

The Adjusted Screened Potential/Excluded Volume (ASPEV) Theory of Strong Electrolytes in Solution

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By analogy with the virial expansion of the equation of state of real gases a Debye-Hückel/Excluded Volume (DHEV) theory is proposed for electrolyte solutions. The second virial coefficients are interpreted as excluded volume between anion and cation using the principle of specific interaction of ions of Brønsted. The calculated ionic radii for many 1–1, 2–1 and 1–2 electrolytes follow a clear-cut pattern, but the radii are too large.

This is explained to be due to the screening effect of counterions which lowers the interaction energy between ions and lowers the contribution to the term in the expression for the activity coefficients proportional to the square root of ionic strength. A statistical-mechanical theory of screened potential is evaluated. The theory yields a semi-quantitative explanation of the effect of screening.

A semi-empirical Adjusted Screened Potential/Excluded Volume (ASPEV) theory is proposed giving an excellent fit for the mean ionic molar activity coefficients f_{\pm} for all combinations of H, Li, Na, K, Rb, Cs and Cl, Br, I in water at 25 °C up to concentrations around 3–5 mol/dm³. In the formula there is only one adjustable parameter – the excluded volume – from which one calculates cationic radii well in accordance with radii derived from ionic conductivities at infinite dilution.

The Debye and Hückel theory of strong electrolytes proposed in 1923¹ has had such far-reaching influence on the later development of electrochemistry that it has to a certain degree overshadowed the many subsequent efforts to rationalise the theory or to extend its applicability to higher electrolyte concentrations. The ionic strength has to stay below 0.001 mol/dm³ for the Debye-Hückel limiting law of electrolytes to be valid. This corresponds to such high dilution that one should properly speak about “slightly polluted solvents” where the activity coef-

ficients are so close to unity that the interest in their calculation is quite low. An exception – of course – is the use of the D.H. theory for making extrapolations to “infinite dilution”.

There has been two general lines of investigation. Some researchers have tried to enlarge the concentration range by making empirical and semi-empirical assumptions. Already the original papers of Debye and Hückel used the concept of distance of closest approach of the two ions (a). Instead of the dependence of activity coefficients on the square root of the ionic strength \sqrt{I} the dependence should rather be on $\sqrt{I}/(1+b\sqrt{I})$ where b is proportional to a and can be fitted individually for each salt. The quantity b has a value around unity and many authors put $b=1 \text{ mol}^{-1/2} \text{ dm}^{3/2}$ (Güntelberg approximation). This approximation is useful up to 0.01 mol/dm³ but it may give deviations to the wrong side of the limiting law in exceptional cases (*e.g.* ammonium halides² and tetraalkyl ammonium iodides³). To account for the minimum and subsequent increase in $\ln \gamma_{\pm}$ vs. \sqrt{I} (γ_{\pm} being the mean ionic molal activity coefficient) – found for most strong electrolytes – an empirical “salting-out” term Bm (m = molality) is also added. Even a third term Cm^2 has been found necessary in some cases and quite recently Pitzer and Mayorga⁴ have claimed the B -coefficient to be a quite complicated function of ionic strength. Those authors have furthermore added still another term proportional to $\ln(1+b\sqrt{I})$. The hydration theory of Bjerrum^{5,6} and later of Robinson and Stokes⁷ seems much simpler and the latter has been widely cited, but it is inconsistent in several respects (see Appendix II). Somewhat more convincing are the later arguments of Glueckauf,⁸ Jacobsen and Skou⁹ and Stokes and Robinson.¹⁰

Other researchers have concentrated more on the fundamental weaknesses of the original D.H. theory. The technique of Debye and Hückel was to combine the statistical Boltzmann-distribution with the macroscopic Poisson eqn. from electrostatics and to solve the linearised Poisson-Boltzmann eqn. For the linearisation to be valid one must have that $z_i F \psi_j / RT$ is much less than unity (ψ_j is the electric potential around the j 'th ion at the position of the i 'th ion with charge z_i). La Mer *et al.*^{11,12} obtained series expansions in $z_i F \psi_j / RT$, and Guggenheim¹³⁻¹⁵ has made computer calculations on the non-linear Poisson-Boltzmann eqn. He concluded that the expansions of La Mer *et al.* do not give significant improvements in comparison to the D. H. solution for aqueous solutions of uni-univalent electrolytes and that the expansion terms are not sufficient for higher valence types.

On a more fundamental level Onsager¹⁶ has shown that the non-linear Poisson-Boltzmann eqn. is inconsistent with the principles of statistical mechanics, since the conditional probability of finding an ion i at $r=r$ given an ion j at $r=0$ is not equal to the conditional probability of finding ion j at r given ion i at 0 for unsymmetrical electrolytes according to the non-linear P.B. eqn. This is due to the mixing of microscopic and macroscopic concepts in the hybrid P.B. eqn. Luckily, however, the inconsistency disappears when the P.B. eqn. is linearised. Onsager also showed that the so-called Debye charging process yields different results from the so-called Güntelberg charging process (see Appendix I) when non-linearities are taken into account – even for symmetrical electrolytes. Nevertheless, solution of the nonlinear P.B. eqn. has become popular among some electrochemists and among researchers studying macro-ions.¹⁷

Mayer¹⁸ applied the principles of statistical mechanics to the problem of finding the thermodynamic properties of an ensemble of charged hard spheres among solvent molecules. He succeeded in deriving a virial expansion by the cluster integral method and found the D.H. limiting law at high dilution avoiding the questionable P.B. eqn. and the problematic charging procedures. The same was done with somewhat different methods by Kirkwood and Poirier.¹⁹ Although the finding of the possibility of stratification of the average space charge around each ion by those latter authors seemed promising – being reminiscent of the space oscillations of the pair correlation functions in simple liquids – the approximations done were too rough

for direct comparison between theory and experiments. In 1968 Résibois (Ref. 20, p. 47) could state – after an excellent survey of the results of applying the Bogolubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy of equations on the electrolyte problem – that “unfortunately, the considerable effort which has been put into this problem has not resulted in much interest. No rigorous theory is presently available beyond the limiting-law region”.

Some light has broken through the dimness in recent years with the appearance of the hypernetted chain theory (HNC) and the mean spherical approximation method (MSA). Friedman and co-workers^{21,22} have performed the first successful calculations for a wide range of concentrations and salts with the HNC-eqns. However, the HNC method invokes the solution of a transcendental integral eqn. and is therefore not apt for rapid and practical calculations. The MSA-model, proposed by Lebowitz and coworkers,^{23,24} seems to be considerably more manageable,²⁵ and Triolo *et al.*²⁶ have fitted osmotic coefficients of 23 uni-univalent salts using this model. We shall see, however, that the fit is somewhat unsatisfactory for the activity coefficient data (see Appendix III) and the cationic radii found are also sometimes less than the Pauling radii and not consistent among different electrolytes with common cations.

In the present paper I shall try to manoeuvre safely between Scylla and Charybdis: on one hand I shall avoid mere curve fitting without fundamental ideas, on the other hand the sophisticated mathematics without practical results. A simple one parameter model is proposed – with the excluded volume between the positive and negative ion as the single adjustable parameter – which can explain the activity data from 0.001 up to 3–5 mol/dm³ for hydrogen- and alkali halides in aqueous solution. Hopefully, the model can also be extended to electrolytes of other valence types and to electrolyte mixtures. Even if the end result appears simple and the sum of radii seems to follow a consistent pattern with hydration numbers of the cations in reasonable accordance with numbers calculable from other sources, the chain of argumentation has many links and subtleties. Therefore, I shall start with the description of a simple Debye-Hückel/Excluded Volume theory (DHEV). This model also yields a consistent pattern of ionic radii, but the radii are generally too large and the concentration range not very big. Next, a modification of the D.H. theory – the “screened potential” theory will be presented,

and it will be explained why plots of $\ln f_{\pm}$ vs. \sqrt{I} for many electrolytes above 0.001 mol/dm³ yield almost straight lines with slopes around 0.7–0.9 times the value predicted by the D.H. limiting law. Finally, the DHEV-theory and the screened potential theory will be merged into a semi-empirical “Adjusted Screened Potential/Excluded Volume” (ASPEV) theory yielding reasonable ionic radii when tested on uni-univalent RX-electrolytes with R=H, Li, Na, K, Rb, Cs and X=Cl, Br, I.

DEBYE-HÜCKEL/EXCLUDED VOLUME (DHEV) THEORY

In this section I shall assume the following formula for the molar activity coefficient in a mixture of n different ionic species in electroneutral solvent (0)

$$\ln f_i = -A_{D.H.} z_i^2 \sqrt{I} + \sum_{j=1}^n B_{ij} c_j \quad (i=1, n) \quad (1)$$

where z_i is the number of unit charges carried by species No. i , $A_{D.H.}$ is the Debye-Hückel slope, I is the ionic strength $= (1/2) \sum c_i z_i^2$ and c_j the concentration of the j th ionic species. The coefficients B_{ij} are just phenomenological interaction coefficients between the ions. We notice that the usual Debye-Hückel expression can be Taylor-expanded in the following way

$$-A_{D.H.} z_i^2 \frac{\sqrt{I}}{1+b\sqrt{I}} \cong -A_{D.H.} z_i^2 \{ \sqrt{I} - bI \} \quad (2)$$

so that the effect of the denominator in the D.H. theory can be approximated by eqn. (1) for ionic strengths small enough. Due to the Maxwell conditions we have

$$\frac{\partial \ln f_i}{\partial c_j} = \frac{\partial \ln f_j}{\partial c_i} \quad (i \neq j) \quad (3)$$

and since

$$\frac{\partial \ln f_i}{\partial c_j} = -\frac{z_i^2 z_j^2}{4} \frac{A_{D.H.}}{\sqrt{I}} + B_{ij} \quad (4)$$

we have the requirements

$$B_{ij} = B_{ji} \quad (5)$$

for purely thermodynamic reasons.

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We now want to calculate the osmotic pressure Π of an electrolyte solution. For the change in chemical potential of the solvent caused by addition of electrolyte we have (at constant T)

$$d\mu_0 = V_0 dp + RT d \ln a_0 \quad (6)$$

where V_0 is the partial molar volume of the solvent and a_0 its activity. If the pressure p is equal to Π we have $d\mu_0 = 0$, i.e.

$$\frac{d\Pi}{RT} = -\frac{d \ln a_0}{V_0} \quad (7)$$

When we combine the Gibbs-Duhem eqn. (const. T , V total volume, n_i number of mol)

$$-V dp + n_0 d\mu_0 + \sum_{i \neq 0} n_i d\mu_i = 0 \quad (8)$$

with the requirement

$$V = n_0 V_0 + \sum n_i V_i \quad (9)$$

and with eqn. (6) and the analogous eqns for $i \neq 0$ we obtain

$$d \ln a_0 = -\frac{1}{c_0} \sum_{i \neq 0} c_i d \ln a_i \quad (10)$$

Inserting (10) into (7) and introducing the molar activity coefficients f_i we have

$$\frac{d\Pi}{RT} = \frac{1}{c_0 V_0} \left\{ \sum_{i \neq 0} dc_i + \sum_{i \neq 0} c_i d \ln f_i \right\} \quad (11)$$

To integrate for the osmotic pressure one should know $c_0 V_0$ as a function of the various salt concentrations. In moderately dilute solutions, however, we have to a good approximation

$$c_0 V_0 \cong 1 \quad (12)$$

We then have for the osmotic pressure

$$\frac{\Pi}{RT} \cong \sum_{i \neq 0} c_i + \sum_{i \neq 0} \int_0^{c_i} c_i' d \ln f_i' \quad (13)$$

Since Π is of course independent of the path of integration, we shall choose the simplest possible. We put

$$c_i' = l c_i \quad (14)$$

where the parameter l runs from 0 to 1. For the integrals in (13) we then obtain [using eqn. (1)]

$$\int_{l=0}^1 c_i' d \ln f_i' = -A_{D.H.} \times \frac{1}{2} c_i z_i^2 \times \frac{2}{3} \sqrt{l} + \frac{1}{2} \sum_{j \neq 0} B_{ij} c_i c_j \quad (15)$$

and for the osmotic pressure

$$\frac{\Pi}{RT} = \sum_{i \neq 0} c_i - \frac{2}{3} A_{D.H.} I^{3/2} + \frac{1}{2} \sum_{i \neq 0} \sum_{j \neq 0} B_{ij} c_i c_j \quad (16)$$

We shall now make an analogy to the case of a mixture of moderately dilute gases. According to Ref. 27, eqns. (7-61) and (7-1) we have for a mixture of gases ($c_{tot} = \sum c_i$, $N_0 =$ Avogadro number)

$$\frac{P}{RT} = c_{tot} + c_{tot}^2 N_0 \sum_i \sum_j x_i x_j B_2(ij) \quad (17)$$

with x_i being the mol fraction of the i 'th species and the second virial coefficients are given by [Ref. 27, eqn. (7.27)]

$$B_2(ij) = -2\pi \int_0^\infty \{e^{-U_{ij}(r_{ij})/kT} - 1\} r_{ij}^2 dr_{ij} \quad (18)$$

where U_{ij} is the pair potential between the i 'th and the j 'th species which is function of the distance r_{ij} . It can be rigorously shown²⁸ that it is allowable to use exactly the same formalism for the osmotic pressure in a moderately dilute solution as for the pressure of a mixture of moderately dilute gases. The pair potential has just to be interpreted as the pair potential of average forces. The average force between two solute molecules separated by a distance of r_{ij} is given by the direct force between the two solute molecules *plus* the average of a fluctuating force due to the fact that two solute molecules fixed at a distance r_{ij} perturb the spherical symmetry of solvent molecules around each solute species. Thus, for a solution of electroneutral species we obtain

$$\frac{\Pi}{RT} = \sum_{i \neq 0} c_i + N_0 \sum_{i \neq 0} \sum_{j \neq 0} c_i c_j B_2(ij) \quad (19)$$

The virial coefficients are given by (18) with U_{ij} interpreted as the potentials of the average force. In this paper we shall consider only the simplest interaction, *i.e.* hard core interaction

$$U_{ij} = \begin{cases} 0 & r_{ij} \geq R_i + R_j \\ \infty & r_{ij} < R_i + R_j \end{cases} \quad (20)$$

From eqn. (18) we then get the second virial coefficients in terms of excluded volumes

$$B_2(ij) = \frac{2\pi}{3} (R_i + R_j)^3 \quad (21)$$

If we compare (19) with (16) we see that they are identical except for the Debye-Hückel term. The simplest assumption is therefore that it is possible to superpose the D.H. osmotic pressure on the hard core osmotic pressure. We then have

$$B_{ij} = 2N_0 B_2(ij) \quad (22)$$

so that the interaction coefficients B_{ij} in (1) may be calculated from assumptions of certain ionic radii.

Two years before the advent of the D.H. theory, Lewis and Randall²⁹ had introduced the concept of ionic strength and stated the principle that "in dilute mixed electrolyte solutions (up to $I=0.05$ mol/kg solvent) the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength". This principle was shortly after repudiated by Brønsted³⁰ who instead advocated his principle of specific interaction of ions: "In a dilute salt solution of constant total concentration ions will be uniformly influenced by ions of their own sign". From the context it appears that Brønsted meant that only ions of opposite signs would have a specific interaction on the activity coefficients of each other. If we interpret "uniformly influenced" to be an influence through the ionic strength and a "specific interaction" to a B_{ij} -interaction, Brønsted's principle combined with the present theory may be stated as follows

$$B_{ij} = \begin{cases} \frac{4\pi N_0}{3} (R_i + R_j)^3 & \text{if } z_i z_j < 0 \\ 0 & \text{if } z_i z_j > 0 \end{cases} \quad (23)$$

The principle of superposition of the D.H. term and the second virial terms supposed in the DHEV-theory is of course far from obvious. One cross-coupling between the $c^{3/2}$ term and the c^2 terms in the expression for the osmotic pressure might very well be, that excluded volumes of ions of like signs should not be accounted for, since the ions are kept apart by the electrostatic forces already accounted

for in the D.H. term. We shall see that this seems to be the case, experimentally.

We shall now concentrate on solutions of single, binary electrolytes dissociating into v_+ cations and v_- anions. The cation is given the number 1 and the anion the number 2. We have now for the mean ionic activity coefficient

$$\ln f_{\pm} = -A_{D.H.} |z_+ z_-| \sqrt{I} + \frac{c_s}{v_+ + v_-} \{B_{11} v_+^2 + 2B_{12} v_+ v_- + B_{22} v_-^2\} \quad (24)$$

where c_s is the salt concentration and $B_{11} = B_{22} = 0$ if Brønsted's principle of specific interaction of ions is valid. Newman³¹ (Chap. 4, Section 30) gives the

following formula for the *molal* activity coefficient (I' = molal ionic strength)

$$\ln \gamma_{\pm} = -|z_+ z_-| \frac{A'_{D.H.} \sqrt{I'}}{1 + b \sqrt{I'}} + \frac{4v_+ v_-}{v_+ + v_-} \beta m \quad (25)$$

together with tables of b and β for various electrolytes in water at 25 °C. Power expanding the denominator according to eqn. (2) we obtain

$$\ln \gamma_{\pm} \cong -A'_{D.H.} |z_+ z_-| \sqrt{I'} + \left\{ \frac{4v_+ v_-}{v_+ + v_-} \beta + \mu |z_+ z_-| A'_{D.H.} b \right\} m \quad (26)$$

with

$$\mu = \frac{1}{2} \{z_+^2 v_+ + z_-^2 v_-\} \quad (27)$$

Table 1. Calculation of DHEV-radii for various 1-1 electrolytes.

Electrolyte	β^a kg/mol ~ dm ³ /mol	B_{12} dm ³ /mol	$R_1 + R_2$ Å	R_2 Å	R_1 Å	R_1 (Pauling) Å	Hydration shell volume (Å ³)	Hydration number
HCl	0.27	1.72	8.8	1.8				
HBr	0.33	1.84	9.0	2.0	7.0(1)	0	1440	48
HI	0.36	1.90	9.1	2.2				
LiCl	-0.21	1.62	8.6	1.8				
LiBr	0.22	1.70	8.8	2.0	6.8(1)	0.61	1320	44
LiI	0.26	1.88	9.1	2.2				
NaCl	0.15	1.48	8.4	1.8				
NaBr	0.17	1.52	8.4	2.0	6.5(1)	0.96	1150	39
NaI	0.21	1.60	8.6	2.2				
KCl	0.10	1.38	8.2	1.8				
KBr	0.11	1.40	8.2	2.0	6.3(1)	1.33	1040	35
KI	0.15	1.48	8.4	2.2				
RbCl	0.06	1.30	8.0	1.8				
RbBr	0.05	1.28	8.0	2.0	6.0(2)	1.48	890	30
RbI	0.04	1.26	7.9	2.2				
CsCl	0.00	1.18	7.8	1.8				
CsBr	0.00	1.18	7.8	2.0	5.8(2)	1.66	800	27
CsI	-0.01	1.16	7.7	2.2				
HNO ₃	0.20	1.58	8.6		7.0			
LiNO ₃	0.21	1.60	8.6		6.8			
NaNO ₃	0.04	1.26	7.9		6.5			
KNO ₃	-0.11	0.96	7.3	1.4(4)	6.3			
RbNO ₃	-0.14	0.90	7.1		6.0			
CsNO ₃	-0.15	0.88	7.0		5.8			

^a All data for water at 25 °C from Ref. 31, Table 30-1. For all electrolytes $b = 1$ (kg/mol)^{1/2} ~ 1 (dm³/mol)^{1/2}. Numbers in parenthesis indicate uncertainty on the preceding cipher.

Table 2. Calculation of DHEV-radii for various 2-1 and 1-2 electrolytes.

Electrolyte	b^a (kg/mol) [‡] ~(dm ³ /mol) [‡]	$2\beta^a$ kg/mol ~dm ³ /mol	B_{12} dm ³ /mol	$R_1 + R_2$ Å	R_2 Å	R_1 Å	R_1 (Pauling) Å
MgCl ₂	1.59	0.36	8.79	15.2	1.8	13.3(1)	0.65
MgBr ₂	1.62	0.50	9.09	15.3	2.0		
CaCl ₂	1.54	0.29	8.45	15.0	1.8		
CaBr ₂	1.62	0.37	8.96	15.3	2.0	13.3(1)	0.99
SrCl ₂	1.56	0.22	8.49	15.0	1.8		
SrBr ₂	1.62	0.30	8.89	15.2	2.0	13.2	1.13
BaCl ₂	1.56	0.11	8.38	14.9	1.8		
BaBr ₂	1.56	0.24	8.51	15.0	2.0	13.0(1)	1.35
Mg(NO ₃) ₂	1.53	0.36	8.47	15.0		13.3	
Ca(NO ₃) ₂	1.39	0.09	7.46	14.4	1.3(4)	13.3	
Sr(NO ₃) ₂	1.39	-0.07	7.30	14.2		13.2	
Li ₂ SO ₄	1.41	-0.11	7.36	14.3		6.8	
Na ₂ SO ₄	1.27	-0.28	6.45	13.7		6.5	
K ₂ SO ₄	1.07	-0.15	5.52	13.0	7.5(7)	6.3	
Rb ₂ SO ₄	1.33	-0.25	6.80	13.9		6.0	
Cs ₂ SO ₄	1.33	-0.20	6.85	14.0		5.8	

^a All data for water at 25 °C from Ref. 31, Table 30-2.

For sufficiently dilute solutions we can neglect the difference between the molality and salt concentration except that we have to use $A_{D,H} = 1.1779 \text{ dm}^3/2 \text{ mol}^{-1/2}$ instead of $A_{D,H} = 1.1762 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ (Ref. 31, Table 28-1). We have then by comparison with (23) and (24)

$$B_{12} \cong 2\beta + \frac{b}{2} \mu \frac{v_+ + v_-}{v_+ v_-} A_{D,H} |z_+ z_-| \quad (28)$$

From the figures in Newman's tables (Ref. 31, Table 30-1 and Table 30-2) we calculate by means of (28) the excluded volume B_{12} for various uni-univalent electrolytes (Table 1) and for various 2-1 and 1-2 electrolytes (Table 2). Furthermore, we get the sum of radii from (23). Comparing the sum of radii for alkali halides with the same cation, we observe that the differences correspond very well to the differences in the crystallographic radii between the halogenide ions. Therefore, the anions are assumed unhydrated and the radii of the cations can be estimated. The hydration numbers of the cations are calculated from the volume in the spherical shell between the calculated radius and the

Pauling radius, assuming that each water molecule occupies 30.0 \AA^3 as in pure water at 25 °C. This is just a rough approximation, since many electrolytes are known to have negative partial molar volumes in water; see Bernal and Fowler (Ref. 32, Table V). However, the approximation is good enough to demonstrate that the hydration numbers calculated by the DMEV-theory are much too large to have any realistic significance.

Apart from that, the pattern shown in Table 1 and Table 2 is fairly consistent. The radii of the series H^+ , Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ as well as the series Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} decrease monotonically, since the smallest ions are the most hydrated. The earth alkali ions are more hydrated than the alkali ions due to the double charge. The "radius" of the NO_3^- ion in alkali nitrates is $1.4 \pm 0.4 \text{ \AA}$ and the "radius" of the SO_4^{2-} ion in alkali sulfates is $7.5 \pm 0.7 \text{ \AA}$. Those values are remarkably constant when one considers that attractive forces and orientation dependent forces must play important roles for those ions - making a simple excluded volume theory quite inappropriate. The constancy of those anionic radii should also be seen in the light of the

wildly fluctuating values of the b - and the β -values taken apart.

The reason for the exaggeration of the values of the sum of radii is that the Debye-Hückel slope $A_{D.H.}$ grossly exaggerates the effect of ionic strength for ionic strengths above 0.001 mol/dm³ due to the screening of ions by their counterions. In the next section it will be explained why slopes less than $A_{D.H.}$ (0.7 to 0.9 $A_{D.H.}$) give a much better fit for electrolytes of all valence types between ionic strengths 0.001 and 0.05 mol/dm³, and why even smaller slopes may be expected for larger ionic strengths. It is then clear that the excluded volume in (24) will be exaggerated.

THEORY OF SCREENED POTENTIAL

The point of departure in the classical theory of Debye and Hückel is the following pair distribution of ion j in the field of ion i

$$n_{ji}(r) = \rho_i \rho_j \exp[-z_j F \psi_i(r)/RT] \quad (29)$$

where ρ_i is the mean number density of the i 'th ion, ψ_i the electric potential due to the i 'th ion in the distance r from this ion and F is the Faraday number. We shall require that

$$F \psi_i / RT \ll 1 \quad (30)$$

The local charge density $\rho_q^{(i)}$ around the i 'th ion can then be approximated by (using the condition of electroneutrality for the mean densities)

$$\rho_q^{(i)} \cong -\frac{2F^2}{RT} I \psi_i \quad (31)$$

Combination of (31) with the Poisson eqn. of electrostatics yields the linearised Poisson-Boltzmann eqn. for the distribution of the electric potential

$$\nabla^2 \psi_i = \kappa^2 \psi_i \quad (32)$$

with the definition

$$\kappa = F \sqrt{\frac{2I}{RT\epsilon}} \quad (33)$$

where ϵ is the absolute permittivity of the solvent medium. The solution to (32) for a point charge z_i is

$$\psi_i^{D.H.} = \frac{z_i F e^{-\kappa r}}{4\pi\epsilon N_0 r} \quad (34)$$

and the charge density around ion i is to a first approximation

$$\rho_q^{(i)}(D.H.) = -\frac{\kappa^2 z_i F e^{-\kappa r}}{4\pi N_0 r} \quad (35)$$

Already at ionic strengths around 0.001 mol/dm³, however, we have a pronounced screening of the interactions between ions due to the atmosphere of the counterions. From (35) we get a first approximation to the charge in the ionic cloud inside a sphere with radius R

$$q_{cloud}^{(D.H.)}(R) = \int_0^R 4\pi r^2 \rho_q^{(i)} dr = -\frac{z_i F}{N_0} \{1 - g(\kappa R)\} \quad (36)$$

with the definition

$$g(\kappa R) = (1 + \kappa R) e^{-\kappa R} \quad (37)$$

To get the total "effective charge" inside the sphere with radius R we have to add the ionic charge $z_i F / N_0$ to q_{cloud} . We obtain

$$z_i^{eff}(R) = g(\kappa R) z_i \quad (38)$$

The basic eqn. (29) was obtained by using simple Boltzmann statistics and noting that the interaction energy of ion j in the field of ion i is $z_j F \psi_i / N_0$. A much better approximation of the interaction energy is, however

$$z_j^{eff}(r) F \psi_i(r) / N_0$$

since $z_j^{eff}(r)$ is the part of the charge z_j effectively "seen" from the central ion i . Just imagine, that the ionic cloud was effectively finished at a distance smaller than r . Then, there cannot be any electrostatic interaction between ion i and ion j , and the local densities of those species are uncorrelated with a pair distribution function $n_{ji}(r) = \rho_i \rho_j$. Replacing z_j with $g(\kappa r) z_j$ in (29) and using the Debye-Hückel condition (30) we obtain as a second approximation for the local charge density (the "screened potential" approximation)

$$\rho_q^{(i)}(SP) = -\frac{2F^2}{RT} I g(\kappa r) \psi_i(r) \quad (39)$$

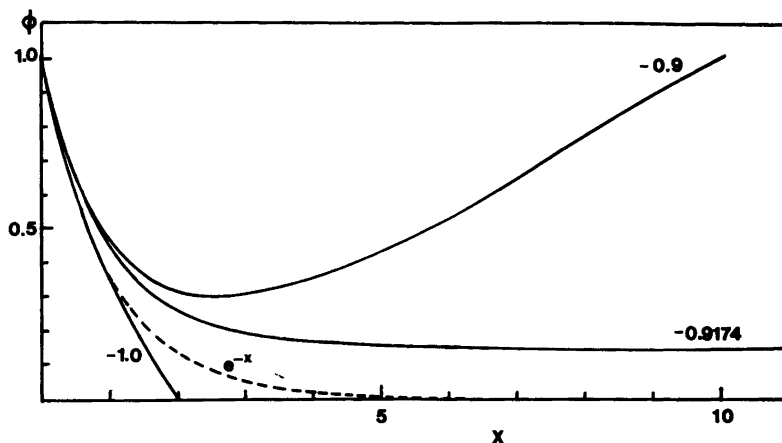


Fig. 1. Finding the screened potential function by trial and error. See text.

Inserting this into the Poisson eqn. we get the "screened potential" version of the linearised P.B. eqn.

$$\nabla^2 \psi_i^{\text{SP}} = \kappa^2 g(\kappa r) \psi_i^{\text{SP}} \quad (40)$$

Introducing the dimensionless variable

$$x = \kappa r \quad (41)$$

the Laplacian in spherical coordinates and the new function

$$\Phi = \psi_i^{\text{SP}} x \quad (42)$$

we get the differential eqn.

$$\frac{d^2 \Phi}{dx^2} = g(x) \Phi \quad (43)$$

This differential eqn. has been solved by computer using a third order Runge-Kutta algorithm with a steplength in x equal to $h=0.1$ and an error of $O(h^4)$; see Ref. 33, No. 25.5.22.

Some results are shown in Fig. 1. One can choose Φ and $d\Phi/dx$ at $x=0$ to be arbitrary values. We choose $\Phi(x=0)$ to be 1, since another value will just amount to a scale factor. For the chosen value of $\Phi(x=0)$ there will only be one value of $[d\Phi/dx]_{x=0}$ with a solution with the property that $\Phi \rightarrow 0$ when $x \rightarrow \infty$ (see Fig. 1). If the initial slope is -0.9173 the $\Phi(x)$ curve finally rises and goes to ∞ when $x \rightarrow 0$. On the other hand, the curve with initial slope -0.9174 cuts the x -axis around $x=4170$, while the

curve with initial slope -0.9175 cuts at $x=202$. The initial slope must therefore be between -0.9173 and -0.9174 , but the curve with slope -0.9174 will be very close to the true curve for x less than 1000. Because of the importance of this potential curve for the present and future studies we have tabulated it in Table 3. We notice especially the long "tail" of the potential curve in comparison to the solution $\exp(-x)$ to the simple linearised P.B.

Table 3. The screened potential function $\phi(x)$.

x	ϕ	x	ϕ
0	1.0000	2.2	0.2406
0.1	0.9131	2.4	0.2245
0.2	0.8353	2.6	0.2113
0.3	0.7657	2.8	0.2003
0.4	0.7035	3.0	0.1912
0.5	0.6479	3.5	0.1744
0.6	0.5982	4.0	0.1638
0.7	0.5538	5.0	0.1525
0.8	0.5140	6.0	0.1478
0.9	0.4784	7.0	0.1459
1.0	0.4465	8.0	0.1450
1.1	0.4179	9.0	0.1447
1.2	0.3922	10.0	0.1445
1.3	0.3691	20.0	0.1441
1.4	0.3483	50.0	0.1430
1.5	0.3296	80.0	0.1419
1.6	0.3127	100.0	0.1413
1.7	0.2975	150.0	0.1396
1.8	0.2837		
1.9	0.2713		
2.0	0.2600		

eqn. The ionic cloud is less concentrated in the screened case since the interactions between ions are weaker.

In the classical Debye-Hückel theory the transition from potential function to activity coefficients is made by various charging processes (Debye charging, Güntelberg charging), but since those procedures can be criticized from several points of view (see Appendix I), we shall apply instead a more satisfactory method given, *e.g.*, in the monograph of Résibois (Ref. 20, pp. 34–40). From simple mathematical properties of the configuration integral and the pair distribution function we obtain for the electrostatic contribution to the Helmholtz free energy per unit volume

$$\frac{A_{el}}{\Omega} = \frac{1}{2} \int_0^1 \frac{d\lambda}{\lambda} \int dr \sum_{ij} \lambda \cdot U_{ij}^{el}(r) n_{ij}(r, \lambda) \quad (44)$$

where λ is a parameter measuring the strength of electrostatic interaction with the Coulombic interaction energy λU_{ij}^{el} given by

$$\lambda U_{ij}^{el} = \frac{\lambda z_i z_j F^2}{4\pi N_0^2 \epsilon_0 r_{ij}} \quad (45)$$

with ϵ_0 being the permittivity of vacuum. The pair distribution function n_{ij} in (44) is determined by the U_{ij}^{el} -interactions as by the short range quantum mechanical forces between ions and between ions and solvent. The Debye-Hückel approximation is now to suppose that the only contribution of short range forces are the ion-dipole forces between ions and solvent molecules, and to assume that those interactions can be adequately accounted for by substituting the permittivity of the solvent ϵ instead of ϵ_0 in (45). Furthermore, the Debye-Hückel pair distribution function is used, *i.e.*

$$n_{ij} \cong \rho_i \rho_j \left[1 - \frac{z_i F \psi_i}{RT} \right] = \rho_i \rho_j \left[1 - \frac{z_i z_j F^2 e^{-\kappa r}}{4\pi RT \epsilon N_0 r} \right] \quad (46)$$

When the interaction strength is only the fraction λ of the full interaction, we can proceed formally by replacing z_i by $\sqrt{\lambda} z_i$. We then have $\kappa' = \sqrt{\lambda} \kappa$ and

$$n_{ij}(r, \lambda) \cong \rho_i \rho_j \left[1 - \frac{\lambda z_i z_j F^2 e^{-\sqrt{\lambda} \kappa r}}{4\pi RT \epsilon N_0 r} \right] \quad (47)$$

Using the electroneutrality condition for the mean densities ρ_i and transforming the variable $dr = 4\pi r^2 dr$ we obtain from (44), modified (45) and (47)

$$\frac{A_{el}}{\Omega} = -\frac{1}{2} \int_0^1 d\lambda \sum_{ij} \left\{ \frac{z_i^2 z_j^2 F^4 c_i c_j}{N_0 4\pi R T \epsilon^2} \int_0^\infty e^{-\sqrt{\lambda} \kappa r} dr \right\} \quad (48)$$

Carrying out the integrations we obtain

$$\frac{A_{el}}{\Omega} = -\frac{RT}{12\pi N_0} \kappa^3 \quad (49)$$

which is exactly the result of Debye and Hückel for point charges.

We are now going to introduce the corrections for screening. According to (39) and (40) the charge distribution around the i 'th ion in the SP-approximation is given by

$$\rho_q^{(i)}(\text{SP}) = -\epsilon \kappa^2 g(\kappa r) \psi_i^{\text{SP}} = -\epsilon \kappa^2 \frac{g(\kappa r)}{\kappa r} C_i \Phi \quad (50)$$

where Φ is given in Table 3 and C_i is a scaling factor for the potential distribution. It can be found by requiring that the total charge in the ionic cloud counterbalances the charge on the central ion

$$\int_0^\infty \rho_q^{(i)} 4\pi r^2 dr = -\frac{4\pi \epsilon}{\kappa} C_i \int_0^\infty g(x) \Phi(x) x dx = -\frac{z_i F}{N_0}$$

so that

$$C_i = \frac{z_i F}{N_0} \frac{\kappa}{4\pi \epsilon \int_0^\infty x g(x) \Phi(x) dx} \quad (51)$$

The potential around the i 'th ion is then given by

$$\Psi_i^{\text{SP}} = \frac{z_i F}{N_0 4\pi \epsilon J_1} \times \frac{\Phi(\kappa r)}{r} \quad (52)$$

with

$$J_1 = \int_0^\infty x g(x) \Phi(x) dx \quad (53)$$

The pair distribution function is given by

$$n_{ij}(r) \cong \rho_i \rho_j \left[1 - \frac{z_i F g(\kappa r) \psi_i^{\text{SP}}}{RT} \right] \quad (54)$$

or – when the Coulombic interaction strength is less than unity –

$$n_{ij}(r, \lambda) \cong \rho_i \rho_j \left[1 - \frac{\lambda z_i z_j g(\sqrt{\lambda} \kappa r) F^2}{4\pi \epsilon N_0 R T J_1} \times \frac{\Phi(\sqrt{\lambda} \kappa r)}{r} \right] \quad (55)$$

The screened potential interaction energy is

$$U_{ij}^{el} = \frac{z_i z_j g^2(\lambda r) F^2}{4\pi N_0^2 \epsilon r_{ij}} \quad (56)$$

Introducing (55) and (56) in (44) and using the electroneutrality condition for the mean densities ρ_i and ρ_j we obtain

$$\frac{A_{el}}{\Omega} = -\frac{1}{2} \times \frac{F^4}{4\pi\epsilon^2 N_0 R T J_1} \int_0^1 \lambda d\lambda \int_0^\infty \sum_{i,j} c_i c_j z_i^2 z_j^2 g^3(\sqrt{\lambda} \kappa r) \Phi(\sqrt{\lambda} \kappa r) dr \quad (57)$$

In the last integral we change variable to $p = \sqrt{\lambda} \kappa r$. Furthermore, we use that

$$\sum_{i,j} c_i c_j z_i^2 z_j^2 = \left(\sum_i c_i z_i^2 \right) \left(\sum_j c_j z_j^2 \right) = 4 I^2 \quad (58)$$

Then (57) can be written

$$\frac{A_{el}}{\Omega} = -\frac{I^2 F^4 J_2}{2\pi\epsilon^2 N_0 R T J_1 \kappa} \int_0^1 \sqrt{\lambda} d\lambda \quad (59)$$

with

$$J_2 = \int_0^\infty g^3(p) \Phi(p) dp \quad (60)$$

Carrying out the λ -integration and using the definition of κ in (33) we obtain

$$\frac{A_{el}}{\Omega} = -\frac{RT}{12\pi N_0} \left(\frac{J_2}{J_1} \right) \kappa^3 \quad (61)$$

The activity coefficient of the i 'th ion is given by

$$RT \ln f_i = \left[\frac{\partial}{\partial c_i} \left(\frac{A_{el}}{\Omega} \right) \right]_{\Omega, T} = - \left(\frac{J_2}{J_1} \right) \frac{\sqrt{2} F^3 z_i^2 \sqrt{I}}{8\pi N_0 \epsilon^{3/2} \sqrt{RT}} \quad (62)$$

or

$$\ln f_i = - \left(\frac{J_2}{J_1} \right) A_{D.H.} z_i^2 \sqrt{I} \quad (63)$$

with the Debye-Hückel constant

$$A_{D.H.} = \frac{\sqrt{2} F^3}{8\pi N_0 (RT\epsilon)^{3/2}} \quad (64)$$

The only difference from the D.H. limiting law is the factor J_2/J_1 which has to be evaluated numerically. The two integrals have been calculated by computer by means of Simpson integration with step length $h=0.1$. We obtain

$$J_1 = 0.8555 \pm 0.0005 \quad J_2 = 0.6055 \pm 0.0005$$

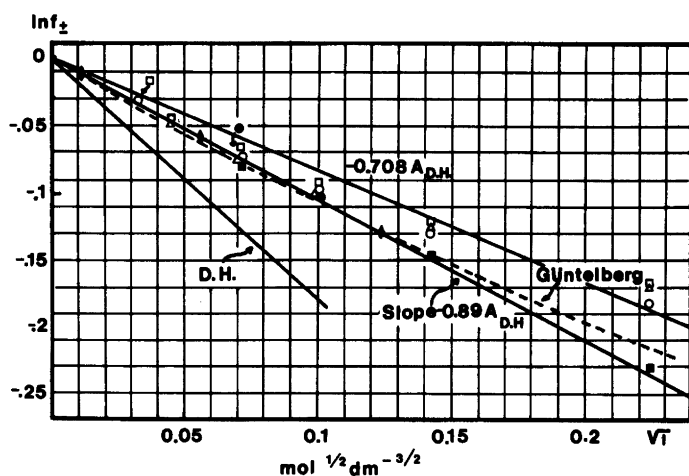


Fig. 2. Logarithm of molar mean ionic activity coefficient vs. square root of molar ionic strength at moderate concentrations for various electrolytes. Water at 25 °C.

○, HCl; □, LiBr; △, KI; ●, RbCl; ■, CsCl + CsBr; ◆, $\text{Co}(\text{NH}_3)_6^{3+} \text{Co}(\text{CN})_6^{3-}$. (Data from Ref. 34 at 18 °C have been multiplied by $(A_{D.H.}^{25}/A_{D.H.}^{18} \times 3^2)$ to make them compatible.)

We have then for the mean ionic molar activity coefficient in the screened potential approximation

$$\ln f_{\pm} = -0.708 |z_+ z_-| A_{D.H.} \sqrt{I} \quad (65)$$

In Fig. 2 we have plotted some experimental results for various electrolytes against the square root of the ionic strength. From the figure it is clear that the D.H. limiting law is grossly in error even at such low concentrations as 0.001 mol/dm³ where measurements start for most electrolytes. The experimental results for the lowest concentrations (up to ionic strengths around 0.01 mol/dm³) seem to follow quite closely a straight line with slope $-0.89 A_{D.H.}$, but around $I=0.02$ mol/dm³ the slope $-0.708 A_{D.H.}$ is more appropriate. The concentration region shown in Fig. 2 is then a transition region between the Debye-Hückel situation and the screened potential situation. We could repeat the whole procedure once more and obtain a third approximation and so on. It is clear from the formalism used that for each new iteration we would find an expression of the same form as (65), but the factor would differ. Sketchy calculations seem to indicate that the factor will diminish even further, but a detailed investigation of this point as well as an investigation of the influence of the ionic size on the effect of screening will be left for future study. Here we shall just anticipate that the empirical facts show (see next paragraph) that the numerical value of the effective slope in (65) diminishes with increasing ionic strength, until it reaches a stationary value which seems to be greater the greater the excluded volume is between anion and cation.

ADJUSTED SCREENED POTENTIAL/ EXCLUDED VOLUME (ASPEV) THEORY

We have seen that the DHEV-theory gave a quite consistent picture of excluded volumes for many electrolytes, but the sum of radii was too big. In the preceding paragraph we showed that the Debye-Hückel limiting law is exaggerating the effect of Coulombic forces, since it doesn't take into account the shielding of ions by their counterions in the expression for the interaction energy between two ions. As a straightforward generalisation of (24) I shall try to apply the following equation

$$\ln f_{\pm} = -A^*x + B^*x^2 \quad (66)$$

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where B^* in conformation with (23) and (24) is given by

$$B^* = \frac{2\mu v_+ v_-}{v_+ + v_-} B_{12} \quad (67)$$

and x is the square root of the ionic strength. In accordance with the points of view in the preceding paragraph, A^* is around $0.7|z_+ z_-| A_{D.H.}$, but it might be varying in an individual way for each electrolyte with varying ionic strength. In the present section we shall fit (66) to the mean ionic activity coefficients of various hydrogen- and alkali halides.

If (66) were a true parabola (*i.e.* A^* and B^* are independent of x) one should have

$$x_{\min} = \frac{A^*}{2B^*} \quad (68a)$$

$$(\ln f_{\pm})_{\min} = -\frac{(A^*)^2}{4B^*} \quad (68b)$$

$$x_{-\frac{1}{2}} = \frac{A^*}{2B^*} \left(1 - \frac{1}{\sqrt{2}}\right) \quad (68c)$$

$$x_{+\frac{1}{2}} = \frac{A^*}{2B^*} \left(1 + \frac{1}{\sqrt{2}}\right) \quad (68d)$$

$$x_0 = \frac{A^*}{B^*} \quad (68e)$$

For the definitions of $x_{-1/2}$, $x_{+1/2}$ and x_0 see Fig. 3. The data for mean ionic activity coefficients (molal) as a function of molality have been collected from various sources.³⁵⁻³⁷ Molal activity coef-

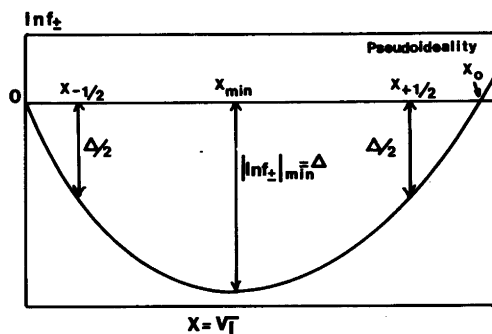


Fig. 3. Various characteristics for $\ln f_{\pm}$ vs. \sqrt{I} curves.

Table 4. Characteristics of the $\ln f_{\pm}$ vs \sqrt{I} curves for various uni-univalent electrolytes.

Electrolyte	$-(\ln f_{\pm})_{\min}$	$x_{-\frac{1}{2}}$	$x_{-0.9}$	x_{\min}	$x_{+0.9}$	$x_{+\frac{1}{2}}$	x_0	Ref. No.
HCl	0.270	0.150		0.60		1.115	1.322	37
HBr	0.240	0.130		0.50		0.965	1.162	37
HI	0.202	0.105		0.42		0.820	0.982	37
LiCl	0.305	0.150		0.65		1.235	1.452	37
LiBr	0.276	0.150		0.60		1.080	1.298	35
LiI	0.214	0.125		0.42		0.930	1.100	37
NaCl	0.400	0.240		1.0		1.855	2.175	37,35
NaBr	0.352	0.240		0.85		1.550	1.845	37
NaI	0.300	0.175		0.65		1.300	—	35
KCl	0.493	0.305		1.3		(2.43) ^a	—	37
KBr	0.452	0.270		1.2		2.20	—	37($I \leq 0.05$), 36($I \geq 0.1$)
KI	0.415	0.245		1.0		1.835	—	35
RbCl	0.533	0.328	0.870	1.3	1.845	—	—	37,35
RbBr	0.540	0.330	0.895	1.4	1.900	—	—	35
RbI	0.528	0.320	0.850	1.3	1.750	—	—	35
CsCl	0.627	0.380	0.960	1.45	1.950	—	—	37,35
CsBr								
CsI	~0.65	~0.4	?	?	?	—	—	35

^a Extrapolated value.

ficients have been transformed to molar activity coefficients and molality to molarity by means of the formula and tabulation for c/m given in Ref. 35, Table (12-1-1A), p. 725. A smooth curve was drawn for $\ln f_{\pm}$ as a function of the square root of ionic strength and x_{\min} , $(\ln f_{\pm})_{\min}$, $x_{-1/2}$, $x_{+1/2}$ and x_0 were found for the investigated electrolytes. The tabulation together with the data sources is given in Table 4. Since $\ln f_{\pm}$ vs. x is not precisely a parabola one has to make some choice about the concentration range of fitting. When $(\ln f_{\pm})_{\min}$, $x_{-1/2}$, $x_{+1/2}$ and x_0 are fixed to their experimental values and A^* is chosen to some value, B^* may be calculated from (68b-e). The B^* -values calculated for the various A^* -values by the four formulae are plotted for HI in water at 25 °C in Fig. 4. One observes that in optimum 1, the depth of the minimum, the x -value of half-minimum to the right of the minimum and the pseudoideal point is reproduced by the parabola, but not the x -value of half-minimum to the left of the minimum. In optimum 2, the depth of the minimum and the $x_{-1/2}$ value fit, but not $x_{+1/2}$ and x_0 . Similar plots

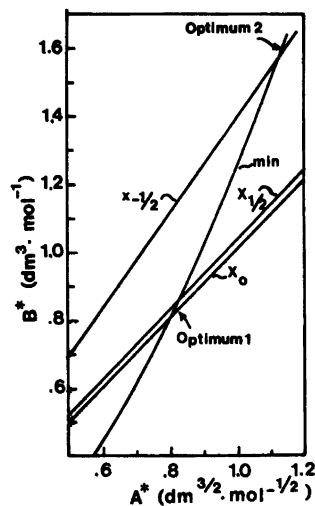


Fig. 4. Finding optimal values for A^* and B^* . Here HI in water at 25 °C.

Table 5. Optimal values of A^* and B^* .

Electrolyte	A_{opt}^* (dm^3/mol) [‡]	B_{opt}^* dm^3/mol	B^* (adjusted to regress.) dm^3/mol	B^* (final adj.) dm^3/mol
HCl	0.83	0.63	0.64	0.64
HBr	0.84	0.74	0.74	0.74
HI	0.82	0.84	0.94	0.94
LiCl	0.865	0.60	0.54	0.54
LiBr	0.87	0.68	0.62	0.62
LiI	0.78	0.71	0.78	0.78
NaCl	0.75	0.35	0.355	0.355
NaBr	0.765	0.415	0.415	0.415
NaI	0.795	0.52	0.52	0.52
KCl	0.705	0.25	0.25	0.27
KBr	0.715	0.28	0.29	0.29
KI	0.78	0.365	0.35	0.35
RbCl	(0.76)	(0.27)	0.26	0.25
RbBr	(0.75)	(0.26)	0.25	0.25
RbI	(0.80)	(0.30)	0.27	0.26
CsCl + CsBr	(0.845)	(0.285)	0.23	0.16
CsI	—	—	—	0.16

were made for most of the electrolytes given in Table 4. In most cases the $x_{+1/2}$ and the x_0 curves even coincided completely.

The values of A^* and B^* in optimum 1 are given in Table 5. Values for rubidium and caesium halides have been estimated from $x_{-0.9}$, $x_{+0.9}$ and $(\ln f_{\pm})_{\text{min}}$, since $x_{+1/2}$ and x_0 could not be safely extrapolated from experimental data. When two data sources disagree about the numerical values of f_{\pm} we have proceeded with the values which seemed to follow the excluded volume pattern most closely. Especially some of the data given by Latimer³⁷ in more concentrated solutions seem to need careful scrutiny before use, see Fig. 11 for an example (KBr).

In Fig. 5 we have plotted the optimum values (optimum 1) of A^* found vs. the optimum values of B^* . There seems to be a linear correlation between the two parameters. The lower the excluded volume, the lower the optimum A^* . A qualitative explanation may be that for smaller ions, the screening effects described in the preceding paragraph — leading to an A^* lower than $A_{\text{D.H.}}$ — are allowed to evolve to a greater extent at increasing ionic strength than for the larger ions where the

excluded volume forces come into action at lower ionic strengths. The linear regression involving all

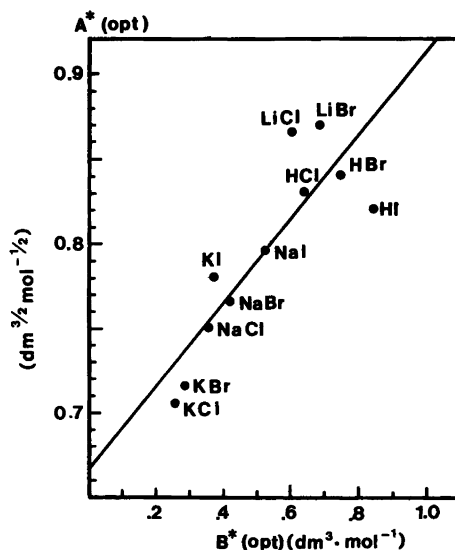


Fig. 5. Linear regression for optimal A^* on optimal B^* .

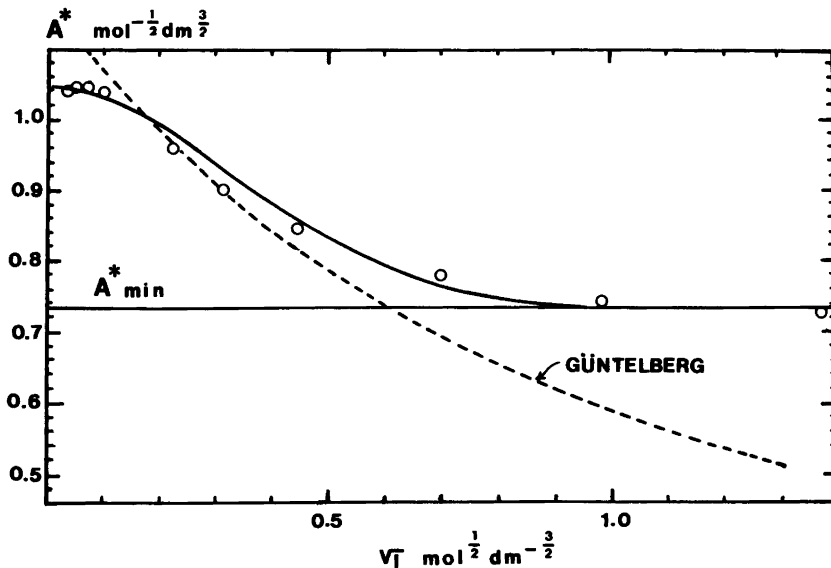


Fig. 6. The variation of A^* with ionic strength. \circ Calculated from experimental data for KCl in water at 25 °C with $B_{opt}^* = 0.27 \text{ dm}^3/\text{mol}$. Full line: $0.734 + (0.89 A_{D.H.} - 0.734) \exp(-18 \times 0.27 I)$.

the points in Fig. 5 (where LiI and Rb and Cs halides have been omitted) is found to be

$$A_{opt}^* = 0.247 B_{opt}^* + 0.667 \quad (69)$$

No systematic variation between the parameters in optimum 2 (Fig. 4) is found. What I have done now is simply to force the deviating points to lie somewhere on the regression line without disturbing the good fit of the parabola too much. In this way I have obtained a one parameter expression for $\ln f_{\pm}$ for concentrations from the minimum in $\ln f_{\pm}$ and above. The chosen B^* values are listed in the fourth column of Table 5. What remains is then the concentration region from around 0.001 mol/dm^3 to the concentrations of minimum $\ln f_{\pm}$. If we calculate A^* as a function of ionic strength by means of

$$A^* = \frac{-\ln f_{\pm} + B_{opt}^* I}{\sqrt{I}} \quad (70)$$

we observe that the variation in A^* is quite well described by the expression (see Fig. 6)

$$A^* = A_{min}^* + (0.89 A_{D.H.} - A_{min}^*) e^{-\alpha} \quad (71)$$

Expressions of the type $\exp(-\alpha\sqrt{I})$ have also been tried, but they yield a bad fit. The classical D.H. expression taking into account ionic size in the electrostatic contribution to $\ln f_{\pm}$ would lead to the following variation of A^* :

$$A^* = \frac{A_{D.H.}}{1 + b\sqrt{I}} \quad (72)$$

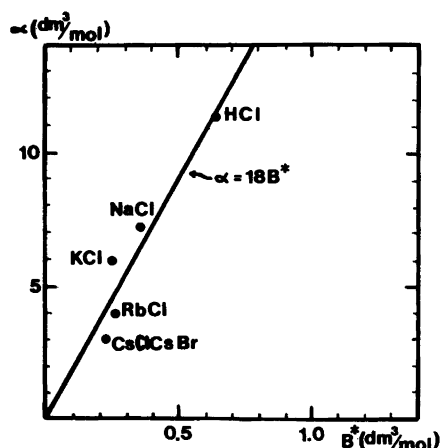


Fig. 7. Regression of α vs. B_{opt}^* .

When $b=1 \text{ mol}^{-1/2} \text{ dm}^{3/2}$ one speaks about the Güntelberg approximation. This is indicated in Fig. 6 by a dashed line. The Güntelberg approximation as well as the more general D.H. relation fail to describe the asymptotic behaviour of A^* towards a minimum value A_{\min}^* ($=A_{\text{opt}}^*$). Notice, that the experimentally determined slope of $0.89A_{\text{D.H.}}$ for small values of \sqrt{I} (see Fig. 2) has been built into (71). This eqn. should therefore not be used for exact calculations below $I=0.001 \text{ mol/dm}^3$.

Some of the α -values are plotted against B^* in Fig. 7. The regression yields a linear correlation given by

$$\alpha = 18.0B^* \quad (73)$$

The final result is that $\ln f_{\pm}$ can be calculated from knowledge of the excluded volume only, by means

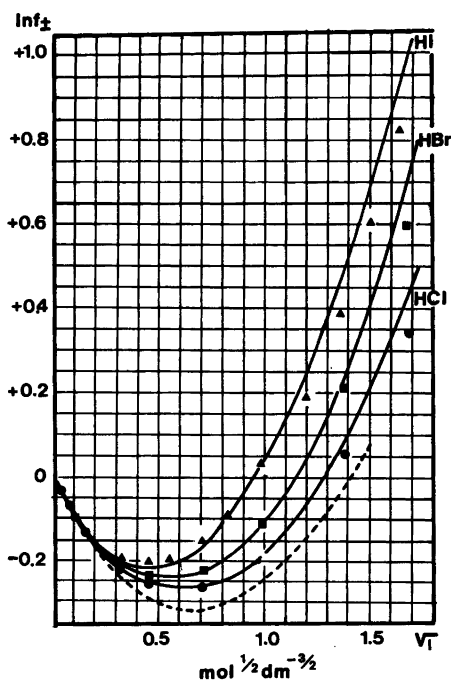


Fig. 8. ●, HCl (Ref. 37); ■, HBr (Ref. 37); ▲, HI (Ref. 37).

Dashed line: Calculation according to MSA-theory for HCl, see Appendix III. Text common to Figs. 8–12: Logarithm of molar mean ionic activity coefficients vs. square root of molar ionic strength in water at 25 °C. Full lines calculated from eqns. (69) and (74).

of the formula

$$\ln f_{\pm} = -\{A_{\min}^* + (0.89 A_{\text{D.H.}} - A_{\min}^*)e^{-1.8B^*I}\} \sqrt{I} + B^*I \quad (74)$$

[with $A_{\min}^* = A_{\text{opt}}^*$ given by (69)] valid for all the uni-univalent electrolytes investigated in this paragraph.

The expression (74) yields very fine correspondence with experimental values, see Figs. 8–12. The values of B^* for Rb and Cs halides were the most uncertainly determined due to lack of data for x_{+1} and x_0 . For these electrolytes, (74) has simply been taken for granted, and B^* has been fitted to give the best correspondence up to the greatest possible ionic strengths. Small changes in B^* have also been made for some of the other electrolytes. In that way, the values in the last column of Table 5 have appeared.

Thus, we have here a very simple one parameter formula which can easily compete with the more complicated two parameter formula of Robinson and Stokes⁷ and with multi-parameter formulae such as given by Pitzer *et al.*⁴ Eqn. (74) is also much simpler than the eqn. derived from the MSA-theory (see Appendix III). Furthermore, it will be shown in the next paragraph that the B^* -values found constitute a nice illustration of the principle of specific interaction of ions of Brønsted and yield values of the radii of the hydrated cations in reasonable accordance with radii estimated from ionic conductivity data.

RADI OF HYDRATED CATIONS FROM ASPEV-THEORY AND FROM CONDUCTANCE DATA

I have calculated the sum of radii ($R_+ + R_-$) from the final values of B^* (Table 5, column 5) using eqns. (67) and (23), *i.e.* the principle of specific interaction of ions of Brønsted is used. The results are given in Table 6. If the anions are assumed to be unhydrated, their radii are given by the Pauling radii and the values of the cationic radii given in Table 6, column 4 are found.

To have an independent check of those radii we have also considered data for ionic conductivities at infinite dilution (λ_i^0). The advantage of those data are that they can be ascribed completely to one single ion in pure solvent. The most obvious idea is to try to apply the Stokes-Einstein formalism, *i.e.* to assume the macroscopic, hydrodynamic, law of

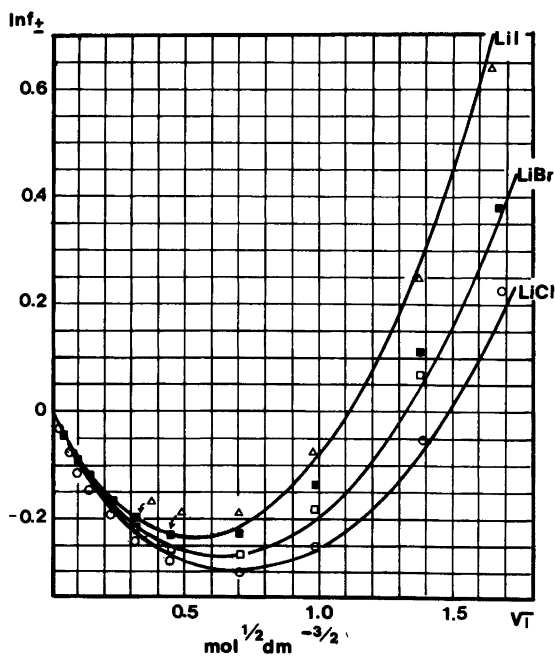


Fig. 9. ○, LiCl (Ref. 37); □, LiBr (Ref. 35); ■, LiBr, probably erroneous data (Ref. 37); △, LiI (Ref. 37).

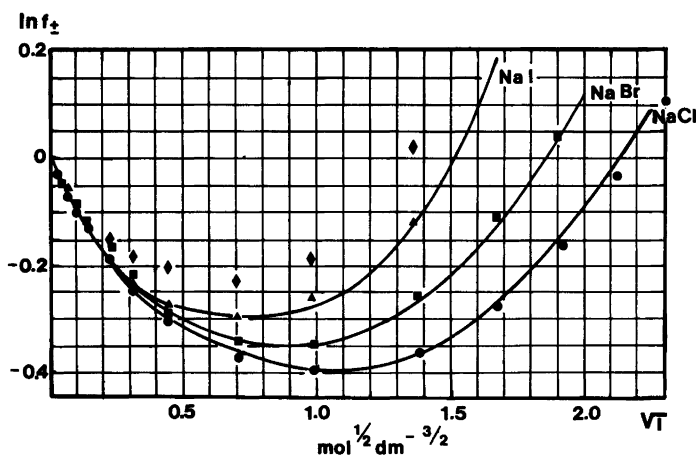


Fig. 10. ●, NaCl (Ref. 37); ■, NaBr (Ref. 37); ▲, NaI (Ref. 35); ◆, NaI, probably erroneous data (Ref. 37).

Stokes valid for the microscopic "friction coefficient". As is well-known, this procedure yields reasonable results for macromolecules. Calculating the cationic radii from

$$R_i = \frac{|z_i| F^2}{6\pi\eta\lambda_i^0} \quad (75)$$

(η = macroscopic viscosity for water at 25 °C) we obtain the values of the cationic radii given in Table 6, column 5. For K^+ , Rb^+ and Cs^+ the

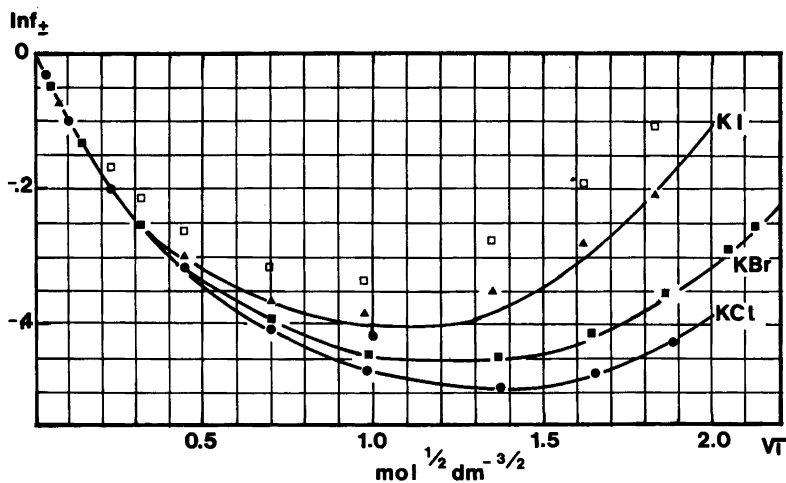


Fig. 11. ●, KCl (Ref. 37); ■, KBr (Ref. 37 $I \leq 0.05$, Ref. 36 $I \geq 0.1$); ▲, KI (Ref. 35); □, KI, probably erroneous data (Ref. 37).

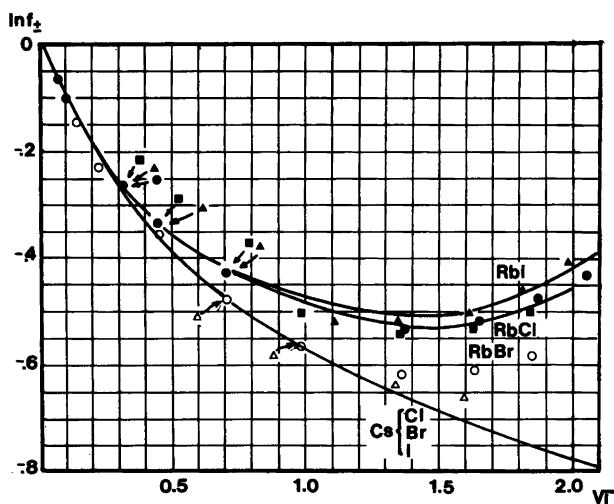


Fig. 12. ●, RbCl (Ref. 37, Ref. 35); ■, RbBr (Ref. 35); ▲, RbI (Ref. 35); ○, CsCl + CsBr (Ref. 37, Ref. 35); △, CsI (Ref. 35).

Stokes radii are less than the Pauling radii which cannot be true.

It is far from obvious, however, that Stokes' law can be used for an ion of approximately the same size as the solvent. One would expect — at least — that a "microscopic" viscosity should be applied instead of the macroscopic viscosity. Furthermore, as Frank³⁸ has pointed out, it seems to be neglected by most researchers that for small ions

in highly dielectric solvents there is a substantial dielectric relaxation drag on a moving ion. In contrast to the so-called "relaxation effect" discussed in Onsager's theory of concentration dependence of equivalent conductivities of strong electrolytes, the ion-dipole relaxation effect operates also at infinite dilution. The effect was first discussed by Born,³⁹ rediscovered by Fuoss⁴⁰ and quantified in terms of modern dielectric theory by Boyd⁴¹

Table 6. Cationic radii from ASPEV-calculations and from other sources.

Electrolyte	$R_+ + R_-$ (ASPEV) Å	R_- (Pauling) Å	R_+ (ASPEV) Å	R_+ (Stokes) Å	R_+ (modif.BFBZ) Å	$R_+ + R_- [\Lambda(c)]$ Å	R_+ (MSA) Å
HCl	6.3	1.80				—	2.07
HBr	6.6	1.95	4.7(3)	—	—	—	2.13
HI	7.2	2.16				—	2.10
LiCl	6.0	1.80				—	1.94
LiBr	6.3	1.95	4.3(2)	2.35	5.35	—	1.95
LiI	6.7	2.16				—	1.94
NaCl	5.2	1.80				3.5 ^a	1.30
NaBr	5.5	1.95	3.5(2)	1.81	4.05	—	1.34
NaI	5.9	2.16	2.16			—	1.29
KCl	4.7	1.80				2.80, ^b 2.85, ^c 3.20 ^d	0.91
KBr	4.9	1.95	2.9(1)	1.23	2.50	—	0.83
KI	5.2	2.16				—	0.75
RbCl	4.6	1.80				—	0.80
RbBr	4.6	1.95	2.6(2)	1.17	2.10	—	0.59
RbI	4.7	2.16				—	0.35
CsCl	4.0	1.80				—	0.58
CsBr	4.0	1.95	2.0(2)	1.17	2.15	—	0.37
CsI	4.0	2.16				2.41, ^b 2.56, ^c 3.49 ^d	0.10

^a Ref. 45. ^b Ref. 46, Table I, $D = 78.54$, first entry. ^c Ref. 46, Table I, $D = 78.54$, second entry. ^d Ref. 46, Table VI, $D = 78.54$.

and Zwanzig.⁴² Here we shall call it the BFBZ-theory. According to this theory one has

$$\lambda_i^0 = \frac{|z_i|AR_i^3}{C + R_i^4} \quad (76)$$

For water at 25 °C and with R_i in Å and λ_i^0 in $\Omega^{-1} \text{ cm}^2/\text{mol}$ we have $A = 91.7$ and C is around 10 Å^4 . We see that for large values of R_i , Stokes' law is approached. It is interesting to observe that the BFBZ-theory predicts a maximum for the ionic conductivity. Such a maximum is actually found for the series F^- , Cl^- , Br^- and I^- when λ_i^0 is plotted against the crystallographic radii (see Fig. 13), but the maximum value of λ_i^0 predicted by the BFBZ-theory is too low. However, in view of the small sizes of the species involved, it is to be expected that the "macroscopic" constants A and C in (76) have to be adjusted. Using the height and the position of the maximum we find for the adjusted constants $A = 209$ and $C = 5.33 \text{ Å}^4$. In this way the

"modified BFBZ" curve in Fig. 13 was found. This curve, together with the values of the limiting ionic conductivities were used for calculation of the cationic radii given in Table 6, column 6. There will be two values of R_+ giving the same λ_i^0 , but the larger of the values was always used.

In Table 6, column 7 some values of $R_+ + R_-$ are given which are derived from the deviation from the simple Onsager formula for equivalent conductivities (Λ) at higher concentrations.⁴⁴⁻⁴⁶ These calculations are very involved and not really clarified, so that those values for the distance of closest approach cannot be regarded with much confidence.

The last column in Table 6 contains the values of R_+ found by Triolo *et al.*²⁶ by fitting the MSA-model to data for the concentration dependence of the osmotic coefficient, using Pauling radii for the anions. For the K, Rb and Cs halides the cationic radii are quite inconsistent and also less than the Pauling radii (see Table 7, column 3). The radii are generally much lower than the radii obtained from

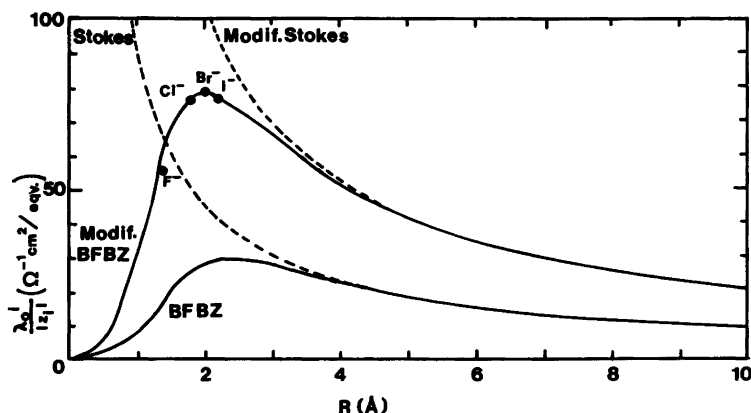


Fig. 13. Estimating ionic radii from Stokes' law and from the Born-Fuoss-Boyd-Zwanzig theory of dielectric relaxation drag; see text.

ASPEV or from modified BFBZ. In Appendix III I have calculated $\ln f_{\pm}$ for HCl from the MSA-theory using the radii of Triolo *et al.* The fit to experimental data is not very good (dashed curve in Fig. 8). Thus, it might be that the other radii given by Triolo *et al.* are not optimally fitted either.

Fig. 14 shows a comparison between the cationic radii calculated by the two independent semi-empirical methods (ASPEV and modified BFBZ). The radii are quite consistent and it is observed, that the ions with the smallest crystallographic radii are the largest, *i.e.* the most hydrated. The hydration numbers are estimated in Table 7. The values of the apparent ionic volumes used to correct the volume in the spherical shell between the Pauling radius and the ASPEV radius are the volumes reported by Bernal and Fowler (Ref. 32, Table V). We have

$$V_{\text{ion}}^{\text{app}} = \frac{4}{3}\pi R_p^3 + n\Delta V \quad (77)$$

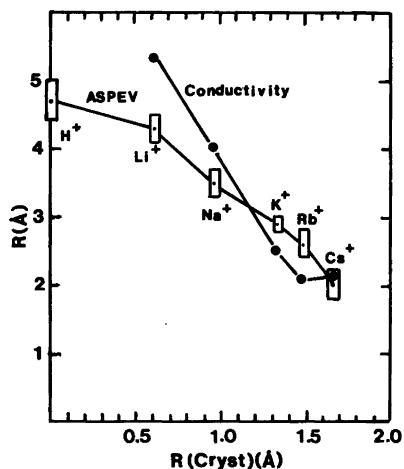


Fig. 14. Radii of hydrated cations calculated from ASPEV-theory compared to radii estimated from conductivity data. Abscissa: crystallographic radii of unhydrated cations.

Table 7. ASPEV-calculations of hydration numbers of cations.

Ion	$R(\text{ASPEV})$ Å	$R(\text{Pauling})$ Å	$(4\pi/3)(R^3 - R_p^3)$ Å ³	$V_{\text{ion}}^{\text{app}}$ Å ³ ^a	Hydration number, n	$n(\text{Ref. 43})$	$n(\text{Ref. 7})$
H ⁺	4.7	0	435	-8	15	-	9 ± 1
Li ⁺	4.3	0.61	332	-8	11	5 ± 1	8 ± 1
Na ⁺	3.5	0.96	176	-8.5	6	5 ± 1	4 ± 1
K ⁺	2.9	1.33	92	+8	3	4 ± 2	2 ± 0.5
Rb ⁺	2.6	1.48	60	+15.5	2	3 ± 1	1 ± 0.3
Cs ⁺	2.0	1.66	14	+27	0.2	-	-

^a Apparent (=partial) ionic volumes taken from Ref. 32.

where ΔV is the volume change per molecule water bound and n is the number of bound water molecules. Since a "normal" water molecule at 25 °C occupies 30.0 Å³ we have

$$\frac{4}{3}\pi(R^3 - R_p^3) = n(30 + \Delta V) \quad (78)$$

From (77) and (78) and the data in Table 7 we can calculate the hydration numbers n shown in Table 7, column 6. They agree with the values of primary hydration numbers given by Bockris and Reddy⁴³ (column 7) except for Li⁺. The ASPEV hydration numbers also agree roughly with the hydration numbers according to the theory of Stokes and Robinson (Ref. 7, Table I) which values are given in Table 7, column 8. This theory is criticized for a number of reasons in Appendix II, however.

The substantial success of the ASPEV-theory in giving radii of cations of uni-univalent electrolytes in agreement with radii and hydration numbers derived from other sources seems promising for future treatment of electrolytes of other valence types, for which the DHEV-theory also gave a consistent picture (though the radii were all too large). It is also my intention to scrutinise the existing data for electrolyte mixtures in the light of the ASPEV theory and to consider temperatures different from 25 °C.

Acknowledgement. The author is grateful to Niels Østerberg, Jørgen Birger Jensen, Jørgen Koefoed, Torben Jacobsen and Sven Atlung for stimulating discussions.

APPENDIX I. CRITIQUE OF COMMONLY APPLIED CHARGING PROCEDURES

The solution to the linearised P.B.-eqn. (32) is given by

$$\psi_i = C_i \frac{e^{-\kappa r}}{r} \quad (A-I-1)$$

The constant C_i can be determined by using (31) and requiring the net charge between $r=a$ and $r=\infty$ to be equal to the charge on the central ion with opposite sign. We obtain

$$\psi_i = \frac{z_i F}{4\pi\epsilon N_0} \times \frac{e^{-\kappa(r-a)}}{r} \quad (A-I-2)$$

Two charging procedures commonplace in literature (see, e.g., Ref. 31, pp. 80–83 and Ref. 47, pp. 21–23) are the Debye charging process and the Güntelberg charging process. In the Debye method we calculate the electrostatic contribution to Helmholtz' free energy as the net work the surroundings have to do by first stripping the ions for their charges in infinite dilution (with a Coulomb-potential around each ion) and then charging all the ions simultaneously at the given concentration. We obtain (with charging and discharging in the distance $r=a$ from the central ions)

$$\begin{aligned} \Delta A_{el} &= \sum_i n_i \frac{z_i^2 F^2}{4\pi N_0 \epsilon a} \left\{ \int_0^1 \left[\frac{\xi}{1+a\kappa\xi} - \xi \right] d\xi \right. \\ &= - \sum_i n_i \frac{z_i^2 F^2 \kappa}{4\pi N_0 \epsilon} \int_0^1 \frac{\xi^2}{1+a\kappa\xi} d\xi \\ &= - \frac{F^2 \kappa}{4\pi N_0 \epsilon} \tau(\kappa a) \sum_i n_i z_i^2 \end{aligned} \quad (A-I-3)$$

where n_i is the number of mol of the i 'th ion and ξ is the charging parameter. We have introduced the function

$$\tau(x) \equiv \frac{1}{x^3} \left[\ln(1+x) - x + \frac{1}{2}x^2 \right] = \frac{1}{3} - \frac{1}{4}x + \frac{1}{5}x^2 - \dots \quad (A-I-4)$$

The electrostatic contribution to the chemical potential of the i 'th ion is now

$$\begin{aligned} \mu_i^{el} &= \left[\frac{\partial(\frac{\Delta A_{el}}{\Omega})}{\partial c_i} \right]_{\Omega, T, c_j} = - \frac{F^2 z_i^2 \kappa}{4\pi N_0 \epsilon} \left[\tau(\kappa a) + \right. \\ &\left. \frac{1}{2} \frac{d}{d(\kappa a)} (\kappa a \tau(\kappa a)) \right] = - \frac{F^2 z_i^2}{8\pi N_0 \epsilon} \times \frac{\kappa}{1+\kappa a} \end{aligned} \quad (A-I-5)$$

The Güntelberg charging process is more direct. Here we charge one single ion in a mixture of ions already charged. The electrostatic contribution to the chemical potential is then

$$\begin{aligned} \mu_i^{el} &= \frac{z_i^2 F^2}{4\pi N_0 \epsilon a} \int_0^1 \left[\frac{\xi}{1+a\kappa\xi} - \xi \right] d\xi \\ &= - \frac{z_i^2 F^2}{8\pi N_0 \epsilon} \times \frac{\kappa}{1+\kappa a} \end{aligned} \quad (A-I-6)$$

identical to the expression (A-I-5). There is a serious drawback in connection with both charging processes, however. For small enough ionic strengths $\kappa a \ll 1$. Then the integrands in both (A-I-3) and (A-I-6) vanish and the electrostatic contribution to the chemical potential becomes nil. But the potential distribution given by (34) is still very different from a Coulomb-distribution (where κr should be approximately zero for all practical r). Then it is absurd that there should be no electrostatic contribution to the chemical potential.

The difficulties arise from the inaccurate use of a as sometimes the distance of closest approach and sometimes the ionic radii. Tanford⁴⁸ has given a more thorough derivation. He considers the potential around the central ion (1) in the following three regions:

I. The "interior" of ion 1.

II. The "excluded volume" between ion 1 and the counterion (2), *i.e.* the region from $r=R_1$ and $r=a=R_1+R_2$.

III. The region of the ionic cloud ($r>a$). In regions I and II there can be no charge (the charge of the central ion is visualized to be smeared out uniformly at the interface between I and II) and the Laplace eqn. therefore applies for the electric potential. In region III the linearised P.B. eqn. applies. Solving those eqns. together with the continuity conditions for ψ and $d\psi/dr$ at the interfaces I/II and II/III one obtains

$$\psi_1^{(I)} = \frac{z_1 F}{4\pi N_0 \epsilon R_1} \left[1 - \frac{\kappa R_1}{1 + \kappa a} \right] \quad (\text{A-I-7a})$$

$$\psi_1^{(II)} = \frac{z_1 F}{4\pi N_0 \epsilon R_1} \left[1 - \frac{\kappa r}{1 + \kappa a} \right] \quad (\text{A-I-7b})$$

$$\psi_1^{(III)} = \frac{z_1 F}{4\pi N_0 \epsilon} \times \frac{e^{\kappa a}}{1 + \kappa a} \times \frac{e^{-\kappa r}}{r} \quad (\text{A-I-7c})$$

For the electrical work in a Güntelberg charging process we have now

$$\mu_1^{el} = \frac{z_1^2 F^2}{4\pi N_0 \epsilon R_1} \left[\int_0^1 \left[1 - \frac{\kappa R_1}{1 + \kappa a} \right] \xi d\xi - \int_0^1 \xi d\xi \right] \quad (\text{A-I-8})$$

and we again find (A-I-5) or (A-I-6) but in a much more satisfactory way, since we can put $\kappa a \ll 1$ before the integration without having $\mu_1^{el} = 0$.

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Also the Tanford charging procedure can be criticised on a more fundamental level, however. For small κa we obtain for the potential at $r=a$ from (A-I-7b and c)

$$\psi_1(r=a) \cong \frac{z_1 F}{4\pi N_0 \epsilon a} \quad (\text{A-I-9})$$

Very near to the central ion, the Debye-Hückel condition therefore takes the form

$$\frac{F^2}{4\pi R T N_0 \epsilon a} \ll 1 \quad (\text{A-I-10})$$

However, calculating the quantity on the l.h.s. of the inequality (A-I-10) with $F=96\,500$ C, $a=5 \times 10^{-10}$ m, $\epsilon=6.9 \times 10^{-10}$ Farad/m, $N_0=6.02 \times 10^{23}$, $T=298$ K and $R=8.31$ J/molK we find the number 1.44! Thus, the assumption behind the linearisation of the P.B. eqn. is far from valid at the position where the solution is applied in the charging process. As rescue for the charging procedures Güntelberg⁴⁹ calculated that 97% of the potential at $r=a$ originated from ions at distances $r>2a$ and 88% from ions at distances $r>5a$ at an ionic strength of 10^{-3} mol/dm³. Since the D.H. assumption is valid at those distances, it does not mean so much that it fails near to the central ion. The whole procedure becomes quite artificial and unpedagogical, however, and the Résibois charging method used in the main text should be applied instead.

APPENDIX II. CRITIQUE OF THE THEORY OF STOKES AND ROBINSON

The hydration theory of Stokes and Robinson⁷ has been much cited in electrochemical textbooks. Here we shall follow the derivation given in Ref. 47, pp. 30–32 which shows the fundamental assumptions more clearly than the original text. For the Gibbs' free energy of a mixture of n_0 mol solvent and one mol electrolyte we have

$$G = n_0 \mu_0 + v_+ \mu_+ + v_- \mu_- = (n_0 - h) \mu'_0 + v_+ \mu'_+ + v_- \mu'_- \quad (\text{A-II-1})$$

h is the number of solvent molecules bound to 1 molecule of the electrolyte, and the primed chemical potentials correspond to the chemical potential of

free solvent and of solvated electrolyte. It is assumed that

$$\mu'_0 = \mu_0 \quad (\text{A-II-2})$$

When the chemical potentials are split up into standard and variable terms one obtains from (A-II-1) and (A-II-2)

$$\begin{aligned} & \frac{v_+(\mu_+^0 - \mu_+^{0'})}{RT} + \frac{v_-(\mu_-^0 - \mu_-^{0'})}{RT} + \frac{h\mu_0^0}{RT} \\ &= -h \ln a_0 - v \ln \frac{n_0 + v - h}{n_0 + v} - v_+ \ln \gamma_+^x - v_- \ln \gamma_-^x \\ &+ v_+ \ln (\gamma'_+)^x + v_- \ln (\gamma'_-)^x \end{aligned} \quad (\text{A-II-3})$$

where $v = v_+ + v_-$ and γ^x are activity coefficients based on mol fractions. At infinite dilution $n_0 \rightarrow \infty$ and all the terms on the r.h.s. of (A-II-3) become zero. The l.h.s. of (A-II-3) must then be zero in all cases. Introducing this in (A-II-3), changing to molal activity coefficients instead of rational activity coefficients using

$$n_0 = 1000/M_0m \quad (\text{A-II-4})$$

$$\gamma_{\pm}^x = \gamma_{\pm}^m [1 + 0.001 v M_0m] \quad (\text{A-II-5})$$

(M_0 = molecular weight of solvent) and introducing mean ionic activity coefficients, we obtain from (A-II-3)

$$\ln \gamma_{\pm}^m = \ln (\gamma'_{\pm})^x - \frac{h}{v} \ln a_0 - \ln [1 + 0.001 M_0(v-h)m] \quad (\text{A-II-6})$$

With the following identification

$$\ln (\gamma'_{\pm})^x = -\frac{A_{D.H.} |z_+ z_-| \sqrt{I}}{1 + b\sqrt{I}} \quad (\text{A-II-7})$$

formula (A-II-6) is the formula used by Stokes and Robinson. The solvent activity coefficient is calculated by means of data for the osmotic coefficient Φ_m

$$\ln a_0 = -0.001 M_0m v \Phi_m = -\frac{c_s v}{c_0} \Phi_m \quad (\text{A-II-8})$$

Whereas the postulate (A-II-2) seems reasonable enough, the identification (A-II-7) has no basis in D.H. theory, whatever. According to D.H. theory

it is $\ln f_{\pm}$ which is equal to the r.h.s. of (A-II-7) and certainly not the logarithm of the rational activity coefficient! Furthermore, data for the osmotic coefficient as a function of concentration has to be used to calculate the r.h.s. of (A-II-6), but from such data activity coefficients can be calculated directly by means of the exact thermodynamic formula

$$-\ln \gamma_{\pm}^m = (1 - \Phi_m) + \int_0^m (1 - \Phi_m) d \ln m \quad (\text{A-II-9})$$

[see Ref. 47, p. 8, eqn. (50)]. Therefore, the whole fitting procedure of Stokes and Robinson seems to be a redundancy. Better derivations of similar hydration theories have been performed later by Glueckauf,⁸ Jacobsen and Skou⁹ and Stokes and Robinson,¹⁰ but the formula (A-II-6) with (A-II-7) and (A-II-8) is the one most cited and used. At any rate, such expressions are two parameter formulae with the distance of closest approach as one parameter (a) and the hydration number (h) as the other. But those parameters are not independent, and are united in the excluded volume parameter in the ASPEV-theory.

APPENDIX III. SAMPLE CALCULATION OF ACTIVITY COEFFICIENTS IN THE MEAN SPHERICAL APPROXIMATION MODEL

Triolo *et al.* [Ref. 26, eqn. (24)] give the following formula for the osmotic coefficient in the mean spherical approximation (MSA) model

$$\Phi_m = \frac{\Pi}{\Pi_{ideal}} = -\frac{\Gamma^3}{3\pi v} + 1 + \beta_2 c_s N_0 + \beta_3 c_s^2 N_0^2 \quad (\text{A-III-1})$$

The generalised inverse Debye length Γ is found as solution to the algebraic eqn. [Ref. 26, eqn. (9)]

$$2\Gamma = \frac{\kappa}{\sqrt{2}} \times f(\Gamma) = \frac{\kappa}{\sqrt{2}} \sqrt{\sum_i v_i z_i^2 / (1 + \Gamma \sigma_i)^2} \quad (\text{A-III-2})$$

where κ is given by eqn. (33) in the main text and σ_i is the hard core diameter of ion number i . The β -terms in (A-III-1) are of the Percus-Yevick type with

$$\beta_2 = \frac{\pi}{2} (\zeta_3/3 + \zeta_1 \zeta_2 / \zeta_0) \quad (\text{A-III-3})$$

Table 8. Example of mean spherical approximation calculation of activity coefficients.^a

Conc. mol/dm ³	$\Gamma_0 = \kappa/2$ \AA^{-1}	Γ_1 \AA^{-1}	Γ_2 \AA^{-1}	Γ_3 \AA^{-1}	Γ_4 \AA^{-1}	$g(\Gamma_4)$	$2\beta_2 N_0 c_s$	$(3/2)\beta_3 N_0^2 c_s^2$	$\ln f_{\pm}$
0.001	0.0052	0.00510			0.00510	-0.0358	0.0003	-	-0.0355
0.005	0.0117	0.0112			0.0112	-0.0770	0.0015	-	-0.0755
0.01	0.0164	0.0154	0.0155		0.0155	-0.1046	0.0030	-	-0.1016
0.05	0.0368	0.0322	0.0327		0.0327	-0.208	0.015	-	-0.193
0.1	0.052	0.0433	0.0445		0.0444	-0.271	0.030	0.0002	-0.241
0.5	0.117	0.0806	0.0892	0.087	0.0870	-0.470	0.148	0.005	-0.322
1.0	0.164	0.101	0.118	0.113	0.114	-0.559	0.295	0.020	-0.244
2.0	0.231	0.122	0.151	0.146	0.148	-0.664	0.590	0.081	+0.007

^a All calculations: Hard core diameters $\sigma_+ = 4.14 \text{ \AA}$, $\sigma_- = 3.60 \text{ \AA}$.

$$\beta_3 = \frac{\pi^2}{36} [\zeta_3^2 + 6\zeta_2(\zeta_1\zeta_3 + \frac{1}{2}\zeta_2^2)/\zeta_0] \quad (\text{A-III-4})$$

and

$$\zeta_n = \sum_i v_i \sigma_i^n \quad (n=0, 1, 2, 3) \quad (\text{A-III-5})$$

Since the ideal osmotic pressure is $\Pi_{id} = RTvc_s$ we have from (A-III-1) that

$$\frac{\Pi}{RT} = h(\Gamma) + vc_s + v\beta_2 N_0 c_s^2 + v\beta_3 N_0^2 c_s^3 \quad (\text{A-III-6})$$

From eqn. (13) in the main text we have

$$\frac{\Pi}{RT} = vc_s + v \int_0^{c_s} c'_s d \ln f'_{\pm} \quad (\text{A-III-7})$$

Introducing

$$\ln f'_{\pm} = g(\Gamma) + Bc'_s + Cc'_s{}^2 \quad (\text{A-III-8})$$

in (A-III-7) we obtain

$$\frac{\Pi}{RT} = v \int_0^{c_s} c'_s \frac{dg}{d\Gamma} \frac{d\Gamma}{dc'_s} dc'_s + vc_s + \frac{v}{2} Bc_s^2 + \frac{2v}{3} Cc_s^3 \quad (\text{A-III-9})$$

Comparison with (A-III-6) makes obvious that the integral amounts to the h -function, and

$$\ln f_{\pm} = g(\Gamma) + 2\beta_2 N_0 c_s + \frac{3}{2} \beta_3 N_0^2 c_s^2 \quad (\text{A-III-10})$$

Blum and Høye [Ref. 25, eqn. (3.11)] have given the following formula for $g(\Gamma)$ according to the MSA-model

$$g(\Gamma) = - \frac{\kappa^2 \Gamma}{16\pi N_0 c_s} \sum \frac{v_i z_i^2}{1 + \Gamma \sigma_i} \quad (\text{A-III-11})$$

This is a very interesting formula, since it is to my knowledge the only example of a modern statistical mechanical theory yielding a formalism somewhat similar to the original D.H. expression (A-I-6). Take a uni-univalent electrolyte, for example, and put $\sigma_+ = \sigma_- = a$. From (A-III-2) it is obvious, that Γ for small concentrations is equal to $\kappa/2$. Inserting this and the definition of κ in (A-III-11) we again find the D.H. expression (A-I-6).

Triolo *et al.* have fitted the MSA-model to osmotic coefficient data for 23 uni-univalent electrolytes. For HCl they have found $\sigma_+ = 4.14 \text{ \AA}$ and $\sigma_- = 3.60 \text{ \AA}$. From those diameters Γ can be calculated from (A-III-2) inserting $\Gamma_0 = \kappa/2$ on the r.h.s., thereby calculating Γ_1 and so on. Three or four iterations are necessary for a precision of 1%. Then $\ln f_{\pm}$ can be calculated by (A-III-10 & 11). The results are given in Table 8 and represented as the dashed line in Fig. 8. The fit to experimental data does not seem very good, so perhaps the values of the hard core diameters found by Triolo *et al.* should be reconsidered.

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