Werner Ebeling H. Künstner

Theorie elektrolytischer Flüssigkeiten

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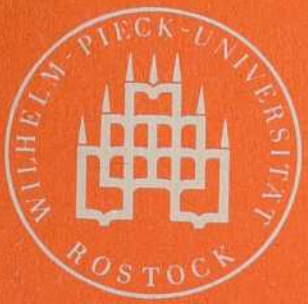

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THEORIE ELEKTROLYTISCHER FLÜSSIGKEITEN

Bearbeiter: Prof. Dr. W. Ebeling
Dipl.-Phys. H. Künstner

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Inhaltsverzeichnis

Vorwort

1949, im Gründungsjahr der Deutschen Demokratischen Republik, wurde Professor Hans Falkenhagen auf den Lehrstuhl für theoretische Physik der Universität Rostock berufen. Es gelang ihm hier, in kürzester Zeit eine Schule der Theorie elektrolytischer Flüssigkeiten aufzubauen.

Als Hans Falkenhagen 1971 nach einem schaffensreichen und erfüllten Leben verstarb, konnte seine Elektrolyt-Gruppe, deren Leitung inzwischen Professor Günter Kelbg übernommen hatte, auf über 200 wissenschaftliche Publikationen zurückblicken. Der vorliegende Band enthält eine Sammlung von Arbeiten zu Problemen, die heute - 30 Jahre danach - Falkenhagens Schüler und ihre Fachkollegen bewegen.

Frau Margarete Thämlitz und Fräulein Hiltrud Prestin sei herzlich gedankt dafür, daß sie wiederum in bewährter zuverlässiger Weise das Schreiben des Manuskriptes übernommen haben.

Prof.Dr.W.Ebeling, Dipl.-Phys.H.Künstner

G. Kelbg

Wilhelm Ostwalds Beitrag zur Elektrolytforschung.

Am 2. September 1978 jährte sich zum 125. Mal der Geburtstag Wilhelm Ostwalds. Dieser Tag gibt uns Anlaß, des großen Gelehrten zu gedenken. Denn Wilhelm Ostwald hat auf vielen Wissenschaftsgebieten Neuland erschlossen und sein Wirken hat die Entwicklung zahlreicher wissenschaftlicher Disziplinen entscheidend beeinflußt. Besondere Bedeutung besitzen seine Arbeiten auf den Gebieten der Katalyse und den chemischen Reaktionsprozessen, für die er am 10. Dezember 1909 den Nobelpreis für Chemie erhielt.

Wilhelm Ostwald hat auch fundamentale Beiträge zur Elektrolytforschung geleistet. Durch Verbreitung und Weiterentwicklung der neuen Ideen seiner Zeit auf diesem Gebiet können wir ihn heute als Mitbegründer der modernen Elektrolyt-Theorie und modernen Elektrochemie ansehen.

Vor allen Dingen ist es das Verdienst Wilhelm Ostwalds, daß sich die Ideen von Svante Arrhenius aus dem Jahre 1883 über den Zerfall der Salze, Säuren und Basen in wässrigen Lösungen in freie Ionen trotz mancher Widerstände der Fachgenossen rasch durchsetzen konnte.

Die in der damaligen Zeit von van't Hoff entwickelte neue Lösungstheorie und das neue Konzept der Theorie der elektrolytischen Dissoziation stützten sich gegenseitig und führten letzten Endes zum Entstehen einer neuen Wissenschaftsdisziplin der physikalischen Chemie.

Die von Ostwald und J.H. van't Hoff neugegründete Zeitschrift für physikalische Chemie enthielt im ersten Band im Jahre 1887 bereits Artikel über die neuen Theorien. In den folgenden Jahren veröffentlichte Wilhelm Ostwald zahlreiche Arbeiten über elektrolytische Dissoziation und damit zusammenhängende physikalisch-chemische Prozesse.

Daß Ostwald die Zusammenhänge besonders klar durchschauen konnte ist auch darauf zurückzuführen, daß er sich lange und

intensiv schon in seinen frühesten Arbeiten mit chemischen Gleichgewichtsproblemen beschäftigt hat. Dem Thema der elektrolytischen Leitfähigkeit hatte er sich schon in Riga zugewendet und Messungen durchgeführt und Dissoziationskonstanten bestimmt.
Nach seiner Berufung von dem kleinen Ordinariat an dem Polytechnikum in Riga im Jahre 1887 nach Leipzig und Übernahme des Lehrstuhls für physikalische Chemie wurden diese Untersuchungen am zweiten chemischen Laboratorium mit großer Intensität und Erfolg fortgeführt.
Wir können sagen, daß die 19 Arbeitsjahre Wilhelm Ostwalds in Leipzig bis 1906 zu den fruchtbarsten in seinem Leben gehören.

Bereits 1888 entwickelte er das nach ihm benannte Ostwaldsche Verdünnungsgesetz, in dem sich die Gedanken der elektrolytischen Dissoziation, der osmotischen Theorie und des Massenwirkungsgesetzes vereinigten.
Diese wissenschaftliche Leistung findet eine besondere Würdigung durch die Gestaltung der Nobelpreis-Urkunde. Der Kopf der zweiten Seite des Diplôms enthält den formelmäßigen Ausdruck des Verdünnungsgesetzes unter einer schematisch gezeichneten Figur des Ostwaldschen Thermostaten,/1/ der bei der Messung der Leitfähigkeit elektrolytischer Lösungen Verwendung fand.
Bemerkenswert ist, daß Wilhelm Ostwald bezüglich der Salzlösungen schon viele Jahre vor Arrhenius und van't Hoff den Ein - fluß gelöster Salze auf die Eigenschaften von Lösungen erkannte. Er kam zur Aussage " das Wasser zersetzt alle Salze ".
Wilhelm Ostwald hat viele schöpferische Kräfte zur Fortentwicklung neuer Ideen und Gedanken freigesetzt. Er durchschaute sein Fachgebiet mit einer seltenen Klarheit und erkannte die entscheidenden Zusammenhänge. Z.B. schreibt Wilhelm Ostwald in seinem Artikel/2/ " Zur Dissoziationstheorie der Elektrolyte ".
" Die nachstehenden Erörterungen über die Salzbildung sind die

erweiterte Wiedergabe des Inhaltes eines Vortrages, welchen ich am 1. Mai 1889 in der chemischen Gesellschaft zu Leipzig gehalten habe. Ich kann von dem sachlichen Inhalt derselben für mich nichts als Eigentum in Anspruch nehmen, denn derselbe ist die Auseinandersetzung einer Reihe von Ideen, welche mein Freund Svante Arrhenius zum Teil ausgesprochen, zum Teil angedeutet hat. Was mir angehört, ist nur die Form der Darstellung. Ich bin durch verschiedene Anfragen von Fachgenossen darüber belehrt worden, daß sie Schwierigkeiten empfinden, sich über die durch die Dissoziationstheorie der Elektrolyte notwendig gewordene Umgestaltung der chemischen Anschauungen Wahrheit zu verschaffen, und es schien mir daher nützlich, zunächst die einfachsten chemischen Vorgänge, wie sie bei der Salzbildung in Frage kommen, im Lichte der neuen Theorie zusammenhängend darzustellen ".

Die Tragfähigkeit der neuen Ideen wurde an den Vorgängen der Salzbildung bei der Mischung von Säuren und Basen demonstriert.

W. Ostwald schreibt weiter:

" Man ist somit zu der Behauptung berechtigt, daß die Dissoziationstheorie der Elektrolyte nicht nur nirgend mit den Tatsachen in Widerspruch gerät, sondern daß sie zum ersten Male eine Anzahl bisher unverstanden und unerklärt gebliebener Beziehungen als notwendig hat voraussehen lassen, wobei der Erfahrung nur der Zahlenwert der auftretenden Konstanten zu entnehmen war ".

Im Übrigen hat auch M. Planck die Richtigkeit der entwickelten Ideen erkannt und sie unterstützt und gegen Angriffe verteidigt.

Die Dissoziation von Ionen in Elektrolyten wird wie jedes andere chemische Gleichgewicht durch das Massenwirkungsgesetz beherrscht. Dieser Gedanke führte Wilhelm Ostwald zum Verdünnungsgesetz. Es stellt eine besonders bedeutende und fruchtbare Entdeckung auf dem Gebiet der Elektrolytforschung dar.

Nahezu 250 verschiedene organische Säuren wurden untersucht[3] und das Gesetz wurde fast durchweg bestätigt gefunden.
Die Messungen Ostwalds zeigen eine hohe Genauigkeit. z.B. wurden von DA. Mc Innes und Th. Shedlovsky die Meßreihe Ostwalds an Essigsäure bei 25 °C im Jahre 1932 unter Präzisionsmeßbedingungen wiederholt. Sie zeigte wie genau die experimentelle Bestimmung der Dissoziationskonstanten von Ostwald mit viel primitiveren Hilfsmitteln war.
Im übrigen ist zu erwähnen, daß die Messungen der Dissozia - tionskonstanten in Riga von nicht erheblichen, doch beständig einseitigen Abweichungen behaftet waren. Der spurenweise Ammoniakgehalt des in Riga benutzten Wassers hatte dies verursacht. Das Leipziger Wasser war von diesen Verunreinigungen frei und so wurden zahlreiche Meßreihen in Leipzig wiederholt und korrigiert.
Das Verdünnungsgesetz, das einen Zusammenhang zwischen der molaren Leitfähigkeit und der molaren Verdünnung beschreibt, wird von Wilhelm Ostwald wie folgt abgeleitet.
Anknüpfungspunkt ist das Massenwirkungsgesetz in partialdruckformulierung

$$\frac{p}{p_1^2} = \text{const.} \qquad (1)$$

wobei p der Druck des unzersetzten und p_1 des zersetzten Anteils ist. Ostwald argumentiert weiter so[4]:

" Nun läßt sich nach den oben erwähnten Arbeiten der "Druck" in der Lösung proportional den vorhandenen Mengen u und u_1 der Stoffe und umgekehrt proportional dem Volumen v setzen; die Gleichung wird, da $p : p_1 = \frac{u}{v} : \frac{u_1}{v}$, zu

$$\frac{u}{u_1^2} v = \text{const.} \qquad (2)$$

Ferner lassen sich die Mengen u und u_1 aus dem elektrischen Leitvermögen berechnen wie Arrhenius (l.c.) gezeigt hat. Nennt man Λ_v die molare Leitfähigkeit eines Elektrolyts beim Volumen v und Λ_∞ den Grenzwert der Leitfähigkeit bei

unendlicher Verdünnung, so ist $u : u_1 = (\Lambda_\infty - \Lambda_v) : \Lambda_v$ da die Leitfähigkeit Λ_v proportional der dissoziierten Menge des Elektrolyts u_1 ist. Daraus folgt als für alle binären Elektrolyte gültige Verdünnungsgesetz

$$\frac{(\Lambda_\infty - \Lambda_v)\, v}{\Lambda_v^2} = \text{const.} \qquad (3)$$

Bedeutet $\alpha = \Lambda_v / \Lambda_\infty$, so ist diese Größe ein Maß für die Dissoziation.
In reziproker Form nach Einführung der Dissoziationskonstanten K und der molaren Konzentration $c \sim 1/v$ lautet das Gesetz

$$\frac{\alpha^2 c}{1 - \alpha} = K \qquad (4)$$

Mit dieser Formel legte Wilhelm Ostwald den Grundstein zur theoretischen Interpretation der Leitfähigkeitseigenschaften schwacher Elektrolyte.

Aus dem Ostwaldschen Verdünnungsgesetz (3) folgt nach einer linearen Näherung nach der molaren Konzentration c, für die molare Leitfähigkeit

$$\Lambda = \Lambda_\infty - c \frac{\Lambda_\infty}{K} \qquad (5)$$

Ein entsprechendes Gesetz ergibt sich nach der Theorie von van't Hoff für die osmotischen Koeffizienten g

$$g = 1 - \frac{1}{2K} c \qquad (6)$$

Danach nimmt die molare Leitfähigkeit und der osmotische Koeffizient linear mit der Konzentration c ab.
Diese Gesetze sind nur für schwache Elektrolyte gültig.

Im Jahre 1900 wies K.F. Kohlrausch nach, daß für die molare Leitfähigkeit im Falle starker Elektrolyte ein Quadratwurzelgesetz besteht

$$\Lambda = \Lambda_\infty - A\sqrt{c} \qquad (7)$$

Ein gleiches Gesetz gilt auch für die osmotischen Koeffizienten starker Elektrolytewie von Lewis und Randall aufgezeigt wurde

$$g = 1 - A'\sqrt{c} \qquad (8)$$

Diese Eigenschaften der starken Elektrolyte hängen mit den beträchtlichen Coulombkräften zwischen den Ionen zusammen. Die elektrischen Wechselwirkungen haben einen entscheidenden Einfluß auf das thermodynamische und Transportverhalten der Lösungen starker Elektrolyte. In diesem Falle ist dann die Leitfähigkeit kein Maß mehr für den Dissoziationsgrad α . Auch Ostwald hatte schon einen Gang für die Dissoziationskonstanten festgestellt. Er deutet diese Abhängigkeit jedoch als Einfluß der Viskosität des Lösungsmittels auf die Ionenbeweglichkeiten.
Der dialektrische Widerspruch zwischen dem linearen Gesetz und dem Quadratwurzelgesetz leitete eine umfangreiche Entwicklung auf diesem Wissensgebiet ein.

Die Berücksichtigung der elektrischen Wechselwirkungen der Ionen führte zu einer neuen Interpretation des Verhaltens hochverdünnter Lösungen. In der modernen Theorie der Elektrolyte im Falle erhöhter Konzentrationen zeigt es sich aber, daß sowohl der Ostwaldsche-Arrheniussche Aspekt der Assoziation-Dissoziation als auch der Aspekt der zwischenionalen Wechselwirkungen gemeinsam berücksichtigt werden müßen. Die Arbeiten Ostwalds über die elektrolytischen Lösungen sind daher als ein erster aber bedeutender Schritt auf dem Wege zu unserer heutigen Erkenntnis auf diesem Fachgebiet anzusehen.

Im Zusammenhang mit Ostwalds Arbeiten über die Dissoziation in Elektrolyten ist bemerkenswert, daß sich diese Untersuchungen gut in die sich Ende des 19. Jahrhunderts immer stärker ausbreitenden Vorstellungen über die atomistische Struktur der Materie

einordneten. Anfang der neunziger Jahre prägte sich bei Ostwald die Tendenz gegen den Atomismus immer stärker aus. Zunächst bezog Ostwald zwar seine Ansichten noch nicht auf den Zustand der freien Ionen in Elektrolyten, dann aber versuchte er auch die Theorie der elektrolytischen Dissoziation mit Hilfe der energetischen Lehre von der Atmovorstellung zu befreien.
Über den Wissenschaftler und Lehrer, den Philosophen Wilhelm Ostwald und sein Leben und sein Wirken gibt das Buch von Rodnyj und Ju.I. Solowjew Auskunft[/5/].

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Anschrift des Verfassers

Prof. Dr. sc.nat.Günter Kelbg
Wilhelm-Pieck-Universität Rostock
Sektion Physik
DDR - 25 Rostock
Universitätsplatz 3

W. Ebeling, K. Scherwinski

Bestimmung thermodynamischer Funktionen aus Potentialparametern für die interionische Wechselwirkung.

Abstract

Thermodynamic properties of strong aqueous 1-1-electrolytes are studied using a simple approximation for the correlation function and a step potential model for the short-range interaction. Predictions for all thermodynamic functions can be made if the potential parameters for the ion-ion interaction are known. As an example the mean activity coefficient is calculated for alkali chlorides on the basis of an earlier determined set of potential parameters. The experimental data are well described up to 0.5 mol/l. Furtheron it is shown for several examples that osmotic coefficients of mixtures can be predicted in the same concentration range using the above mentioned set of potential parameters and simple approximations for the potential parameters of the interaction between two unlike anions or two unlike cations respectively.

1. Thermodynamische Funktionen in der DHX-Näherung.

Die thermodynamischen Exzeßfunktionen elektrolytischer Lösungen hängen nach einem Satz von Mc Millan und Mayer[1] allein von den Potentialen der mittleren Kräfte zwischen den Ionen ab. Für den Bereich kleiner und mittlerer Konzentrationen, auf den wir uns in dieser Arbeit beschränken, lassen sich relativ einfache analytische Gleichungen für die thermodynamischen Funktionen finden[2]. In der vorliegenden Arbeit werden ausgehend von bereits bestimmten Parametern für die Potentiale der mittleren Kräfte zwischen den Ionen thermodynamische Exzeßgrößen für wässrige 1-1 Elektrolyte berechnet.

Wir beschränken uns auf den Fall von Paarwechselwirkungen. Mit Hilfe der binären Verteilungsfunktionen $F_{ab}(u_1 u_2)$ berechnen wir den osmotischen Koeffizienten g aus der Virialformel

$$g = 1 - \frac{2\pi n}{3kT} \sum_{a,b} x_a x_b \int_\sigma^\infty r^3 \frac{\partial \Psi_{ab}}{\partial r} F_{ab}(r)\, dr \qquad (1.1)$$

und die freie Exzeßenergie über einen Aufladeprozeß

$$\frac{\mathcal{F}^{ex}}{NkT} = 2\pi n \sum_{a,b} x_a x_b \int_\sigma^1 d\lambda^2 \int_\sigma^\infty dr\, r^2\, \Psi_{ab}(r) F_{ab}(r,\lambda). \qquad (1.2)$$

Hierbei ist $n=N/V$ die Gesamtteilchendichte der Ionen, x_a der Molenbruch der Teilchensorte a und λ ein Aufladungsparameter.

Ein anderer Weg zur Berechnung der freien Exzeßenergie führt über eine Volumenintegration des osmotischen Druckes

$$\mathcal{F}_V^{ex} = -\int_\infty^V \left[P_{osm} - P_{osm}^{id} \right] dV. \qquad (1.3)$$

Den mittleren rationalen Aktivitätskoeffizienten $f_\pm$ erhalten wir aus der bekannten Beziehung

$$\ln f_\pm = \frac{1}{kTV} \left(\frac{\partial \mathcal{F}^{ex}}{\partial n} \right)_{T,V,x_i}. \qquad (1.4)$$

Das Wechselwirkungspotential Ψ_{ab} beschreiben wir durch ein sortenabhängiges Stufenpotentialmodell

$$\Psi_{ab}(r) = \begin{cases} \infty & r < R_{ab}, \\ h_{ab} & R_{ab} \le r < R'_{ab}, \\ \frac{e_a e_b}{D_o r} & r \ge R'_{ab}, \end{cases} \qquad (1.5)$$

$$R_{ab} = R_a + R_b,$$
$$R'_{ab} = R_{ab} + d.$$

Dabei ist D_0 die makroskopische DK des Lösungsmittels, d ein mittlerer Durchmesser eines Lösungsmittelmoleküls (d=2.76 Å für H_2O) und R_a, R_b sind die kristallographischen Ionenradien. Die Stufenhöhe h_{ab} ist ein sortenabhängiger freier Parameter, der eine spezifische Beschreibung kurzreichender Wechselwirkungen ermöglicht. Für einfache Elektrolyte wurden die Stufenhöhen durch Anpassungen an den osmotischen Koeffizienten[3] und an Daten der elektrischen Leitfähigkeit[4] für alle Alkalihalogenide bestimmt. Die so ermittelten Potentialparameter erlauben es, Aussagen über individuelle Ionenwechselwirkungen zu treffen und ermöglichen theoretische Voraussagen über weitere thermodynamische Größen.

Tabelle 1: Potentialparameter βh_{ij} für Alkalihalogenide in H_2O bei 25 °C.

Table 1: The potential parameters βh_{ij} for alkali halides in water at 25 °C.

	$\beta h_{ii} \rightarrow$ / $\downarrow \beta h_{ij}$	F^-	Cl^-	Br^-	J^-
	0.92	1.44	1.19	1.28	
Li^+	0.84	(- 0.70)	- 0.66	- 0.53	-0.03
Na^+	0.68	- 1.20	- 1.09	- 0.99	-0.95
K^+	0.91	- 1.06	- 1.28	- 1.22	-1.19
Rb^+	1.94	- 1.08	- 1.42	- 1.40	-1.42
Cs^+	1.54	- 0.99	- 1.48	- 1.45	-1.47

Aus den in /3/ angegebenen verschiedenen Varianten wählten wir im folgenden den in Tabelle 1 angegebenen Satz von Potentialparametern aus. Da für die Li-F-Wechselwirkung bisher kein Parameterwert bekannt ist, haben wir die vorliegenden Daten interpoliert. Zielstellung dieser Arbeit ist, daß mit Hilfe dieser Parameter der mittlere Aktivitätskoeffizient und der osmotische Koeffizient von Mischungen voraussagbar sind.

Für die binäre Verteilungsfunktion F_{ab} verwenden wir eine nichtlineare Debye-Hückel-Näherung (DHX-Näherung)/5/.

$$F_{ab}^{DHX} = \exp\left\{-\beta \Phi_{ab}\right\}. \tag{1.6}$$

Hier ist Φ_{ab} das Potential der mittleren Kraft

$$\Phi_{ab} = \begin{cases} \infty & r < R_{ab}\,, \\ h_{ab} - \dfrac{e_a e_b \varkappa}{D_0(1+\varkappa R'_{ab})} & R_{ab} \le r < R'_{ab}\,, \\ \dfrac{e_a e_b}{D_0 r} \cdot \dfrac{\exp[\varkappa R'_{ab} - \varkappa r]}{1+\varkappa R'_{ab}} & r \ge R'_{ab}\,. \end{cases} \tag{1.7}$$

Dabei ist der reziproke Debye Radius

$$\varkappa^2 = \frac{4\pi \sum_a n_a e_a^2}{D_0 kT}\,,$$

und $\beta = (kT)^{-1}$.

Berechnet man mit (1.5) und (1.6) den osmotischen Druck nach (1.1), so erhält man nach (1.3), (1.4) für den mittleren Aktivitätskoeffizienten

$$\ln f_{\pm}^{V} = -\frac{2\pi n}{3}\sum_{a,b} x_a x_b \Big\{ l_{ab} R_{ab}'^{2} + l_{ab}^{2}\Big[\frac{1}{\varkappa(1+\varkappa R_{ab}')} + \frac{2}{\varkappa^{2} R_{ab}'^{2}}\ln(1+\varkappa R_{ab}')\Big]$$
$$+ \Big[R_{ab}'^{3} + (R_{ab}^{3} - R_{ab}'^{3})\exp\Big\{-\beta h_{ab} + \frac{l_{ab}}{R_{ab}'}\Big\} \times$$
$$\times\Big\{Y_{ab} - \exp\Big(-\frac{l_{ab}}{R_{ab}'(1+\varkappa R_{ab}')}\Big)\Big\}\Big]$$
$$+ 2M_{ab} + n\frac{\partial M_{ab}}{\partial n}\Big\}, \qquad (1.8)$$

$$M_{ab} = \int_{\infty}^{1}\frac{d\mu}{\mu^{2}}\int_{R_{ab}'}^{\infty} r\Big[e^{-\beta\Phi_{ab}'} - 1 + \beta\Phi_{ab}'\Big]dr,$$

$$\Phi_{ab}' = \frac{e_a e_b}{D_0 r}\cdot\frac{\exp[\varkappa' R_{ab}' - \varkappa' r]}{1+\varkappa' R_{ab}'},$$

$$\varkappa' = \frac{\varkappa}{\sqrt{u}}, \qquad l_{ab} = \frac{e_a e_b}{D_0 kT}.$$

Die Funktionen Y_{ab} sind gegeben durch

$$Y_{ab} = \frac{1}{\varkappa^{2} R_{ab}'^{3}}\Big\{\exp\Big(-\frac{l_{ab}}{R_{ab}'(1+\varkappa R_{ab}')}\Big)\Big[R_{ab}' - \varkappa^{2} R_{ab}'^{3} +$$
$$l_{ab} + \varkappa l_{ab} R_{ab}'\Big] - \exp\Big(-\frac{l_{ab}}{R_{ab}'}\Big)\Big[R_{ab}' + l_{ab}\Big] +$$
$$\Big(\frac{l_{ab}^{2}}{R_{ab}'} + 2l_{ab}\Big)\Big[Ei\Big(-\frac{l_{ab}}{R_{ab}'(1+\varkappa R_{ab}')}\Big) - Ei\Big(-\frac{l_{ab}}{R_{ab}'}\Big)\Big]\Big\}.$$

2. Vergleich mit HNC- und MSA - Daten für das Modell geladener starrer Kugeln.

Nach (1.1) berechnen wir den osmotischen Koeffizienten für ein Modell geladener starrer Kugeln. Ψ_{ab} hat dabei die Form

$$\Psi_{ab} \begin{cases} \infty & r < R_{ab} \\ \frac{e_a e_b}{D_o r} & r > R_{ab} \end{cases} \qquad (2.1)$$

Die Resultate werden in Tabelle 2 mit HNC-Daten von Rasaiah[6] ($R_+ = R_- = 4.2$ Å) und von Rasaiah und Friedman[7] verglichen. In Spalte 3 sind zusätzlich die aus der MSA Theorie[8] folgenden Werte für g angegeben, wobei für den Anteil der ungeladenen starren Kugeln eine Formel von Carnahan und Starling[9] benutzt wurde. Aus der Tabelle ist erkennbar, daß die Abweichungen der DHX-Theorie von den HNC Werten bis zu c = 0.5 mol/Liter kleiner als 1 % sind.

Die für $c > 0.5$ auftretenden größeren Abweichungen sind in erster Linie auf die Nichtberücksichtigung des 3. Virialkoeffizienten für ungeladene starre Kugeln zurückzuführen. Für $c \leq 0.1$ liefert die DHX-Theorie eine bessere Übereinstimmung mit den HNC Daten als MSA. Für höhere Konzentrationen liefert die MSA-Theorie kleinere Abweichungen. Der Vergleich deutet auf einen Gültigkeitsbereich der DHX-Theorie bis zu c = 0.5 mol/l hin.

3. Der mittlere rationale Aktivitätskoeffizient.

Nach (1.8) wurden die mittleren Aktivitätskoeffizienten für Alkalichloride unter Verwendung der in Tabl.1 angegebenen Parameter für die Wechselwirkungsparamter berechnet und mit experimentellen Werten verglichen. Die thermodynamischen Funktionen beziehen sich in der statistischen Theorie auf ein osmotisches Gleichgewicht für ein vorgegebenes Volumen V und vorgegebene Temperatur T (Mc Millan-Mayer-System), während

Tabelle 2. Osmotischer Koeffizient für das Modell geladener starrer Kugeln für wässrige 1-1-Elektrolyte bei 25 °C. c ist die Konzentration in mol/l.

Table 2. Osmotic coefficient for the model of charged hard spheres for aqueous solutions of 1-1-electrolytes at 25 °C. C is the concentration in moles/liter.

c	HNC	MSA	DHX
	$R_+ = R_- = 2.1$ Å		
0.001	0.9885	0.9885	0.9885
0.0.1	0.9691	0.9694	0.9689
0.1	0.9442	0.9443	0.9439
0.2	0.9479	0.9480	0.9480
0.4	0.9719	0.9727	0.9716
1.0	1.0829	1.0872	1.0687
	$R_+ = 0.95$ Å, $R_- = 1.81$ Å		
0.002	0.9832	0.9836	0.9833
0.02	0.9534	0.9545	0.9543
0.1	0.9179	0.9186	0.9151
0.2	0.9021	0.9019	0.8985
0.4	0.8911	0.8894	0.8870
1.0	0.8973	0.8945	0.8932
	$R_+ = 1.8$ Å, $R_- = 2.8$ Å		
0.05	0.9547	0.9547	0.9544
0.1	0.9542	0.9541	0.9539
0.2	0.9669	0.9669	0.9663
0.5	1.035	1.037	1.028
0.7	1.092	1.095	1.074
1.0	1.191	1.196	1.147

die experimentellen Daten für ein System mit vorgegebenem Druck P und vorgegebener Temperatur T vorliegen. Die experimentellen Daten müssen deshalb vor dem Vergleich mit der Theorie ins MMM-System umgerechnet werden. Außerdem muß man berücksichtigen, daß für die Meßdaten die Konzentration in mol/kg Lösungsmittel angegeben wird, während die Theorie auf eine molare Konzentration (c = mol/Liter Lösung) führt. Zur Umrechnung wurden die Formeln[10] /10/

$$\ln f_{\pm}(c) = \ln \gamma_{\pm}(m) + \ln\left(\frac{m d_0}{c}\right) - \frac{2\beta_0 \nu c RT}{1000} + \frac{c \bar{\phi}_v}{1000} \qquad (3.3)$$

und

$$c = m d_0 - A m^2 + B m^3 \qquad (3.2)$$

benutzt. Hier sind d_0 und β_0 Dichte bzw. Kompressibilität des Lösungsmittels und $\bar{\phi}_v$ ist das scheinbare partielle molare Volumen der Lösung. Die Koeffizienten der empirischen Formel (3.2) wurden dem Werk von Harned-Owen[11] /11/ entnommen.

In Fig.1 ist der mittlere Aktivitätskoeffizient für KCl in wässriger Lösung mit dem Experiment verglichen. Außerdem wurde nach /5/ der Aktivitätskoeffizient über (1.2), (1.4) für dieselben Potentialparameter berechnet. Der nach (1.8) erhaltene Aktivitätskoeffizient stimmt bis zu c = 1 mol/l sehr gut mit den experimentellen Werten überein. Die bei der Berechnung von $\ln f_{\pm}$ über die Aufladeformel gemachten Näherungen sind die Ursache für die größeren Abweichungen im angegebenen Konzentrationsbereich. In Abbildung 2 sind die nach (1.8) erhaltenen Resultate für die Alkalichloride gezeigt. Bis zu c=0.5 mol/l werden die experimentellen Daten von allen Kurven gut beschrieben. Dies entspricht der Übereinstimmung von Theorie und Experiment, wie sie in /3/ bei der Anpassung der Potentialparameter an osmotische Koeffizienten erzielt wurde. Die angepaßten Potentialparameter ermöglichen also eine äquivalent gute Beschreibung des mittleren Aktivitätskoeffizienten durch Gl.(1.8). Es ist daher zu erwarten, daß die Poten-

tialparameter zur Voraussage aller thermodynamischer Funktionen benutzt werden können.

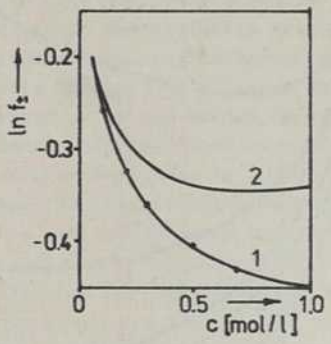

Fig.1: Mittlerer Aktivitätskoeffizient für KCl (25 °C).• Experiment /11/;
1 - Theorie nach (1.8); 2 - Theorie berechnet über eine Aufladeformel für die freie Energie.

Fig.1: Mean activity coefficient for KCl at 25 °C.
• Experimental values /11/; 1 - theoretical result according to Eq.(1.8);
2 - calculated, using a charging process to obtain the free energie (Eq.(1.2)).

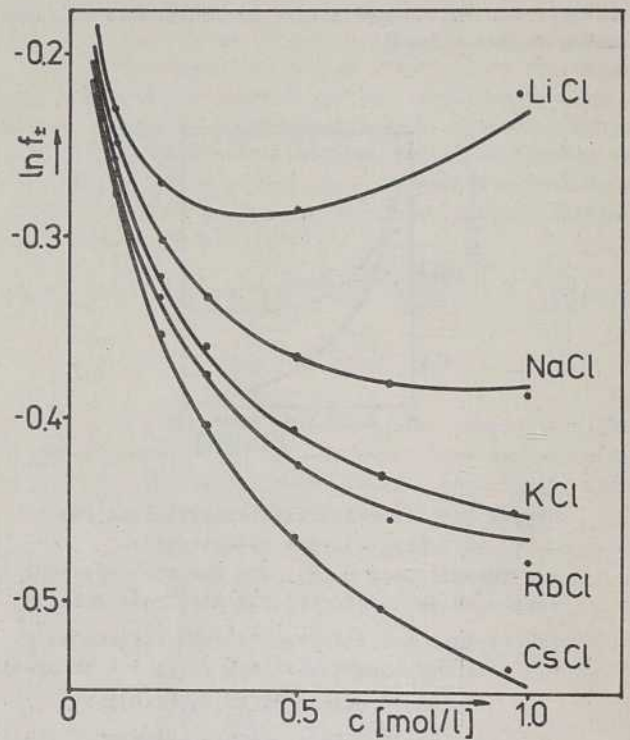

Fig.2: Mittlerer Aktivitätskoeffizient für wässrige Alkalichloride bei 25 °C. • Experiment /11/; – theoretischer Verlauf nach (1.8).

Fig.2: Mean activity coefficient for alkalichlorides in water at 25 °C. • experimental values /11/; – theoretical curves obtained from Eq.(1.8).

4. Osmotischer Koeffizient für Mischungen von wässrigen 1-1-Elektrolyten mit einem gemeinsamen Ion.

Für die meisten einfachen Elektrolyte stehen bei Raumtemperaturen für den osmotischen Koeffizienten Meßreihen über einen großen Konzentrationsbereich zur Verfügung. Im Gegensatz dazu gibt es für gemischte Elektrolyte nur eine geringe Zahl von Meßdaten, die außerdem meist auf wenige Mischungsverhältnisse beschränkt sind. Daher sind jene theoretischen Formeln und Ausdrücke von besonderem Wert, die es erlauben, für eine große Anzahl von Mischungen in einem bestimmten Konzentrationsbereich relativ genaue Vorhersagen für die thermodynamischen Eigenschaften zu treffen. Im folgenden wird nach (1.1) der osmotische Koeffizient in der DHX-Näherung für Mischungen von 1-1-Elektrolyten mit einem gemeinsamen Ion für Konzentrationen bis zu I = 0.5 mol/l (I ist die Ionenstärke. $I = \frac{1}{2} \sum_i c_i z_i^2$; z_i - elektrochemische Wertigkeit) berechnet.

Wir betrachten eine Mischung aus einem Elektrolyten A und einem Elektrolyten B. Für die Potentiale der mittleren Kräfte zwischen den Ionen benutzen wir die in Tab.1 angegebenen Stufenpotentialparameter βh_{ij} für die einfachen Elektrolyte. Die zusätzlich in der Mischung auftretenden Stufenhöhen der Anion A - Anion B bzw. Kation A - Kation B Wechselwirkungen werden zunächst als freie Parameter betrachtet, deren Wert durch Anpassung an experimentelle Meßdaten bestimmt wird. Vor einer Anpassung müssen die experimentellen Daten ins MMM-System umgerechnet werden. Dazu wurde eine von Krienke /10/ angegebene Formel benutzt. In Fig.3 sind die Resultate der Anpassung für drei Mischungen von Alkalihalogeniden für I=0.5 mol/l in Abhängigkeit vom Ionenstärkebruch y_B des Elektrolyten B ($y_B = I_B/I$) angegeben. Sowohl für die NaCl-KCl Mischung als auch für die NaBr-KBr Mischung folgt aus der Anpassung βh_{Na-K} = 0.68, für die Natrium-Cäsium Wechselwirkung folgt βh_{Na-Cs} = 1.22. Aus der Abbildung ist ersichtlich, daß die theoretischen Kurven die experimentellen Daten gut beschreiben. Die

größeren Abweichungen der Kurve 3 von den experimentellen Meßwerten sind im wesentlichen darin begründet, daß die in /3/ verwendeten Meßdaten für reines CsCL von den Daten in der Mischung abweichen. Es ist also für eine möglichst genaue Bestimmung des in der Mischung zusätzlich auftretenden Wechselwirkungsparameters notwendig, daß die experimentellen Meßwerte für die Mischung eine gleichgute Qualität besitzen, wie die zur Bestimmung der Wechselwirkungsparameter der reinen Stoffe herangezogenen Meßdaten. Für den Fall der hier betrachteten Mischungen mit 3 verschiedenen Ionen ist bereits ein einziger Meßwert ausreichend, um den Potentialparameter der beiden ungleichen Kationen bzw. der beiden ungleichen Anionen zu bestimmen. Damit läßt sich dann der osmotische Koeffizient für beliebige Ionenstärken $I \leq 0.5$ mol/l berechnen.

In Fig.4 wurde für eine NaBr-KBr Mischung der Einfluß des βh_{Na-K} Parameters auf den osmotischen Koeffizienten der Mischung untersucht. Der Vergleich der Kurven 2 und 3 zeigt, daß eine Änderung des βh_{Na-K} Parameters um etwa 15 % nur eine Änderung von φ um rund 0.1 % bewirkt. Dieser geringe Einfluß auf den osmotischen Koeffizienten ermöglicht es, durch Wahl einer geeigneten Näherung für βh_{Na-K} eine Anpassung zu umgehen.

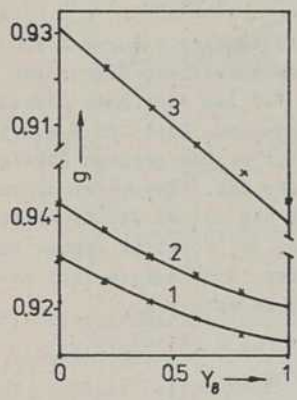

Fig.3: Osmotischer Koeffizient für Mischungen von 1-1-Elektrolyten. Der Potentialparameter für die Wechselwirkung ungleicher Kationen wurde angepaßt. I = 0.5 mol/l.
1-NaCl-KCl; 2 NaBr-KBr;
3 NaCl-CsCl; x Experiment /12/.

Fig.3: The osmotic coefficient for mixtures of 1-1-electrolytes with fitted potential parameter for the interaction of unlike cations I = 0.5 mol/l.
1 NaCl-KCl; 2 NaBr-KBr;
3 NaCl-CsCl; x experimental values /12/.

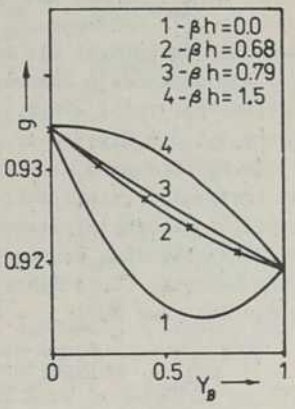

Fig.4: Osmotischer Koeffizient einer wässrigen NaBr-KBr Lösung für einige Werte des Potentialparameters der Na-K Wechselwirkung. I = 0.3 mol/l.
x Experiment /12/.

Fig.4: Osmotic coefficient of an aqueous NaBr-KBr solution for several values of the potential parameter of the Na-K interaction.
I = 0.3 mol/l.
x experimental values /12/.

Wir wählen den Parameter so, daß er sich als arithmetisches Mittel aus den Potentialparametern der Na-Na und K-K Wechselwirkung ergibt, d.h.

$$\beta h_{Na-K} = \frac{1}{2}\beta h_{Na-Na} + \frac{1}{2}\beta h_{K-K} \tag{4.1}$$

Dieser Wahl entspricht die bereits diskutierte Kurve 3 in Fig.4. Wir testen die Näherung an zwei weiteren Mischungen (Fig.5 und 6). Für I = 0.1 und I = 0.3 ist eine gute Übereinstimmung mit dem Experiment festzustellen. Noch für I = 0.5 sind die Abweichungen kleiner als 0.3 %. Die größten Abweichungen treten für reines NaCl bzw. KBr auf. Dies weist darauf hin, daß die Potentialparameter für die reinen Stoffe nicht genau genug bestimmt worden sind und ist nicht in erster Linie auf die Näherung (4.1) zurückzuführen. Eine andere Möglichkeit der Wahl des βh_{Na-K} - Parameters wäre z.B.

$$\beta h_{Na-K} = \sqrt{\beta h_{Na-Na} \cdot \beta h_{K-K}} \tag{4.2}$$

Für die hier untersuchten Mischungen unterscheiden sich die beiden Varianten (4.1) und (4.2) nur geringfügig, so daß eine in etwa gleich gute Beschreibung der experimentellen Daten erfolgt.

Die Anzahl der Mischungskomponenten ist durch die Theorie nicht begrenzt. Aus Alkalihalogeniden können etwa 450 verschiedene Mischungen gebildet werden. Durch Benutzung einfacher Mittelungsregeln für die Wechselwirkungen ungleicher Anionen bzw. ungleicher Kationen z.B.

$$h_{ij}^{A} = \frac{1}{2} h_{ii}^{A} + \frac{1}{2} h_{jj}^{A}$$

$$h_{ij}^{K} = \frac{1}{2} h_{ii}^{K} + \frac{1}{2} h_{jj}^{K} \tag{4.3}$$

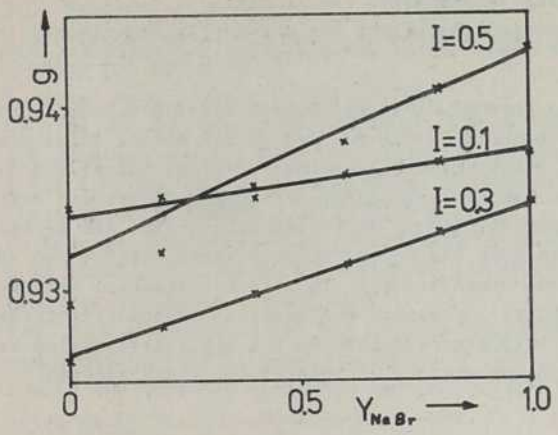

Fig.5: Osmotischer Koeffizient für NaCl-NaBr in Wasser bei 25 °C. Der βh_{Cl-Br}- Parameter wurde nach Gl.(4.3) bestimmt. x Experiment /12/.

Fig.5: Osmotic coefficient for NaCl-NaBr in water at 25 °C. The βh_{Cl-Br}-parameter is obtained from Eq.(4.3). x experimental values /12/.

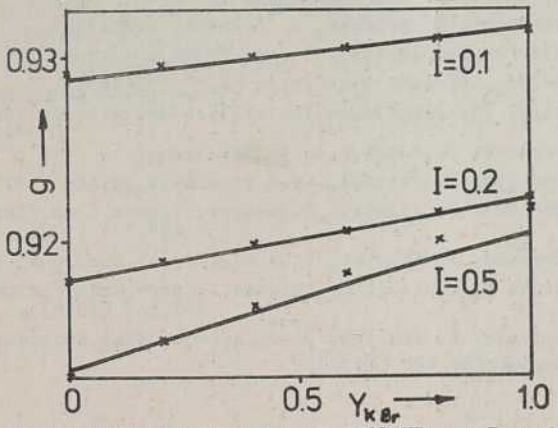

Fig.6: Osmotischer Koeffizient für KCl-KBr. x Experiment/12/.

Potentialparameter wie in Fig.5.

Fig.6: Osmotic coefficient for KCl-KBr. x experimental values. For the value of the potential parameter see Fig.5.

können alle thermodynamischen Größen bis $I \leq 0.5$ mol/l hinreichend gut beschrieben werden. Der großen Anzahl möglicher Mischungen steht dabei eine relativ geringe Anzahl von 29 notwendigen Wechselwirkungsparametern gegenüber. Bis auf den genauen Wert für die Li-F-Wechselwirkungen sind die Wechselwirkungsparameter zumindest näherungsweise bekannt und können der Tab.1 entnommen werden. Die hier beschriebene Methode ist damit zumindest im Prinzip geeignet, die thermodynamischen Funktionen beliebiger Mischungen von Alkalihalogeniden bis zu Ionenstärken von etwa 0.5 M theoretisch vorherzusagen.

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Anschrift der Verfasser:

Prof.Dr.W. Ebeling und Dipl.-Phys.K. Scherwinski
Wilhelm-Pieck-Universität Rostock
Sektion Physik
DDR - 25 Rostock
Universitätsplatz 3

H.L. Friedman, W. Ebeling.

Theory of a Fluid of Interacting and Reactive Particles

Abstract.

Density and fugacity expansions of the thermodynamic functions are combined in a way that preserves the best features of each. The pressure of a given system of interacting and reactive particles is divided into two parts. The first contribution represents the pressure of a reference system which is computationally simple and is treated in the density representation. The deviations from the reference pressure are treated by a fugacity expansion.

1. Introduction.

The aim of this work is to find an effective method for estimating the equilibrium properties of those Hamiltonian model systems in which the attractive forces within specified small sets of particles are relatively strong so that complexes such as dimers or trimers are dominant structural features in the model fluid. Furtheron we try to find a representation which is at the same time computationally simple and is imbedded in a stronger formulation. The simplest representations satisfying the requirement of computational simplicity seem to be the cluster series in the density[1] or in the fugacity respectively[2,3]. The problem connected with the use of these expansions is that density and fugacity expansions have quite different convergence properties depending on the nature of the forces between the particles[4]. As is well known for systems with only repulsive interactions, e.g. hard sphere systems, the density expansion converges morerapidly than the fugacity expansion. In order to show this we have represented in Fig.1 the result of the density expansion up to the n^2-term as well as of the fugacity expansion up to

the z^2-term in comparision with the exact result which was calculated by using the Carnahan - Starling formula. On the other hand for system with attracting forces the convergence of fugacity series is much batter. This is also true for Coulomb systems in the region where the hard core contributions are not dominant. In order to show this we compare the known density series up to the second order[1,5] for a primitive model

$$\beta p = 2n - \frac{1}{24\pi}(8\pi n l)^{3/2} - 8\pi n^2 a^3 k_0(l/a) \qquad (1.1)$$

n - density, a - diameter, $l = \beta e^2/D_0$

$$k_0(b) = -\frac{1}{3} - \frac{b^2}{2} + \sum_{m=2}^{\infty} \frac{b^{2m}}{(2m)!(2m-3)} \qquad (1.2)$$

with the corresponding fugacity expansion for the same model up to the z^2- term

$$\beta p = 2z + \frac{1}{12\pi}(8\pi z l)^{3/2} + 8\pi z^2 a^3 \left[k_0\left(\frac{l}{a}\right) + \frac{1}{4}\left(\frac{l}{a}\right)^3\right]$$

$$n = z + \frac{1}{16\pi}(8\pi z l)^{3/2} + 8\pi z^2 a^3 \left[k_0\left(\frac{l}{a}\right) + \frac{1}{4}\left(\frac{l}{a}\right)^3\right] \qquad (1.3)$$

The results for a 2-2-electrolyte with $a = 4.2$ A°, D=78,358, T = 298,16 K have been compared with the HNC-calculations (Fig.2). The fugacity expansion has a better overall shape but clearly it is wrong at high densities where the hard core contributions dominate. Recently fugacity expansions were successfully applied to partially ionized plasmas by Rogers and De Witt[6] applied to ionic solutions by Wood, Lilley and Thompson[3]. It is the aim of this paper to find a mixed representation which is some where between density and fugacity expansions. As described below, density and fugacity expansions may be combined in a way that seems to preserve the best features of each. This work is a generalization of

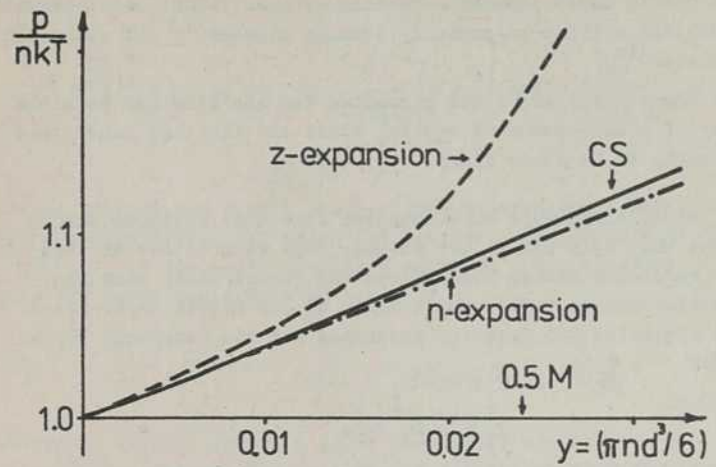


Fig.1 Comparision of a density expansion up to n^2 with a fugacity expansion up to z^2 and with the (exact) Carnahan-Starling expression for a hard sphere system.

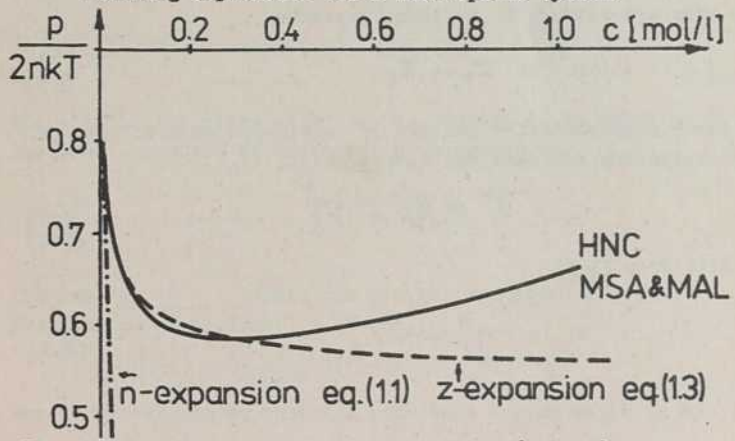


Fig.2 Comparision of a density expansion (eq.1.1) with a fugacity expansion (eq.1.3) and with HNC-results for a charged hard sphere system.

the use of mixed expansion techniques used in earlier papers [4,7] which was applied to partially ionized plasmas [2] and weak electrolytes [5].

The basic ideas are first presented for the simplest possible case of a one-component neutral fluid and then are genralized to apply to an ionic fluid.

2. Association in a One-Component Non-Ionic Fluid. We assume first that only dimers are formed. Then we consider an idealized reference system with attracting forces which make big positive second order coefficients b_2^*. If higher order terms are neglected the fugacity expansion for the reference system reads

$$\begin{aligned} \beta p^* &= z + z^2 b_2^* \\ n &= z + 2z^2 b_2^* \end{aligned} \tag{2.1}$$

Introducing the fugacities of monomers z_1^* and dimers z_2^* by

$$z_1^* = z \quad , \quad z_2^* = z^2 b_2^* \tag{2.2}$$

the pressure reduces to an ideal pressure

$$\beta p^* = z_1^* + z_2^* \tag{2.3}$$

In the " star-picture " the gas is considered as a mixture of noninteracting monomers and dimers. Using

$$n_i^* = z_i^* \, \partial(\beta p^*)/\partial z_i^* \tag{2.4}$$

we find from (2.1)

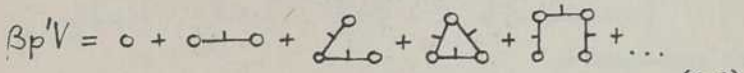
$$n = n_1^* + 2n_2^* \tag{2.5}$$

Also we notice that the Helmholtz free energy corresponding to βp^* is

$$-\frac{\beta}{V}A^*(n_1^*,n_2^*) = n_1^*\left[1+\ln\frac{1}{n_1^*\Lambda_1^3}\right]+n_2^*\left[1+\ln\frac{b_2^*}{n_2^*\Lambda_1^6}\right] \quad (2.6)$$

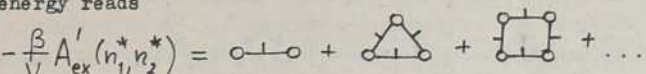
$$\Lambda_1 = h\left[2\pi m_1 k\bar{T}\right]^{-3/2} \quad (2.7)$$

Let us include now simple interactions between the quasispecies using a Hamiltonian for which the cluster function is $f'(r) =$ ——1—— . In the usual graphical notation[1] the pressure of this new reference system is given by



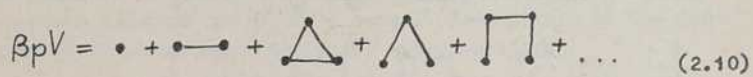
(2.8)

where the circles denote a z_1^* - factor. We assume that we have still a convenient and accurate approximation method for the calculation of the free energy $A'(n_1^*, n_2^*)$ of this new reference system. The density expansion of the excess free energy reads



(2.9)

The equation of state (2.8) may be considered in relation to the exact equation of state of the given system



(2.10)

the bounds ——— denote the cluster functions for the Hamiltonian of interest

$$f(r) = \exp(-\beta u(r)) - 1 = \text{———} \quad (2.11)$$

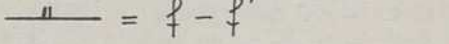
Now it is our aim to choose a reference system which is as

near as possible to the original system. A procedure for doing this is described below.

Let us split the pressure of the real system into the contribution of the reference system and the remaining contributions

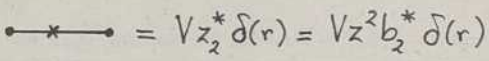
$$p = p' + p'' \tag{2.12}$$

Now we examine the remaining contributions which are due to the difference between f-bonds in the real system and f'-bonds in the reference system and due to introducing z^{*} - circles instead of z-circles. For a graphical representation of p we introduce the f''- bonds by



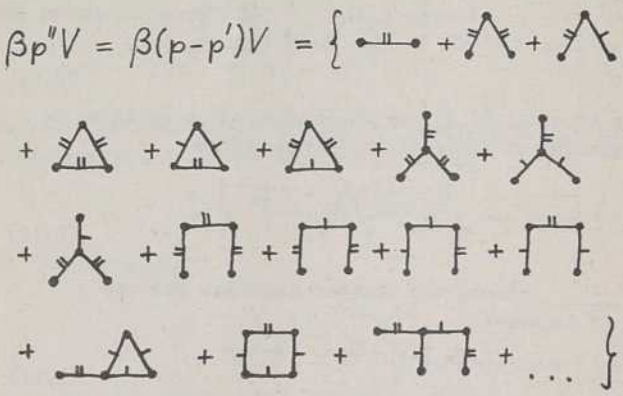
$$= f - f' \tag{2.13}$$

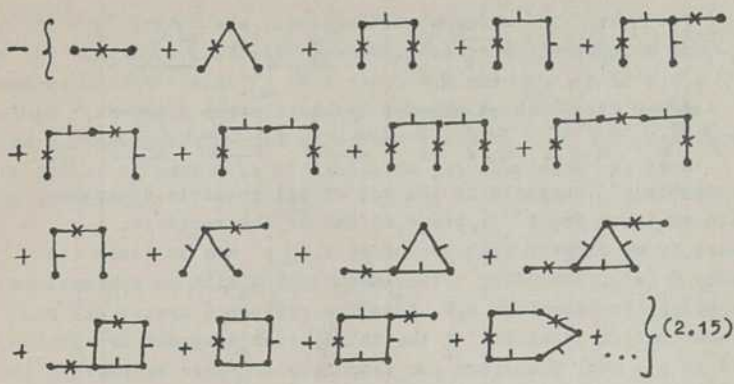
and star-bonds by



$$= V z_2^{*} \delta(r) = V z^2 b_2^{*} \delta(r) \tag{2.14}$$

Using this notation the remaining contribution may be represented by the following graphs

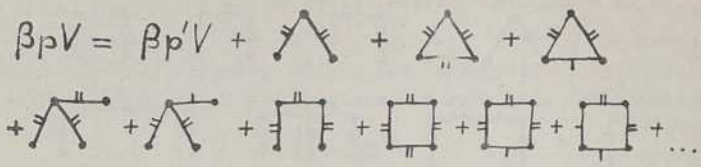




(2.15)

Note that here all circles are z-circles.
The remaining contributions appear as the difference of two parts were in the first paren theses all terms are collected which are due to the difference between the f- and f'- bonds. The second paren thesis contains the terms which are due the expression of z^{*}- circles by z-circles. As the examples illustrate the replacement of z^{*}-circles by z-circles introduces star-bonds into a graph of f'- bonds in all possible ways subject to the constraint that no two star-bonds meet at a vertex. Clearly the star-bond i.e. the expression for b_2^{*} can be adjusted to cancel a f''- bond. By choosing b_2^{*} in such a way many diagrams in eq.(2.5) cancel. The numbers at the diagrams show which terms in (2.15) are cancelled.

Assuming that the calculation of the pressure for the refe - rence system is a solved problem the estimation of the pressure for the real system reduces to the calculation of the following diagram expression



Evidently p'' consists of the set of all possible diagrams with at least two f'' - bonds at one of the vertices. There is no diagram with two nodes i.e. p' has at least the order O (z^3). Including trimer association with an appropriate trimerization constant $b_3^{\equiv}$ into the reference system one can reach that at least two of the third order diagrams are included in p' etc. Therefore the technique of mixed representation seems to be a systematic procedure to include the contribution of more and more important diagrams into a reference system which is computationally simple in the density representation. The remaining terms are to be calculated in the fugacity representation with fugacities which are given by the free-particle fugacities $z_1^{\equiv} = z$ in the reference system.

3. Assoziation in Many-Component Ionic Fluids.

Let us consider an ionic system consisting of s components $i = 1,2,\ldots s$ with the cluster expansion

$$\beta p = \sum_a z_a + \sum z_a z_b b_{ab} + \sum z_a z_b z_c b_{abc} + \ldots + \sum z_{a_1} \ldots z_{a_\ell} b_{a_1 \ldots a_\ell} + \ldots \qquad (3.1)$$

If a cluster coefficient contains a big positive contribution caused by attracting forces $b^*_{a_1 \ldots a_\ell}$ we shall interpret the expression

$$z^*_\ell = z^*_{a_1 \ldots a_\ell} = \gamma_{a_1 \ldots a_\ell} b^*_{a_1 \ldots a_\ell} z_{a_1} \ldots z_{a_\ell} \qquad (3.2)$$

as the fugacity of the corresponding complex[4]. Here $\gamma_{a_1 \ldots a_\ell}$ is the number of different permutations corresponding to the same composition, e.g. $\gamma_{ab} = 1$ if a = b and $\gamma_{ab} = 2$ if $a \neq b$. Assume that there are t kinds of complex species with densities n_ℓ^* charges e_ℓ^* and effective radii R_ℓ^*. If ν_i^ℓ denotes the number of particles of kind i in the complex ℓ we have the relations

$$n_i = n_i^* + \sum_{\ell=s+1}^{t} \nu_i^\ell n_\ell^* \tag{3.3}$$

$$\sum_{i=1}^{s} n_i^* e_i + \sum_{\ell=s+1}^{t} n_\ell^* e_\ell^* = 0 \tag{3.4}$$

$$(R_\ell^*)^3 = f \cdot \sum_{i=1}^{s} \nu_i^\ell R_i^3 \tag{3.5}$$

where n_i^* are the densities of free ions, R_i their effective radii and f certain factor $f > 1$ which takes into account the incomplete filling of the space by spheres. Now we choose as the reference system a chemical model including mass action equilibrium between the complexes and the free particles and interaction terms described by the mean spherical approximation[9]. Assume that the free energy of the reference system is given by

$$-\frac{\beta}{V} A'(n_k^*, V, T) = \sum_{i=1}^{s} n_i^* \left[1 + \ln \frac{1}{n_i^* \Lambda_i^3} \right] + \sum_{\ell=s+1}^{t} n_\ell^* \left[1 + \ln \frac{K_\ell(T)}{n_\ell^* \Lambda_\ell^{*3}} \right] - \frac{\beta}{V} A_{ex}^{MSA}(n_k^*, V, T) \tag{3.6}$$

where A_{ex}^{MSA} is the known MSA-expression for the excess free energy of a system of hard charged spheres which is for sym - metrical systems of the form

$$A_{ex}^{MSA} = -\frac{1}{12\pi R^3}\left[6x + 3x^2 + 2 - 2(1+2x)^{3/2}\right]$$

$$x = R(8\pi\beta n e^2)^{1/2} \tag{3.7}$$

Furtheron the mass action constant K_ℓ and the thermal wave length Λ_ℓ^* are defined by

$$K_\ell(T) = \gamma_{a_1 \ldots a_\ell} b^*_{a_1 \ldots a_\ell}(T) \; ; \; \Lambda_\ell^* = \prod_{i=1}^{s} \Lambda_i^{\nu_i^\ell} \tag{3.8}$$

Using these expressions we find the set of particle numbers $n_1^* \ldots n_t^*$ by minimizing of A with respect to changes of n_k^* taking into account the balance relations (3.3). Now we define fugacities by

$$z_k^* = n_k^* \exp\left[\frac{\partial}{\partial n_k^*}\left(\frac{\beta}{V} A_{ex}^{MSA}\right)\right] \qquad k = 1, \ldots, t+s \tag{3.9}$$

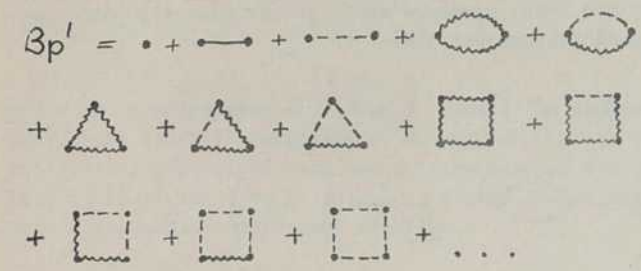
Note that consistency requires

$$z_k^* = z_k \quad \text{if} \quad k = 1, 2, \ldots, s \tag{3.10}$$

and the relations (3.2) if $k = s+1, \ldots, s+t$. The equations (3.2) may be considered as mass action laws for the complex formation. The pressure of the reference system follows from

$$\beta p'(n_1^*, \ldots, n_{s+t}^*, T) = -\left(\partial A / \partial V\right)_T$$
$$= \sum_{k=1}^{s+t} n_k^* - \left(\partial F_{ex}^{MSA} / \partial V\right)_T \tag{3.11}$$

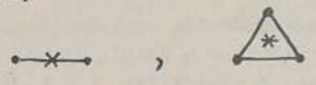
These expressions define a certain set of diagrams. In the density representation we have for the reference system



(3.12)

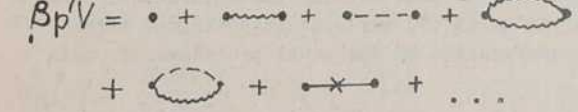
Here the way lines correspond to Coulomb interactions outside the hard core and optimized interactions inside (Φ - bonds in the sense of Andersen and Chandler[8]) The dashed lines correspond to hard core Mayer bonds. The black circles are affected with n_k^* - factors.

In the fugacity representation we find the same diagrams including additionally all the reducible combinations and with z_k^* - factors at the nodes. Similar as in part 2 we may introduce now instead of the z_k^* - circles star-bonds corresponding to eqs.(3.2)



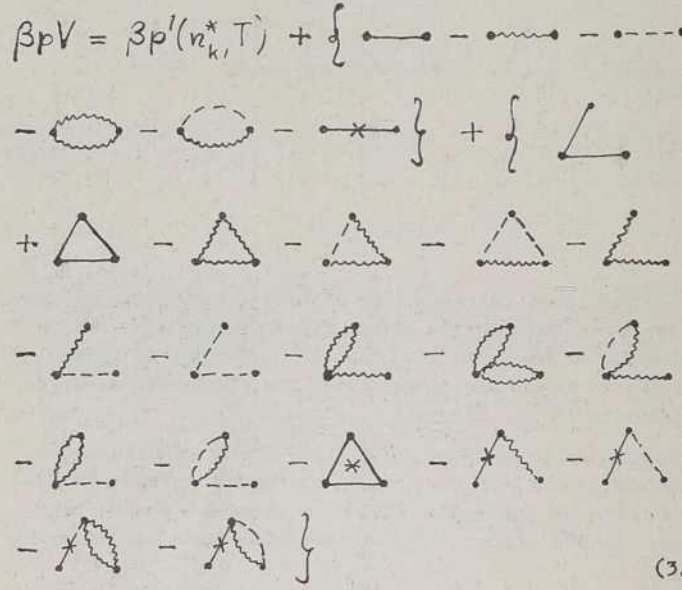
(3.13)

Therefore we find the graphical expansion in terms of the original fugacities



(3.14)

Now we are able to write down the graphical expression for the remainding terms by subtracting eq.(3.14) from eq.(3.1). It follows for the total pressure which is the sum of p' and these remainding contributions



(3.15)

Here the black circles correspond to the original fugacities which may be calculated from eqs.(3.9 - 3.10). Clearly the star-bonds in eq.(3.15), i.e. the choice for K_2, K_3 etc., can be adjusted to cancel as much diagrams as possible. Especially the second-order contribution can always made to be zero. This is a kind of optimization of the reference system by choosing appropriate values for the mass action constants. Clearly the diagram expansion in eq.(3.15) may contain divergent terms which are to be renormalized by the usual procedure of chain

summations[1]. Therefore the final result will have the form

$$\beta p = \beta p'(n_k^*, T) + \sum_{ab} z_a z_b \tilde{b}''_{ab} + \sum_{abc} z_a z_b z_c \tilde{b}''_{abc} + \dots \qquad (3.16)$$

where the coefficients $\tilde{b}''_{ab}$, $\tilde{b}''_{abc}$ denote the renormalized convergent cluster coefficients. In contradiction to the common density expansions were one screens usually all the Coulomb lines it seems to be useful to screen in the fugacity expansion only the divergent diagrams.

4. The Distribution Functions.

The unspecified pair distribution functions for our system may be obtained by functional differentiation of thermodynamic potentials. Due to our assumption $p = p' + p''$ the pair distribution function consist of two parts

$$n_{ab}(r) = n'_{ab}(r) + n''_{ab}(r) \qquad (4.1)$$

where the first part corresponds to the reference system. By functional differentiation of eq.(3.6) follows

$$n'_{ab}(r) = \frac{\delta A'}{\delta(-\beta u^*_{ab})} = \frac{n^*_{ab}}{b^*_{ab}} \frac{\delta b^*_{ab}}{\delta(-\beta u^*_{ab})} + \sum_c \frac{n^*_{abc}}{b^*_{abc}} \frac{\delta b^*_{abc}}{\delta(-\beta u^*_{ab})} + \dots + n^{MSA}_{ab}(r) \qquad (4.2)$$

where u^*_{ab} denotes the short range part of the interactions, n^*_{ab} the density of (ab)-complexes, n^*_{abc} the density of (abc)-complexes etc. and $n^{MSA}_{ab}(r)$ the MSA-expression for the p.d.f.. The second part of the p.d.f. we calculate by functional differentiation of eq.(3.16)

$$n''_{ab}(r) = \frac{\delta(\beta p'')}{\delta(-\beta u^*_{ab})} = z_a z_b \frac{\delta \tilde{b}''_{ab}}{\delta(-\beta u^*_{ab})} + z_a z_b \sum_c z_c \frac{\delta \tilde{b}''_{abc}}{\delta(-\beta u^*_{ab})} + \dots \qquad (4.3)$$

Therefore the final result is

$$n_{\alpha\beta}(r) = n_\alpha^* n_\beta^* g_{\alpha\beta}^{PY}(r) + n_\alpha^* n_\beta^* C_{\alpha\beta}^{PY}(r)$$

$$+ \left(\frac{n_{\alpha\beta}^*}{b_{\alpha\beta}^*} \frac{\partial b_{\alpha\beta}^*}{\partial(-\beta u_{\alpha\beta}^*)} + z_\alpha z_\beta \frac{\partial \tilde{b}_{\alpha\beta}''}{\partial(-\beta u_{\alpha\beta}^*)} \right)$$

$$+ \left(\sum_\gamma \frac{n_{\alpha\beta\gamma}^*}{b_{\alpha\beta\gamma}^*} \frac{\partial b_{\alpha\beta\gamma}}{\partial(-\beta u_{\alpha\beta\gamma}^*)} + z_\alpha z_\beta \sum_\gamma z_\gamma \frac{\partial b_{\alpha\beta\gamma}^*}{\partial(-\beta u_{\alpha\beta\gamma}^*)} \right) + \ldots \qquad (4.4)$$

Here $g_{\alpha\beta}^{PY}$ denotes the Percus-Yevick expression for the hard sphere reference system and $C_{\alpha\beta}^{PY}$ the generalized chain sum evaluation using the PY-approximation for the short range bonds and using a perturbation inside the core that makes

$$C_{\alpha\beta}^{PY}(r) = 0 \quad \text{if} \quad r < (R_\alpha + R_\beta) \qquad (4.5)$$

This optimization procedure was discussed e.g. by Andersen and Chandler[9].

5. Ion Association in the Primitive Model.

Consider of charged hard spheres with the diameters a. Three kinds of ion complexes will be considered:

(1) ion pairs (+ −)

(2) ion triples (+ − +) and (− + −)

For simplicity we shall assume here that in the reference system the complexes have also the diameters a . Then the free energy and the pressure of the reference system reads

$$-\frac{\beta}{V}A' = n_+^*\left[1+\ln\frac{1}{n_+^*\Lambda_+^3}\right]+n_-^*\left[1+\ln\frac{1}{n_-^*\Lambda_-^3}\right]$$

$$+n_{+-}^*\left[1+\ln\frac{K_{+-}}{n_{+-}^*\Lambda_+^3\Lambda_-^3}\right]+n_{+-+}^*\left[1+\ln\frac{K_{+-+}}{n_{+-+}^*\Lambda_+^6\Lambda_-^3}\right]$$

$$+n_{-+-}^*\left[1+\ln\frac{K_{-+-}}{n_{-+-}^*\Lambda_-^6\Lambda_+^3}\right]+\frac{(\varkappa^*)^3}{12\pi}\tau(\varkappa^*a) \qquad (5.1)$$

$$\beta p' = \left(n_+^*+n_-^*+n_{+-}^*+n_{+-+}^*+n_{-+-}^*\right)\frac{(1+y+y^2-y^3)}{(1-y)^3}$$

$$-\frac{(\varkappa^*)^3}{24\pi}\varphi(\varkappa^*a) \qquad (5.2)$$

$$\varkappa^* = 4\pi\beta e^2\left(n_+^*+n_-^*+n_{+-+}^*+n_{-+-}^*\right)/D_0 \qquad (5.3)$$

where

$$y = \frac{1}{6}\pi a^3\left(n_+^*+n_-^*+n_{+-+}^*+n_{-+-}^*+n_{+-}^*\right) \qquad (5.4)$$

The concentrations n_k^* are found by minimization of the free energy under the constraint

$$n_+ = n_- = n_+^* + n_{+-}^* + 2n_{+-+}^* + n_{-+-}^* \tag{5.5}$$

Here we may use the symmetry condition

$$n_+^* = n_-^* \quad ; \quad n_{+-+}^* = n_{-+-}^* \tag{5.6}$$

The optimal choice for the dimerization constant is

$$K_{+-}(T) = 2b_{+-}^* = \int d^3r\, e^{-\beta u_{+-}^*} \left(e^{\ell/r} + e^{-\ell/r} - 2 - \frac{\ell^2}{r^2} \right)$$

$$= 8\pi a^3 \sum_{m=2}^{\infty} \frac{\xi^{2m}}{(2m)!(2m-3)} \tag{5.7}$$

$$\ell = \frac{e^2}{D_0 kT} \quad ; \quad \xi = \frac{e^2}{D_0 kTa} \tag{5.8}$$

This is exactly the choice which makes the second order contributions $O(z^2)$ to p'' to zero and therefore one has at least

$$p'' = O(z^{5/2}) \tag{5.9}$$

The mass action constant (5.7) was already used in earlier papers[11] based on more intuitive arguments.

For Coulomb systems there is no possibility to make the higher order contributions also exactly to zero by an appropriate choice of the trimerization constant. Therefore all what we can do, is to make the contribution of the third order integrals as small as possible. A reasonable choice seems to be

$$K_{abc} = \frac{1}{2!V} \int d^3r_1 d^3r_2 d^3r_3 \exp\left[-\beta u_{aa}^*(12) - \beta u_{ab}^*(13) - \beta u_{ab}^*(23) \right]$$

$$\cdot \exp\left[-\ell_{aa}/r_{12}\right]\cdot\left\{\left(e^{\ell_{ab}/r_{13}}-1-\frac{\ell_{ab}}{r_{13}}-\frac{\ell_{ab}^2}{2r_{13}^2}\right)\right.$$

$$\cdot\left(e^{\ell_{ab}/r_{13}}-1-\frac{\ell_{ab}}{r_{23}}-\frac{\ell_{ab}^2}{2r_{23}^2}\right)+\left(e^{-\ell_{ab}/r_{13}}-1+\frac{\ell_{ab}}{r_{13}}-\frac{\ell_{ab}^2}{2r_{13}^2}\right)$$

$$\left.\cdot\left(e^{-\ell_{ab}/r_{23}}-1+\frac{\ell_{ab}}{r_{23}}-\frac{\ell_{ab}^2}{2r_{23}^2}\right)\right\} \qquad (5.10)$$

where $b \neq a$ i.e. we have the configurations $(- + -)$ or $(+ - +)$. The asymptotic expression for this integral is given by[10]

$$K_{aba} = 8\pi^2 R_{ab}^6 \frac{\exp\left[(2\ell_{ab}/R_{ab})+(\ell_{aa}/2R_{ab})\right]}{(-\ell_{aa}/2R_{ab})\left[(\ell_{ab}/R_{ab})+(\ell_{aa}/2R_{ab})\right]} \qquad (5.11)$$

In order to check these formulae the pressure has been calculated from eqs.(5.1-5.8) neglecting the trimer formation. The resulting system of equations is up to the different treatment of the hard core contribution identical to the MSA-MAL-theory by Ebeling and Grigo[5]. For a model 2-2-electrolyte with d = 4.2 A° the result of explicite calculations is in very good agreement with the HNC-calculations by Rasaiah ; the deviations are in the whole region $c < 2$ M smaller than 3% (see Fig.1). Therefore we may conclude that

the representation given here yields a reasonable description of associating electrolytes. A continuation of this work is in preparation /12/.

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Anschrift der Verfasser

Prof.Dr. Harold L. Friedman
Department of Chemistry
State University of New York
Stony Brook, N.Y. 11794, U S A

Prof. Dr. habil.rer.nat. Werner Ebeling
Wilhelm-Pieck-Universität Rostock
Sektion Physik
DDR - 25 Rostock
Universitätsplatz 3

W. Ebeling and H. Krienke

Statistical Thermodynamics and Conductance of Strong Electrolytes with Exponential Interaction Potential

Abstract

Some formulae for equilibrium and transport excess properties of electrolytes on the MMM-level are developed, based on more realistic solvent-averaged ionic interaction potentials especially in the region of cosphere overlapping. For several 1-1 aqueous ionic solutions the parameters of specific ionic interactions for two potential models are given, consisting of a hard core part and combination of Yukawa-terms.

1. Introduction

In recent years several models were used for the description of the potentials of mean forces between ions in solution /1-5/. They mostly propose an more or less hard core for the Pauli-exclusion region of the interaction of the ions, and an adjustable functional form in the overlapping region of the first solvation shells around the ions where very little is known about the exact form of interionic interactions up to now. To this class belonges e.g. the step potential

$$\psi_{ab} = \begin{cases} \infty & ; \; r < R_a + R_b \\ h_{ab} & ; \; R_a + R_b \leq r < R_a + R_b + d \\ \frac{e_a e_b}{D_0 r} & ; \; r \geq R_a + R_b + d \end{cases} \qquad (1)$$

(R_a, R_b - crystallographic radii of the ions, d - diameter of a solvent molecule).

For this potential thermodynamics as well as transport properties were calculated recently /4,5,8/. A disadvantage of the step potential are unrealistic edges or jumps at distances $r = (R_a+R_b)$ and $r = (R_a+R_b+d)$. In order to avoid this difficulty we shall develope here the first approximation to a statistical theory for exponential potentials of the following type

$$\psi_{ab} = V'_{ab} + V_{ab} \qquad (2)$$

where $$V'_{ab} = \begin{cases} \infty & ; \quad r \le (R_a + R_b) \\ 0 & ; \quad r > (R_a + R_b) \end{cases}$$

and $$V_{ab} = \frac{e_a e_b}{D_0 r} + B_{ab} \frac{(R_a + R_b + d)}{r} \exp\left(-\frac{r}{R_a + R_b + d}\right) \qquad (3)$$

or in another variant

$$V_{ab} = \frac{e_a e_b}{D_0 r}\left(1 - e^{-\alpha r}\right) + A_{ab} \frac{1}{r\gamma}\left(e^{-\gamma r} - e^{-\alpha r}\right) \qquad (4)$$

The parameters α and γ may be correlated with the thickness of the solvation shell (Gurney-cosphere), for instance we will make the choice

$$\alpha = \frac{2}{d} \quad ; \quad \gamma = \frac{1}{2d} \qquad (5)$$

Both variants are rather equivalent with respect to their behaviour for $r > (R_a + R_b)$. An advantage of the variant (4) is the nonsingular behaviour in the point r=0 which gives rise to rather shortrange Fourier transforms $V_{ab}(k)$. In Fig. 1 we present the shape of the potential for parameters which should correspond to KCl-solutions (see Tab.1)/3/

$$\begin{aligned} B_{KCl} &= 0.30 & A_{KCl} &= 0.27 \\ B_{KK} &= -0.84 & A_{KK} &= -0.78 \\ B_{ClCl} &= -0.03 & A_{ClCl} &= 0.04 \end{aligned} \qquad (6)$$

2. Pairdistribution functions and thermodynamic potentials in equilibrium

For the class of fouriertransformable potentials discussed here it seems to be of advantage to use the standard method of cluster expansions for the pairdistribution function (p.d.f.) /6/. Defining the first order correlation function g_{ab} as the solution of the screening integral equation for the non hard core part of ψ_{ab} :

$$g_{ab}(1,2) + \beta V_{ab}(1,2) + \beta \sum_c \eta_c \int V_{ac}(1,3)\, g_{bc}(2,3)\, d3 = 0 \qquad (7)$$

we find in the low density regime for the p.d.f. the cluster expansion $F^{o}_{ab}(r) = e^{g_{ab} - \beta V'_{ab}} \{1 + \sum_c n_c \int d3 \left((e^{g_{ac} - \beta V'_{ac}} - 1) \cdot (e^{g_{bc} - \beta V'_{bc}} - 1) - g_{ac} g_{bc} \right) + \dots \}$ (8)

(V'_{ab} is the hard core potential).

For higher densities another expansion with the full hard core p.d.f. F^{HC}_{ab} as reference p.d.f. may be useful. We can start from an perturbation expansion of the excess free energy (see e.g. /9/)

$$F^{ex} = F^{M} + F^{D} - kT (B_2 + B_3 + \dots) \tag{9}$$

$$F^{M} = \frac{1}{2} \sum_{a,b} \frac{N_a N_b}{\vartheta} \int V^{C}_{ab} (F^{HC}_{ab}(r) - 1) \, d\vec{r} \quad ; \quad V^{C}_{ab} = \frac{e_a e_b}{D_0 r} \tag{10}$$

and

$$F^{D} = \frac{1}{2} \sum_{a,b} \frac{N_a N_b}{\vartheta} \int d\vec{r} \int_0^{e^2} de^2 \left(\frac{\partial V^{C}_{ab}}{\partial e^2} \right) g_{ab} \tag{11}$$

are mean field and modified Debye-terms, respectively, and from the higher order virial coefficients B_2 has the structure

$$B_2 = \frac{1}{2} \sum_{a,b}' \frac{N_a N_b}{\vartheta} \int \left\{ F^{HC}_{ab} \left(e^{g_{ab}} - 1 - g_{ab} - \frac{1}{2} g^2_{ab} \right) + \frac{1}{2} g^2_{ab} (F^{HC}_{ab} - 1) \right\} d\vec{r} \tag{12}$$

Functional differentiation of (9) with respect to the potentials V_{ab} gives us the p.d.f. F^{o}_{ab} . In a first approximation we get /9/:

$$F^{o}_{ab}(r) = F^{HC}_{ab} e^{g_{ab}} \tag{13}$$

Possible is also another choice of the reference system: the inclusion of the coulombic part of V_{ab} in $\dot{a}$. In this case the reference p.d.f. will be that of hard charged spheres, which may be approximated by its MSA variant (at least for electrolytes in the low Bjerrum-parameter regime). We can follow the lines of thermodynamic perturbation theory /10/ and put

$$\frac{F^{ex}}{NkT} = \bar{F} = \bar{F}^{MSA} - \frac{1}{2} n \sum_{a,b} x_a x_b \int F^{MSA}_{ab}(1,2) e_{ab}(1,2) d1 d2 + \dots \quad ; \left(x_a = \frac{N_a}{N} \right) \tag{14}$$

contains in a proper form the perturbation part of the potential, e.g.

$$e_{ab} = -\beta \bar{V}_{ab}(r) \quad \text{or} \quad e_{ab} = e^{-\beta \bar{V}_{ab}(r)} - 1 \tag{15}$$

The equilibrium p.d.f. Which corresponds to this approximation we may construct as

$$F^{\circ}_{ab} = F^{MSA}_{ab}\, e^{-\beta \bar{V}_{ab}} \quad \text{or on the basis} \tag{16}$$

of a definition of a renormalized perturbation potential as in mode-expansion-theories [11] as

$$F^{\circ}_{ab} = F^{MSA}_{ab}\, e^{\bar{g}_{ab}} \tag{17}$$

where $\bar{g}_{ab}$ is the solution of (7) for the potential

$$\bar{V}_{ab} = V_{ab} - V^{C}_{ab}$$

The solution of eq.(7) may be easily found by the Fourier-transformation technique. We follow in this direction earlier work of Kelbg [12]. In general the correlation function is connected with the screened potential $\widetilde{V}_{ab}$ by $g_{ab} = -\beta \widetilde{V}_{ab}$

We note that the Fourier-transforms of the potentials (3) and (4) are given by

$$\hat{V}_{ab}(k) = \frac{4\pi e_a e_b}{k^2} + B_{ab} \frac{4\pi (R_a + R_b + d)^3}{1 + k^2 (R_a + R_b + d)^2} \tag{18}$$

resp.

$$\hat{V}_{ab}(k) = \frac{1}{k^2 + \alpha^2} \left\{ \frac{4\pi e_a e_b \alpha^2}{D_0 k^2} + A_{ab} \frac{4\pi}{\gamma} \frac{(\alpha^2 - \gamma^2)}{(k^2 + \gamma^2)} \right\} \tag{19}$$

Transforming eq.(7) into the Fourier-space and defining matrices C and H with elements

$$C_{ab}(k) = \sqrt{n_a n_b}\, \beta \hat{V}_{ab}(k) \quad ; \quad H_{ab}(k) = \sqrt{n_a n_b}\, \beta \hat{g}_{ab}(k) \tag{20}$$

we can solve the resulting algebraic matrix equation to

$$H = C * \{ I + C \}^{-1} \tag{21}$$

($*$ denotes a convolution and $\{\}^{-1}$ the inverse of a matrix).

For potentials of typ (18) and (19) the Fourier-transforms $H_{ab}(k)$ are rational functions of k^2, i.e. quotients of poly-

noms of k^2. We find

$$H_{ab} = \frac{Q_{ab}(k^2}{P(k^2)} \quad , \qquad (22)$$

$$P(k^2) = \sum_{\ell=0}^{5} P_\ell \, k^{2\ell}$$

in both cases.

For two-component electrolytes (a,b=1,2) we find for B-type potentials (19):

$$P_0 = \varkappa^2 \alpha_{12}^4 \alpha_{11}^2 \alpha_{22}^2 + \alpha_{12}^4 (\alpha_{11}^2 \varkappa_1^2 \bar{B}_{22} + \varkappa_{22}^2 \varkappa_2^2 \bar{B}_{11}) -$$
$$2\alpha_{12}^2 \alpha_{11}^2 \alpha_{22}^2 \varkappa_1 \varkappa_2 \bar{B}_{12}$$

$$P_1 = \alpha_{11}^2 \alpha_{22}^2 \alpha_{12}^4 + \varkappa^2 (\alpha_{12}^4 (\alpha_{11}^2 + \alpha_{22}^2) + 2\alpha_{12}^2 \alpha_{11}^2 \alpha_{22}^2) + \alpha_{12}^4 (\alpha_{11}^2 \bar{B}_{22} +$$
$$\alpha_{22}^2 \bar{B}_{11}) + \alpha_{12}^4 (\varkappa_1^2 + \bar{B}_{11})(\varkappa_2^2 + \bar{B}_{22}) - \alpha_{11}^2 \alpha_{22}^2 (\varkappa_1 \varkappa_2 + \bar{B}_{12})^2$$

$$P_2 = (\alpha_{11}^2 + \alpha_{22}^2) \alpha_{12}^4 + 2\alpha_{12}^2 \alpha_{11}^2 \alpha_{22}^2 + \varkappa^2 (\alpha_{11}^2 \alpha_{22}^2 + 2\alpha_{12}^2 (\alpha_{11}^2 + \alpha_{22}^2) + \alpha_{12}^4) +$$
$$\bar{B}_{11} (\alpha_{12}^4 + 2\alpha_{12}^2 \alpha_{22}^2) + \bar{B}_{22} (\alpha_{12}^4 + 2\alpha_{12}^2 \alpha_{11}^2) + \bar{B}_{11} \varkappa_1^2 (\alpha_{22}^2 + 2\alpha_{12}^2) +$$
$$\bar{B}_{22} \varkappa_2^2 (\alpha_{11}^2 + 2\alpha_{12}^2) - 2\bar{B}_{12} \varkappa_1 \varkappa_2 (\alpha_{11}^2 + \alpha_{22}^2 + \alpha_{12}^2) + 2\alpha_{12}^2 \bar{B}_{11} \bar{B}_{22} -$$
$$(\alpha_{11}^2 + \alpha_{22}^2) \bar{B}_{12}^2$$

$$P_3 = \alpha_{11}^2 \alpha_{22}^2 + \alpha_{12}^4 + (\varkappa^2 + \bar{B}_{11} + \bar{B}_{22})(\alpha_{11}^2 + \alpha_{22}^2 + 2\alpha_{12}^2) +$$
$$(\varkappa_1^2 + \bar{B}_{11})(\varkappa_2^2 + \bar{B}_{22}) - (\varkappa_1 \varkappa_2 + \bar{B}_{12})^2 \qquad (23)$$

$$P_4 = \alpha_{11}^2 + \alpha_{22}^2 + 2\alpha_{12}^2 + \varkappa^2 + \bar{B}_{11} + \bar{B}_{22} \quad , \quad P_5 = 1$$

$$\varkappa_a^2 = \frac{4\pi n_a e_a^2}{D_0 kT} \quad ; \quad \varkappa^2 = \varkappa_1^2 + \varkappa_2^2 \quad ; \quad \alpha_{ab} = (R_a + R_b + d)^{-1}$$

$$\bar{B}_{ab} = \frac{4\pi \sqrt{n_a n_b}\, B_{ab}}{kT \, \alpha_{ab}}$$

For A-type potentials we have:

$$P_0 = \alpha^2\alpha^4\gamma^4 + (\alpha_1^2\bar{A}_{11} + \alpha_2^2\bar{A}_{22} - 2\alpha_1\alpha_2\bar{A}_{12})(\alpha^2-\gamma^2)\alpha^2\gamma^2$$

$$P_1 = \alpha^4\gamma^4 + \alpha^2\alpha^2\gamma^2(\alpha^2+\gamma^2) + (\alpha^2\alpha^2 + (\bar{A}_{11}-\bar{A}_{22}))(\alpha^2-\gamma^2)\alpha^2\gamma^2 + (\alpha_1^2\bar{A}_{11} + \alpha_2^2\bar{A}_{22} - 2\alpha_1\alpha_2\bar{A}_{12})\alpha^2(\alpha^2-\gamma^2) + (\bar{A}_{11}^2 + \bar{A}_{22}^2 - 2\bar{A}_{12}^2)(\alpha^2-\gamma^2)^2$$

$$P_2 = 2(\alpha^2\gamma^4 + \gamma^2\alpha^4) + \alpha^2\alpha^2\gamma^2 + (\alpha^2\alpha^2 + (\bar{A}_{11}-\bar{A}_{22})(\alpha^2-\gamma^2))(\alpha^2+\gamma^2)$$

$$P_3 = 4\alpha^2\gamma^2 + \alpha^4 + \gamma^4 + \alpha^2\alpha^2 + (\bar{A}_{11}-\bar{A}_{22})(\alpha^2-\gamma^2)$$

$$P_4 = 2(\alpha^2+\gamma^2) \quad , \quad P_5 = 1$$

$$\bar{A}_{ab} = \frac{4\pi\sqrt{n_a n_b}\, A_{ab}}{kT\gamma}$$

(24)

The Q_{ab}-polynomials are:

$$Q_{12}(k^2) = (\alpha_{12}^2\alpha_1\alpha_2 + k^2(\alpha_1\alpha_2 + \bar{B}_{12}))(\alpha_{11}^2+k^2)(\alpha_{22}^2+k^2)(\alpha_{12}^2+k^2)$$

$$Q_{11}(k^2) = (\alpha_{11}^2\alpha_1^2 + k^2(\alpha_1^2+\bar{B}_{11}))(\alpha_{11}^2+k^2)(\alpha_{12}^2+k^2)^2 + k^{-2}\{(\alpha_1^2\alpha_{11}^2 + k^2(\alpha_1^2+\bar{B}_{11}))\cdot(\alpha_2^2\alpha_{22}^2 + k^2(\alpha_2^2+\bar{B}_{22}))(\alpha_{12}^2+k^2)^2 - (\alpha_1\alpha_2\alpha_{12}^2 + k^2(\alpha_1\alpha_2+\bar{B}_{12}))^2\cdot(\alpha_{11}^2+\bar{B}_{11})(\alpha_{22}^2+\bar{B}_{22})\} \qquad (25)$$

respective

$$Q_{12}(k^2) = (\alpha_1\alpha_2\alpha^2(k^2+\gamma^2) + \bar{A}_{12}(\alpha^2-\gamma^2)k^2)(k^2+\alpha^2)(k^2+\gamma^2)$$

$$Q_{11}(k^2) = (\alpha_1^2\alpha^2(k^2+\gamma^2) + \bar{A}_{11}(\alpha^2-\gamma^2)k^2)(k^2+\alpha^2)(k^2+\gamma^2) + (\alpha_1^2\bar{A}_{11} + \alpha_2^2\bar{A}_{22} - 2\alpha_1\alpha_2\bar{A}_{12})\alpha^2(k^2+\gamma^2)(\alpha^2-\gamma^2) + (\bar{A}_{11}^2 + \bar{A}_{12}^2 - 2\bar{A}_{12}^2)(\alpha^2-\gamma^2)k^2 \qquad (26)$$

for A-type according to eq.(19).

The back transform may be performed to give

$$\sqrt{n_a n_b}\,\tau + g_{ab}(r) = \int_0^\infty k\, H_{ab}(k) \sin(rk)\, dk = \pi \sum_\ell \tau_{ab}^{(\ell)} \qquad (27)$$

$\sum_\ell \tau_{ab}^{(\ell)}$ is the sum over the residues of

$$f(z) = \frac{z\, Q_{ab}(z^2)}{P(z^2)}\, e^{izr} \qquad (28)$$

in the upper half-plane. $f(z)$ must be regular on the positive real axis. If all poles of $f(z)$ are simple, the residuum $\tau_{ab}^{(\ell)}$ is given by

$$\tau_{ab}^{(\ell)} = \frac{Q_{ab}(z_\ell^2)\, e^{izr_\ell}}{2 \prod_{k,\, k\neq\ell} (z_\ell^2 - z_k^2)} \qquad (29)$$

with

$$P(z_\ell^2) = P(z_k^2) = 0 \qquad (30)$$

In the low density limit with nearly equal radii we can prove that the z_ℓ are all on the imaginary axis, so that

$$g_{ab}(r) = \sum_{k=1}^{5} C_{ab}^{(k)}(s_k)\, \frac{\exp(-s_k r)}{r} \qquad (31)$$

with

$$C_{ab}^{(k)}(s_k) = \frac{(is_k)\, Q_{ab}\left((is_k)^2\right)}{\sqrt{n_a n_b}\, P'\left((is_k)^2\right)} \quad ; \; s_k > 0 \qquad (32)$$

3. Pair distribution function in nonequilibrium and conductance

If an external field E is applied to the electrolyte the p.d.f. is disturbed

$$F_{ab} = F_{ab}^{0} + F_{ab}^{1} \qquad (33)$$

Following other papers /5,7/ we represent the perturbation in the following way

$$F_{ab}^{1} = F_{ab}^{0}\left[\rho_{ab}^{1} + g_{ab}^{1}\right] \qquad (34)$$

where f_{ab}^{1} is defined as the solution of

$$\Delta f_{ab}^{1} + \nabla g_{ab} \cdot \nabla f_{ab}^{1} = \mu_{ab}\left(\vec{E}/E\right) \cdot \nabla g_{ab} \tag{35}$$

with

$$\mu_{ab} = \beta\left(e_a w_a^{\,b} - e_b w_b^{\,a}\right); \quad w_a^{\,b} = \frac{1}{\varrho_a}\left(\frac{1}{\varrho_a} + \frac{1}{\varrho_b}\right)^{-1} \tag{36}$$

(ϱ_a, ϱ_b - friction coefficients).

Neglecting the nonlinear terms and introducing the expression (31) we get the d.e.

$$\Delta f_{ab}^{1} = \mu_{ab}\left(\vec{E}/E\right) \cdot \nabla\left[\sum_{k=1}^{5} C_{ab}^{(k)}(s_k) \frac{\exp\left(-s_k \tau\right)}{\tau}\right] \tag{37}$$

The solution is easily found to be

$$f_{ab}^{1} = \mu_{ab}\left(\vec{E}/E\right) \cdot \nabla\left[\sum_{k=1}^{5} C_{ab}^{(k)}(s_k) \frac{\left(\exp\left(-s_k \tau\right) - 1\right)}{s_k^{2} \tau}\right] \tag{38}$$

For the function g_{ab}^{1} holds in certain approximation /5/

$$\Delta g_{ab}^{1} = q \varkappa^{2} F_{ab}^{\,0}\left[f_{ab}^{1} + g_{ab}\right] \tag{39}$$

Strictly speaking we have neglected here the influence of short-range forces on g_{ab}^{1}. In the linear approximation $F_{ab}^{\,0}$ may be replaced by one and we find the d.e.

$$\left(\Delta - q\varkappa^{2}\right) g_{ab}^{1} = \frac{\varkappa^{2}}{2} \mu_{ab}\left(\vec{E}/E\right) \cdot \nabla\left[\sum_{k} C_{ab}^{(k)}(s_k) \frac{\left(\exp\left(-s_k \tau\right) - 1\right)}{s_k^{2} \tau}\right] \tag{40}$$

where $q = 0.5$ for symmetrical electrolytes.

This equation is solved by

$$g_{ab}^{1} = \mu_{ab}\left(\vec{E}/E\right) \cdot \nabla \sum_{k}{}' C_{ab}^{(k)}\left(\frac{q\varkappa^{2}}{\left(s_k^{2} - q\varkappa^{2}\right)} \frac{e^{-s_k \tau}}{s_k^{2} \tau} + \frac{1}{\left(s_k^{2} - q\varkappa^{2}\right)} \frac{e^{-\varkappa r/\sqrt{q}}}{\tau} + \frac{1}{s_k^{2} \tau}\right) \tag{41}$$

Finally the molar conductance may be expressed by the set of formulae

$$\Lambda = \Lambda_0\left(1 + S^{Rel} + S^{Ext} + S^{Int}\right) \tag{42}$$

$$S^{Rel} = \frac{-(n_1\varrho_2 + n_2\varrho_1)}{\varrho_1+\varrho_2}\,\frac{4\pi}{3}\int_0^\infty d\tau\,\tau^2\,\frac{\partial(\beta\psi_{12})}{\partial\tau} = \frac{\partial}{\partial\tau}\Big[\sum_{k=1}^{5} C_{12}^{(k)} \cdot \frac{\exp(-s_k\tau) - \exp(-\tau\varkappa\sqrt{q})}{(s_k^2 - q\varkappa^2)\,\tau}\Big] \qquad (43)$$

$$S^{Ext} = \Big(\frac{e_1}{\varrho_1} - \frac{e_2}{\varrho_2}\Big)^{-1}\big[n_1 e_1 (G_{11} - G_{12}) + n_2 e_2 (G_{22} - G_{21})\big]\,; \quad G_{ab} = \frac{2}{3\eta_0}\int_0^\infty d\tau\,\tau\,F_{ab}^{\circ} \qquad (44)$$

$$S^{Int} = -\Big(\frac{1}{\varrho_1} + \frac{1}{\varrho_2}\Big)^{-1}(n_1 + n_2)\,J_{12} \qquad (45)$$

$$J_{12} = -\frac{1}{3\eta_0}\int_0^\infty d\tau\,\tau\Big[1 - \frac{\varrho_1^2 + \varrho_2^2}{108\,\pi^2\eta_0^2\tau^2}\Big]\frac{\partial F_{12}^{\circ}}{\partial\tau}\,\frac{\partial}{\partial\tau}\sum_k C_{12}^{(k)}\,\frac{\exp(-s_k\tau)}{s_k^2\,\tau} \qquad (46)$$

By means of these formulae the calculation of conductance is reduced to simple integrations.

4. Potential parameters

A calculation of the potential parameters A_{ab} and B_{ab} from first principles is difficult at the present stage of our knowledge on the interionic forces. In order to get an idea about the order of magnitude of these parameters we have calculated here the A_{ab} and B_{ab} from the parameters of the step potential h_{ab} which are known from earlier work. Similar as in the theory of real gases we have assumed that two potentials are equivalent if they include the same area with the x-axis. Therefore a step potential and an exponential potential are equivalent if

$$\int_{R_a+R_b}^{\infty} dr\,\big(\psi_{ab}^{Step} - V_{ab}^{C}\big) = \int_{R_a+R_b}^{\infty} dr\,\big(\psi_{ab}^{exp} - V_{ab}^{C}\big) \qquad (47)$$

The Coulombic part was subtracted in order to make the integrals convergent. Introducing the formulae (3) or (4) into eq.(47) the B_{ab} and A_{ab}-parameters can be calculated from the h_{ab}. We have used for the alkali halides a weighted mean of

the h_{ab}-parameters from thermodynamic data (factor 2/3) and from conductance data (factor 1/3). For the acids, ammonium salts, nitrates as well as for the tetraalkyl-ammonium salts we have used new results of Paigl and Krienke /8/. All parameters refer to 25°C with the exception of the tetraalkyl-ammonium solutions which correspond to 0°C. In combination with the formulae presented in parts 2-3 of this paper the potential parameter A_{ab} and B_{ab} given in Tab. 1 should fit the thermodynamic and conductance data in the region up to 0.1 M in a reasonable way.

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Anschrift der Verfasser:
Prof. Dr. Werner Ebeling und Dr. Hartmut Krienke
Wilhelm-Pieck-Universität Rostock
Sektion Physik
DDR - 25 Rostock
Universitätsplatz 3

Tab. 1

	FF	ClCl	BrBr	JJ	NO_3NO_3	OH-OH
h_{ab}	0.92	1.44	1.19	1.28	1.02	
B_{ab}	-0.80	-0.03	-0.18	0.00	-0.06	
A_{ab}	-0.74	0.04	0.22	-0.05	-0.13	
HH						
1.30		-0.50+				
-1.67		1.38				
-0.65		1.12				
LiLi						
0.84+		-0.78	-0.53	-0.03	-1.10	-1.77
-1.75+		1.06	1.22	1.58	0.45	0.36
-0.88		0.89	1.11	1.61	0.46	0.21
NaNa						
0.68	-1.20	-1.11	-0.90	-0.92	-1.42	-1.19
-1.42	0.74	0.63	0.75	0.65	0.05	0.68
-2.35	0.54	0.55	0.74	0.70	-0.01	0.52
KK						
0.91	-1.06	-1.30	-1.18	-1.17	-1.58	-1.18
-0.84	0.69	0.30	0.36	0.29	-0.19	0.52
-0.78	0.61	0.27	0.38	0.34	-0.37	0.47
RbRb						
1.94+	-1.08	-1.42	-1.35	-1.42	-1.61	
0.21	0.61	0.14	0.16	0.04	-0.25	
0.35	0.55	0.08	0.13	-0.02	-0.48	
CsCs						
1.54+	-0.99	-1.55	-1.50	-1.51	-1.61	
-0.01	0.61	-0.04	-0.03	-0.10	-0.29	
0.08	0.63	-0.14	-0.13	-0.22	-0.59	
NH_4NH_4						
0.98		-1.33			-1.45	
-0.69		0.24			-0.10	
-0.66		0.21			-0.22	
Me_4NMe_4N						
0.00		-1.25	-1.30	-1.45		
-0.68		-0.14	-0.20	-0.35		
-2.92		-0.44	-1.21	-1.09		

FF	ClCl	BrBr	JJ	NO_3NO_3	OH-OH
Et_4NEt_4N					
0.40	-1.28	-1.40	-1.55		
-0.27	-0.22	-0.34	-0.48		
-1.60	-0.78	-1.18	-1.57		
Pr_4NPr_4N					
0.45	-1.30	-1.44	-1.62		
-0.17	-0.29	-0.42	-0.57		
-1.34	-1.16	-1.68	-2.44		
Bu_4NBu_4N					
0.60	-1.40	-1.44	-1.60		
-0.03	-0.40	-0.45	-0.58		
-0.15	-1.79	-2.05	-2.83		

Tab. 1:
Parameters of specific ionic interactions in aqueous 1-1 electrolyte solutions for different models:
h_{ab} from (1), B_{ab} from (3) and A_{ab} from (4). (in $k\bar{T}$)

The TAA-halides refer to solutions of 0°C, all other to such at 25°C. In hard core R_a are Pauling-radii for alkali- and halide-ions and Robinson-Stokes-radii for TAA-ions. The remaining were taken:

$$R_{OH} = 1.50,\ R_H = 0.45,\ R_{NO_3} = 2.46\ \text{Å}.$$

To estimate the A_{ab} parameters we have taken the choice

$$\alpha = \frac{2}{d} \quad \text{and} \quad \gamma = \frac{1}{2d} \quad \text{with } d = 2.76\ \text{Å}.$$

Values in parentheses are extrapolated.

+) $h_{ab} = \frac{9}{10} h_{ab}(eq) + \frac{1}{10} h_{ab}(neq)$, all other $h_{ab} = \frac{2}{3} h_{ab}(eq) + \frac{1}{3} h_{ab}(neq)$

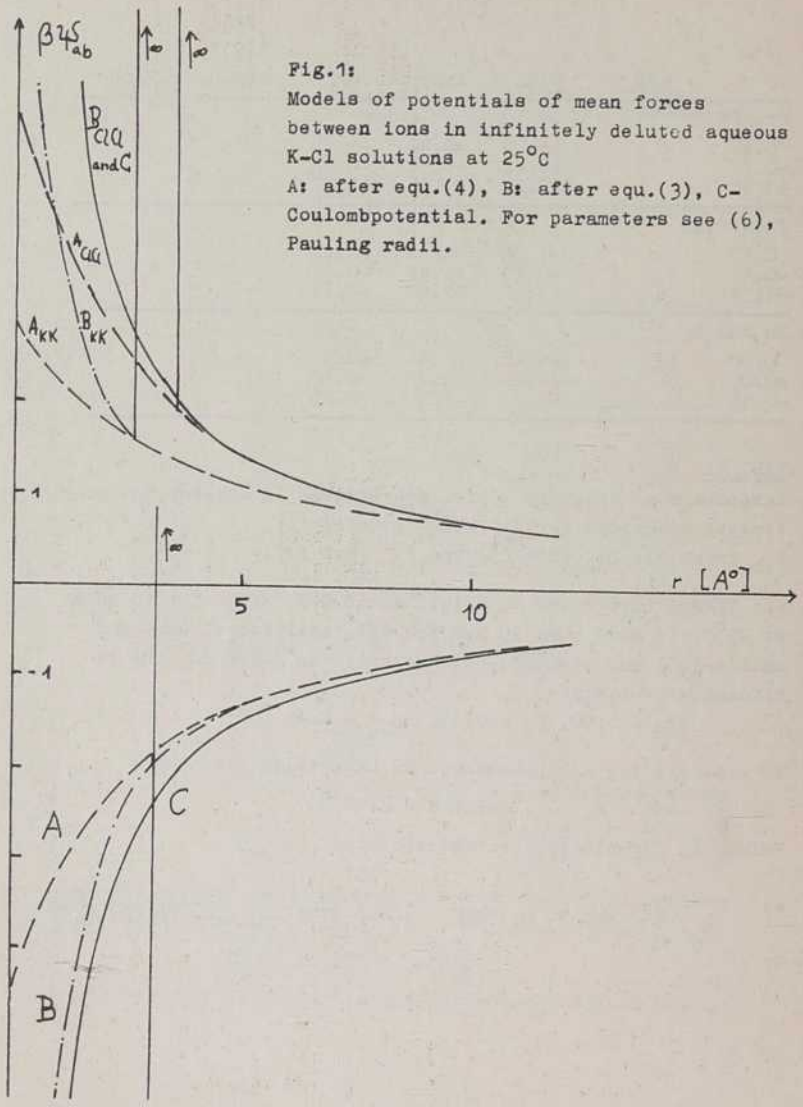

Fig.1:
Models of potentials of mean forces between ions in infinitely deluted aqueous K-Cl solutions at 25°C
A: after equ.(4), B: after equ.(3), C- Coulombpotential. For parameters see (6), Pauling radii.

D. Kremp, U. Lau and W.D. Kraeft

Conductance theory for electrolytes at higher concentration

1. Introduction. Basic equations

One of the most essential tasks in the theory of the electrolytic conductance turns out to be the generalization of previous theories (e.g. of the KKE theory[1]) towards higher concentration ranges[2]. In this paper, we want to propose such an improvement of the theory by introducing a better approximation of the three particle distribution function F_{abc}. -
The starting point for a conductance theory is the current density of the ions

$$j = \sum_a n_a e_a \bar{u}_a = \sigma E .$$

The problem of the statistical theory of the conductivity consists mainly in the derivation of a relation for the calculation of the mean velocity $\bar{u}_a$ of the ions from the external fields and the interactions between the ions. Such a theory is, e.g., the well-known Debye-Onsager-Falkenhagen theory. That theory shows especially that the square root law found experimentally by Kohlrausch has its origin in the long range character of the Coulomb interaction.

Experimental investigations show that at higher concentrations different electrolytes show different deviations from the Kohlrausch behaviour. These individual behaviours are determined by short range interactions, e.g. by the influence of different ionic radii.

The Onsager-Falkenhagen theory is not appropriate to take into account in a systematic way the short range interactions. Only in the simplest case of the hard sphere potential, Kelbg succeded in taking into account these interactions in the theory by boundary conditions. Further progress in the theory of the conductance was achieved on the basis of more rigorous methods of the statistical mechanics. A statistical theory of the conduc-

tance was formulated by Falkenhagen and Ebeling[3] and further developed by Kremp, Kraeft and Ebeling (KKE)[1].

The basic idea is as follows. A system of N_0 neutral particles and N ions is considered under the condition $N_0 >> N$. The state of the ions is then determined by the distribution functions of the ions, $F_N(r^{(N)} p^{(N)})$.

For the determination of F_N, by Klimontovich and Ebeling[4] the so-called stochastic or Brownonian model was developed. In this model, the motion of the ions is combined of the mechanical motion of the ions under the influence of the external forces and the interactions with the ions, which is characterized by the Liouvillean L_N, and of the stochastic motion caused by the collisions between the ions and the neutral solvent particles, which is characterized by the collision operator S_N. The basis of this model is the stochastic Liouville equation

$$\frac{\partial F_N}{\partial t} = L_N F_N + S_N F_N \quad . \tag{1}$$

As a consequence of the high collision frequency, the momentum distribution approaches in a very short time to that of a local Maxwell distribution. For this reason, the basic equations of the transport theory are balance equations in the configuration space, which follow from (1) by hydrodynamic approximations. We use the Falkenhagen-Ebeling transport equations in the following shape

- the equation of motion for the mean velocity

$$\bar{u}_a F_a = \frac{n_a}{\rho_a}\left[e_a E - \sum_b n_b \int dr_b F_{ab}\left\{\frac{\partial \psi_{ab}}{\partial r_a} - \frac{\rho_a u_a^b}{8\pi\eta_0 r}\left(\delta + \frac{\vec{r}\vec{r}}{r^2}\right)\right\}\right] \tag{2}$$

- the equation of continuity for the two particle flux

$$\frac{\partial F_{ab}}{\partial t} + \frac{\partial}{\partial r_a} u_a^b F_{ab} + \frac{\partial}{\partial r_b} u_b^a F_{ba} = 0 \tag{3}$$

- the equation of motion for the two particle flux

$$u_a^b F_{ab} = \frac{1}{\rho_a}\left[e_a E F_{ab} - kT \frac{\partial}{\partial r_a} F_{ab} - F_{ab} \frac{\partial}{\partial r_a} \hat{\phi}_a^b\right] \tag{4}$$

$$\frac{\partial}{\partial r_a}\hat{\Phi}_a^b = \frac{\partial \psi_{ab}}{\partial r_a} - \sum_c n_c \int \frac{\partial}{\partial r_c}\psi_{ac}\,\frac{F_{abc}}{F_{ab}}\,dr_c \,. \qquad (5)$$

Here, as usual, F_a, F_{ab} and F_{abc} are the single, two and three particle distribution functions, U_a^b are the relative velocities, ρ_a are friction constants, ψ_{ab} is the true two particle potential, and $\hat{\Phi}_a^b$ is the effective two particle potential. The Falkenhagen-Ebeling equations (2-5) have a clear physical meaning. They may be interpreted as particle and force balances for the motion of particles in a liquid under the influence of friction forces.

From eq.(2) we see that the two particle distribution function is the key information quantity for the determination of transport properties. This function must be determined from eqs. (3-5). Here we meet the difficulty, which is characteristic of all interacting many particle systems, that F_{ab} is coupled with higher distribution functions. For systems with short range interactions, in the case of small concentrations the binary collisions play the most important role, and one could neglect the higher distribution functions, i.e. $F_{abc} \approx 0$. Because of the collective behaviour of systems having Coulomb forces in systems of ions such an approximation is not appropriate. Formally, this approximation would lead to the well-known Coulomb divergencies. In this paper we apply a generalization of the previously developed theory /1/ using the nonlinear approximation /5/

$$F_{abc} = F_{ab}F_{bc} \qquad (6)$$

In this approximation we get for the effective potential $\hat{\Phi}_a^b$, using $\psi_{ab} = V'_{ab} + V_{ab}$,

$$\frac{d}{dr_a}\hat{\Phi}_a^b = \frac{d}{dr_a}(V'_{ab} + V_{ab}) - \sum_c n_c \int dr_c \frac{d}{dr_a}(V'_{ac} + V_{ac})F_{bc} \,. \qquad (7)$$

Thus the equations (3,4,7) represent a system of equations from which F_{ab} may be determined selfconsistently. $\hat{\Phi}_a^b$ may be interpreted as a screened potential.

Because the short range potential V_{ab} must not be screened necessarily, in the integral of (7) we shall only retain the Coulomb potential V_{ab}:

$$\hat{\phi}_a^b = V'_{ab} + \phi_a^b \; ; \; \frac{d}{dr_a}\phi_a^b = \frac{d}{dr_a}\left(V_{ab} + \sum_c n_c \int dr_c V_{ac} F_{bc}\right). \tag{8}$$

The structure of the equations then implies the substitution

$$F_{ab} = e^{-\beta V'_{ab}} \bar{F}_{ab} \; . \tag{9}$$

Combining (3) and (4) we get after some rearrangements for the stationary case and using $r_a - r_b = r$, $F_{ab}(r) = F_{ba}(-r)$

$$e^{-\beta V'_{ab}}\left\{kT\Delta\bar{F}_{ab} + \nabla\bar{F}_{ab}\cdot\nabla\phi_{ab} + \bar{F}_{ab}\Delta\phi_{ab} - \mu_{ab}\nabla\bar{F}_{ab}\frac{E}{|E|}\right\}$$
$$+\nabla e^{-\beta V'_{ab}}\left\{kT\nabla\bar{F}_{ab} + \bar{F}_{ab}\nabla\phi_{ab} - kT\mu_{ab}\bar{F}_{ab}\frac{E}{|E|}\right\} = 0 \; . \tag{10}$$

Here we used (Ebeling, Feistel et al.[2]):

$$\phi_{ab} = w_a^b\phi_a^b + w_b^a\phi_b^a \; , \tag{11}$$

where w_a^b are the relative friction coefficients

$$w_a^b = \frac{1}{\rho_a}\left(\frac{1}{\rho_a} + \frac{1}{\rho_b}\right)^{-1} \tag{12}$$

and

$$\mu_{ab} = \beta(e_a w_a^b - e_b w_b^a)|E| = \beta q (e_a - e_b),$$
$$q = (e_a w_a^b - e_b w_b^a)(e_a - e_b)^{-1}, \quad a \neq b. \tag{13}$$

As usual, F_{ab} fulfills the following conditions

-1- $\lim_{r\to\infty} \bar{F}_{ab}(r) = 1$

-2- $F_{ab}\, e^{\beta V'_{ab}} = \bar{F}_{ab}(r)$ – continuous (14)

-3- $e^{-\beta V'_{ab}} \frac{\vec{r}}{r}\cdot\left\{\nabla\bar{F}_{ab} + \bar{F}_{ab}\nabla\beta\phi_{ab} - \beta q (e_a - e_b) E \bar{F}_{ab}\right\}$ – continuous.

The first property is known as the decay of the correlation, while the second property follows from that of the integro-differential equation (8), (10) for F_{ab}. The third condition re-

presents the continuity of the particle flux, which follows immediately from the equation of continuity (4). We will see that this third property in the case of stepwise constant short range potentials (hard spheres, square well) will act as boundary condition at the discontinuity points of the potential V_{ab}.

2. Boundary value problem for the determination of the distribution function

The main task in the theory of electrolyte conductance is the determination of the binary distribution function. The corresponding equations are given in section 1. - In order to get explicit solutions for F_{ab}, we adopt some simplifications.

The most essential one is the restriction to small external electrical fields, i.e. we consider only small deviations from the equilibrium distribution. This means that we shall consider only the range of validity of Ohm's law.

In this case all quantities are expanded in the manner

$$\bar{F}_{ab} = \bar{F}^{0}_{ab} + \bar{F}^{(1)}_{ab} + O(E^2) ,$$
$$\phi^{b}_{a} = \phi^{b0}_{a} + \phi^{b(1)}_{a} + O(E^2) .$$

With these expansions we get from (3-5) or (8), (10) respectively for the equilibrium quantities

$$\nabla \bar{F}^{0}_{ab} + \beta \bar{F}^{0}_{ab} \nabla \phi^{b0}_{a} = 0 , \tag{15}$$

$$\phi^{b0}_{a} = V_{ab} + \sum_{c} n_c \int V_{ac} (F_{bc} - 1) \, dr_c . \tag{16}$$

The solution of (15) yields together with (9)

$$F^{0}_{ab} = e^{-\beta (V'_{ab} + \phi^{b0}_{a})} . \tag{17}$$

The explicit expression for ϕ^{b0}_{a} depends on the special choice of the short range potential. In this paper we shall use a hard sphere potential which is defined by

$$V'_{ab}(r) = \begin{cases} 0, & r \geq a \\ \infty, & r < a \end{cases}$$

independently of the species. From (16) and (17) we get then with a linearization of (17) with respect to

$$\phi_a^{b\circ}(r) = e_a e_b \cdot \frac{e^{\varkappa a}}{1+\varkappa a} \cdot \frac{e^{-\varkappa r}}{r} \equiv \phi_{ab}^{\circ} \quad . \tag{18}$$

This is the well known Debye-Hückel potential. This approximation indicates the character of the theory we get in this way: We deal with the nonlinear Debye-Hückel theory which was discussed extensively during the course of the last years[6]. It was shown that this approximation provides for a calculation of thermodynamic properties of 1-1 valent electrolytes up to an accuracy which is comparable with that of HNC and Monte Carlo calculations.

For this reason we may assume that a conductance theory on the basis of (8), (10), (18) gives formulae which are valid at higher concentration ranges.

For the deviations from the equilibrium we get from (10)

$$\begin{aligned} & e^{-\beta V'_{ab}} \{ \Delta \bar{F}_{ab}^{(1)} + \nabla \bar{F}_{ab}^{(1)} \cdot \nabla \beta \phi_{ab}^{\circ} + \nabla \bar{F}_{ab}^{\circ} \cdot \nabla \beta \phi_{ab}^{(1)} + \\ & + \bar{F}_{ab}^{\circ} \Delta \beta \phi_{ab}^{(1)} + \bar{F}_{ab}^{(1)} \Delta \beta \phi_{ab}^{\circ} - \mu_{ab} \frac{\vec{E}}{|E|} \nabla \bar{F}_{ab}^{\circ} \} = \\ & = -\nabla e^{-\beta V'_{ab}} \{ \nabla \bar{F}_{ab}^{(1)} + \bar{F}_{ab}^{\circ} \nabla \beta \phi_{ab}^{(1)} + \bar{F}_{ab}^{(1)} \nabla \beta \phi_{ab}^{\circ} - \mu_{ab} \frac{\vec{E}}{|E|} \bar{F}_{ab}^{\circ} \} . \end{aligned} \tag{19}$$

A simplification of (19) is achieved using the substitution[2]

$$\bar{F}_{ab}^{(1)} = \bar{y}_{ab}(r)\, e^{-\beta \phi_{ab}^{\circ}} \quad . \tag{19a}$$

For $\bar{y}_{ab}$ we get the equation

$$\begin{aligned} & e^{-\beta V'_{ab}} \{ \Delta \bar{y}_{ab} + \nabla \bar{y}_{ab} \cdot \nabla \beta \phi_{ab}^{\circ} - \nabla \beta \phi_{ab}^{\circ} \cdot \nabla \beta \phi_{ab}^{(1)} + \\ & + \Delta \beta \phi_{ab}^{(1)} - \mu_{ab} \frac{\vec{E}}{|E|} \beta \phi_{ab}^{\circ} \} = \\ & = -\nabla e^{-\beta V'_{ab}} \{ \nabla \bar{y}_{ab} + \nabla \beta \phi_{ab}^{(1)} - \mu_{ab} \frac{\vec{E}}{|E|} \} \quad . \end{aligned} \tag{20}$$

For the hard sphere potential we may write

$$\nabla e^{-\beta V'_{ab}} = \frac{\vec{r}}{|r|}\,\delta(r-a)\,.$$

In the eq.(20) for $\bar{y}_{ab}$ we have thus a singularity at r=a, which may be excluded by subdividing the total r-interval into two regions:

$$0 < r \leq a \;;\quad a < r \leq \infty\,.$$

The differential equation must be fulfilled in the regions and must fulfill the boundary conditions at r=a and r= ∞ . The boundary condition at r=a is given by the expression in curly brackets at the right hand side of (20) and corresponds to (14,3).

We restrict ourselves to a system having two species with $e_1=-e_2$. Taking into account the electroneutrality and

$$F^{(1)}_{aa} = F^{(1)}_{bb} = 0 \;;\quad F^{(1)}_{ab} = -F^{(1)}_{ba}$$

we get the following equation for the determination of the effective potential

$$\Delta\phi^{(1)}_{ab} = -q\varkappa^2 F^{(1)}_{ab}\,. \tag{21}$$

In eq.(20) we will neglect the term $\nabla\beta\phi^{\circ}_{ab}\cdot\nabla\beta\phi^{(1)}_{ab}$.
The direction of the external field is arbitrarily fixed to the x-axis, and for $\bar{y}$ we apply the substitution

$$\bar{y}_{12}(\vec{r}) = \mu_{12}\, y_{12}(r)\cos\vartheta\,, \tag{22}$$

where

$$\cos\vartheta = \vec{r}\cdot\vec{E}/(rE)\,.$$

With (21) and (22) we get from (20) the following boundary value problem for $y_{12}\equiv y$

$$\frac{d^2}{dr^2}y + \frac{d}{dr}y\left(\frac{2}{r} - \frac{l}{r^2}\right) - \left(\varkappa^2 + \frac{2}{r^2}\right)y = l\omega\,\frac{d}{dr}\,\frac{e^{-\varkappa r}}{r}\;;\; r>a.$$

$$y(r)\big|_{r\to\infty} = 0\;;\quad \left[\frac{d}{dr}y + \mu_{12}\frac{d}{dr}(\beta\phi^{(1)}_{ab}) - 1\right]_{r=a} = 0. \tag{23}$$

Here two more approximations were applied: The potential ϕ°_{ab} in the nonlinear term $\nabla \bar{y}_{ab} \cdot \nabla \phi^{\circ}_{ab}$ was replaced by a Coulomb one, and the expression (21) was used replacing the exponential $\exp(-\beta \phi^{\circ}_{ab})$ occuring in $F^{(1)}_{ab}$ by unity. The abbreviations mean $\omega = e^{\varkappa a}/(1+\varkappa a)$ and $\ell = e^2/(kT D_o)$ - Landau length; $\alpha^2 = q \varkappa^2$.

The boundary value problem (23) differs from that derived in previous work /1/ by the following points:

- There is an opposite sign in the ℓ/r^2-term,
- The function y is only influenced by the order ℓ of the equilibrium distribution function, and
- the boundary conditions are simpler.

These differences have their origin in the special approximation for F_{abc}.

The nonlinear approximation used here seems to be more appropriate not only because it extends probably the range of validity but also because now it is possible (as a result of the special structure of the approximation) to isolate the equilibrium distribution function, $\exp(-\beta \phi^{\circ}_{ab})$, see (19a).

The remaining boundary value problem has thus a simpler structure than that in /1/.

3. Determination of the binary distribution function

As in /1/, we cannot find here a closed analytical solution of the boundary value problem (23).

For this reason we apply a perturbation procedure and determine y up to the order ℓ^2. However, especially on account of the fact that association effects shall be taken into account we are not allowed to consider ℓ a small quantitiy; thus we determine the higher power contributions of y with respect to ℓ from the so-called unscreened problem (23), i.e. with $\varkappa \to 0$, $\alpha = \sqrt{q}\,\varkappa \to 0$. Such a procedure is justified, because the Coulomb divergencies occuring during the course of the calcu-

lation of σ are restricted to the orders ℓ and ℓ^2, and consequently only the lower orders must be screened. Thus y is decomposed as follows

$$y = y_0 + y_1 + y_2 + y_R \quad . \tag{24}$$

The perturbation theory yields for the k'th order of ℓ

$$\frac{d^2 y_k}{dr^2} + \frac{2}{r}\frac{dy_k}{dr} - \left(\alpha^2 + \frac{2}{r^2}\right) y_k = \delta_{k,1}\, \ell\omega \frac{d}{dr}\frac{e^{-\alpha r}}{r} + \frac{\ell}{r^2}\frac{dy_{k-1}}{dr} \tag{25}$$

with the boundary conditions

$$\left[\frac{dy_k}{dr} - \delta_{k,0}\right]_{a=r} = 0 \; ; \quad y_k(r)\big|_{r=\infty} = 0 \; . \tag{25a}$$

In the boundary condition the term with $\phi_{ab}^{(1)}$ was neglected because it leads to higher concentration contributions.

The general shape of the solutions is

$$y_k = A_k \frac{d}{dr}\frac{e^{-\alpha r}}{r} + y_k^{part.} \quad , \tag{26}$$

$$A_k = \left(-\frac{d}{dr} y_k^{part.} + \delta_{k,0}\right) \Big/ \left(\frac{2}{a^3} T(\alpha a)\right) \; , \tag{26a}$$

$$T(\alpha a) = e^{-\alpha a}\left(1 + \alpha a + \tfrac{1}{2}\alpha^2 a^2\right) \; .$$

Consequently, the most essential problem consists in the determination of the particular solutions $y_k^{part.}$ of each order. This task is solved by means of the method of the "variation of the constants", i.e.

$$y_k^{part.} = C_k^1(r)\, y_{R1} + C_k^2(r)\, y_{R2}$$

with $C_k^1(r) = \int_r^\infty \frac{dr}{\Delta}\, y_{R1}\, I_k(r)$, $C_k^2(r) = -\int_r^\infty \frac{dr}{\Delta}\, y_{R2}\, I_k(r)$.

Here $I_k(r)$ is the inhomogeneity of (25), y_{R1} and y_{R2} are linearily independent solutions of the homogeneous equation (25) which are for any k

$$y_{R1} = \frac{d}{dr}\frac{e^{-\alpha r}}{r} \quad , \quad y_{R2} = \frac{d}{dr}\frac{e^{\alpha r}}{r}$$

with the Wronskian $\Delta = 2\alpha^3/r^2$.
In this way we get for the zeroth order

$$y_0^{part.} = \frac{1}{2}\frac{a^3}{T(\varkappa a)}\frac{d}{dr}\frac{e^{-\alpha r}}{r} \tag{27}$$

and for the first order

$$y_1^{part.} = \frac{\varrho\omega}{(\varkappa^2-\alpha^2)}\frac{d}{dr}\frac{e^{-\varkappa r}}{r} + \frac{\varrho a^3}{4T(\varkappa a)}\left[\frac{1}{r^3}+\frac{\alpha}{r^2}\right]e^{-\alpha r}. \tag{28}$$

For the constant A_1 we get

$$A_1 = -\frac{a^3}{2T(\varkappa a)}\left[\frac{\varrho\omega}{\alpha^2}\frac{2}{a^3}T(\varkappa a) - \frac{\varrho a^3 e^{-\alpha a}}{4T(\varkappa a)}\left(\frac{3}{a^4}+\frac{3\alpha}{a^3}+\frac{\alpha^2}{a^2}\right)\right]. \tag{29}$$

The second order $y_2^{part.}$ is determined by the inhomogeneities

$$I_2^{(1)} = \frac{\varrho}{r_2}\left\{A_1 e^{-\alpha r}\left(\frac{2}{r^3}+\frac{2\alpha}{r^2}+\frac{\alpha^2}{r}\right)\right\},$$

$$I_2^{(2)} = \frac{\omega\varrho}{\alpha^2}\left\{\frac{2}{r^3}+\frac{2\varkappa}{r^2}+\frac{\varkappa^2}{r}\right\}e^{-\varkappa r},$$

$$I_2^{(3)} = -\frac{\varrho a^3}{4T(\varkappa a)}\left\{\frac{3}{r^4}+\frac{3\alpha}{r^3}+\frac{\alpha^2}{r^2}\right\}e^{-\alpha r}.$$

The corresponding particular solutions read then

$$y_2^{part,1} = \frac{\varrho}{2}A_1 e^{-\alpha r}\left(\frac{1}{r^3}+\frac{\alpha}{r^2}\right), \tag{30a}$$

$$y_2^{part,2} = \frac{\varrho^2\omega}{\alpha^2}\left\{\left(\frac{1}{4}\frac{\varkappa^3}{\alpha^2 r_2}+\frac{1}{4}\frac{\varkappa}{r_2}+\frac{1}{2r^3}\right)e^{-\varkappa r} + \frac{1}{8r_2}\left(\frac{\varkappa^4}{\alpha^3}-\alpha\right)(U-\alpha r G)\right\}, \tag{30b}$$

$$y_2^{part,3} = -\frac{\varrho^2 a^3}{8T(\varkappa a)}\left\{e^{-\alpha r}\left(\frac{3}{5r^4}+\frac{3\alpha}{5r^3}+\frac{-\alpha^2}{15r^2}\right) + \frac{2\alpha^2}{15}Ei(-2\alpha r)\,e^{\alpha r}\left(\frac{1}{r^2}-\frac{\alpha}{r}\right)\right\}. \tag{30c}$$

Here we used the abbreviation

$$\begin{Bmatrix} U \\ G \end{Bmatrix} = -e^{\alpha r}Ei(-(\varkappa+\alpha)r) + \begin{Bmatrix} + \\ - \end{Bmatrix}e^{-\alpha r}Ei(-(\varkappa-\alpha)r),$$

and $Ei(x)$ is the exponential integral function. The constant A_2 is determined to be

$$A_2 = \frac{1}{2T(\varkappa a)}\Big[\frac{\ell^2 e^{-\varkappa a}}{2T(\varkappa a)}\Big(\frac{3}{a}+3\varkappa+\varkappa^2 a\Big)\Big\{-\frac{\omega}{\varkappa^2}T(\varkappa a)+$$

$$+\frac{a^2 e^{-\varkappa a}}{8T(\varkappa a)}(3+3\varkappa a+\varkappa^2 a^2)\Big\}+\frac{\ell^2\omega}{\varkappa^2}\Big\{e^{-\varkappa a}\Big(\frac{\varkappa^4 a}{4\varkappa^2}+\frac{\varkappa^3}{2\varkappa^2}+$$

$$+\frac{\varkappa^2 a}{4}+\frac{3}{2a}+\varkappa\Big)+\frac{1}{4}\Big(\frac{\varkappa^4}{\varkappa^3}-\varkappa\Big)\big(U(a)-\varkappa a\,G(a)\big)-$$

$$-\frac{1}{8}\Big(\frac{\varkappa^4 a}{\varkappa^3}-\varkappa a\Big)\big(2\varkappa e^{-\varkappa a}-\varkappa^2 a\,U(a)\big)\Big\}-\frac{\ell^2 a^3}{8T(\varkappa a)}*$$

$$*\Big\{e^{-\varkappa a}\Big(\frac{12}{5a^2}+\frac{12\varkappa}{5a}-\frac{7\varkappa^2}{15}-\frac{\varkappa^3 a}{15}\Big)-\frac{2}{15}Ei(-2\varkappa a)\,e^{\varkappa a}*$$

$$*\,\varkappa^2(-\varkappa^2 a^2+2\varkappa a-2)-\frac{2\varkappa}{15a}(\varkappa a-\varkappa^2 a^2)e^{-\varkappa a}\Big\}\Big]. \qquad (31)$$

By eqs.(26-31) the distribution function is known up to the order ℓ^2. Now we have to determine the higher power contribution, i.e. y_R.

As already mentioned, we consider now the equation

$$\frac{d^2}{dr^2}y+\frac{d}{dr}y\Big(\frac{2}{r}-\frac{\ell}{r^2}\Big)-\frac{2}{r^2}y=\ell\,\frac{d}{dr}\frac{1}{r}\ . \qquad (32)$$

The general solution $y^{un.}$ of the unscreened eq.(32) is given by

$$y^{un.}=C_1 e^{-\ell/r}\Big(1+\frac{2r}{\ell}\Big)+C_2\Big(1-\frac{2r}{\ell}\Big)+r\ . \qquad (33)$$

$y^{un.}$ contains all powers of ℓ, and it is easily to be seen that (33) does not fulfill the boundary conditions (25a). But we shall not use the entire solution $y^{un.}$, but only a part of it, y_R. Thus we may determine the constants C_1 and C_2 in the following way: One of the constants is fixed in such a way that the highest power with respect to r of (33) vanishes; the other one is then determined by the first boundary condition (25a) which reads

$$\big(dy^{un.}/dr-1\big)\big|_{r=a}=0 \qquad (34)$$

while the vanishing coefficient of r gives

$$C_1 \cdot 2/\ell - C_2 \cdot 2/\ell + 1 = 0 . \tag{35}$$

From (34) and (35) we get

$$C_1 = \left[e^{-\ell/a}\left(\frac{2}{a} + \frac{\ell}{a^2} + \frac{2}{\ell}\right) - \frac{2}{\ell}\right]^{-1} , \quad C_2 = C_1 + \frac{\ell}{2} . \tag{36}$$

Thus we get

$$y^{un.}(r) = \frac{\ell}{2} + \left[e^{-\frac{\ell}{r}}\left(1+\frac{2r}{\ell}\right) + 1 - \frac{2r}{\ell}\right]\left[e^{-\frac{\ell}{a}}\left(\frac{2}{a}+\frac{\ell}{a^2}+\frac{2}{\ell}\right) - \frac{2}{\ell}\right]^{-1} . \tag{37}$$

y_R follows from (37) by sub traction of the terms of the orders ℓ^0, ℓ^1 and ℓ^2 and turns out to be

$$y_R = \left[e^{-\ell/r}\left(1+\frac{2r}{\ell}\right) + 1 - \frac{2r}{\ell}\right]\left[e^{-\ell/a}\left(\frac{2}{a}+\frac{\ell}{a^2}+\frac{2}{\ell}\right) - \frac{2}{\ell}\right]^{-1} + \\ + \frac{a^3}{2r^2}\left(1 + \frac{3\ell}{4a} + \frac{21}{80}\frac{\ell^2}{a^2} - \frac{\ell}{2r} - \frac{3\ell^2}{8ra} + \frac{3\ell^2}{20r^2}\right) . \tag{38}$$

4. Relations to the theory[1]

An immediate comparison between the theory given here and those versions given in [1] and by Ebeling et al. [2] is not possible because in the present work the exponential $\exp(-\beta\phi^0_{ab})$ was separated. For the comparison with, e.g., the KKE theory[1] we must consider the expression

$$e^{-\beta\phi^0_{ab}}(y_0 + y_1 + y_2) + e^{-\beta\phi^0_{ab}} y_R . \tag{39}$$

This expression (39) must be expanded according to ϕ^0_{ab}-powers, and the corresponding powers of ℓ must be compared. As a result we get (using $\tilde{y} = y \exp(-\beta\phi^0_{ab})$)

$$\tilde{y}_0 = y_0^{KKE}$$

and for the orders ℓ and ℓ^2

$$\tilde{y}_1 = -\beta y_0 \phi^0_{ab} + y_1 \tag{40}$$

$$\tilde{y}_2 = \frac{y_0}{2}(\beta\phi^0_{ab})^2 - \beta\phi^0_{ab} y_1 + y_2 \tag{41}$$

For the first order we get

$$\tilde{y}_1 = A_1 \frac{d}{dr}\frac{e^{-\alpha r}}{r} + \frac{\ell a^3}{4r}\cdot\frac{1}{\Gamma(\alpha a)}\frac{d}{dr}\frac{e^{-\alpha r}}{r} +$$

$$+\frac{\omega\ell}{(\varkappa^2-\alpha^2)}\frac{d}{dr}\frac{e^{-\varkappa r}}{r}+\frac{\ell a^3}{4rT(\varkappa a)}(\omega e^{-\varkappa r}-1)\frac{d}{dr}\frac{e^{-\alpha r}}{r}. \qquad (40a)$$

Taking into account the different definitions of A_1, we find

$$\frac{\alpha^2}{\ell\omega}A_1 = A_1^{KKE}+O(\varkappa^3a^3)=1+\frac{3}{8}a^2\alpha^2+O(\varkappa^3).$$

It follows that eq.(40a) coincides with the corresponding quantitiy y_1^{KKE} only up to higher powers in $\varkappa a$, i.e. if the last term in (40a) is neglected.

For $\tilde{y}_2$ we may not achieve a full correspondence between the theories. There is only agreement for the lower orders with respect to $\varkappa$. Let us now consider the quantitiy $\tilde{y}_R = y_R \exp(-\beta\phi^0_{ab})$. In the "unscreened limit" the exponential reads $\exp(\ell/r)$. From (33) follows

$$\tilde{y}^{un.} = y^{un.}\exp(\tfrac{\ell}{r}) = y^{un,KKE}.$$

For the remainder, $\tilde{y}_R$, we have to consider obviously

$$\tilde{y}_R = \exp(\tfrac{\ell}{r})y^{un.} - (1+\tfrac{\ell}{r}+\tfrac{\ell^2}{2r^2})(y^{un,0}+y^{un,1}+y^{un,2}).$$

For the product of the two brackets we get

$$\frac{a^3}{2r^2}\left[1+\ell\left(\frac{3}{4a}+\frac{1}{2r}\right)+\ell^2\left(\frac{21}{80a^2}+\frac{3}{8ra}+\frac{3}{20r^2}\right)-\frac{\ell r^2}{a^3}-\frac{\ell^2 r}{a^3}\right].$$

Thus we have, up to some approximation with respect to higher concentrations, agreement between $y_R \exp(-\beta\phi^0_{ab})$ and y_R^{KKE}.

5. Relaxation and Electrophoresis

The conductance must be determined from

$$\sigma = \frac{1}{E}\sum_a n_a e_a \bar{u}_a, \qquad \bar{u}_a = u_a^{rel.}+u_a^{el}.$$

Using (2) we get after carrying out the integration over the angles[1]

$$\sigma=\sigma_0+\sum_{ab}\frac{4\pi}{3\rho_a}n_a n_b\frac{e_a^2 e_b}{D_0}\frac{\mu_{ab}}{E}\int_a^\infty e^{-\beta\phi^\circ_{ab}}y(r)\,dr+$$

$$+\sum_{ab}\frac{4\pi}{3\rho_a}e_a kT a^2 n_a n_b\frac{\mu_{ab}}{E}e^{-\beta\phi^\circ_{ab}(a)}y(a)+$$

$$+\sum_{ab}\frac{e_a n_a n_b}{3\eta_0}\left\{\int_a^\infty dr\,r\left[2e_b F^\circ_{ab}+\frac{\mu_{ab}}{E}y e^{-\beta\phi^\circ_{ab}}\frac{dV_{ab}}{dr}\right]\right.$$

$$\left.-kTa\frac{\mu_{ab}}{E}y(a)e^{-\beta\phi^\circ_{ab}(a)}\right\},\qquad(43)$$

with $\sigma_0=\frac{n_1e_1^2}{\rho_1}+\frac{n_2e_2^2}{\rho_2}$, conductance at infinite dilution, and η_0 -viscosity. The second and third terms represent the relaxation contribution, while the remaining contributions are due to electrophoretic effects. Now the summation over the species is carried out. Here we take into account

$$\mu_{aa}=\mu_{bb}=0,\quad \mu_{ab}=-\mu_{ba},\quad n_a e_a=-n_b e_b.$$

For a two component symmetric electrolyte we get

$$\sigma=\sigma_0-\frac{q\sigma_0}{3D_0}\varkappa^2\left[\int_a^\infty e^{-\beta\phi^\circ_{12}(r)}y(r)\,dr-\frac{a^2}{\ell}e^{-\beta\phi^\circ_{12}(a)}y(a)\right]$$

$$+\varkappa^2\frac{nkT D_0}{24\pi\eta_0}\left[4\int_a^\infty dr\,r\left(e^{\beta\phi^\circ_{12}(r)}-e^{-\beta\phi^\circ_{12}(r)}\right)+\right.$$

$$\left.+2\ell\int_a^\infty\frac{dr}{r}y(r)\,e^{-\beta\phi^\circ_{12}(r)}-2a\,e^{-\beta\phi^\circ_{12}(a)}y(a)\right].\qquad(44)$$

Eq.(44) is written as in earlier work

$$\frac{\sigma}{\sigma_0}=1-\frac{\varkappa ab}{6(1+\sqrt{q})}+\frac{(\varkappa ab)^2}{12}\left[Q^{rel.}(\varkappa a,b)+\ln\varkappa ab\right]$$

$$-\frac{1}{8}A\,\varkappa ab+\frac{A}{8}(\varkappa ab)^2\left[Q^{el.}(\varkappa a,b)-A\ln\varkappa ab\right],$$

$$A=\rho_1\rho_2 D_0 kT/(3\pi\eta_0(\rho_1+\rho_2)e_1^2)\ .$$

In contrast to /1/ the functions $Q^{rel.}$ and $Q^{el.}$ are now functions of $\varkappa a$. These quantities are defined by the integrals

$$Q^{rel}(\varkappa a,b) = -\frac{2}{a^2b^2}\Big[\int_a^\infty e^{-\beta\phi_{12}^\circ(r)}\, y(r)\,dr - \frac{ba}{\varkappa(1+\varkappa a)} - \frac{a}{b}\exp(-\beta\phi_{12}^\circ(a))\, y(a)\Big] - \ln \varkappa ab\,; \quad (46)$$

$$Q^{el}(\varkappa a,b) = -\frac{1}{a^2b^2}\Big[4\int_a^\infty dr\, r\,(\exp[\beta\phi_{12}^\circ(r)] - \exp[-\beta\phi_{12}^\circ(r)]) \quad (47)$$
$$+2\ell\int_a^\infty e^{-\beta\phi_{12}^\circ(r)}\, y(r)\,\frac{dr}{r} - 2a\, e^{-\beta\phi_{12}^\circ(a)}\, y(a) - \frac{Aab}{8\varkappa}\Big] + A\ln \varkappa ab.$$

Now the solutions (26-38) and (18) may be applied, and the functions (46,47) may be evaluated numerically. This task will be solved in a subsequent paper.

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Anschrift der Verfasser:

Prof.Dr.habil. D. Kremp und
Dr. U. Lau
PH Liselotte Hermann, Sektion Physik/Mathematik
26 Güstrow
Goldberger Str.12

Prof.Dr.sc.W.D. Kraeft
EMA -Universität, Sektion Physik/Elektronik
22 Greifswald
Domstr. 10 a

R. Sändig, R. Feistel, H. Künstner

The z - φ - theory of electrolytic conductance.

1. Basic Equations for the binary distribution functions.

In recent papers [1,2] was demonstrated how to calculate the electrical molar conductivity Λ and the individual conductivities Λ_a, respectively, in the stationary case

$$\Lambda = \sum_a \Lambda_a = \frac{1000}{C} \sum_a \frac{n_a e_a}{g_a} \left[e_a + \frac{K_a^{Rel}}{E}(\{F_{ab}\}) + \frac{K_a^{El}}{E}(\{F_{ab}\}) \right] \qquad (1.1)$$

Here the Λ's are measured in $[cm^2/(\Omega \cdot mol)]$; $C = \sum_a c_a / \sum_a \nu_a$ is the stoichiometric concentration in [mol/l]; ν_a is the number of ions of kind " a " forming a salt molecul; $\delta = \frac{1}{9} 10^{11} [s/\Omega cm]$, n_a is the particlenumber density in $[cm^{-3}]$ of the ions of kind " a " with the electrical charge e_a in electrostatic units ($e_0 = 4.80298 \cdot 10^{-10}$ $[cm^{-3/2} g^{1/2} s^{-1}]$) and g_a is the ions friction coefficient in [g/s]).

The electrical field strength $\vec{E}$ in $[V/cm]$ is supposed to be small. The relaxation force $\vec{K}_a^{Rel}$ and the electrophoretic force $\vec{K}_a^{El}$ are functionals of the set of binary distribution functions $\{F_{ab}\}$. Neglecting the three-body electrophoretic contributions the Falkenhagen - Ebeling equation for F_{ab} reads [1,2,3]

$$\nabla \left\{ (\underline{\underline{\delta}} - \chi_{ab}) \left[\nabla F_{ab} + F_{ab} \nabla \beta \Phi_{ab} - \mu_{ab} F_{ab} \frac{\vec{E}}{E} \right] \right\} = 0 \qquad (1.2)$$

Here $\underline{\underline{\delta}}$ is the unit tensor and χ_{ab} is the hydrodynamic coupling tensor. With $\beta = 1/kT$ the nonequilibrium perturbation parameter μ_{ab} has the form

$$\mu_{ab} = \beta (w_a \bar{K}_a - w_b \bar{K}_b) \cdot \frac{\vec{E}}{E} \qquad (1.3)$$

with $w_a = \varrho_a^{-1}\left(\varrho_a^{-1}+\varrho_b^{-1}\right)^{-1}$ and the effective external force

linearized theory: $\bar{K}_a = e_a \vec{E}$

feedback theory: $\bar{K} = e_a \vec{E} + \vec{K}_a^{Rel} + \vec{K}_a^{El}$ (1.4)

μ may be interpreted as a reciprocal perturbation length of order $\Lambda 10^2\,[V^{-1}] \approx E\,[V/cm]$. Under the usual experimental conditions ($E \sim 10$ V/cm) the deviation from the equilibrium state may be restimated by the ratio $\mu_{ab}\,\ell_{ab} \sim 10^{-5}\,[cm/V] \cdot E\,[V/cm]$. Eq. (1.2) is the continuity equation for the relative probability flow. The boundary conditions for F_{ab} were first derived by Kelbg [4].

(i) $F_{ab}(r \to \infty) = 1$ (1.5)

(ii) $\exp(\beta \Psi_{ab})\, F_{ab}$ is continuous $\forall \vec{r}$ (1.6)

(iii) the relative probability flow proportional to

$$\left[\nabla F_{ab} + F_{ab} \nabla \beta \Phi_{ab} - \mu_{ab} F_{ab} \frac{\vec{E}}{E}\right] \text{ is continuous } \forall \vec{r} \quad (1.7)$$

The two particle relaxation force in eq.(1.2)approximated by $-\nabla \Phi_{ab}$ is given by

$$\nabla \Phi_{ab}(\vec{r}) = w_a \nabla \Phi_a^b(\vec{r}) - w_b \nabla \Phi_b^a(\vec{r})$$

$$\nabla \Phi_a^b(\vec{r}) = \sum_c n_c \int \nabla \Psi_{ac}(|\vec{r}-\vec{r}'|)\left[\frac{\tilde{F}_{abc}}{F_{ab}} - F_{ac}\right] d\vec{r}' \quad (1.8)$$

Here Ψ_{ab} is the Mc Millan/Mayer interionic potential at infinite dilution. Further $\tilde{F}_{abc}$ denotes any approximation of the ternary distribution function which guarantees the conservativity of the two particle relaxation force. This is a restrictive assumption for the nonequilibrium contributions of F_{ab} only.

Now we expand F_{ab} and Φ_{ab} with respect to the external electrical field strength

$$F_{ab}(\vec{r}) = F_{ab}^{0}(r) + F_{ab}^{1}(r,\vartheta) + \sigma(E^2)$$

$$\Phi_{ab}(\vec{r}) = \Phi^{\circ}_{ab}(r) + \Phi^{\wedge}_{ab}(r,\vartheta) + \mathcal{O}(E^2)$$

$$F^{\circ}_{ab}(r) = \exp\{-\beta\,\Phi^{\circ}_{ab}(r)\}$$

$$F^{\wedge}_{ab}(r,\vartheta) = \mu_{ab}\,F^{\circ}_{ab}(r)\,[z_{ab}(r) - \varphi_{ab}(r)]\cos\vartheta \qquad (1.9)$$

$$\Phi^{\wedge}_{ab}(r,\vartheta) = kT\,\mu_{ab}\,\varphi_{ab}(r)\cos\vartheta$$

Here ϑ denotes the angle between $\vec{r}$ and $\vec{E}$. In what follows we assume that the equilibrium radial distribution function F°_{ab} is known.

Inserting eq. (1.9) in eq. (1.2) we get an ordinary differential equation for $z_{ab}(r)$

$$\left(1-\chi^{(1)}_{ab}-\chi^{(2)}_{ab}\right)\left[z''_{ab} + \left(\frac{2}{r} + \frac{F^{\circ\prime}_{ab}}{F^{\circ}_{ab}}\right) z'_{ab} - \frac{2}{r^2}\,z_{ab} - \frac{F^{\circ\prime}_{ab}}{F^{\circ}_{ab}}\right]$$

$$+ \chi^{(2)}_{ab}\left[\frac{2}{r}\,z'_{ab} - \frac{2}{r^2}\,z_{ab}\right] = 0 \qquad (1.10)$$

with the hydrodynamic functions

$$\chi^{(1)}_{ab} = \left(\frac{1}{\beta_a} + \frac{1}{\beta_b}\right)^{-1} \frac{1}{4\pi\eta_0\,r}\left[1 + \frac{1}{3}\,\frac{1}{(6\pi\eta_0)^2}\,\frac{\beta_a^2+\beta_b^2}{r^2}\right]$$

$$\chi^{(2)}_{ab} = \left(\frac{1}{\beta_a} + \frac{1}{\beta_b}\right)^{-1} \frac{1}{4\pi\eta_0\,r}\left[1 + \frac{1}{(6\pi\eta_0)^2}\,\frac{\beta_a^2+\beta_b^2}{r^2}\right] \qquad (1.11)$$

In what follows we neglected the r^{-3} contributions in $\chi^{(1,2)}_{ab}$ and restrict ourselves to binary symmetrical electrolytes. We suppress now the index (ab) keeping in mind that

$$\mu \equiv \mu_{+-} = -\mu_{-+}\,; \quad F \equiv F_{+-}\,; \quad z \equiv z_{+-}\,; \quad F^{\wedge}_{aa} \equiv 0 \ \text{ etc.}$$

Then eq. (1.11) reads

$$\chi^{(1)} = \chi^{(2)} = 6h\,\frac{\ell}{r} \qquad (1.12)$$

with $h = \nu_+\nu_- H/(\nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ)$; $H = DkTN_L\delta/24\pi\eta_\circ$

and $\ell \equiv \ell_{+-} = -e_+e_-/DkT$

Now we expand z in eq. (1.10) with respect to the dimensionless hydrodynamic parameter h and get the following equations

$$z = z_\circ + h\cdot z_1 + \mathcal{O}(h^2) \tag{1.13}$$

$$z_\circ'' + \left(\frac{2}{r} + \frac{F^{\circ\prime}}{F^\circ}\right) z_\circ' - \frac{2}{r^2} z_\circ = \frac{F^{\circ\prime}}{F^\circ} \tag{1.14}$$

$$z_1'' + \left(\frac{2}{r} + \frac{F^{\circ\prime}}{F^\circ}\right) z_1' - \frac{2}{r^2} z_1 = -12\,\frac{\ell}{r}\left(\frac{z_\circ}{r}\right)' \tag{1.15}$$

The higher order contributions z_2 etc. may be neglected since $h \ll 1$ for the usual electrolytes. The boundary conditions for z are derived from eq.(1.5 - 1.7) and eq. (1.9)

(i) $z(r \to \infty) = 0$ (1.16)

(ii) z is continuous $\forall r$ (1.17)

(iii) $F^\circ(z'-1)$ is continuous $\forall r$ (1.18)

Now we shall give the equation for $\hat{\phi}^1$.
Here we start with the following approximation for F_{abc} (unsymmetric superposition approximation after Kremp [5] for the nonequilibrium part)

$$\frac{F_{abc}}{F_{ab}} - F_{ac} = \left(\frac{F^\circ_{abc}}{F^\circ_{ab}} - F^\circ_{ac}\right) + F^\circ_{ac} F^1_{bc} \tag{1.19}$$

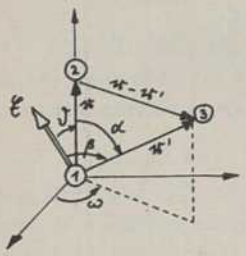
Then eq.(1.8) reads

$$\nabla\beta\hat{\phi}(\vec{r}) = \int \left[w_+ n_+ \nabla E_{++}(|\vec{r}-\vec{r}'|) + w_- n_- \nabla E_{--}(|\vec{r}-\vec{r}'|) \right] * \\ * F^1(\vec{r}')\, d\vec{r}' \tag{1.20}$$

with the Kirkwood function

$$E_{ab}(r) = \int_r^\infty F^\circ_{ab}(r')\, \frac{d}{dr'}\left(\beta\psi_{ab}(r')\right)\, dr' \tag{1.21}$$

Introducing spherical coordinates in eq.(1.20) we shall derive an inhomogeneous Fredholm integral equation of 2.kind for the radial part of Φ^1. We get



$$\int d\vec{r} = \int_0^{2\pi} d\omega \int_0^{\pi} d\alpha \sin\alpha \int_0^{\infty} dr\, r^2$$

and

$$\cos\beta = \sin\alpha \cos\omega \sin\vartheta + \cos\alpha \cos\vartheta \qquad (1.22)$$

From eq. (1.20) together with eq.(1.9) and (1.22) we find

$$\Psi(r) = f(r) + \int_0^{\infty} K(r,r')\, \Psi(r')\, dr' \qquad (1.23)$$

with the kernel

$$K(r,r') = -2\pi r'^2 F^0(r') \int_0^{\pi} \left[w_- n_- E_{--}(|\vec{r}-\vec{r}'|) + w_+ n_+ E_{++}(|\vec{r}-\vec{r}'|) \right] \cdot \sin\alpha \cdot \cos\alpha \, d\alpha \qquad (1.24)$$

$$|\vec{r}-\vec{r}'| = \left(r^2 + r'^2 - 2rr'\cos\alpha\right)^{1/2}$$

and the inhomogenity

$$f(r) = -\int_0^{\infty} K(r,r')\, z(r')\, dr' \qquad (1.25)$$

The solution of eq.(1.23) may be obtained using the facilities of modern computers. In this paper we do not discuss this possibility.

To solve eq.(1.20) analytically we approximate in eq.(1.21) F_{ab}^0 by 1 and Ψ_{ab} by the Coulomb potential $V_{ab} = e_a e_b / D \cdot r$. Then E_{ab} has the form

$$E_{ab} = \beta\, V_{ab} \qquad (1.26)$$

and the divergence of eq.(1.20) may be calculated taking into

account that $\Delta \frac{1}{r} = -4\pi\delta(\vec{r})$

$$\Delta \Phi^{1} = -kT\varkappa^{2}F^{1} \tag{1.27}$$

with $\alpha^{2} = q\varkappa^{2}$; $q = (1/\varrho_{+}+1/\varrho_{-})^{-1}\left(e_{+}/\varrho_{+} - \frac{e_{-}}{\varrho_{-}}\right)(e_{+}-e_{-})^{-1}$

and $\varkappa^{2} = 4\pi \sum_{a} n_{a} e_{a}^{2} / DkT$

For the radial part of Φ^{1} we get now after expansion with respect to the hydrodynamic parameter h

$$\begin{aligned} &\varphi(r) = \varphi_{0}(r) + h\,\varphi_{1}(r) + O(h^{2}) \\ &\frac{d}{dr}\left(\varphi_{i}' + \frac{2}{r}\varphi_{i}\right) = -\alpha^{2}F^{\circ}(z_{i} - \varphi_{i}) \end{aligned} \tag{1.27}$$

or

$$\varphi_{i}'' + \frac{2}{r}\varphi_{i}' - \left(\frac{2}{r^{2}} + \alpha^{2}F^{\circ}\right)\varphi_{i} = -\alpha^{2}F^{\circ}z_{i} \tag{1.29}$$

The boundary conditions for the φ_{i} are

(i) $\varphi_{i}(r \to \infty) = 0$ (1.30)

(ii) φ_{i} is continuous $\forall r$ (1.31)

(iii) φ_{i}' is continuous $\forall r$ (1.32)

2. Analytical solution for $z(r)$ for hard core potential.

For charged hard core systems the potential $\psi \equiv \psi_{+-}$ has the form

$$\psi = \begin{cases} \infty & o < r < R \\ -\frac{l}{r} & R \leq r < \infty \end{cases} \tag{2.1}$$

In what follows we use the Debye-Hückel approximation for F°

$$F^{\circ} = \begin{cases} 0 & o < r < R \\ \exp\{g(r)\} & R \leq r < \infty \end{cases} \tag{2.2}$$

with $g(r) = \tilde{\ell}\, e^{-\varkappa r}/r$; $\tilde{\ell} = \ell\, e^{\varkappa R}/(1+\varkappa R)$

and $\ell = -e_+ e_-/\mathcal{D}kT$

2.1 Zeroth order in electrophoresis z_0

In the region $R \leq r < \infty$ the eq. (1.14) has the following general solution

$$z_0 = A_h z_0^h + A_g z_0^g + z_0^p \tag{2.3}$$

Here z_0^g and z_0^h are two independent solutions of the homogeneous equation where $z_0^h (r \to \infty)$ is divergent. z_0^p is a partial solution of the inhomogeneous equation. From the boundary condition eq. (1.16) we get $A_h = 0$
and from eq.(1.18)

$$F^*(R-0)\left[A_g z_0'^g(R-0) + z_0'^p(R-0) - 1\right] = F^*(R+0)\left[A_g z_0'^g(R+0) + z_0'^p(R+0)\right]$$

or together with eq. (2.2)

$$A_g = \left[1 - z_0'^p(R)\right] / z_0'^g(R) \tag{2.4}$$

To solve eq.(1.14) we expand z_0^x $(x = h, g, p)$ with respect to powers of $\tilde{\ell}$

$$z_0^x = \sum_{n=0}^{\infty} z_{0n}^x \tag{2.5}$$

where $z_{0n}^x \sim \tilde{\ell}^n$ and $z_{0n}^x \equiv 0$ for $n < 0$.
Then we get the system of perturbation equations

$$z_{0n}''^x + \frac{2}{r} z_{0n}'^x - \frac{2}{r^2} z_{0n}^x = \delta_{x,p}\, g' - g' z_{0n-1}'^x \tag{2.6}$$

Here $\delta_{a,b}$ is the Kronecker symbol. A fundamental system of solutions of eq. (2.6) is

$$z_I = r^{-2} \quad \text{and} \quad z_{II} = r$$

with the Wronskian $W = 3\, r^{-2}$. Then the partial solutions are

calculated using the method of variation of constants ($R_n(r) \equiv$ $\equiv$ r.h.s. ; proportional to $\tilde{\ell}^n$)

$$z_{on}^{x} = -z_I \int z_{II} \frac{R_n(r')}{W(r')}\, dr' + z_{II} \int z_I \frac{R_n(r')}{W(r')}\, dr' \tag{2.7}$$

All the appearing r.h.s. of eq.(2.6) and the corresponding solutions after eq.(2.7) are given in table 1 up to order $\tilde{\ell}^2$ The result is

$$z_{oo}^{h} = z_I \tag{2.8}$$

$$z_{oo}^{g} = z_I$$

$$z_{o1}^{g} = z_{(1)} \tag{2.9}$$

$$z_{o2}^{g} = z_{(2)}$$

$$z_{oo}^{r} = 0$$

$$z_{o1}^{r} = z_{(3)} + \frac{\tilde{\ell}}{\varkappa^2} z_I \tag{2.10}$$

$$z_{o2}^{r} = z_{(4)} + \frac{1}{12} \frac{\tilde{\ell}^2}{\varkappa^4} z_I + \frac{\tilde{\ell}}{\varkappa^2} z_{(1)}$$

The higher order parts z_{on}^{h} $(n>2)$ are not of interest here. In z_{o1}^{r} and z_{o2}^{r} convergent homogeneous solutions were added to avoid divergencies at $\varkappa \to 0$. To calculate approximately the remainders ($x = g, \rho$)

$$z_{or}^{x} \approx \sum_{n=3}^{\infty} z_{on}^{x} \tag{2.11}$$

we use the following procedure. For vanishing concentration $\varkappa \to 0$ we have $F''/F' = \frac{q'}{q} \longrightarrow -\beta v' = -\ell/r^2$
Then eq.(1.14) reads with $\bar{z}_o \equiv z_o \ (\varkappa \to 0)$

$$\bar{z}_o'' + \left(\frac{2}{r} - \frac{\beta}{r^2}\right) \bar{z}_o' - \frac{2}{r^2} \bar{z}_o = -\frac{\ell}{r^2} \tag{2.12}$$

with the solution

$$\bar{z}_o = \alpha_h \bar{z}_o^{h} + \alpha_g \bar{z}_o^{g} + \bar{z}_o^{r} \tag{2.13}$$

$$\bar{z}_o^h = r - \ell/2 \tag{2.14}$$

$$\bar{z}_o^g = \frac{12\,r}{\ell^3}\left[\left(1+\frac{\ell}{2r}\right)\exp\{-\ell/r\} - 1 + \frac{\ell}{2r}\right]$$

$$= \frac{6}{r^2}\sum_{k=0}^{\infty}\frac{k+1}{(k+3)!}\left(-\ell/r\right)^k \tag{2.15}$$

$$\bar{z}_o^f = \ell/2 \tag{2.16}$$

Since the boundary condition eq.(1.16) cannot be fulfilled in the unscreened case $\varkappa \to 0$ we shall demand that the divergent at $r \to \infty$ contribution $\bar{z}_o^h$ vanishes or $a_h = 0$. The Solution $\bar{z}$ does not diverge at $r \to \infty$. The constant a_g is to be determined by the boundary condition at $r = R$ eq.(2.4)

$$a_g = \frac{1}{\bar{z}_o'^g(R)} = \frac{\ell^3}{12\,[T(b) - 1]} \tag{2.17}$$

with the Bjerrumparameter $b = \ell/R$ and

$$T(x) = e^{-x}\,(1 + x + x^2/2)$$

To calculate the remainders $z_{or}^{\varkappa}$ we neglect the lowest ℓ - orders in eq.(2.15) and eq.(2.16) up to ℓ^2 and resubstitute $\ell \Rightarrow -r^2 g' = \tilde{\ell}\,D(\varkappa r) \equiv G(r)$, with $D(x) = e^{-x}(1+x)$
This last step first proposed by Ebeling we shall call the "<u>static screening of the higher ℓ - ordes</u>".

Formally this means

$$z_{or}^{\varkappa} = \left[\bar{z}_o^{\varkappa}(r,\ell) - \text{all } \ell\text{-orders up to } \ell^2\right]_{\ell \Rightarrow \tilde{\ell} D(\varkappa r) \equiv G(r)} \tag{2.18}$$

Now we find immediately $z_{or}^{f} \equiv 0$ (2.19)

and

$$z_{0r}^{g} = \frac{12r}{G^3(r)}\left[\left(1+\frac{G(r)}{2r}\right)e^{-\frac{G(r)}{r}} - 1 + \frac{G(r)}{2r} - \frac{G^3(r)}{12r^3} + \frac{G^4(r)}{24r^4} - \frac{G^5(r)}{80r^5}\right]$$

$$= \frac{6}{r^2}\sum_{k=3}^{\infty}\frac{k+1}{(k+3)!}\left(-\frac{G(r)}{r}\right)^k \qquad (2.20)$$

The function

$$z_0 = A_g\left(z_{00}^{g} + z_{01}^{g} + z_{02}^{g} + z_{0r}^{g}\right) + z_{01}^{r} + z_{02}^{r} \qquad (2.21)$$

has the properties to be solution of eq.(1.14) and (1.16–1.18) up to ℓ^2 and to solve this equations correct in the limiting case $\varkappa \to 0$.

Finally we give the complete expansion with respect to ℓ ($z_{0n} \sim \ell^n$)

$$z_{00} = A_{g0}\, z_{00}^{g} \qquad (2.22)$$

$$z_{01} = A_{g1}\, z_{00}^{g} + A_{g0}\, z_{01}^{g} + z_{01}^{r}$$

$$z_{02} = A_{g2}\, z_{00}^{g} + A_{g1}\, z_{01}^{g} + A_{g0}\, z_{02}^{g} + z_{02}^{r}$$

with

$$A_{g0} = \left[1/z_{00}'^{g}\right]_{r=R}$$

$$A_{g1} = -\left[\left(z_{01}'^{g} + z_{00}'^{g} z_{01}'^{r}\right)/\left(z_{00}'^{g}\right)^2\right]_{r=R} \qquad (2.23)$$

$$A_{g2} = -\left[\left(z_{00}'^{g} z_{02}'^{g} - \left(z_{01}'^{g}\right)^2 - z_{00}'^{g} z_{01}'^{g} z_{01}'^{r} + \left(z_{00}'^{g}\right)^3 z_{02}'^{r}\right)/\left(z_{00}'^{g}\right)^3\right]_{r=R}$$

2.2 First order in electrophoresis z_1

In the region $R < r < \infty$ the eq.(1.15) has the following general solution

$$z_1 = B_h\, z_0^{h} + B_g\, z_0^{g} + z_1^{p} \qquad (2.24)$$

We note that the homogeneous solutions are the same as for z_0. From the boundary conditions we get

$$B_h = 0$$

$$B_g = -z_1'^{p}(R) \,/\, z_0'^{g}(R) \tag{2.25}$$

To get the function z_1^p we follow the procedure described in ch.2.1. with

$$z_1^p = \sum_{n=0}^{\infty} z_{1n}^p \tag{2.26}$$

and $z_{1n}^p \sim l^n$ we get the perturbation equations

$$z_{1n}''^{p} + \frac{2}{r} z_{1n}'^{p} - \frac{2}{r^2} z_{1n} = -g' z_1^p{}_{(n-1)} - \frac{12\,l}{r}\left(\frac{z_{0(n-1)}}{r}\right)' \tag{2.27}$$

All the appearing r.h.s. of eq.(2.27) and the corresponding solutions after eq.(2.7) are given in table 1 up to order l^2. The result is

$$z_{10}^p = 0$$

$$z_{11}^p = A_{g0}\, z_{(5)} \tag{2.28}$$

$$z_{12}^p = A_{g0}\, z_{(6)} + A_{g1}\, z_{(5)} + z_{(7)} - \frac{18\,l}{x^2} z_{(4)} + \frac{4\,\tilde{l}\,l}{x^2} z_I$$

The unscreened equation for $\bar{z}_1 = z_1\,(x \to 0)$ reads

$$\bar{z}_1'' + \left(\frac{2}{r} - \frac{l}{r^2}\right)\bar{z}_1' - \frac{2}{r^2}\bar{z}_1 = -12\,\frac{l}{r}\left(\frac{\bar{z}_0}{r}\right)' \tag{2.29}$$

with the solution

$$\bar{z}_1 = b_h \bar{z}_0^h + b_g \bar{z}_0^g + \bar{z}_1^p \tag{2.30}$$

The homogeneous solutions $\bar{z}_0^h$ and $\bar{z}_0^g$ are given in eqn. (2.14, 2.15). A partial solution created by $a_g\,\bar{z}_0^g$ in eq. (2.29) has the form

$$\bar{Z}^{p}_{1\alpha} = \frac{144\,r}{\ell^3}\,a_9\Big\{\Big(1-\frac{\ell}{2r}\Big)\Big[Ei\Big(-\frac{\ell}{r}\Big)-\ln\frac{\ell}{r}-c\Big]$$

$$+\Big(1+\frac{\ell}{2r}\Big)\Big[Ei\Big(\frac{\ell}{r}\Big)-\ln\frac{\ell}{r}-c\Big]\,e^{-\ell/r}$$

$$+\Big(1+\frac{3\ell}{2r}+\frac{\ell^2}{2r^2}\Big)e^{-\ell/r}-1-\frac{\ell}{2r}\Big\} \qquad (2.31)$$

The expansion with respect to ℓ gives

$$\bar{Z}^{p}_{1\alpha} = -12\,r\sum_{k=0}^{\infty} f_k\big(\ell/r,\ \ell/R\big)\ ;\quad f_k\sim\ell^k$$

and (2.32)

$$f_0(x,b) = \frac{1}{2}\,\frac{x^3}{b^3}$$

$$f_1(x,b) = -\frac{7}{16}\,\frac{x^4}{b^3}+\frac{3}{8}\,\frac{x^3}{b^2}$$

$$f_2(x,b) = \frac{29}{160}\,\frac{x^5}{b^3}-\frac{21}{64}\,\frac{x^4}{b^2}+\frac{21}{160}\,\frac{x^3}{b}$$

A further partial solution comes from $\bar{z}^{p}_{0}$ in eq.(2.29)

$$\bar{Z}^{p}_{1\beta} = 12\,r\Big\{\Big[Ei\Big(\frac{\ell}{r}\Big)-\ln\frac{\ell}{R}-c\Big]\,e^{-\ell/r}\Big(1+\frac{\ell}{2r}\Big)$$

$$-\Big(1-\frac{\ell}{2r}\Big)\ln\frac{R}{r}-2\Big\} \qquad (2.33)$$

Here the ℓ - expansion gives

$$\bar{Z}^{p}_{1\beta} = 12\,r\Big\{-2+\frac{\ell}{r}-\frac{1}{4}\,\frac{\ell^2}{r^2}+\Big(\frac{1}{12}\ln\frac{R}{r}-\frac{5}{72}\Big)\frac{\ell^3}{r^3}+\mathcal{O}(\ell^4)\Big\} \qquad (2.34)$$

Now the unscreened solution $\bar{Z}_1 = b_4\,\bar{z}^{3}_{0}+\bar{Z}^{p}_{1\alpha}+\bar{Z}^{p}_{1\beta}$
is complete with $b_4 = 0$ as argued in ch.2.1 and

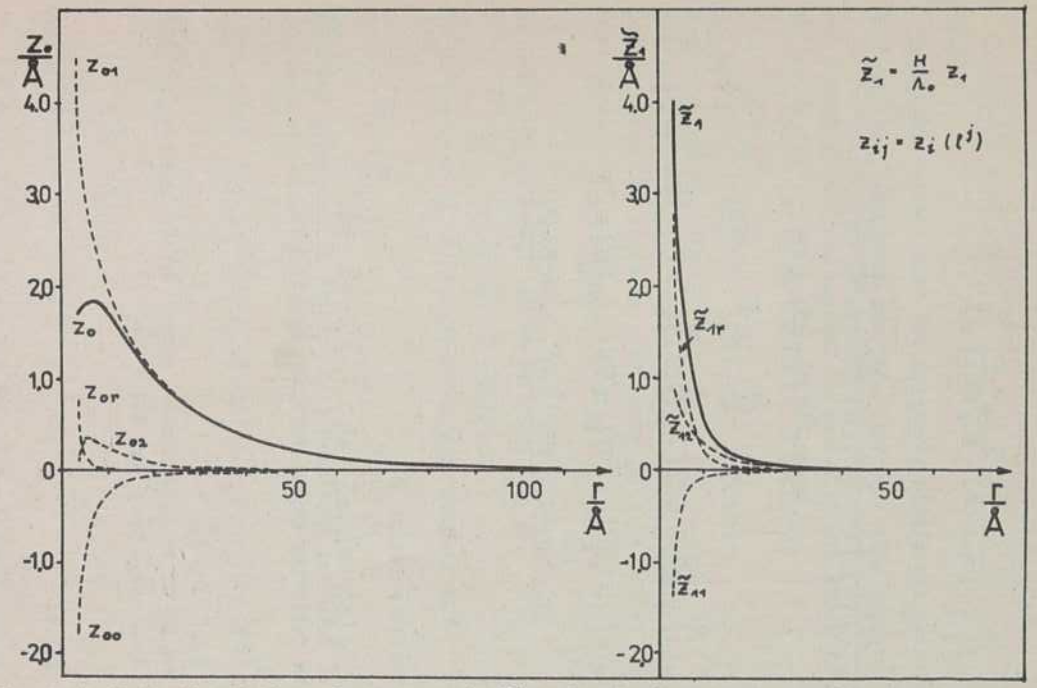


Fig.1: Analytical solutions for $z_o(r)$ and $\tilde{z}_1(r)$ for hard core potential
($\varkappa$ = 0.10405 Å^{-1}, R = 3.576 Å, l = 7.1522 Å, Λ_o = 150.0 cm^2 Ω^{-1} mol^{-1})

$$b_g = -\left(\bar{z}^{\prime f}_{1\alpha}(R) + \bar{z}^{\prime f}_{1\beta}(R)\right) / \bar{z}^{\prime g}_{0}(R) \tag{2.35}$$

After doing the static screening the higher-order remainder reads

$$\begin{aligned} z^{f}_{1r} = \frac{12r}{T(\frac{G(R)}{R})-1} \Big\{ & (1-\tfrac{G(r)}{2r})\left[Ei(-\tfrac{G(r)}{r}) - \ln\tfrac{G(r)}{r} - c\right] \\ & + (1+\tfrac{G(r)}{2r})\, e^{-\frac{G(r)}{r}}\left[Ei(\tfrac{G(r)}{r}) - \ln\tfrac{G(r)}{r} - c\right] \\ & + (1+\tfrac{3G(r)}{2r}+\tfrac{G^2(r)}{2r^2})\, e^{-\frac{G(r)}{r}} - 1 - \tfrac{G(r)}{2r} \Big\} \\ & + 12r\left\{ f_0(\tfrac{G(r)}{r}, \tfrac{G(R)}{R}) + f_1(\tfrac{G(r)}{r}, \tfrac{G(R)}{R}) + f_2(\tfrac{G(r)}{r}, \tfrac{G(R)}{R})\right\} \\ & + 12r\Big\{ (1+\tfrac{G(r)}{2r})\, e^{-\frac{G(r)}{r}}\left[Ei(\tfrac{G(r)}{r}) - \ln\tfrac{G(r)}{R} - c\right] \\ & - (1-\tfrac{G(r)}{r})\ln\tfrac{R}{r} - \tfrac{G(r)}{r} + \tfrac{1}{4}\,\tfrac{G^2(r)}{r^2} \Big\} \end{aligned} \tag{2.36}$$

The complete solution z_1

$$z_1 = B_g\left(z^{g}_{00} + z^{g}_{01} + z^{g}_{02} + z^{g}_{0r}\right) + z^{f}_{11} + z^{f}_{12} + z^{f}_{1r} \tag{2.37}$$

has the following expansion with respect to ℓ

$$\begin{aligned} z_{10} &= 0 \\ z_{11} &= B_{g1}\, z^{g}_{00} + z^{f}_{11} \\ z_{12} &= B_{g2}\, z^{g}_{00} + B_{g1}\, z^{g}_{01} + z^{f}_{12} \end{aligned} \tag{2.38}$$

with

$$B_{g0} = 0 \tag{2.39}$$

$$B_{g1} = -\left[z^{\prime f}_{11} / z^{\prime g}_{00}\right]_{r=R}$$

$$B_{gz} = \left[\left(z'^{f}_{+2}\, z'^{g}_{00} - z'^{f}_{+1}\, z'^{g}_{01} \right) / \left(z'^{g}_{00} \right)^2 \right]_{r=R}$$

3. Analytical solutions for $\varphi(r)$ for hard core potentials.

The potential and the approximation for F^0 are given in ch.2. In the region $0 < r \leq R$ eq.(1.29) reads

$$\varphi_i'' + \frac{2}{r}\varphi_i' - \frac{2}{r^2}\varphi_i = 0 \tag{3.1}$$

with the solution $\varphi_{iI} = r$ and $\varphi_{iII} = r^{-2}$. Since φ_i is limited for $r \to 0$. φ_{iI} is the only relevant solution in this region. Then the boundary conditions eq.(1.31, 1.32) are equivalent to

$$\varphi_i(R-0) = \varphi_i(R+0)$$
$$\varphi_i'(R-0) = \varphi_i'(R+0) \tag{3.2}$$

or (with $\varphi_i(r) = r\,\varphi_i'(r)$ in $0 < r \leq R$)

$$\varphi_i(R+0) = R \cdot \varphi_i'(R+0) \tag{3.3}$$

As in the case of z_i we expand φ_i with respect to l

$$\varphi_i = \sum_{n=0}^{\infty} \varphi_{in} \qquad \text{with} \qquad \varphi_{in} \sim l^n \tag{3.4}$$

Then the perturbation differential equations for both φ_0 and φ_1 have the structure ($x = g, h, p$)

$$\varphi_{in}^{\prime\prime x} + \frac{2}{r}\varphi_{in}^{\prime x} - \left(\frac{2}{r^2} + \alpha^2\right)\varphi_{in}^{x} = \delta_{x,p}\left(-\alpha^2 \left[F^0 z_i\right]_n\right) + \alpha^2 \left[\left(F^0 - 1\right)\varphi_i^x\right]_n \tag{3.5}$$

Here $[f]_n$ denotes the l^n-order contribution of f. We get

$$\begin{aligned} \left[F^0 z_i\right]_0 &= z_{i0} \\ \left[F^0 z_i\right]_1 &= z_{i1} + q\, z_{i0} \\ \left[F^0 z_i\right]_2 &= z_{i2} + q\, z_{i1} + \frac{1}{2} q^2 z_{i0} \end{aligned} \tag{3.6}$$

$$[(F^{\circ}-1)\varphi_i^{\varkappa}]_0 = 0$$

$$[(F^{\circ}-1)\varphi_i^{\varkappa}]_1 = q\,\varphi_{i0}^{\varkappa} \tag{3.6}$$

$$[(F^{\circ}-1)\varphi_i^{\varkappa}]_2 = q\,\varphi_{i1}^{\varkappa} + \tfrac{1}{2}q^2\varphi_{i0}^{\varkappa}$$

Since even the correct solution of eq.(3.5) up to l^2 is rather complicated we restrict ourselves in what follows on symmetrical electrolytes i.e. $\alpha^2 = \frac{1}{2}\varkappa^2$ or $q = 1/2$

In the region $R < r < \infty$ the eq.(3.5) has the following general solutions

$$\varphi_0 = C_h\varphi_0^h + C_q\varphi_0^q + \varphi_0^p$$
$$\varphi_1 = D_h\varphi_0^h + D_q\varphi_0^q + \varphi_1^p \tag{3.7}$$

Here φ_0^h and φ_0^q are the homogeneous solutions divergent and convergent in the limit $r \to \infty$ respectively. From the boundary condition eq.(1.30) follows $C_h = 0$ and $D_h = 0$. Further we get after eq.(3.3) for the constants

$$C_q = -\left[(\varphi_0^p(r) - r\,\varphi_0'^p(r))/(\varphi_0^q(r) - r\,\varphi_0'^q(r))\right]_{r=R} \tag{3.8}$$

and

$$D_q = -\left[(\varphi_1^p(r) - r\,\varphi_1'^p(r))/(\varphi_0^q(r) - r\,\varphi_0'^q(r))\right]_{r=R}$$

A fundamental system of solution of eq.(3.5) is $\varphi_I = D(\alpha r)/r^2$ and $\varphi_{II} = D(-\alpha r)/r^2$ with the Wronskian $W = -2\alpha^3 r^{-2}$. Using the partial solutions given in table 2 we get the following expressions

$$\varphi_0^q = \varphi_{00}^q + \varphi_{01}^q + \varphi_{02}^q + \varphi_{0r}^q \tag{3.9}$$

with

$$\varphi_{00}^q = \varphi_I$$
$$\varphi_{01}^q = \varphi_{(1)}$$
$$\varphi_{02}^q = \varphi_{(2)}$$

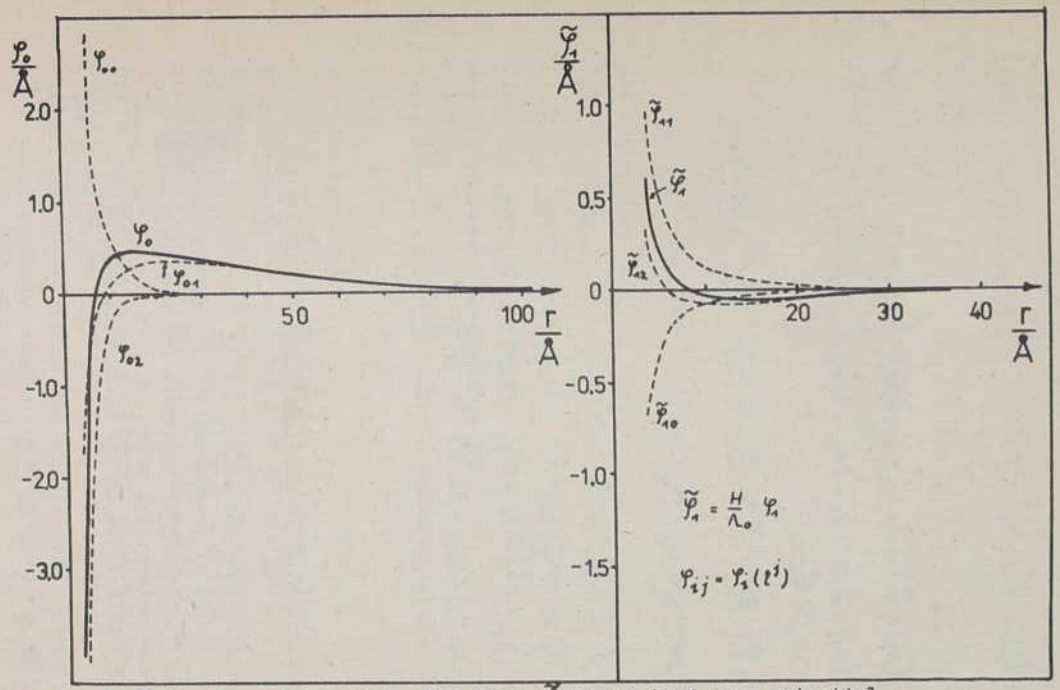


Fig.2 Analytical solutions for $\varphi_0(r)$ and $\tilde{\varphi}_1(r)$ for hard core potential
($\varkappa$ = 0.10405 Å^{-1}, R = 3,576 Å , l = 7.1522 Å, Λ_0 = 150,0 cm^2 Ω^{-1} mol^{-1}.

$$\varphi_0^P = \varphi_{00}^P + \varphi_{01}^P + \varphi_{02}^P + \varphi_{0r}^P \qquad (3.10)$$

with

$$\varphi_{00}^P = A_{g_0} z_I$$

$$\varphi_{01}^P = (A_{g_1} + \tilde{\ell}/\varkappa^2) z_I + A_{g_0} \varphi_{(3)} - z_{(3)} - 2\tilde{\ell}/\varkappa^2 \cdot \varphi_I$$

$$\varphi_{02}^P = (A_{g_2} + \frac{1}{12}\frac{\tilde{\ell}^2}{\varkappa}) z_I + (A_{g_1} + \tilde{\ell}/\varkappa^2)\varphi_{(3)} + A_{g_0}\varphi_{(4)}$$
$$+ \varphi_{(5)} - \frac{2\tilde{\ell}}{\varkappa^2}\varphi_{(1)}$$
$$+ \tilde{\ell}\left\{ \frac{5}{4\varkappa} - \frac{1}{2\alpha} + \frac{1}{16\alpha} \ln\frac{\varkappa-\alpha}{\varkappa+\alpha} - \frac{7}{16\alpha}\ln\frac{2\varkappa-\alpha}{2\varkappa+\alpha}\right\}\varphi_I$$

and

$$\varphi_1^P = \varphi_{10}^P + \varphi_{11}^P + \varphi_{12}^P + \varphi_{1r}^P \qquad (3.11)$$

with

$$\varphi_{10}^P = 0$$

$$\varphi_{11}^P = B_{g_1} z_I + A_{g_0}\varphi_{(6)}$$

$$\varphi_{12}^P = (B_{g_2} - 8\frac{\tilde{\ell}\ell}{\varkappa})z_I + (B_{g_1} - 18\ell/\varkappa^2)\varphi_{(3)} + A_{g_0}\varphi_{(7)}$$
$$+ A_{g_0}\varphi_{(6)} + \varphi_{(8)} + 39\frac{\tilde{\ell}\ell}{8\alpha}\ln\frac{\varkappa+\alpha}{\varkappa-\alpha}\varphi_I$$

The higher ℓ - order remainders φ_{0r}^2, φ_{0r}^P and φ_{1r}^P are not yet calculated.

4. Comparison of the z-φ-theory with other formulations.

In this chapter we show the connection of the z-φ-theory with the u - theory of Kremp/Kraeft [7] and the y-theory of Falkenhagen/Kelbg/Ebeling/Kremp/Kraeft [8] in the special case of hard core potentials. Both u- and y - formulation are valid for the zeroth order in the electrophoresis only.

4.1 The u - theory.

We define

$$u_0 = \dot{z}_0 - \varphi_0 \tag{4.1}$$

Then we get an ordinary differential equation for u_0 using eq.(1.14) and eq.(1.29)

$$u_0'' + \left(\frac{2}{r} - \frac{\ell}{\mu^2}\right) u_0' - \left(\frac{2}{r^2} + \alpha^2\right) u_0 = -\beta \Phi^{0\prime} + \mathcal{D}_u \tag{4.2}$$

The remainder $\mathcal{D}_u$ neglected in the u - theory has the form

$$\mathcal{D}_u = \beta \Phi^{0\prime} \cdot \varphi_0' + \left(\beta \Phi^{0\prime} - \frac{\ell}{\mu^2}\right) u_0' + \alpha^2 (F^0 - 1) u_0 \Rightarrow 0 \tag{4.3}$$

The neglection $\mathcal{D}_u \equiv 0$ means

(i) single φ_0 - terms are to be omitted

(ii) approximate on the l.h.s. Φ^0 by V (4.4)

(iii) approximate on the l.h.s. F^0 by 1

For the boundary conditions we get

$$u_0 (r \to \infty) = 0$$

$$u_0' (R) = 1 + R_u \tag{4.5}$$

Here the remainder (4.6)

$$R_u \equiv \varphi_0' (R) \Rightarrow 0$$

vanishes using the approximation eq.(4.4(i)).
Comparing the perturbation expansion with respect to ℓ we see that $u_{00} (\sim \ell^0)$ agrees with the z-φ - theory. In $u_{0i} (\sim \ell^i, i>0)$ discrepances appear with respect to z-φ from two reasons

(i) created by the approximation eq.(4.4(i)) some φ - contributions disappear

(ii) higher c-contributions of u_{0i} and $c_{0i} - \varphi_{0i}$ $(i>1)$ do not conincide completely because of the approximations eq.(4.4 (ii) and (iii)).

We note that the static screened higher ℓ - order contributions are the same in both formulations.

4.2 The y - theory.

We define

$$y_0 = F^0 u_0 = F^0 (z_0 - \varphi_0) \tag{4.7}$$

Using eq.(4.2) we find

$$y_0'' + \left(\frac{2}{r} + \frac{\beta}{r^2}\right) y_0' - \left(\frac{2}{r^2} + \alpha^2\right) y_0 = F^{0\prime} + D_y \tag{4.8}$$

The remainder Dy neglected in the y - theory reads

$$D_y \equiv -F^{0\prime}\varphi_0' - \left(\beta\Phi^{0\prime} - \frac{\ell}{r^2}\right) y_0'$$
$$+\left[\alpha^2(F^0 - 1) - \beta\Phi^{0\prime\prime} - \frac{2}{r}\beta\Phi^{0\prime}\right] y_0 \Rightarrow 0 \tag{4.9}$$

The neglection Dy $\equiv$ 0 is correct under the approximations given in eq.(4.4). So we can conclude that the approximation level of the u - and the y - theory is the same with respect to the solution of the differential equations (4.2) and (4.8). From eq.(4.5) and (4.7) we get for the boundary conditions

$$y_0(r \to \infty) = 0$$

$$y_0'(R) + \beta\Phi^{0\prime}(R)\, y_0(R) = F^0(R) + R_y \tag{4.10}$$

Here R is to be understood as R + 0. Now the remainder Ry has the form

$$R_y \equiv F^0(R)\, \varphi_0'(R) \Rightarrow 0 \tag{4.11}$$

As noted above the fundamental solutions and the partial solution of eq.(4.8) coincide with the corresponding solutions of eq.(4.2) after expansion with respect to ℓ and to the concentration. Also constants agree if we use the boundary condition eq.(4.10) . Usually in the y-theory eq.(4.10) is further

simplified $d\beta\Psi^{0}(R)/dr \Rightarrow \ell/R^{2}$. Then differences appear in the concentration expansion of the integration constants for the homogeneous solutions as first mentioned by Kremp.

5. The conductivity functions for stairslike potentials.

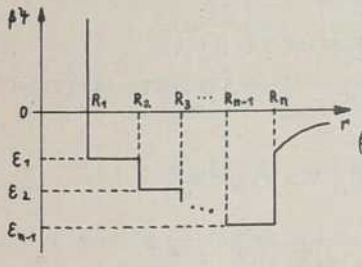
To calculate the conductance Λ after eq.(1.1) it is necessary to know the relaxation force

$$\vec{K}_a^{Rel} = -\sum_b n_b \int \nabla \psi_{ab} F_{ab} \, d\vec{r}_b \tag{5.1}$$

and the electrophoretic force

$$\vec{K}_a^{El} = \varrho_a \sum_b n_b \int \frac{\chi_{ab}}{\varrho_b} \left[e_b \vec{E} + \vec{K}_b^{RH} + \vec{K}_{ab} \right] F_{ab} \, d\vec{r}_b \tag{5.2}$$

We define a stairslike potential as follows:



$$\beta\psi = \begin{cases} \infty & \text{if } 0 < r \leq R_1 \\ \varepsilon_1 & \text{if } R_1 < r \leq R_2 \\ \vdots & \text{if } R_{n-1} \leq r \leq R_n \\ \varepsilon_{n-1} & \\ -\frac{\ell}{r} = \beta V & \text{if } R_n < r < \infty \end{cases} \tag{5.3}$$

obviously the well known hard core and step potentials are special cases of the potential given above.

5.1 The relaxation force.

We are interested in the contribution proportional to the external electrical field only. Then eq.(5.1) reads

$$\vec{K}_a^{Rel} = -\sum_b n_b \int \nabla \psi_{ab} F_{ab}^{1} \, d\vec{r}_b \tag{5.4}$$

Since $F^{*}_{aa} = 0$ and $F^{*}_{+-} = -F^{*}_{-+} = F^{*}$ we get

$$\vec{K}_{+}^{Rel} = -\frac{n_-}{n_+}\vec{K}_{-}^{Rel} = \vec{K}^{Rel} \tag{5.5}$$

with $\vec{K}^{Rel} = -n\int \nabla \psi_{+-} F^{*} d\vec{r} = \vec{K}_1^{Rel} + \vec{K}_2^{Rel}$. Here $\vec{K}_1^{Rel}$ denotes

$$\vec{K}_1^{Rel} = -n_- \int \nabla V F^{*} d\vec{r} \tag{5.6}$$

We discuss two ways to calculate $\vec{K}_1^{Rel}$:

(i) with $F^{*} = \mu F^{0}(z-\varphi)\cos\vartheta = \mu\, y(r)\cos\vartheta$ for $r > R_1$ and $F^{*} = 0$ for $r < R_1$ we get

$$\vec{K}_1^{Rel} = -\frac{4\pi}{3} n_- kT l \mu \frac{\vec{E}}{E}\int_{R_1}^{\infty} y(r)\, dr \tag{5.7}$$

(ii) We start from the connection after eq. (1.27) $\Delta\Phi^{*} = -kT\alpha^2 F^{*}$ which is correct in the Kremp approximation eq.(1.19). Then $\vec{K}_1^{Rel}$ reads

$$\vec{K}_1^{Rel} = -n_-\int \nabla V F^{*} d\vec{r} = \frac{n_-}{kT\alpha^2}\int \nabla V\, \Delta\Phi^{*} d\vec{r}$$

$$= \frac{n_-}{kT\alpha^2}\int \left[\nabla(\nabla V\cdot\nabla\Phi^{*}) - \Delta V\, \nabla\Phi^{*}\right] d\vec{r} \tag{5.8}$$

($\nabla(\nabla V\cdot\nabla\Phi^{*})$ integrates to 0 by Gauss; $\Delta V = -4\pi\delta(\vec{r})\,kT l$)

$$= \frac{4\pi n_- l}{\alpha^2}\,\nabla\Phi^{*}(\vec{r}=0)$$

$$= \frac{4\pi l kT n_-}{\alpha^2}\,\mu\frac{\vec{E}}{E}\,\varphi'(0)$$

For $\vec{K}_2^{Rel}$ we get with $V' \equiv \psi - V$

$$\vec{K}_2^{Rel} = -n_- \int \nabla V' F^{-1} \, d\vec{r}$$

$$= \frac{4\pi}{3} n_- kT \mu \frac{\vec{E}}{E} \cdot$$

$$\cdot \Big\{ \sum_i^n R_i^2 \left[z(R_i) - \varphi(R_i) \right] \cdot \left[F^\circ(R_i+0) - F^\circ(R_i-0) \right]$$

$$+ l \int_{R_n}^{R_n} F^\circ(r) \left[z(r) - \varphi(r) \right] dr \Big\} \qquad (5.9)$$

We note that the covolume contribution $\vec{K}_2^{Rel}$ is valid for square well potentials too after neglecting the integral in eq.(5.9).
Now we define the relaxation function $S^{Rel}[1]$ by

$$\vec{K}^{Rel} = kT \mu \frac{\nu_+ \Lambda_+^\circ + \nu_- \Lambda_-^\circ}{\nu_+ \Lambda_0} \frac{\vec{E}}{E} S^{Rel} \qquad (5.10)$$

or

$$S^{Rel} = -\frac{\nu_+ n_- \Lambda_0}{\nu_+ \Lambda_+^\circ + \nu_- \Lambda_-^\circ} \cdot$$

$$\cdot \Big\{ \frac{4\pi}{3} \sum_{i=1}^n R_i^2 \left[z(R_i) - \varphi(R_i) \right] \cdot \left[F^\circ(R_i+0) - F^\circ(R_i-0) \right] + I \Big\} \qquad (5.11)$$

In the version (i) given above I reads

$$I = -\frac{4\pi}{3} l \int_{R_n}^{\infty} y(r) \, dr \qquad (5.12a)$$

In the case (ii) we get

$$I = -\frac{4\pi l}{3\alpha^2} \varphi'(0) + \frac{4\pi}{3} l \int_{R_n}^{R_n} F^\circ (z - \varphi) \, dr$$

$$= -\frac{4\pi l}{3\alpha^2} \left[\varphi'(R_n) + \frac{2}{R_n} \varphi(R_n) \right] \qquad (5.12b)$$

5.2 The electrophoretic force.

Starting from eq.(5.2) we approximate the two particle relaxation force $\vec{K}_{ab}$ by $-\nabla\Phi_{ab}$. Further we split up $\vec{K}_a^{El}$ into two parts

$$\vec{K}_a^{El} = \vec{K}_a^{El,Ext} + \vec{K}_a^{El,Int} \tag{5.13}$$

The external part $\vec{K}_a^{El,Ext}$ reads

$$\vec{K}_a^{El,Ext} = \varrho_a \sum_b n_b \int \frac{\chi_{ab}}{\varrho_b} \left[e_b \vec{E} + \vec{K}_a^{Rel} \right] F_{ab}^{\circ} \, d\vec{r}_b \tag{5.14}$$

As shown in [1] it is useful to define the external electrophoretic function S^{Ext} by

$$S^{Ext} = S_+^{Ext} + S_-^{Ext}$$

and

$$S_a^{Ext} = n_+ e_+ \left(\frac{e_+}{\varrho_+} - \frac{e_-}{\varrho_-} \right)^{-1} \left[G_{aa} - G_{+-} \right] \tag{5.15}$$

with $G_{ab} = \frac{2}{3\eta_0} \int_0^\infty r \, F_{ab}^{\circ}(r) \, dr$

The internal response is given by

$$\begin{aligned} \vec{K}_a^{El,Int} &= -\varrho_a \sum_b n_b \int \frac{\chi_{ab}}{\varrho_b} \nabla \Phi_{ab} F_{ab} \, d\vec{r}_b \\ &= -\varrho_a \sum_b n_b \int \frac{\chi_{ab}}{\varrho_b} \nabla \Phi_{ab} \, e^{-\beta \Phi_{ab}} \left[1 + \mu_{ab} z(r) \cos\vartheta + O(E^2) \right] d\vec{r}_b \\ &= kT \varrho_a \sum_b n_b \int \frac{\chi_{ab}}{\varrho_b} \mu_{ab} z(r) \cos\vartheta \, \nabla F_{ab}^{\circ} \, d\vec{r}_b \end{aligned} \tag{5.16}$$

Here we introduce the internal electrophoretic function

$$S^{Int} = -\left(\frac{1}{\varrho_+} + \frac{1}{\varrho_-} \right)^{-1} (n_+ + n_-) \, \mathcal{J} \tag{5.17}$$

and

$$\mathcal{J} = \frac{1}{3\eta_0} \int_0^\infty r \, z(r) \frac{\partial F^{\circ}(r)}{\partial r} \, dr \tag{5.18}$$

For stairslike potential we get

$$\gamma = \frac{1}{3\eta_0}\left\{\int_0^\infty r\,z(r)\,F^\circ(r)\,\frac{dg(r)}{dr}\,dr + \int_{R_1}^{R_n}\frac{1}{r}\,z(r)\,F^\circ(r)\,dr + \sum_{i=1}^{n} R_i\,z(R_i)\left[F^\circ(R_i+0)-F^\circ(R_i-0)\right]\right\} \tag{5.19}$$

6. The method of numerical calculation of z and φ for hard core potentials.

To solve the ordinary differential equations (1.14, 1.15 and 1.29) for z_0, z_1, φ_0 and φ_1 in the region $R < r < \infty$ it is convenient to substitute $r \longrightarrow x = R/r$. In what follows we have to understand z_0 as $z_0(x)$ etc. The following relations are straightforward

$$\frac{d}{dr} = -\frac{x^2}{R}\frac{d}{dx} \qquad \text{and} \qquad \frac{d^2}{dr^2} = \frac{x^4}{R^2}\left[\frac{d^2}{dx^2} + \frac{2}{x}\frac{d}{dx}\right] \tag{6.1}$$

The resulting equations were solved by the Runge-Kutta algorithm with Gill's modification [6] in the region $0 \leq x \leq 1$. In table 3 a survey of all appearing equations is given.

6.1 Calculation of $z(x)$

In the x - space the differential equation for the homogeneous solution z_0^g reads

$$\frac{d^2 z_0^g(x)}{dx^2} - \frac{d\beta\Phi^0(x)}{dx}\cdot\frac{d z_0^g(x)}{dx} - \frac{2}{x^2} z_0^g(x) = 0 \tag{6.2}$$

Here we have introduced $-\beta\Phi^0 \equiv \ln F^0$

From the behaviour at $x \to 0$

$$z_0^g(x \to 0) = x^2 \tag{6.3}$$

we get the initial conditions

$$z_0^g(0) = 0$$
$$\frac{d}{dx} z_0^g(0) = 0 \tag{6.4}$$

The differential equation for the partial solution z_0^f has the form

$$\frac{d^2 z_0^f(x)}{dx^2} - \frac{d\beta\Phi^0(x)}{dx}\cdot\frac{d z_0^f(x)}{dx} - \frac{2}{x^2} z_0^f(x) = \frac{R}{x^2}\frac{d\beta\Phi^0(x)}{dx} \tag{6.5}$$

Here the initial conditions

$$z_0^p(0) = 0$$

$$\frac{d}{dx} z_0^p(0) = 0 \qquad (6.6)$$

come from

$$z_0^p(x \to 0) = A_p x^2 \qquad (6.7)$$

with

$$A_p = \tilde{l}/\varkappa^2 R^2 + \tilde{l}^2/12\,\varkappa R^2 \qquad \text{after eq.(2.10)}$$

For the complete z_0 solution we get

$$z_0 = A_g z_0^g + z_0^p \qquad (6.8)$$

The constant A_g is to be determined from the boundary condition eq.(2.4) in the x - space

$$A_g = -\left(R + \frac{d}{dx} z_0^p(1)\right) \Big/ \frac{d}{dx} z_0^g(1) \qquad (6.9)$$

For $x \to 0$ the function z_0 behaves as

$$z_0(x \to 0) = A x^2 = (A_g + A_p) x^2 \qquad (6.10)$$

From eq.(1.15) and eq.(6.1) we derive the differential equation for the partial solution z_1^p

$$\frac{d^2 z_1^p(x)}{dx^2} - \frac{d\beta\Phi^0(x)}{dx} \cdot \frac{d z_1^p(x)}{dx} - \frac{2}{x^2} z_1^p(x) = 12 \frac{l}{R} \frac{1}{x} \frac{d}{dx}(x \cdot z_0(x)) \qquad (6.11)$$

with the initial conditions

$$z_1^p(0) = 0$$

$$\frac{d}{dx} z_1^p(0) = 0 \qquad (6.12)$$

coming from

$$z_1^p(x \to 0) = B_p x^2 + 9 \frac{l}{R} A x^3 \qquad (6.13)$$

Here is $B_p = -\rho l \tilde{l}/\varkappa R^2$ after eq. (2.28). For z_1 we get

$$z_1 = B_g z_0^g + z_1^p \qquad (6.14)$$

with

$$B_g = - \frac{d}{dx} z_{-1}^{g}(1) \Big/ \frac{d}{dx} z_0^{g}(1) \tag{6.15}$$

Now it is easily found

$$z_{-1}(x \to 0) = B x^2 + \frac{g\,l}{R} A x^3 \equiv (B_g + B_f) x^2 + g \frac{l}{R} A\, x^3 \tag{6.16}$$

Last not least we give the connection between $z(r)$ and $z(x)$:

$$\begin{aligned} z_0^{g}(r) &= R^{-2} z_0^{g}(x = R/r) \\ z_{-1}^{f}(r) = z_0^{f}(x = R/r) \;&;\; z_{-1}^{f}(r) = z_{-1}^{f}(x = R/r) \\ z_0(r) = z_0(x = R/r) \;&;\; z_{-1}(r) = z_{-1}(x = R/r) \\ A_g[r] = R^2 A_g[x] \;&;\; B_g[r] = R^2 B_g[x] \end{aligned} \tag{6.17}$$

6.2 Calculation of $\varphi(x)$

The differential equation for the homogeneous solution φ_0^{g} has the form

$$\frac{d\,\varphi_0^{g}(x)}{dx^2} - \left(\frac{2}{x^2} + \frac{\alpha^2 R^2 F^{\circ}}{x+} \right) \varphi_0^{g}(x) = 0 \tag{6.18}$$

The analytical solution eq.(3.9) shows the exponential vanishing of $\varphi_0^{g}(x \to 0)$. To avoid numerical difficulties connected with his behaviour we substitute

$$\varphi_0^{g}(x) = \mathcal{D}\left(\frac{\alpha R}{x}\right) g(x) \tag{6.19}$$

and get

$$\frac{d^2 g(x)}{dx^2} + \frac{2\,\alpha^2 R^2}{x^2 (x + \alpha R)} \cdot \frac{dg(x)}{dx} \tag{6.20}$$

$$- \left[\frac{2}{x^2} + \frac{4\alpha^2 R^2}{x^3 (x + \alpha R)} + \frac{\alpha^2 R^2 (F^{\circ} - 1)}{x+} \right] g(x) = 0$$

with the initial conditions

$$q(0) = 0$$

$$\frac{d}{dx} q(0) = 0 \tag{6.21}$$

since $q(x \to 0) = x^2$.

The differential equation for both partial solutions φ_0^P and φ_1^P reads ($i = 0, 1$)

$$\frac{d^2 \varphi_i^P(x)}{dx^2} - \left(\frac{2}{x^2} + \frac{\alpha^2 R^2 F^0}{x^4} \right) \varphi_i^P(x) = - \frac{\alpha^2 R^2 F^0}{x^4} z_i(x) \tag{6.22}$$

Here the behaviour for $x \to 0$ is the following

$$\varphi_0^P(x \to 0) = A x^2$$

$$\varphi_1^P(x \to 0) = B x^2 \tag{6.23}$$

The constants A and B are defined in eq.(6.10) and eq.(6.16) respectively. Therefore we get for the initial conditions

$$\varphi_i^P(0) = 0$$

$$\frac{d}{dx} \varphi_i^P(0) = 0 \tag{6.24}$$

Now the complete solutions may be determined

$$\varphi_0(x) = C_1 \varphi_0^1(x) + \varphi_0^P(x)$$

$$\varphi_1(x) = D_1 \varphi_0^1(x) + \varphi_1^P(x) \tag{6.25}$$

Here the constants C_1 and D_1 have to be calculated fulfilling the boundary conditions eq.(1.31) and eq.(1.32) or eq. (3.3)

$$C_1 = - \left(\varphi_0^P(1) + \frac{d}{dx} \varphi_0^P(1) \right) / \left(\varphi_0^1(1) + \frac{d}{dx} \varphi_0^1(1) \right) \tag{6.26}$$

$$D_1 = - \left(\varphi_1^P(1) + \frac{d}{dx} \varphi_1^P(1) \right) / \left(\varphi_0^1(1) + \frac{d}{dx} \varphi_0^1(1) \right)$$

The connection between $\varphi(r)$ and $\varphi(x)$ is given now by

$$\varphi_0^1(r) = R^{-1}\varphi_0^1(x=R/r)$$

$$\varphi_0^P(r) = \varphi_0^P(x=R/r)\ ;\ \varphi_1^P(r) = \varphi_1^P(x=R/r)$$

$$\varphi_0(r) = \varphi_0(x=R/r)\ ;\ \varphi_1(r) = \varphi_1(x=R/r)$$

$$C_g[r] = R^2 C_g[x]\ ;\ D_g[r] = R^2 D_g[x]$$

Table 1 Solutions of the differential equation

$$\frac{d^2z}{dr^2} + \frac{2}{r}\frac{dz}{dr} - \frac{2}{r^2} z = R(r)$$

$R_I = 0$

$z_I = r^{-2}$

$z_I' = -2r^{-3}$

$R_{II} = 0$

$z_{II} = r$

$z_{II}' = 1$

$R_{(1)} = -g' z_I'$

$z_{(1)} = \frac{\tilde{\ell}}{12 r^3}\left\{ e^{-\varkappa r}(-6 + 2\varkappa r - \varkappa^2 r^2 + \varkappa^3 r^3) + \varkappa^6 r^6 \, Ei(-\varkappa r)\right\}$

$z_{(1)}' = \frac{\tilde{\ell}}{12 r^4}\left\{ e^{-\varkappa r}(18 + 2\varkappa r - \varkappa^2 r^2 + \varkappa^3 r^3) + \varkappa^6 r^6 \, Ei(-\varkappa r)\right\}$

$R_{(2)} = -g' z_{(1)}'$

$z_{(2)} = \frac{\tilde{\ell}^2}{3 r^5}\left\{ e^{-2\varkappa r}\left(\frac{9}{20} - \frac{1}{10}\varkappa r + \frac{19}{20}\varkappa^2 r^2 - \frac{1}{15}\varkappa^3 r^3 + \frac{2}{15}\varkappa^6 r^6\right) + \frac{4}{15}\varkappa^5 r^5 \, Ei(-2\varkappa r) + \frac{1}{4}\varkappa^2 r^2 \, D(\varkappa r)\, Ei(-\varkappa r)\right\}$

$z_{(2)}' = \frac{\tilde{\ell}^2}{3 r^6}\left\{ e^{-2\varkappa r}\left(-\frac{9}{5} - \frac{3}{5}\varkappa r - \frac{11}{60}\varkappa^2 r^2 - \frac{19}{60}\varkappa^3 r^3 + \frac{2}{15}\varkappa^6 r^6\right) - \frac{1}{2}\varkappa^2 r^2 \, T(\varkappa r)\, Ei(-\varkappa r) + \frac{4}{15}\varkappa^5 r^5 Ei(-2\varkappa r)\right\}$

$R_{(3)} = g'$

$z_{(3)} = -\frac{\tilde{\ell}}{\varkappa^2 r^2} D(\varkappa r)$

$z_{(3)}' = \frac{2\tilde{\ell}}{\varkappa^2 r^3} T(\varkappa r)$

$$R_{(0)} = -g' z'_{(3)}$$

$$z_{(4)} = \frac{\tilde{l}}{4\varkappa^2 r^4} e^{-2\varkappa r} (2+\varkappa r)$$

$$z'_{(4)} = -\frac{\tilde{l}}{2\varkappa^2 r^4} e^{-2\varkappa r} (3+3\varkappa r+\varkappa^2 r^2)$$

$$R_{(5)} = -12 \frac{l}{r} \frac{d}{dr} \left(\frac{z_1}{r}\right)$$

$$z_{(5)} = 9l/r^3$$

$$z'_{(5)} = -27\, l/r^4$$

$$R_{(6)} = -12 \frac{l}{r} \frac{d}{dr} \left(\frac{z_{(4)}}{r}\right) - g' z'_{(5)}$$

$$z_{(6)} = -\frac{l\tilde{l}}{5r^4} \left\{ e^{-\varkappa r} \left(\frac{51}{2} - \frac{9}{2}\varkappa r + \frac{7}{3}\varkappa^2 r^2 - \frac{7}{6}\varkappa^3 r^3 + \frac{7}{6}\varkappa^4 r^4\right) + Ei(-\varkappa r)\, \frac{5}{2}\varkappa^2 r^2 \left(1 + \frac{7}{16}\varkappa^3 r^3\right) \right\}$$

$$z'_{(6)} = -\frac{l\tilde{l}}{5r^5} \left\{ e^{-\varkappa r} \left(-102 - 12\varkappa r + \frac{7}{3}\varkappa^2 r^2 - \frac{7}{6}\varkappa^3 r^3 + \frac{7}{6}\varkappa^4 r^4\right) - Ei(-\varkappa r)\, \varkappa^2 r^2 \left(5 - \frac{7}{6}\varkappa^3 r^3\right) \right\}$$

$$R_{(7)} = -12 \frac{l}{r} \frac{d}{dr} \left(\frac{z_{(5)}}{r}\right)$$

$$z_{(7)} = -\frac{l\tilde{l}}{2\varkappa^2 r^3} \left\{ e^{-\varkappa r} (18 + 2\varkappa r - \varkappa^2 r^2 + \varkappa^3 r^3) + \varkappa^4 r^4\, Ei(-\varkappa r) \right\}$$

$$z'_{(7)} = \frac{l\tilde{l}}{2\varkappa^2 r^4} \left\{ e^{-\varkappa r} (54 + 22\varkappa r + \varkappa^2 r^2 - \varkappa^3 r^3) - \varkappa^4 r^4 Ei(-\varkappa r) \right\}$$

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with the functions

$$D(x) = (1+x)\, e^{-x} \qquad ; \qquad T(x) = (1 + x + \tfrac{1}{2}x^2)\, e^{-x}$$

and

$$\left.\begin{matrix} Eq(x,y) \\ Es(x,y) \end{matrix}\right\} = \frac{e^{-y}}{x^2} \left[D(x)\, Ei(y+x) \left\{\begin{matrix} - \\ + \end{matrix}\right\} D(-x)\, Ei(y-x) \right]$$

Table 2: Solutions of the differential equation

$$\frac{d^2\varphi}{dr^2} + \frac{2}{r}\frac{d\varphi}{dr} - \left(\frac{2}{r^2} + \alpha^2\right)\varphi = S(r)$$

The solutions $\varphi_{(1)} \cdots \varphi_{(4)}$ are valid for $\alpha^2 = 1/2\,\varkappa^2$ only!

$S_I \equiv 0$ $\varphi_I = D(\alpha r)/r^2$	$S_{II} \equiv 0$ $\varphi_{II} = D(-\alpha r)/r^2$
$S_{(1)} = \alpha^2 g\,\varphi_I$ $\varphi_{(1)} = \frac{\gamma}{2r^2}\, e^{-\alpha r - \varkappa r}\,(\varkappa r - \alpha r)$	
$S_{(2)} = \alpha^2 g\,\varphi_{(1)} + \frac{1}{2}\alpha^2 g^2\,\varphi_I$ $\varphi_{(2)} = \frac{\tilde{\gamma}^2\alpha}{12r^2}\Big\{ e^{-2\varkappa r - \alpha r}(5\alpha r - \varkappa r) + 4\varkappa r\, D(\alpha r)\, Ei(-2\varkappa r)$ $-2(2\varkappa r + \alpha r)\, D(-\alpha r)\, Ei(-2\varkappa r - 2\alpha r)\Big\}$	
$S_{(3)} = -\alpha^2 z_{(1)}$ $\varphi_{(3)} = \frac{\tilde{\gamma}\varkappa}{12r^2}\Big\{ e^{-\varkappa r}\left(-1 - \varkappa r + \varkappa^2 r^2 - \frac{3}{2}\alpha\varkappa r^2 \cdot Ea(\alpha r, -\varkappa r)\right) + \varkappa^3 r^3 Ei(-\varkappa r)\Big\}$	
$S_{(4)} = -\alpha^2 z_{(2)} - \alpha^2 g\, z_{(1)} + \alpha^2 g\,\varphi_{(3)}$ $\varphi_{(4)} = \frac{\tilde{\gamma}^2\alpha^2}{180r^2}\Big\{ -e^{-2\varkappa r}\Big(\frac{293}{2} + 8\varkappa r - 16\varkappa^2 r^2$ $+ \frac{3}{4}\alpha^2 r^2\left(9\,Ea(\alpha r, -2\varkappa r) + 143\,\frac{\varkappa}{\alpha}\,Es(\alpha r, -2\varkappa r)\right)\Big)$ $- 30\, D(\varkappa r)\, Ei(-\varkappa r) + 32\,\varkappa^3 r^3\, Ei(-2\varkappa r)$ $+ \frac{45}{4} e^{-\varkappa r}\left(e^{-\alpha r}\left(1 - \frac{\varkappa}{\alpha}\right) Ei(\alpha r - \varkappa r) + e^{\alpha r}\left(1 + \frac{\varkappa}{\alpha}\right) Ei(-\alpha r - \varkappa r)\right)\Big\}$	

$$S_{(5)} = -\alpha^2 z_{(4)}$$

$$\varphi_{(5)} = -\frac{\tilde{\rho}^2}{4\varkappa r^2} e^{-2\varkappa r}\left\{1 + \frac{7\varkappa}{4}\alpha r^2 Ea(\alpha r, -2\varkappa r)\right\}$$

$$S_{(6)} = -\alpha^2 z_{(5)}$$

$$\varphi_{(6)} = \frac{g}{4}\ell\alpha^3 Ea(\alpha r, 0)$$

$$S_{(7)} = -\alpha^2 z_{(6)} - \alpha^2 g z_{(5)} - \alpha^2 g \varphi_{(6)}$$

$$\varphi_{(7)} = \frac{\rho\tilde{\ell}\alpha^2}{30 r^2}\left\{ e^{-\varkappa r}(-1 + 14\varkappa r - 14\varkappa^2 r^2 + \frac{69}{2}\alpha r^2 Es(\alpha r, -\varkappa r) - \frac{21\varkappa}{2}\alpha r^2 Ea(\alpha r, -\varkappa r) - \frac{135}{4}\alpha r\, Ea(\alpha r, 0)) + \frac{135}{4\alpha r}\left(D(\alpha r)\, V(\alpha r, 0) - D(-\alpha r)\, V(-\alpha r, 0)\right)\right\}$$

$$S_{(8)} = -\alpha^2 z_{(7)}$$

$$\varphi_{(8)} = \frac{\ell\tilde{\rho}}{2\varkappa r^2}\left\{ e^{-\varkappa r}\left(13 + \varkappa r - \varkappa^2 r^2 + \frac{15\alpha^3}{2\varkappa} Ea(\alpha r, -\varkappa r)\right) - \varkappa^3 r^3 Ei(-\varkappa r)\right\}$$

$$S = -\alpha^2 z_I \qquad \varphi = 1/r^2$$

$$S = -\alpha^2 z_{(3)} \qquad \varphi = \frac{\tilde{\rho}}{\varkappa^2 r^2} D(\varkappa r)$$

with

$$V(ar, br) = \frac{r}{\alpha}\int_{\infty}^{r} \frac{e^{-ar'}}{r'} \frac{d}{dr'}\left\{ r' e^{-\varkappa r'} \frac{d}{dr'}\left[\frac{e^{\alpha r'}}{r'} Ei(br' - \alpha r') - \frac{e^{-\alpha r'}}{r'} Ei(br' + \alpha r')\right]\right\} dr'$$

$$= (ar + br - \varkappa r)\, Ei(ar + br - \varkappa r) - e^{ar - \varkappa r + \alpha r} + \frac{1}{2\alpha r}\left\{(1 + ar + \varkappa r + \alpha r)\, Ei(br + \alpha r)\, e^{ar - \varkappa r - \alpha r} - (1 + ar + \varkappa r - \alpha r)\, Ei(br - \alpha r)\, e^{ar - \varkappa r + \alpha r}\right\}$$

for $a = +\alpha, -\alpha$ and $b = \sigma, -\varkappa$

Table 3 : Differential equation and initial conditions

Region : $0 \le x \le 1$

$$y_1'(x) = y_2(x)$$
$$y_2'(x) = f(x, y_1(x), y_2(x))$$

z_o^g	$y_1 = z_o^g \quad ; \quad y_2 = \frac{d}{dx} z_o^g$ $f = \frac{d}{dx}(\beta\Phi^\circ) y_2 + \frac{2}{x^2} y_1$ $y_1(0) = 0 \quad ; \quad y_2(0) = 0 \quad ; \quad f(0) = 2$
z_o^f	$y_1 = z_o^f \quad ; \quad y_2 = \frac{d}{dx} z_o^f$ $f = \frac{d}{dx}(\beta\Phi^\circ) y_2 + \frac{2}{x^2} y_1 + \frac{R}{x^2} \frac{d}{dx}(\beta\Phi^\circ)$ $y_1(0) = 0 \quad ; \quad y_2(0) = 0 \quad ; \quad f(0) = 2A_p$
z_1^p	$y_1 = z_1^p \quad ; \quad y_2 = \frac{d}{dx} z_1^p$ $f = \frac{d}{dx}(\beta\Phi^\circ) y_2 + \frac{2}{x^2} y_1 + \frac{12\,l}{Rx} [z_o(x) + x \frac{d}{dx} z_o(x)]$ $y_1(0) = 0 \quad ; \quad y_2(0) = 0 \quad ; \quad f(0) = 2B_p$
φ_o^g	$\varphi_o^g(x) = D(\frac{\alpha R}{x}) g(x) \; ; \; \frac{d}{dx}\varphi_o^g(x) = g \frac{dD}{dx} + D \frac{dg}{dx} \; ; \quad D(x) = e^{-x}(1+x)$ $y_1 = g \quad ; \quad y_2 = \frac{d}{dx} g$ $f = -\frac{2\alpha^2 R^2}{x^2(x+\alpha R)} y_2 + [\frac{2}{x^2} + \frac{4\alpha^2 R^2}{x^3(x+\alpha R)} + \frac{\alpha^2 R^2 (F^\circ - 1)}{x^4}] y_1$ $y_1(0) = 0 \quad ; \quad y_2(0) = 0 \quad ; \quad f(0) = 2$
φ_o^f	$y_1 = \varphi_o^f \quad ; \quad y_2 = \frac{d}{dx}\varphi_o^f$ $f = [\frac{2}{x^2} + \frac{\alpha^2 R^2 F^\circ}{x^4}] y_1 - \frac{\alpha^2 R^2 F^\circ}{x^4} z_o(x)$ $y_1(0) = 0 \quad ; \quad y_2(0) = 0 \quad ; \quad f(0) = 2A$
φ_1^p	$y_1 = z_1^p \quad ; \quad y_2 = \frac{d}{dx} z_1^p$ $f = [\frac{2}{x^2} + \frac{\alpha^2 R^2 F^\circ}{x^4}] y_1 - \frac{\alpha^2 R^2 F^\circ}{x^4} z_1(x)$ $y_1(0) = 0 \quad ; \quad y_2(0) = 0 \quad ; \quad f(0) = 2B$

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Anschrift der Verfasser:
Dr. R. Sändig, Dr. R. Feistel, Dipl.-Phys. H. Künstner
Wilhelm-Pieck-Universität Rostock
Sektion Physik
DDR - 25 Rostock
Universitätsplatz 3

H. Ulbricht und G. Kessler

Individuelle Eigenschaften der Ionen in wäßrigen Elektrolytlösungen

Abstract

The cation transference number of Li-, Na-, and K-ions in water is analyzed by the Ebeling-Sändig-Feistel transference number theory. The limiting transference number of Na-ion obtained is $t_+^o(Na)=0.39636$. The limiting ion conductances of Li-, Na-, K-, Cs-, Rb-, F-, Cl-, Br-, and I-ions in water have been calculated.

Verschiedene Arbeiten auf dem Gebiet der Leitfähigkeit[1], die in den letzten Jahren entstanden sind, gestatten die Ermittlung der Grenzleitfähigkeiten und der Kation-Anion-Wechselwirkung eines Elektrolyten. Die Kation-Kation- und Anion-Anion-Wechselwirkungsparameter wurden dabei aus thermodynamischen Ergebnissen[2] entnommen. Die Grenzleitfähigkeiten der einzelnen Ionen können nur bis auf einen Beitrag Δ bestimmt werden[4].

Wir wenden uns nun den individuellen Eigenschaften der Ionen in einer Elektrolytlösung zu. Aus der molaren Leitfähigkeit

$$\Lambda = \alpha \mathcal{F} (u_+ + u_-) \qquad (1)$$

wobei α der Dissoziationsgrad, u_i die Beweglichkeit des i-ten Ions (i=+,-) und $\mathcal{F}$ die Faradaysche Konstante sind, läßt sich die individuelle Leitfähigkeit für das i-te Ion mit

$$\lambda_i = \alpha \mathcal{F} u_i \qquad (2)$$

ablesen.

In dem von uns betrachteten Konzentrationsbereich bis 1 mol/l kann der Dissoziationsgrad α für die Alkalihalogenide praktisch gleich 1 gesetzt werden. Eine ausführliche Darstellung

der Zusammenhänge findet sich in den Arbeiten von Haase[3].

Die individuellen Leitfähigkeiten werden nicht gemessen, sondern über die Beziehung

$$\lambda_i = t_i \Lambda \tag{3}$$

berechnet. Für die Überführungszahlen t_i erhielten Kelbg, Ebeling, Sändig und Feistel[1,2] in der feedback-Theorie als Ergebnis

$$t_+ = \frac{(t_+^\circ + S_+^{ext})(1 - S_-^{int}) + (t_-^\circ + S_-^{ext}) S_+^{int}}{1 + S^{ext}} \tag{4}$$

mit

$$t_+^\circ = \Lambda_+^\circ / \Lambda_\circ \tag{5}$$

Linearisiert man diese Gleichung, ergibt sich

$$t_+ = t_+^\circ (1 - S^{ext} - S^{int}) + S_+^{ext} + S_+^{int} \tag{6}$$

Da Gleichung (4) jedoch den Verlauf der Überführungszahlen wesentlich besser beschreibt, wird im folgenden stets diese Gleichung verwendet.

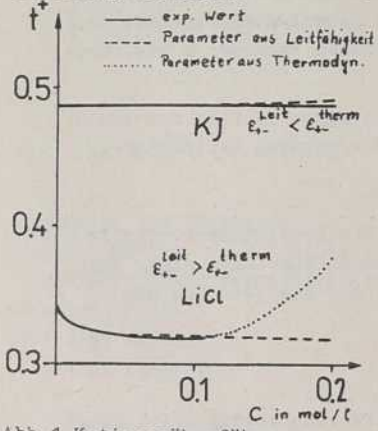

Abb.1 Kationenüberführungszahlen, berechnet nach Gleichung ( )

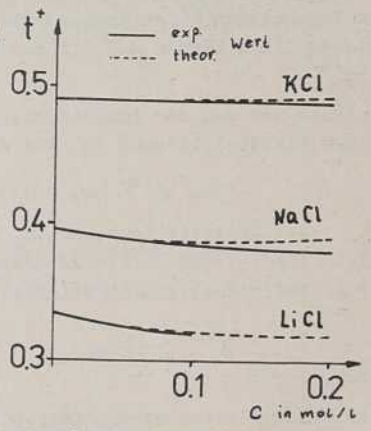

Abb.2 Kationenüberführungszahlen für LiCl, NaCl, KCl

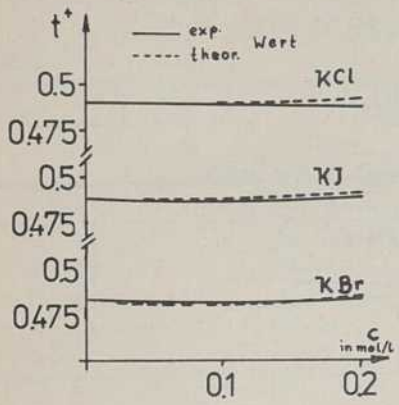

Abb.3 Kationenüberführungszahlen für KCl, KI, KBr

Für das Stufenpotential wurden mit den aus der Leitfähigkeit gemäß[1,2] erhaltenen ε_{+-}-Parametern Überführungszahlen berechnet, die in Abb.2 und 3 dargestellt sind. Beide Abbildungen zeigen die gute Übereinstimmung der nach Gl. (5) ermittelten theoretischen Kurven mit den experimentellen Daten.

Abb.1 zeigt uns das Verhalten der Überführungszahlen, bei denen der ε_{+-}-Parameter aus der Bestimmung der osmotischen Koeffizienten verwendet wurde. Für KI ist $\varepsilon_{+-}^{leitf} < \varepsilon_{+-}^{therm}$, für LiCl gilt dagegen $\varepsilon_{+-}^{leitf.} > \varepsilon_{+-}^{therm}$. Wie der Abb.1 zu entnehmen ist, werden die experimentellen Ergebnisse auch hier zufriedenstellend wiedergegeben.

Um die Grenzleitfähigkeiten der Ionen genau zu bestimmen, genügt es, die Überführungszahlen für ein Ion exakt zu ermitteln. Die übrigen lassen sich dann tabellarisch berechnen[2,5]. Abb.4 zeigt uns eine solche Anpassung für NaCl bei T=25°C bis zu einer Konzentration von 0.05 mol/l. Für den ε_{+-}-Parameter ergab sich dabei ε_{+-}=-2.10638 und für t_0^+=0.39636.

Mit der Gleichung für die individuelle Leitfähigkeit

$$\Lambda_+ = \frac{\Lambda_+^\circ\left[\left(1+\frac{\Lambda_-^\circ}{\Lambda_+^\circ} S_+^{ext}\right)\left(1-\frac{\nu}{\nu_+} S_+^{int}\right)+\left(\frac{\Lambda_-^\circ}{\Lambda_+^\circ}+\frac{\Lambda_0^\circ}{\Lambda_+^\circ} S_-^{ext}\right)\frac{\nu_-}{\nu_+} S_-^{int}\right.}{1 - S^{rel} - S^{int} - S^{rel}\cdot S^{ext}} \qquad (7)$$

und der Bestimmung von Λ_0^+ und Λ_0^- nach

$$\Lambda_+^\circ = t_+^\circ \Lambda_0 \qquad (8)$$

ließen sich die Anion- und Kationleitfähigkeit in Abb.5 berechnen.

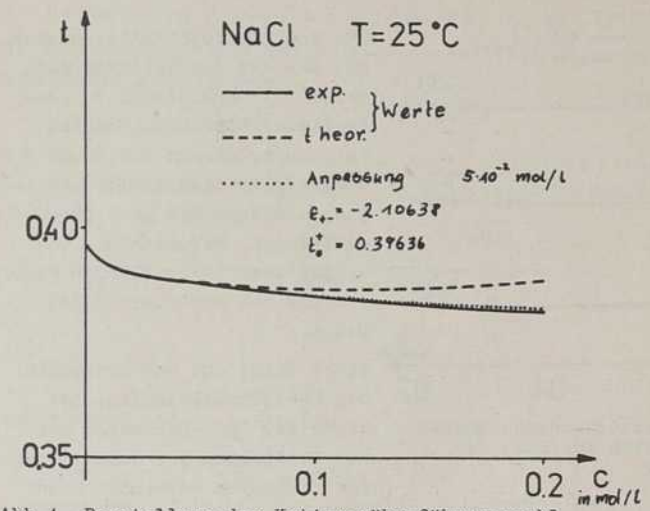

Abb.4 Darstellung der Kationenüberführungszahl.

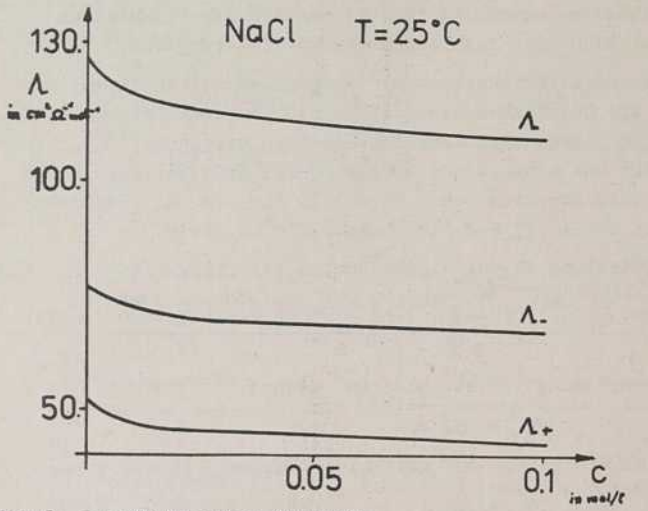

Abb.5 Leitfähigkeiten für NaCl

In Tabelle 1 sind schließlich die Grenzleitfähigkeiten der Ionen der Alkalihalogenide aufgeführt.

Tabelle 1
Grenzleitfähigkeiten der Ionen der Alkalihalogenide
$T = 25^{\circ}C$

Ion	$\lambda_{\circ}^{+}$	Ion	$\lambda_{\circ}^{-}$
Li	38.723	F	55.637
Na	50.183	Cl	76.427
K	73.503	Br	78.147
Rb	77.193	I	76.957
Cs	77.013		

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Anschrift der Verfasser
Prof. Dr. Heinz Ulbricht und Dipl.-Phys. Gisela Kessler
Wilhelm-Pieck-Universität Rostock
Sektion Physik
DDR - 25 Rostock
Universitätsplatz 3

W. Ebeling

Theory of Ion Pairing for Gurney-Friedman Models of Electrolytes.

Abstract.

Assuming the existence of a theory of the thermodynamic functions and of the conductance in a binary approximation the extension of the theory to associating electrolytes is given.

1. Introduction.

The statistical theory of electrolytes usually starts from the theory of nonassociating electrolytes. In earlier work we have studied already the question how the theory of nonassociated electrolytes may be extended to associating electrolytes[1,2,3]. The main idea of this work has been the idea of consistency between a physical formulation and the chemical picture in terms of a mass action law. It is the aim of this paper to give a generalization of the method developed earlier[1,2,3] to higher concentration. For simplicity we shall restrict us to a binary symmetrical electrolyte with the anion number density n_+ and the cation number density n_- where

$$n_+ = n_- = n \tag{1.1}$$

due to electroneutrality.

2. The Definition of Ion Pairs and the Mass Action Law.

As well known[1] there is no unique prescription for the definition of an ion pair. In the following we shall follow a generalized Bjerrim-convention. An ion pair is considered as bound if the pair energy satisfies the condition

$$\psi_{+-}(r) < -2kT \tag{2.1}$$

Such a configuration is relative stable with respect to the thermal agitation. Note that the definition (2.1) applies to any short range potential and reduces in the case of a primitive model to the original Bjerrum convention

$$R_{+-} \leq r < q = (Z^2 e^2 / 2 D_0 kT) \tag{2.2}$$

R_{+-} - contact distance of the ion pair.
The mass action law will be written as

$$n = n^* + (n^*)^2 \tilde{K}(T, n^*) \tag{2.3}$$

$\tilde{K}$ - effective mass action constant
n^* - density of free anions or free cations respectively.
For the mass action constant we propose here two variants:

(1) Using the activity coefficient the MAC reads in the common form

$$\tilde{K}(T, n^*) = K(T) f_{\pm}^2 \tag{2.4}$$

$$K(T) = \int_{q_0}^{q_1} dr \, 4\pi r^2 \exp\left[- \psi_{+-}(r)/kT \right] \tag{2.5}$$

where q_0 and q_1 are the two roots of

$$\psi_{+-}(q_i) = - 2kT \tag{2.6}$$

For the primitive model one finds

$$q_0 = R_{+-} \quad ; \quad q_1 = (Z^2 e^2 / 2 D_0 kT)$$

(2) If the pair distribution function $\overline{T}_{+-}(r)$ and the corresponding potential of mean force

$$\overline{\Phi}_{+-}(r) = - kT \ln \overline{T}_{+-}(r) \tag{2.7}$$

are explicitely known we may define the binding region as

$$\bar{q}_0 \leq r < \bar{q}_1 \tag{2.8}$$

where $\bar{q}_0$ and $\bar{q}_1$ are the roots of

$$\Phi_{+-}(\bar{q}_i) = -2kT \tag{2.9}$$

Here the region of bound states is defined by the distances where the first peak of the pair distribution function exceeds the value exp (2) = 7.389 .... The corresponding mass action constant is defined by

$$\tilde{K}(T, n^*) = \int_{\bar{q}_0}^{\bar{q}_1} dr\, 4\pi r^2 \mathcal{F}_{+-}(r; n^*, T) \tag{2.10}$$

3. Association Theory of the Pressure

Assume that in the frame work of the physical picture an expression for the pressure including the pair interactions is available which reads

$$P(n) = P_0(n) + \delta P(n) = 2nkT - 2kTn^2 B_2(n) + \ldots \tag{3.1}$$

where $P_0(n)$ is the ideal pressure and $B_2(n)$ a kind of second virial coefficient. In the framework of the chemical picture we propose to replace eq.(3.1) by

$$P^*(n) = P_0(n) + \delta P(n^*) = 2nkT - 2kT(n^*)^2 B_2(n^*) + \ldots \tag{3.2}$$

An equivalent representation is

$$P^*(n) = 2kT(n - n^*) + P(n^*) \tag{3.3}$$

where the function $P(n^*)$ is to be taken from eq.(3.1). The underlying physical assumption leading to eqs.(3.2-3) is that pair interactions act only between free ion which have the density n^*. The value of n^* as function of n and T is defined by the mass action law (2.3). Another possibility of splitting which could be of advantage is

$$P(n) = P_{HC}(n) + \Delta P(n) \tag{3.4}$$

where P_{HC} denotes the pressure of a hard core system and the remainding part of the second virial coefficient. In the chemical picture eq.(3.4) is to be replaced by

$$P^*(n) = P_{HC}(n) + \Delta P(n^*) \tag{3.5}$$

where again n^* follows from the massaction law (2.3) but using in eq.(2.4) activity coefficients without hard core contribution.

Due to the result obtained by iteration of eq.(2.3)

$$n^* = n + O(n^2) \tag{3.6}$$

the chemical representations (3.2) as well as (3.5) are automatically consistent with eqs.(3.1) or (3.4) respectively.

4. Conductivity.

Assume that the specific conductivity of a binary symmetrical electrolyte is given by the following formula

$$\sigma(n) = \sigma_0(n) + \delta\sigma(n) \tag{4.1}$$

where $\delta\sigma(n)$ is the contribution resulting from pair interactions and

$$\sigma_0(n) = An \quad ; \quad A = \left(\frac{z^2 e^2}{g_1} + \frac{z^2 e^2}{g_2} \right) \tag{4.2}$$

In a more explicite form given by Ebeling, Feistel and Geisler we have e.g.

$$\delta\sigma(n) = nAS^{rel}(n) + nB\left[S^{el}(n) + S^{so}(n)\right] \tag{4.3}$$

where

$$B = \frac{D_0 kT\delta}{24\pi\eta_0} \tag{4.4}$$

The S-functions are defined elsewhere /4/
For the chemical description we propose the formulae

$$\Sigma^*(n) = \Sigma_0(n) + \delta\Sigma(n^*) \tag{4.5}$$

where n^* follows by solution of the mass action law.
An equivalent form reads

$$\Sigma^*(n) = (n-n^*)A + \Sigma(n^*) \tag{4.6}$$

The construction (4.5) or (4.6) reduces in the case of small concentrations to the classical procedure for the derivation of conductance formulae for associating electrolytes due to Fuoss. The physical assumption underlying this construction is that only the free ions may interact by the law corresponding to the original Hamiltonian. The construction (4.5) guarantees automatically the consistency with the physical picture (4.1) up to higher orders in n due to the condition (3.6).
In order to transform eq.(4.6) to a more practical form we rewrite it for the molar conductance

$$\Lambda^*(c) = (1-\alpha)\Lambda_0 + \alpha\Lambda(\alpha c) \tag{4.7}$$

where α is the degree of dissociation and $\Lambda(c)$ is the molar conductance in the physical picture. Another equivalent form is

$$\Lambda^*(c) = \Lambda_0 + \alpha\delta\Lambda(\alpha c) \tag{4.8}$$

where $\delta\Lambda(c)$ is the deviation from the limiting value in the physical picture which is defined by

$$\Lambda(c) = \Lambda_o + \delta\Lambda(c) \tag{4.9}$$

5. Application to $CuSO_4$ - Solutions at 25 °C.

In order to give an example the method presented here has been applied to $CuSO_4$ - solutions at 25 °C in the region $C < 0.01$ M. Following an earlier paper the interactions are described by the following model

$$\psi_{++}(r) = \begin{cases} \infty & \text{if } r < 4.2\,A^\circ \\ 4e^2/D_o r & \text{if } r \geq 4.2\,A^\circ \end{cases} \tag{5.1}$$

$$\psi_{--}(r) = \begin{cases} \infty & \text{if } r < 4.6\,A^\circ \\ 5\,kT & \text{if } 4.6 \leq r < 7.4\,A^\circ \\ 4e^2/D_o r & \text{if } r \geq 7.4\,A^\circ \end{cases}$$

$$\psi_{+-}(r) = \begin{cases} \infty & \text{if } r < 3.0\,A^\circ \\ -5.6\,kT & \text{if } 3.0 \leq r < 5.8\,A^\circ \\ -4e^2/D_o r & \text{if } 5.8 \leq r \end{cases}$$

Following the conductance theory without feedback effect as developed in [16] (LT-variant) it follows the lower curve in Fig.1. The upper curve given in Fig.1 was calculated using eq.(4.8) and the mass action law eq.(2.3) and (2.4). The mass action constant was calculated to be

$$K(T) = 4\pi \int_{R_{+-}}^{R'_{+-}} dr\, r^2 \exp(5.6) + 4\pi \int_{R'_{+-}}^{2e^2/D_o kT} dr\, r^2 \exp\left(\frac{4e^2}{D_o kT r}\right) \tag{5.2}$$

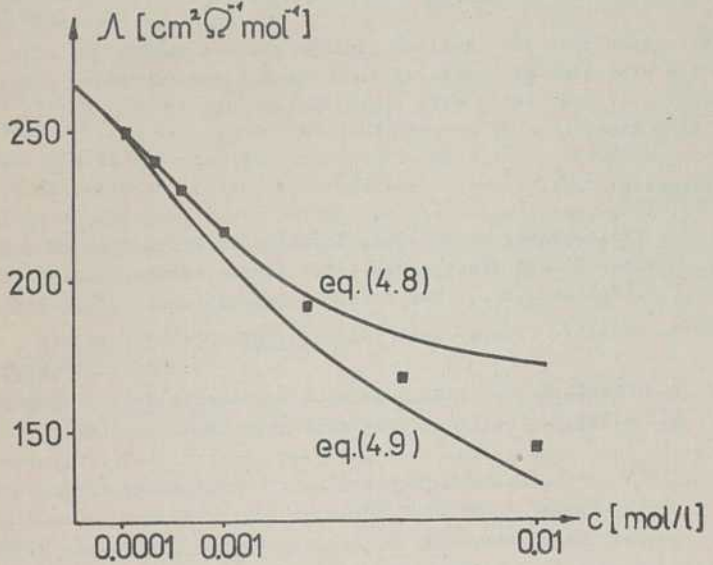

Fig.1: Comparision of the chemical description using eq. (4.8) and the mass action law eqs.(2.3-2.4) with the physical description after eq.(4.9) and following and with the experimental points for $CuCO_4$ at 25 °C.

In the mol/l scale follows

$$K_c(T) = 6.023 \cdot 10^{20} K(T) \approx 154.48 \qquad (5.3)$$

Fig.1 shows that the chemical picture gives a rather good fit of the experimental points up to 0.001 M.A more extended comparision of the theory with experimental data is referred to a later paper.

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Anschrift des Verfassers

Prof.Dr.W. Ebeling
Wilhelm-Pieck-Universität Rostock
Sektion Physik
DDR - 25 Rostock
Universitätsplatz 3

W. Ebeling, J. C. Justice

Frequency Dependent Conductance and Dielectric Permittivity of Electrolytes.

Abstract.

Starting from the basic equations for the pair distribution function in non-equilibrium, electrolytes in low-frequency fields are investigated theoretically. For explicite calculations of the pair distribution functions the strong coupling approximations for distances smaller than the Bjerrum distance is used. The influence of rotating ion pairs on the dielectric permittivity is discussed.

1. Introduction.

Complex permittivity measurements in a wide frequency range (10^7 - 10^{11} Hz) show the existence of ionic relaxation processes. In the limit of very small concentrations the effects due to the relaxation of the ion sphere have been explained by the Debye-Falkenhagen theory[1]. An extension of this theory to strong electrolytes at higher concentrations was given by Kraeft[2] for the so-called primitive model. The aim of this paper is the study of the influence of ion pair formation on the dielectric properties. Experimental work shows that ion pair rotation yields really an observable contribution to the polarization but evidently there exist other significant effects[3,4]. In recent work Badiali et al.[3,5] have studied the relaxation effects in electrolytes by using the technique of memory functions. In the present work a new concept of the conductance theory of electrolytes is applied to the problem of frequence dependence[6].

Let us assume an external electrical field with the time dependence

$$\vec{E} = \vec{E}_0 \exp(i\omega t) \tag{1.1}$$

producing a total current

$$\vec{j} = \vec{j}^{(i)} + \vec{j}^{(d)} \tag{1.2}$$

consisting by a first part $\vec{j}^{(i)}$ due to the center of mass motion of the solved ions and $\vec{j}^{(d)}$ due to the dicplacement of internal charges in the solvent molecules and eventually also in the ions. Further let us introduce a specific conductivity $\sigma^*(\omega)$ and a dielectric permittivity $\varepsilon^*(\omega)$ by[1,7]

$$\vec{j}^{(i)} = \sigma^*(\omega)\vec{E}$$

$$\vec{j}^{(d)} = \frac{1}{4\pi}\frac{\partial}{\partial t}\vec{P} = \frac{i\omega}{4\pi}\left[\varepsilon^*(\omega)-1\right]\vec{E} \tag{1.3}$$

$$\vec{j} = \left\{\sigma^*(\omega) + \frac{i\omega}{4\pi}\left[\varepsilon^*(\omega)-1\right]\right\}\vec{E}. \tag{1.4}$$

Here

$$\sigma^* = \sigma' - i\sigma'' \quad , \quad \varepsilon^* = \varepsilon' - i\varepsilon'' \tag{1.5}$$

are complex functions. In the following we deal exclusively with $\sigma^*(\omega)$. Note that in an earlier paper systems of ions and dipoles, both present in low concentration, have been treated neglecting ion pair effects[7]. From the physical point of view the conductance may be splitted into two parts σ_L and σ_S originating in free ion movement (long interionic distances) and bound ion pair movement (short interionic distances)

$$\sigma^*(\omega) = \sigma_L(\omega) + \sigma_S(\omega) \tag{1.6}$$

Evidently this splitting is not free of arbitrariness. Let us quote here again the comment made by Onsager 1968 in Montpellier: " The distinction between free ions and associate pairs depends on an arbitrary convention. Bjerrum's choice is good but we could vary it within reason. In a complete theory this would not matter; what we remove from one page of the ledger would be entered elsewhere with the same effect ". Following earlier papers let us introduce here a characteristical distance R which is identical or near to the Bjerrum distance $(e^2/2D_0kT)$. We split the interionic distance into two parts:
The short range part S corresponding to $0 \leq r < R$
and the long range part L corresponding to $R \leq r < \infty$
Both parts will be treated with different approximation methods. The contribution to the short range part $\sigma_S(\omega)$ corresponding to ion pair rotation contributes mostly to the imaginary part of $\sigma^*(\omega)$. It seems to make sense to interpret this contribution as a dielectric contribution $\Delta\varepsilon$ corresponding to

$$\sigma_S(\omega) = \frac{i\omega}{4\pi}\Delta\varepsilon(\omega) + \Delta\sigma(\omega) \tag{1.7}$$

Therefore we obtain finally

$$\vec{j} = \left\{ \sigma_L(\omega) + \Delta\sigma(\omega) + \frac{i\omega}{4\pi}\left[\varepsilon^*(\omega) + \Delta\varepsilon(\omega) - 1\right]\right\}\vec{E} \tag{1.8}$$

It is the aim of this paper to present explicite expressions for $\sigma^*(\omega)$, $\sigma_L(\omega)$, $\Delta\sigma$ and $\Delta\varepsilon$ for symmetrical electrolytes $e_2 = -e_1 = e$ using the so-called strong coupling approximation.

2. Basic Equations for the Pair Distribution Function.

In the foregoing paper[6] the following equation for the dimensionless perturbation of the p.d.f. was derived

$$\nabla\cdot\left[\nabla Y_{21}(\vec{r})+g^{\circ}_{21}(r)\nabla\left(Z_{21}(\vec{r})-r\cos\vartheta\right)\right.$$
$$\left.-Y_{21}(\vec{r})\nabla\ln g^{\circ}_{21}(r)\right]+i\upsilon Y_{21}(\vec{r})=0 \qquad (2.1)$$

$$\upsilon=\frac{\omega}{kT(\omega_1+\omega_2)} \qquad (2.2)$$

where g°_{21} is the equilibrium p.d.f., Z_{21} the perturbation of the potential and ω_1, ω_2 the mobilities of the ions. Following the method proposed earlier[6] we solve the equation (2.1) for the region $R \leq r < \infty$ by perturbation methods with boundary conditions corresponding to the primitive model with radius R.

In the simplest approximation the outside solution of eq.(2.1) is given by[1,2]

$$Y_{21}(\vec{r})=\frac{e^2\cos\vartheta}{D_0kT(\varkappa^2-\zeta^2)}\frac{d}{dr}\left[\frac{e^{-\varkappa r}}{r}+A_1\frac{e^{-\zeta r}}{r}\right]\frac{e^{\varkappa R}}{1+\varkappa R} \qquad (2.3)$$

$$\zeta=\varkappa\left[(1+i\omega\tau)/2\right]^{1/2}\ ;\quad \tau^{-1}=\frac{1}{2}\varkappa^2kT(\omega_1+\omega_2) \qquad (2.4)$$

$$A_1=-e^{\zeta R-\varkappa R}\left\{\left[1+\varkappa R+\tfrac{1}{2}\varkappa^2R^2\right]-\tfrac{1}{2}R^2(\varkappa^2-\zeta^2)\cdot\right.$$
$$\left.\cdot\left[1+\frac{D_0kTR}{e^2}(1+\varkappa R)\right]\right\}\left[1+\zeta R+\tfrac{1}{2}\zeta^2R^2\right]^{-1} \qquad (2.5)$$

The second approximation was also given by Kraeft[1.2]. In order to get the inside solution for the region $0 \leq r < R$ we shall use the strong coupling approximation which includes the assumptions that

1) The perturbation of the potential may be neglected: $Z_{21} \equiv 0$

2) The radial flow may be neglected:

$$\frac{\partial}{\partial r} Y_{21} - g^{\circ}_{21} \frac{\partial}{\partial r}(r\cos\vartheta) - Y_{21} \frac{\partial}{\partial r} \ln g^{\circ}_{21} = 0 \tag{2.6}$$

Introducing $Y(r)$ by $Y_{21}(\vec{r}) = Y(r)\cos\vartheta$ and $\varphi = -\ln g^{\circ}_{21}$ we get from (2.6)

$$Y'(r) - e^{-\varphi} + Y(r)\varphi'(r) = 0 \tag{2.7}$$

Differentiation of eq.(2.7) yields

$$Y'' + \varphi' e^{-\varphi} + Y'\varphi' + Y\varphi'' = 0 \tag{2.8}$$

On the other hand we find from eq.(2.1)

$$Y'' + \frac{2}{r}Y' - \frac{2}{r^2}Y + Y'\varphi' + Y\varphi'' + \frac{2}{r}Y\varphi' + \varphi' e^{-\varphi} + iv_1 Y = 0 \tag{2.9}$$

By subtraction of eq.(2.8) from eq.(2.9) we find

$$Y' - \frac{1}{r}Y + Y\varphi' + \frac{1}{2}irvY = 0 \tag{2.10}$$

The exact solution of this equation reads

$$Y(r) = r\exp\left[-\varphi - \frac{i}{4}vr^2\right] \tag{2.11}$$

and therefore the p.d.f. is given by

$$Y_{21}(\vec{r}) = r\cos\vartheta\, g^{\circ}_{21}(r)\exp\left[-\frac{i}{4}vr^2\right] \tag{2.12}$$

In the static case $\omega=0$ i.e. $\upsilon=0$ follows the static strong coupling solution given in [6].

3. The Frequency - dependent Conductance.

As shown in earlier papers [6,8] there are two different variants to express the conductance as a functional of the p.d.f.

(a) The linear theory

$$\sigma^*(\omega) = \sigma_0\left[1-T^{rel}-T_1^{el}+T_2^{el}\right] \tag{3.1}$$

(b) The feedback theory (echo theory)

$$\sigma^*(\omega) = \sigma_0\,\frac{1-T_1^{el}}{1+T^{rel}\left(1-T_1^{el}\right)-T_2^{el}}\,. \tag{3.2}$$

Here the T - functions may be expressed by the p.d.f. [6]. In the case of small correlations one may develope with respect to the T - functions i.e. (3.2) coincides then with (3.1). As shown earlier [6,8] in principle eq.(3.1) as well as (3.2) are exact, but strictly speaking, we have to use in each case another solution for Y_{21} and therefore another T - functions. In some respect the linear theory is similar to the virial formula for the pressure and the feedback theory (echo theory) is the analogon of the compressibility equation [6,8]. Therefore a comparision of both expressions may be used for a test of the accuracy of the p.d.f. In the frame work of our simple approximations for the p.d.f. Y_{21} both variants are not consistent except for the case of very low densities. Therefore we shall prefer eq.(3.1) for applications to strong electrolytes, eq.(3.2) for applications to weakly associating electrolytes and eq.(3.1) in combination with a mass action law for applications to strongly associating electrolytes. As shown

earlier[6,8], the feeback-or echo - method corresponds to taking into account mass-action-effects in a first order.

Now we have to calculate the T - function. Using the formulae given in[6] and [8] and the splitting in short-range and long-range terms we get for a symmetrical electrolyte with

$$e_2 = -e_1 = e \; ; \quad n_2 = n_1 = n$$

$$T^{rel} = T_L^{rel} + T_S^{rel} \; ; \quad T_i^{el} = T_{iL}^{el} + T_{iS}^{el} \; ; \tag{3.3}$$

$$T_L^{rel} = \frac{e^2 \varkappa}{6 D_0 kT (1 + [(1+i\omega\tau)/2]^{1/2})} + \frac{(\varkappa R)^2}{6}\left(\frac{e^2}{D_0 kTR} + \frac{1}{2}\right) - (2\pi/3) n R^3 \; ; \tag{3.4}$$

$$\varkappa = (8\pi n e^2 / D_0 kT)^{1/2} \; ; \quad \tau = 2[\varkappa^2 kT(\omega_1 + \omega_2)]^{-1} \tag{3.5}$$

$$T_{1L}^{el} = \frac{\varkappa}{3\pi\eta(\omega_1+\omega_2)(1+\varkappa R)} \; ; \quad T_{2L}^{el} = 0 \tag{3.6}$$

$$T_S^{rel} = 4\pi n \int_0^R dr\, r^2 g_{21}^0(r) \exp\left[-\frac{i}{4} v r^2\right] \tag{3.7}$$

$$T_{1S}^{el} = \frac{2n}{3\eta(\omega_1+\omega_2)} \int_0^R dr\, r \left(g_{21}^0 + g_{12}^0 - g_{11}^0 - g_{22}^0\right) \tag{3.8}$$

$$T_{2S}^{el} = \frac{4n}{3\eta(\omega_1+\omega_2)} \int_0^R dr\, r\, g_{21}^0(r) \exp\left[-\frac{i}{4} v r^2\right] . \tag{3.9}$$

Calculating the short-range parts we have neglected certain contributions from the upper boundary $r = R$ which seems to be within the limits of the accuracy of the strong-coupling approximation.

The combination of the feedback- (echo)- formula eq.(3.2) with the expressions (3.3) to (3.9) should describe the complex conductivity of weakly associating electrolytes. By inspection one sees that T_L^{rel}, T_S^{rel} and T_{2S}^{el} are complex functions which have to be calculated. The physical meaning of these contributions will be clearer in the chemical picture given in the next section.

4. Chemical Description and Discussion

Led us start from eq.(3.1) ând develope with respect to the concentration $c = n \cdot 10^3 N_L^{-1}$. It follows

$$\varepsilon^*(\omega) = \varepsilon_0 \Big\{ 1 - \big[\alpha^*(\omega) + \beta \Lambda_0^{-1}\big] c^{1/2} + \Big[2E_1' \Big(\frac{2}{\xi} + \frac{1}{\xi^2} - \frac{1}{\xi^3} \Big) + \frac{E_2'}{\Lambda_0 \xi} + \frac{C(R, U_{11}, U_{12})}{\Lambda_0} \Big] c - \big[1 - i\omega\tau_1(\omega) \big] K_A c - \frac{i\omega}{4\pi} \tau_2(\omega) \frac{4}{3a\eta(\omega_1 + \omega_2)} K_A c + O(c^{3/2}) ; \quad (4.1)$$

$$\alpha^*(\omega) = \Big\{ 1 + \big[(1 + i\omega\tau)/2 \big]^{1/2} \Big\}^{-1} ; \quad \xi = (e^2/D_0 kTR) \quad (4.2)$$

$$\tau_1(\omega) = \frac{\int_0^R dr\, r^2 \exp\Big(-\frac{U_{12}}{kT}\Big) \Big[\exp\Big(-\frac{i}{4} \vartheta r^2\Big) - 1 \Big]}{(-i\omega) \int_0^R dr \cdot r^2 \exp\Big(-\frac{U_{12}}{kT}\Big)} \quad (4.3)$$

$$\tau_2(\omega) = \frac{a\int_0^R dr\, r \exp\left(-\frac{U_{12}}{kT}\right)\left[\exp\left(-\frac{i}{4}\upsilon r^2\right)-1\right]}{(-i\omega)\int_0^R dr\, r^2 \exp\left(-\frac{U_{12}}{kT}\right)} \qquad (4.4)$$

$$K_A = \frac{4\pi N_L}{1000}\int_0^R dr\, r^2 \exp\left(-\frac{U_{12}}{kT}\right) \qquad (4.5)$$

$$C(R, U_{11}, U_{22}) = \frac{2\Lambda_0 N_L}{3000\eta(\omega_1+\omega_2)}\int_0^R dr\, r\left(e^{-\frac{U_{11}}{kT}} + e^{-\frac{U_{22}}{kT}}\right) \qquad (4.6)$$

Here a is the contact distance and the coefficients α, β, E_1' E_2' have the usual meaning[6].
Using eqs. (1.6 - 1.7) we get

$$\Delta\varepsilon(\omega) = 4\pi e^2 \frac{cN_L}{1000}\left[(\omega_1+\omega_2)\tau_1(\omega) - \frac{\tau_2(\omega)}{3\pi\eta a}\right]K_A c \qquad (4.7)$$

Now the mass action law will be introduced by

$$(1-\gamma) = \gamma^2 f_\pm^2 (K_A c) \qquad (4.8)$$

γ - degree of dissociation, $f_\pm$ mean activity coefficient.
The receipt for the transition to the chemical picture reads: Replace everywhere a single c by γc and a factor $K_A c^2$ by $(1-\gamma)c$. Then eq.(4.7) is transformed to

$$\Delta\varepsilon(\omega) = 4\pi e^2 \frac{(1-\gamma)cN_L}{1000}\left[(\omega_1+\omega_2)\tau_1(\omega) - \frac{\tau_2(\omega)}{3\pi\eta a}\right] \qquad (4.9)$$

Furtheron eq.(4.1) is transformed to

$$\sigma^*(\omega) = \gamma\varepsilon_0\Big[1-[\kappa^*(\omega)+\beta\Lambda_0^{-1}](\gamma c)^{1/2}+\Big[2E_1'\Big(\frac{2}{\xi}+\frac{1}{\xi^2}-\frac{1}{\xi^3}\Big)$$
$$+\frac{E_2'}{\Lambda_0\xi}+C(R,U_{11},U_{22})\Big](\gamma c)+\frac{i\omega}{4\pi}\Delta\varepsilon(\omega)+O(c^{3/2}) \qquad (4.10)$$

For the physical interpretation of eq.(4.9) it is useful to look at the asymptotic value of the relaxation functions at **large** (e^2/D_0kTa) which read

$$\tau_1 \approx \tau_2 \approx \frac{1}{i\omega}\Big[1-\exp\Big(-\frac{i\omega a^2}{4kT(\omega_1+\omega_2)}\Big)\Big] \qquad (4.11)$$

$$= \frac{1}{\omega}\sin\Big(\frac{1}{2}\omega\tau_D\Big)+\frac{i}{\omega}\Big[\cos\Big(\frac{1}{2}\omega\tau_D\Big)-1\Big]. \qquad (4.12)$$

$$\tau_D = a^2\big[2kT(\omega_1+\omega_2)\big]^{-1} \qquad (4.13)$$

Now one can see that eq.(4.9) is quite similar to the result of the simple Debye theory which yields for rotating dipoles consisting of two charges $(+e)$ and $(-e)$ at the distance a the dielectric contribution[7]

$$\Delta\varepsilon(\omega) = \frac{8\pi}{3}n_D(\omega_1+\omega_2)\frac{e^2\tau_D}{1+i\omega\tau_D} \qquad (4.14)$$

n_D-number density of the dipoles. Evidently the first term in eq.(4.8) may by interpreted as a Debye contribution of rotating ion pairs with the number density $(1-\gamma)cN_L/1000)$. The second contribution originates from hydrodynamic coupling of the two charges in the rotating pair.

Finally we mention that the long-range contribution to eq. (4.10) may be easily improved by taking into account the second approximation of Kraeft's theory[1,2]. Furtheron we have to mention that the upper frequency limit for the validity of the strong coupling approximation is not yet known.

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Adresse der Autoren:

W. Ebeling
Wilhelm-Pieck-Universität Rostock
Sektion Physik
DDR - 25 Rostock
Universitätsplatz 3

J.C. Justice, Laboratoire d'Electrochimie
Université Pierre et Marie Curie
75230 Paris
Frankreich

Anmerkungen

Koeffizient für Mischungen von wässrigen ...rten mit einem gemeinsamen Ion.

...einfachen Elektrolyte stehen bei Raumtempera... ...motischen Koeffizienten Meßreihen über einen ...cionsbereich zur Verfügung. Im Gegensatz dazu ...schte Elektrolyte nur eine geringe Zahl von ...Berdem meist auf wenige Mischungsverhältnisse ... Daher sind jene theoretischen Formeln und ...sonderem Wert, die es erlauben, für eine große ...ngen in einem bestimmten Konzentrationsbe... ...haue Vorhersagen für die thermodynamischen ... treffen. Im folgenden wird nach (1.1) der ...izient in der DHX-Näherung für Mischungen von ... mit einem gemeinsamen Ion für Konzentrationen ...ol/l (I ist die Ionenstärke. $I=\frac{1}{2}\sum_i c_i z_i^2$; z_i - Wertigkeit) berechnet.

...ine Mischung aus einem Elektrolyten A und ...en B.Für die Potentiale der mittleren Kräfte ...en benutzen wir die in Tab.1 angegebenen ...arameter βh_{ij} für die einfachen Elektrolyte. ...n der Mischung auftretenden Stufenhöhen der ...B bzw. Kation A - Kation B Wechselwirkungen ...als freie Parameter betrachtet, deren Wert ...an experimentelle Meßdaten bestimmt wird. Vor ...müssen die experimentellen Daten ins MMM-Sys... ...werden. Dazu wurde eine von Krienke[10] ange... ...nutzt. In Fig.3 sind die Resultate der Anpas... ...schungen von Alkalihalogeniden für I=0.5 mol/l ...vom Ionenstärkebruch y_B des Elektrolyten B ...eben. Sowohl für die NaCl-KCl Mischung als ...r-KBr Mischung folgt aus der Anpassung βh_{Na-K} ...Natrium-Cäsium Wechselwirkung folgt βh_{Na-Cs} ...Abbildung ist ersichtlich, daß die theoreti... ... experimentellen Daten gut beschreiben. Die