Mean Activity Coefficients in Aqueous Electrolyte Mixtures. 2. The Generalized DHX Model and its Resolution of Some Seemingly Paradoxical Experimental Results

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The so-called DHX model is generalized to arbitrary mixtures of ions of different charges and different sizes. The idea is to use the Debye-Hückel screened electric potential around the ions to calculate the potential of mean force between two ions a and b (w_{ab}). The potential of mean force determines the radial distribution functions through the relations $g_{ab}(r) = \exp(-w_{ab}/kT)$ The model is tested by some Monte Carlo simulations. The generalized DHX model (GDHX) seems to be almost exact in dilute systems, where the radial distribution functions calculated by ordinary Debye-Hückel theory are grossly in error close to contact. Even at quite high concentrations (around 1 mol l^{-1} in water at 25 °C) and in mixtures of three ions of very different sizes, the radial distribution functions calculated by GDHX are in qualitative agreement with Monte Carlo simulations. The GDHX model does not fulfil the electroneutrality condition exactly. However, it is possible to calculate salt activities in mixtures from the Kirkwood-Buff formalism using only a subset of the GDHX radial distribution functions together with electroneutrality. When all the radial distribution functions are taken as GDHX functions, the Kirkwood-Buff equations may be inverted and single ionic activities calculated. Taken individually, these activities are meaningless, but they may be combined to salt activities which are close to the salt activities calculated by the Kirkwood-Buff equations with electroneutrality. A comparison between data for the mean ionic activity coefficients of KF and KCl in water at 25 °C (pure solutions and 1:1 mixtures) and GDHX calculations is made. The GDHX model is able to explain the fact that the mean activity coefficients of KF and KCl are almost the same in pure solutions and in mixtures at the same ionic strength, corresponding to Harned coefficients close to zero.

Paradoxically, a number of other mixed systems exhibit almost equivalent trace activities of the two salts. The GDHX model is also able to reproduce that behaviour with other choices of the ionic radii.

In a previous paper[1] we have reported some experimental results for the mean ionic activity coefficients of KCl and KF in KCl−KF−H₂O mixtures at 25 °C. One curious result is that the mean molar activity coefficients ($y_{\pm}$) for KCl dissolved in water seem to be statistically indistinguishable from the activity coefficients for KCl in 1:1 mixed solutions of KCl and KF having the same ionic strength. The same result was found for the activity coefficient of KF in pure and mixed solutions. This *mutual insensitivity* of a thermodynamic property of one salt on the presence of another is quite remarkable. The mutual insensitivity seems to hold even in the extreme case of the activity coefficients of a trace of one salt in a great excess of another! Bagg and Rechnitz[2] and Leyendekkers[3] have demonstrated that the activity coefficients of a *trace* of KF (0.0001 mol dm⁻³) in NaCl, KCl, KBr and KI solutions with concentrations ≤4 mol dm⁻³ are the same as the activity coefficients in KF solutions of the same ionic strength as in the mixed solutions.

Chap. 15 of the monograph by Robinson and Stokes[4] summarizes the thermodynamics of a variety of mixed electrolyte systems. Many mixed electrolyte solutions follow the so-called *Harned's rule*. This rule states that at *constant total ionic strength* the logarithm of the mean molal activity coefficient for one salt depends linearly on the molal concentration of the other salt:

$$\ln \gamma_{\pm}(B) = \ln \gamma_{\pm}(B,0) - \alpha_B \, m_C \qquad (1)$$

$$\ln \gamma_{\pm}(C) = \ln \gamma_{\pm}(C,0) - \alpha_C \, m_B \qquad (2)$$

The two *Harned coefficients* α_B and α_C are usually functions of the total ionic strength(I), but the Maxwell condition for cross-differentiation of the chemical potentials requires that their sum is independent of the total ionic strength:

$$\alpha_B + \alpha_C = \text{constant (independent of } I) \qquad (3)$$

This condition was first derived by Glueckauf, McKay and Mathieson.[5] Robinson and Stokes also treat a more general

form of eqn. (3), where quadratic terms may be included in eqns. (1) and (2).

It is seen that the peculiar behaviour of the KCl−KF system is not in conflict with eqns. (1)–(3), but the two Harned coefficients are zero in this system. In a number of other cases the $\ln \gamma_{\pm}$ vs. $\sqrt{I}$ curves are different for each pure electrolyte solution, but the trace activity coefficient of electrolyte B in great excess of the other (C), and the trace activity coefficient of electrolyte C in great excess of B, follows the same or almost the same $\ln \gamma_{\pm}$ vs. $\sqrt{I}$ curve [see e.g. Fig. 15.1 in Ref. 4 (HCl−NaCl−H$_2$O)]. Obviously, this cannot be the case for a system with Harned coefficients equal to zero.

So far, the above observations have not been subjected to theoretical analysis, and one might wonder about the nature of a theoretical model being able to explain simultaneously the mutual insensitivity exhibited by some electrolyte systems and the near equivalence of trace activities found in other electrolyte mixtures. Will it be necessary to involve highly specific interactions between ions (and ions and water), or can the findings be *roughly* explained using only the naive picture associated with the *primitive model* of electrolytes (charged, hard spheres in a dielectric continuum)?

Although one might be tempted to exclude the latter possibility, we shall show in this paper that a certain approximation for the radial distribution functions in the primitive model (the generalized DHX model) is able to generate results similar to those for both of the above-mentioned situations. Furthermore, the contact distances between the ions found by comparison with experimental KF−KCl data seem to be quite realistic as a crude measure of the extensions of the repulsive potentials between the ions in solution. The DHX estimate for the radial distribution function has been confirmed − at least in dilute solutions − by Monte Carlo simulation of the restricted primitive model (anions and cations of equal size).[6,7,8] We generalize the expressions to unequal sizes of ions, supporting the generalisation with a Monte Carlo simulation in a dilute solution with a Bjerrum parameter B_{+-} = 1.546 and in a quite concentrated solution with B_{+-} = 2.272. For mixtures, one has further to assume *pairwise autonomy* of the radial distribution functions, i.e. we assume that the functional form of the radial distribution function between two ions is unaffected by the presence of other ions except for the presence of the common Debye-Hückel screening constant ($\varkappa$) in the expressions. This assumption is backed up by a single Monte Carlo simulation with a mixture of ions of three different sizes.

First, we present the generalized DHX assumption together with some supporting Monte Carlo simulations. Next, we present some different routes which can be followed from radial distribution functions to activity coefficients. We then focus on the *principle of electroneutrality*, which makes calculation of *single-ion activity coefficients* from the Kirkwood-Buff formalism *impossible* in principle. We also provide an explanation for the observed mutual insensitivity of the activity coefficients found experimentally. Finally, we shall see that many other systems may well exhibit the near equivalence of trace activity coefficients found in NaCl−HCl and several other mixtures.

The generalized DHX model for the radial distribution functions

The historical origin of the so-called DHX model is somewhat obscure. Card and Valleau[9] found in their Monte Carlo studies of the restricted, primitive model (RPM) that the DHX expressions for the radial distribution functions were quite good approximations, especially at low concentrations. Recently, high precision Monte Carlo simulations including up to 1000 ions and greater than one million configurations have been performed in our laboratory in the ultradilute region for a Bjerrum parameter value of 1.546 for the RPM.[6-8] In those studies, the radial distribution functions obtained by statistical analysis were *indistinguishable* from the DHX profiles in the region between one and four contact distances (see especially Figs. 6 and 7 in Ref. 8). The idea behind the DHX model is the following: The *screened, mean electric potential* around a selected ion with valence z_a at a distance r is given according to the Debye-Hückel theory by:

$$\Phi_a(r) = z_a e_0 (4\pi \, \epsilon r)^{-1} (1 + \varkappa a_{ab})^{-1} \exp(-\varkappa[r - a_{ab}]) \quad (4)$$

In eqn. (4), e_0 is the elementary charge, $\varkappa$ is the inverse Debye-Hückel screening length and ϵ is the absolute permittivity of the medium. Thus, the dimensionless electrostatic interaction between an ion a and an ion b at a distance r including the screening effect of the other ions may be approximated by eqn. (5):

$$w_{ab}(r)/kT = z_a \, z_b \, e_0^2 \, (4\pi \, \epsilon kTr)^{-1} (1 + \varkappa \, a_{ab})^{-1}$$
$$\times \exp(-\varkappa[r - a_{ab}]) \quad (5)$$

The *potential of mean force* between two particles is in general defined by the equation $g_{ab}(r) = \exp(-w_{ab}/kT)$, where $g_{ab}(r)$ is the radial distribution function. If we take eqn. (5) for this mean potential, we obtain:

$$g_{ab}(r) = \exp[-z_a z_b B (1 + d_{ab}\varkappa a)^{-1} (s_{ab} + d_{ab})^{-1}$$
$$\times \exp(-\varkappa \, a \, s_{ab})] \quad (6)$$

$$B \equiv e_0^2/(4\pi \, \epsilon \, k \, T \, a) \quad (7)$$

$$s_{ab} \equiv (r/a) - d_{ab} \quad (8)$$

$$d_{ab} \equiv a_{ab}/a \quad (9)$$

In eqns. (6)–(9), the length a is some suitable mean value of the contact distances. In the present paper we shall make the following choice for a system containing n *different kinds of ions*:

$$a = (1/n) \sum_{b=1}^{n} a_{bb} \tag{10}$$

We shall call the assumption (6) the *generalized DHX model* (GDHX). This model has not been investigated before. For the RPM with equal radii and symmetric charges (z), we have the DHX model:

$$\left. \begin{array}{c} g_{+-}(s) \\ g_{++}(s) = g_{--}(s) \end{array} \right] = \exp[\pm z^2 B (1+\varkappa\, a)^{-1} (s+1)^{-1} \times \exp(-\varkappa\, a\, s)] \tag{6a}$$

$$s \equiv (r/a) - 1 \quad (\text{RPM})$$

In all cases, the radial distribution functions are of course zero for distances smaller than the contact distances:
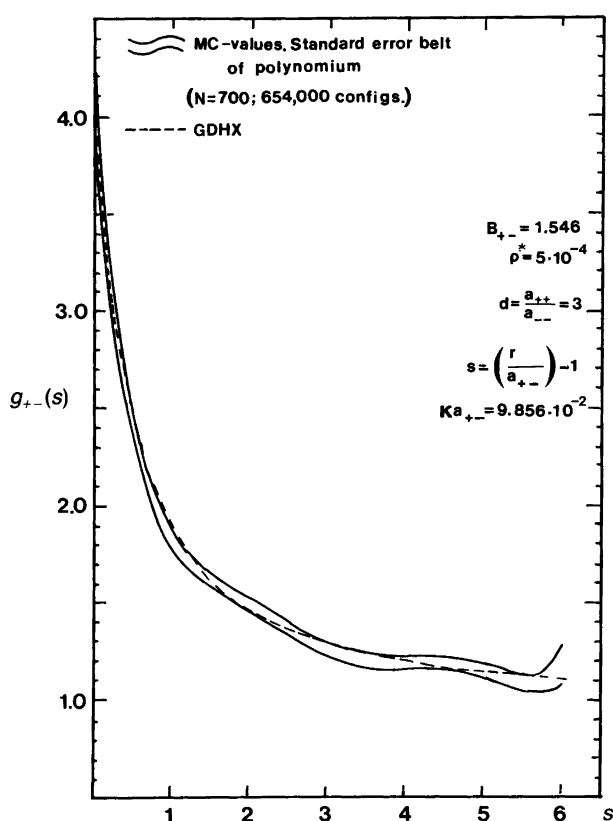
$$g_{ab}(r) = 0 \quad r < a_{ab} \tag{11}$$

Fig. 1. The radial distribution function $g_{+-}(s)$ in a dilute electrolyte solution $(\varrho_{tot}^* = 5 \cdot 10^{-4})$ with a cation three times larger than the anion $(a_+-/a_{--} = 3)$. Bjerrum parameter $B = 1.546$. The belt is the standard error belt of the smoothened least-squares values (6th-degree polynomial most significant at the 95 % level) of Monte Carlo samplings in 60 spherical shells between one and seven contact distances. 799 ions were used and 654,000 Metropolis configurations investigated. The dashed curve calculated from the GDHX assumption is statistically indistinguishable from the Monte Carlo values.
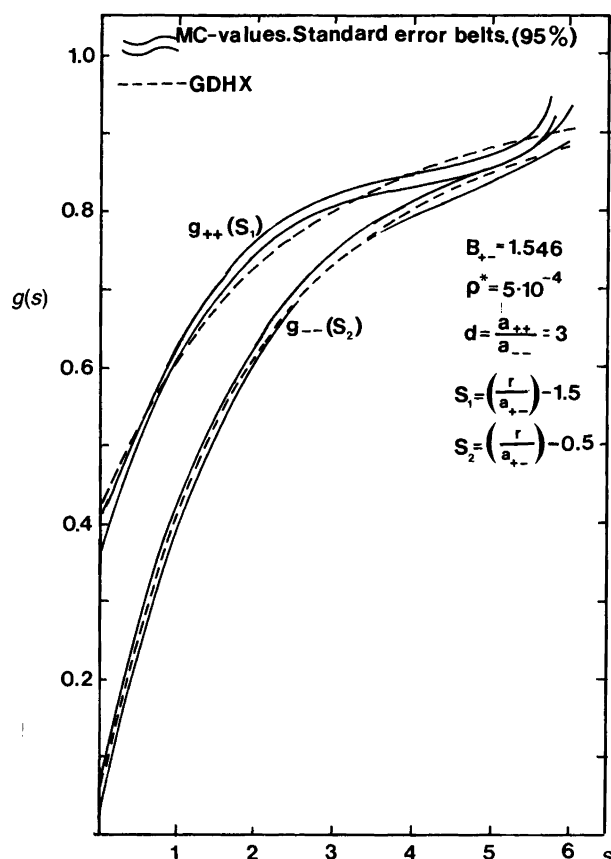
Fig. 2. The radial distribution functions $g_{++}(s)$ and $g_{--}(s)$ for the same system as in Fig. 1. The small anions are seen to repel each other much more strongly than the larger cations. Again, the GDHX values (dashed curves) are indistinguishable from the Monte Carlo values as judged from the uncertainty belt of the smoothened polynomial values (3rd degree at 95 % level).

In Ref. 8 we have shown that for dilute RPM systems with $B = 1.546$ and $z = 1$, the radial distribution functions found by Monte Carlo simulations are statistically identical to the values calculated by eqn. (6a). Figs. 1 and 2 in the present paper show that the same is the case with the GDHX model, in a case where the cation is 3 times larger than the anion. The dimensionless concentration is $\varrho_{tot}^* = 5 \cdot 10^{-4}$. In all cases treated in the present paper, the dimensionless concentration is defined as the total particle concentration times the cube of a, where a is given by eqn. (10). One would expect deviations for higher concentrations, however. Figs. 3 and 4 show a situation with $B = 2.272$ and $\varrho_{tot}^* = 8.39 \cdot 10^{-2}$. The sizes of the cations and the anions do not differ very much (ratio 0.858). The situation seems to be quite similar in a ca. 2 mol dm^{-3} solution of KF in water at 25 °C, if the primitive model of electrolytes has any relevance at this concentration (see section 4). It is quite surprising to see from (Figs. 3 and 4) that the GDHX is not a bad approximation for the radial distribution functions even at such high concentrations. Fig. 5 shows that even in a three-ion mixture with $B = 2$, $a_{11}/a_{22}/a_{33} = 3/2/1$ and $\varrho_{tot}^* = 0.05$, the radial distribution functions calculated by
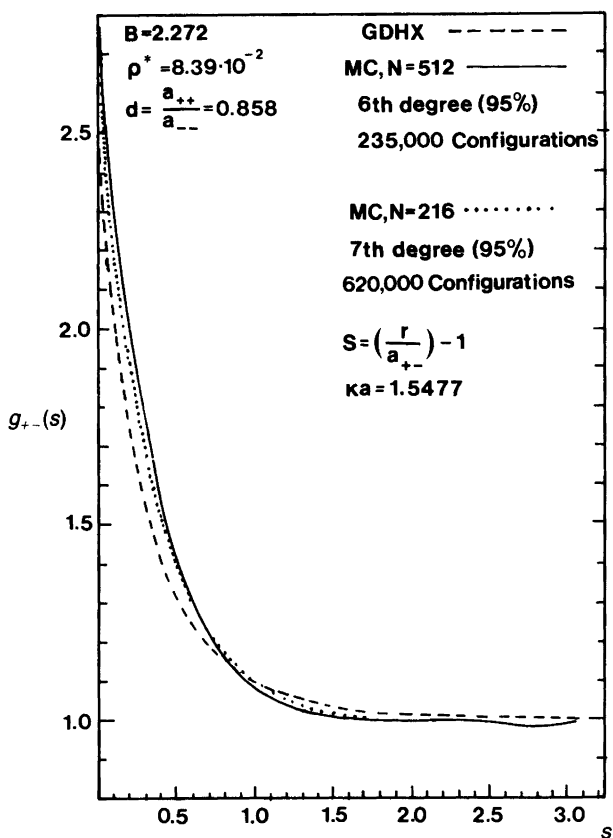
Fig. 3. The radial distribution function $g_{+-}(s)$ in a quite concentrated electrolyte solution ($\varrho^{*}_{tot} = 0.0839$). $B = 2.272$ and $a_{++}/a_{--} = 0.858$. The smoothened values of two Monte Carlo samplings are shown (solid curve: 512 ions, 235,000 configurations, 6th-degree polynomial; dotted curve: 216 ions, 620,000 configurations, 7th-degree polynomial. Samplings in 60 shells from one to four contact distances). The GDHX values (dashed curve) do not differ substantially more from the Monte Carlo values than the Monte Carlo values differ among themselves.

the GDHX formula are in semi-quantitative agreement with Monte Carlo calculations using 250 of the large cations, 125 of the medium-sized anions and 125 of the small anions (Fig. 5). Thus, it also seems to be a fair assumption that the radial distribution functions in mixtures, $g_{ab}(r)$, may be calculated from x and the corresponding value of a_{ab} alone, i.e. we have approximately *pairwise autonomy* of the radial distribution functions in electrolyte mixtures.

From radial distribution functions to activity coefficients

When the form of the radial distribution functions is known, several methods exist for the calculation of activity coefficients. One may calculate the mean dimensionless excess energy per particle (under the assumption of no temperature variation of the dielectric permittivity). We state here the formula for E (ex)/k T in the general case of n types of ions (see for example Ref. 10, section 5.3):

$<E$ (ex, constant ϵ) $> / kT =$

$$(2\pi/\varrho_{tot} k\ T) \sum_{a} \sum_{b} \varrho_{a}\varrho_{b} \int_{a_{ab}}^{\infty} g_{ab}(r)\ U_{ab}(r)r^{2}\ dr. \qquad (12)$$

The summations over a and b run over all the n types of ions, the ϱ's are particle densities and ϱ_{tot} the total density of particles. The McMillan–Mayer pair potential is given by eqn. (13):

$$U_{ab}(r)/k\ T = Z_{a} Z_{b} B a/r. \qquad (13)$$

With eqn. (13), the integrals in eqn. (12) seem to be divergent, since $g_{ab}(r) \to 1$ for $r \to \infty$. The situation is rescued by electroneutrality, however. Integrating first from a_{ab} to the mean diameter a and then from a to a large value of the radial distance (insertion rule for integration), we observe that the common integral in the second term may be factorized out, and the remaining sum vanishes because
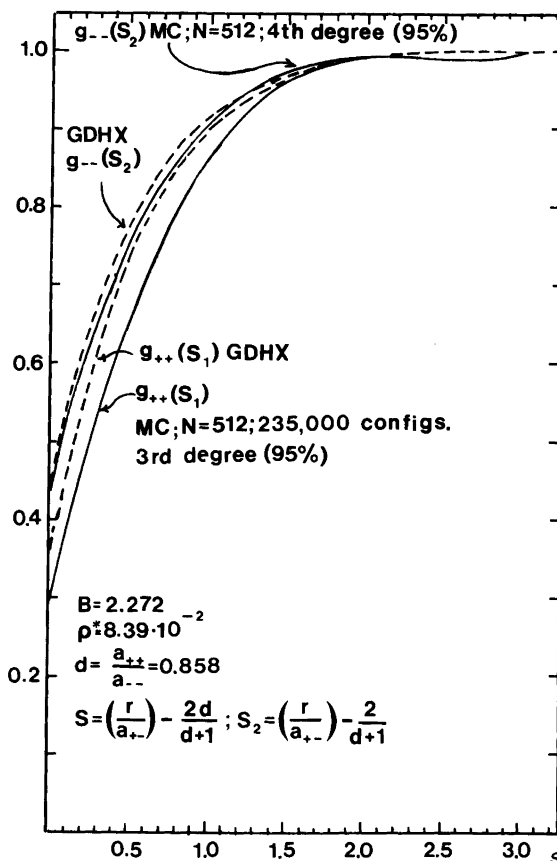

Fig. 4. The radial distribution functions $g_{++}(s)$ and $g_{--}(s)$ for the same system as in Fig. 3. The cations are seen to repel each other somewhat more than the slightly larger anions, both in the Monte Carlo simulations ($N = 512$; 235,000 configurations) and the GDHX calculations. The correspondence is acceptable in the case of $g_{--}(s)$, but is at most semi-quantitative in the case of $g_{++}(s)$.
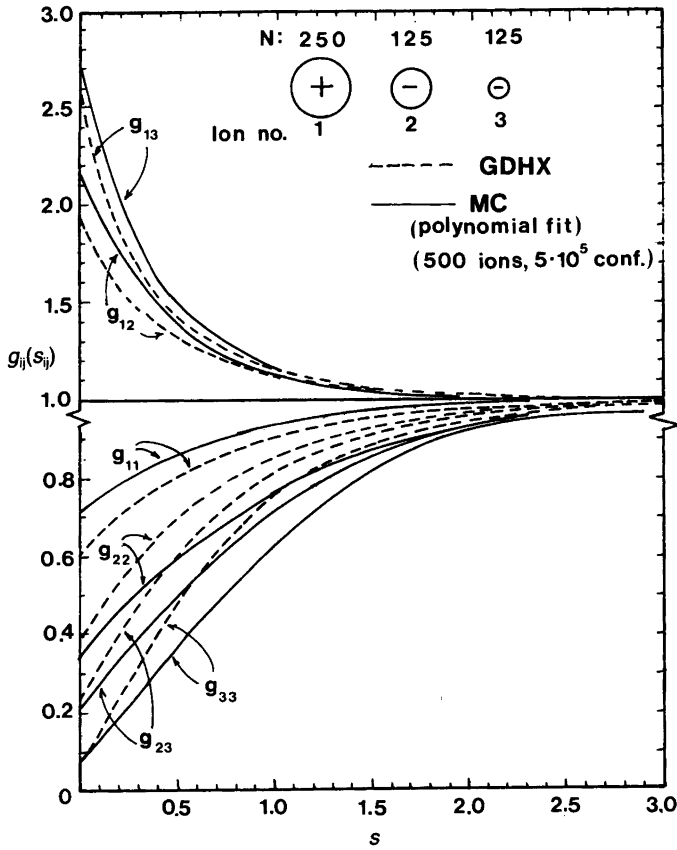
Fig. 5. The six radial distribution functions in a ternary electrolyte system with a large cation, a medium-sized anion and a small anion (ratio between ionic radii 3:2:1). The concentration is quite high ($\varrho^*_{tot} = 0.05$) and the value of the Bjerrum parameter is $B = 2$ (both dimensionless quantities are based on the mean diameter of the three ions). The Monte Carlo results (solid curves) are for 500,000 configurations with 250 cations and 2×125 anions with samplings in 60 shells from one to four contact distances. The succession of the GDHX curves (dashed) is the same as the MC curves, but especially the distribution functions between charges of equal sign are distorted in the intermediary region (neither close to nor far from contact).

of electroneutrality. For clarity we may rewrite eqn. (12) as follows:

$$<E(\text{ex, constant } \varepsilon)>/k\,T =$$

$$(\pi/\varrho^*)\ B\ \Sigma_a\ \Sigma_b\ Z_a Z_b\ \varrho^*_a \varrho^*_b$$

$$\times \left\{2 \int\limits_{d_{ab}}^{\infty} [g_{ab} - 1](r/a)\mathrm{d}(r/a) + 1 - d^2_{ab}\right\}. \tag{14}$$

We have defined the following dimensionless particle densities:

$$\varrho^* \equiv \varrho_{tot}\ a^3;\quad \varrho^*_a \equiv \varrho_a\ a^3;\quad \varrho^*_b \equiv \varrho_b\ a^3. \tag{15}$$

The d_{ab}'s are given in eqn. (9) and B in eqn. (7) with the mean contact distance a given by eqn. (10). For eqn. (14) we use the shorthand notation:

$$<E(\text{ex, constant } \varepsilon)>/k\,T =$$

$$(\pi/\varrho^*)\ B\ \Sigma_a \Sigma_b\ Z_a Z_b\ \varrho^*_a \varrho^*_b\ \{2e_{ab} + 1 - d^2_{ab}\} \tag{16}$$

$$e_{ab} \equiv \int\limits_{0}^{\infty} [g_{ab}-1](s_{ab}+d_{ab})\mathrm{d}s_{ab}. \tag{17}$$

The s_{ab}'s are given by eqn. (8). The excess osmotic coefficient may be found by (follows from Ref. 10, section 5.3):

$$\varphi - 1 = <E(\text{ex, constant } \varepsilon)>/3k\,T + VOL \tag{18}$$

$$VOL \equiv (2\pi/3)\varrho^*$$

$$\times [\Sigma_a \Sigma_b (\varrho_a/\varrho_{tot})(\varrho_b/\varrho_{tot})(a_{ab}/a)^3 g_{ab}(a_{ab})] \tag{19}$$

Eqns. (18)–(19) yield the osmotic coefficient correctly at a given temperature, whether or not there is a temperature dependence of ε. Finally, when only *two kinds of ions are present*, the value of $\ln y_\pm$ may be calculated by the well-known *Gibbs–Duhem integration* from concentration zero to the concentration studied.

When *three or more kinds of ions* are present, this method will not be applicable when one wants to calculate $\ln y_\pm$ for two or more electrolytes in a mixed solution. In such a case the generalized compressibility equations of Kirkwood and Buff may be used instead (Ref. 10, eqn. 70, or Ref. 11). The equations are the following (the μ's are the *electrochemical potentials* of the single ions and δ_{ab} is Kronecker's delta):

$$k\,T[\partial\varrho_a/\partial\mu_b] = \varrho_a\delta_{ab} + 4\pi\ \varrho_a\varrho_b\int\limits_{0}^{\infty} [g_{ab}(r)-1]r^2\mathrm{d}r. \tag{20}$$

μ_c constant   (a and b from 1 to n)
($c \neq b$)

The most obvious idea is to invert the system of eqn. (20) in order to obtain *single ion activities* as a function of concentration. However, we shall see in section 3 that when we have *strict electroneutrality*, this inversion is *in principle impossible*. Nevertheless, *in practice* many approximations for the radial distribution function – which are quite satisfactory in other respects (for example the DHX approximation; Ref. 21) – do not fulfil strict electroneutrality, and eqn. (20) may then be inverted. The single ion activities are then spurious quantities without physical meaning, but when combined to salt activities they – strangely enough – often make sense (Ref. 10, section 7.5, p. 131). However, it is also possible to use strict electroneutrality to obtain salt activities directly without inversion from the eqn. (20), using only a subset of the approximations for the radial

distribution functions (section 3) (it should be mentioned here that it *is* possible to calculate single ion activities from first principles. A method is described in Refs. 20 and 22).

The Kirkwood-Buff equations for two ions at constant temperature, solvent activity and electric potential (since the *electrochemical* potentials of all but one species remain constant in each equation) are given as:

$$kT\partial\varrho_+^*/\partial\mu_+ = 4\pi(\varrho_+^*)^2[i_{++}-(1/3)d_{++}^3] + \varrho_+^* \tag{21a}$$

$$kT\partial\varrho_+^*/\partial\mu_- = 4\pi(\varrho_+^*)(\varrho_-^*)[i_{+-}-(1/3)] \tag{21b}$$

$$kT\partial\varrho_-^*/\partial\mu_+ = 4\pi(\varrho_+^*)(\varrho_-^*)[i_{+-}-(1/3)] \tag{21c}$$

$$kT\partial\varrho_-^*/\partial\mu_- = 4\pi(\varrho_-^*)^2[i_{--}-(1/3)d_{--}^3] + \varrho_-^* \tag{21d}$$

$$i_{++} = \int_0^\infty [g_{++}(s)-1](s+d_{++})^2 ds \tag{22a}$$

$$i_{--} = \int_0^\infty [g_{--}(s)-1](s+d_{--})^2 ds \tag{22b}$$

$$i_{+-} = \int_0^\infty [g_{+-}(s)-1](s+1)^2 ds. \tag{22c}$$

It is interesting to observe that the Kirkwood-Buff equations are *independent* of any assumption of the form of the pair potential. Incidentally, these generalized compressibility equations do not even require the assumption of pairwise additivity of the McMillan-Mayer potential. The special expressions (21)–(22) written above are valid for all hard core potentials.

In the case of three ions, the Kirkwood-Buff equations may be written in matrix form:

$$\begin{bmatrix} d\varrho_1^* \\ d\varrho_2^* \\ d\varrho_3^* \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{bmatrix} \begin{bmatrix} d(\mu_1/kT) \\ d(\mu_2/kT) \\ d(\mu_3/kT) \end{bmatrix} \tag{23}$$

$$A_{ab} = A_{ba} = 4\pi \varrho_a^* \varrho_b^* [i_{ab}-(1/3\ d_{ab}^3] + \delta_{ab}\ \varrho_a^* \tag{24}$$

$$i_{ab} = \int_0^\infty [g_{ab}(s)-1](s+d_{ab})^2 ds. \tag{25}$$

The generalisation to mixtures of n types of ions is straightforward.

Electroneutrality and the Kirkwood–Buff formalism

The formulae used in the Kirkwood–Buff formalism involve integration to infinity. In the simple form given here they are valid only for *spherically symmetric* pair distribution functions and for *infinite systems*. For such systems, *strict electroneutrality* has to hold. The reason is that

electric potential satisfies the equation of Poisson. This equation has as solution an *infinite potential* in each point when the system is infinite, and has a constant charge density differing from zero. Therefore, not only the electrostatic energy but also the electrostatic energy density in each point tends to infinity in the thermodynamic limit of an infinite system.

Of course, real systems (electrolytes, electrodes, etc.) are not infinite. Rather, they are finite systems separated by interfacial boundary layers wherein the charge density is not zero. The incorporation of such boundary layers would require integration of generalized, anisotropic radial distribution functions through the boundary layers. The simple Kirkwood–Buff formalism does not work anymore. Thus, we shall restrict ourselves to cases with strict electroneutrality. Another reason is that we have assumed in the derivation of eqns. (21) and (23) that the electric potential in the solution is kept constant when the concentrations are varied. Thus, the concentration variations have to be constrained by the electroneutrality condition.

The electroneutrality condition around a central ion of the b'th kind is given as (we relax in this section the strict hard core condition):

$$z_b = -4\pi \sum_{a=1}^n Z_a\ \varrho_a^* \int_0^\infty (g_{ab}(r)-1)r^2 dr. \tag{26}$$

$(b = 1,2...n)$

We define the following quantities (of dimension volume):

$$G_{ab} = G_{ba} = 4\pi \int_0^\infty (g_{ab}-1)\ r^2\ dr. \tag{27}$$

Therefore we have the constraints:

$$\sum_{a=1}^n Z_a\ \varrho_a\ G_{ab} = -Z_b \quad (b = 1,2...n). \tag{28}$$

The Kirkwood–Buff equations may now be written in a somewhat more general form than eqns. (21) or (23), since we do not need to assume a hard-sphere core here. For three types of ions we have, for example:

$$\begin{bmatrix} d\ \varrho_1 \\ d\ \varrho_2 \\ d\ \varrho_3 \end{bmatrix} \begin{bmatrix} M_{11} & M_{12} & M_{13} \\ M_{21} & M_{22} & M_{23} \\ M_{31} & M_{32} & M_{33} \end{bmatrix} \begin{bmatrix} d(\mu_1/kT) \\ d(\mu_2/kT) \\ d(\mu_3/kT) \end{bmatrix} \tag{29}$$

$$M_{ab} = M_{ba} = \varrho_a\ \varrho_b\ G_{ab} + \delta_{ab}\ \varrho_b. \tag{30}$$

From eqns. (28) and (30) we obtain:

$$\sum_{a=1}^n Z_a\ M_{ab} = 0. \quad (b = 1,2...n) \tag{31}$$

Thus, we have linear dependency between the rows in the matrix **M**. Therefore, the determinant det**M** = 0 and the

Kirkwood–Buff system of equations *cannot* be inverted to find the *single ionic chemical potentials* from the ionic densities (or from the salt densities). This is a consequence of strict electroneutrality. However, one should be able to find the variation in the *chemical potentials of complete salts* in any mixture by solving the Kirkwood–Buff equations. The condition for finding such solutions is also exactly the electroneutrality constraint. We shall show this in the case of two kinds of ions and three kinds of ions, respectively.

The general conditions for compatible solutions to linear equations with zero determinant is that the *augmented matrix* aug(M) has the *same rank* as M (Ref. 12). In the case of *two kind of ions* we have:

$$\text{aug}(M) = \begin{bmatrix} M_{11} & M_{12} & d\varrho_1 \\ M_{21} & M_{22} & d\varrho_2 \end{bmatrix} \tag{32}$$

The matrix **M** has a rank = 1. Therefore, all 2×2 sub-determinants of aug(M) have to be zero. Apart from det(M) = 0 we have:

$$M_{11}d\varrho_2 - M_{21}d\varrho_1 = 0 \tag{33a}$$

$$M_{12}d\varrho_2 - M_{22}d\varrho_1 = 0. \tag{33b}$$

From eqns. (30) and (31) we have:

$$z_1 M_{11} + z_2 M_{21} = 0 \tag{34a}$$

$$z_1 M_{12} + z_2 M_{22} = 0 \tag{34b}$$

$$M_{12} = M_{21}. \tag{34c}$$

Alternatively:

$$M_{11} = -(z_2/z_1)M_{12}; \quad M_{22} = -(z_1/z_2)M_{12}. \tag{35}$$

Inserting the eqn. (35) into eqns. (33a–b), we see that both of the two compatibility eqns. (33a–b) lead to the same condition:

$$z_1 d\varrho_1 + z_2 d\varrho_2 = 0. \tag{36}$$

That is, all the concentration variations should be *constrained by the electroneutrality condition*. Therefore, we may write:

$$d\varrho_1 = \nu_1 \, d\varrho_s; \quad d\varrho_2 = \nu_2 \, d\varrho_s. \tag{37}$$

The density of "salt molecules" is denoted ϱ_s, and ν_1, ν_2 are stoichiometric coefficients of the ions in the salt. Using the two Kirkwood–Buff equations together with eqns. (35) and (37) and the condition for *stoichiometric electroneutrality* ($z_1\nu_1 + z_2\nu_2 = 0$) we obtain from both equations:

$$d\mu_s = \nu_1 \, d\mu_1 + \nu_2 \, d\mu_2 = (kT \, \nu_1 \, \nu_2/M_{12}) \, d\varrho_s. \tag{38}$$

The chemical potential of the whole salt is denoted μ_s. In the case of *three ions* we have:

$$\text{aug}(M) = \begin{bmatrix} M_{11} & M_{12} & M_{13} \\ M_{12} & M_{22} & M_{23} \\ M_{13} & M_{23} & M_{33} \end{bmatrix} \begin{bmatrix} d\varrho_1 \\ d\varrho_2 \\ d\varrho_3 \end{bmatrix} \tag{39}$$

The rank of the augmented matrix should be 2, since this is the rank of **M**. Thus, all 3×3 subdeterminants of aug(M) have to be zero. The conditions for det(M) = 0 are given by eqn. (31), which may be written:

$$M_{11} = -(z_2 \, M_{12} + z_3 \, M_{13})/z_1 \tag{40a}$$

$$M_{22} = -(z_1 \, M_{12} + z_3 \, M_{23})/z_2 \tag{40b}$$

$$M_{33} = -(z_1 \, M_{13} + z_2 \, M_{23})/z_3. \tag{40c}$$

Another subdeterminant condition is the following:

$$\begin{vmatrix} M_{11} & M_{12} & d\varrho_1 \\ M_{12} & M_{22} & d\varrho_2 \\ M_{13} & M_{23} & d\varrho_3 \end{vmatrix} = 0. \tag{41}$$

Evaluating this determinant and inserting eqns. (40a–c) we obtain, after tedious calculations:

$$\alpha \cdot (z_1 d\varrho_1 + z_2 d\varrho_2 + z_3 d\varrho_3) = 0 \tag{42}$$

$$\alpha \equiv z_1 M_{12}M_{13} + z_2 M_{12}M_{23} + z_3 M_{13}M_{23}. \tag{43}$$

Exactly the same condition is obtained from the two other subdeterminant conditions analogous to eqn. (41). It is seen once more that the Kirkwood–Buff equations are compatible (soluble) if the concentration variations are *constrained to electroneutrality*:

$$z_1 \, d\varrho_1 + z_2 \, d\varrho_2 + z_3 \, d\varrho_3 = 0 \; (\alpha \neq 0). \tag{44}$$

It can be safely assumed that $\alpha \neq 0$, since matrix elements in **M** are functions of the ionic densities [eqn. (30)]. Therefore, α can at most be zero for certain specific concentrations, and not in general.

We now try to solve the three Kirkwood–Buff equations (29) for the two independent chemical potentials of the electroneutral salts (13 and 23, ion No. 3 is the common ion). We denote the stoichiometric coefficients in salt 13 by ν_1 and ν_3 ($\nu \equiv \nu_1 + \nu_3$). The stoichiometric coefficients in salt 23 are called η_2 and η_3 ($\eta \equiv \eta_2 + \eta_3$). We have the stoichiometric conditions:

$$\nu_1 \, z_1 + \nu_3 \, z_3 = 0; \quad \eta_2 \, \zeta_2 + \eta_3 \, z_3 = 0. \tag{45}$$

We now write:

$$d\varrho_1 = \nu_1 d\varrho_{13}; \quad d\varrho_2 = \eta_2 d\varrho_{23}; \quad d\varrho_3 = \nu_3 d\varrho_{13} + \eta_3 d\varrho_{23}. \tag{46}$$

Eqn. (46) are inserted in the three Kirkwood–Buff equation (29). The matrix elements M_{11}, M_{22} and M_{33} are eliminated by eqns. (40a–c). The equations are combined so that only changes in the chemical potentials of the two salts appear, using the relations (45). As a result, the two independent linear eqn. (47) are derived:

$$
\begin{bmatrix}
(M_{13} - [\eta_3/\eta_2]M_{12}/\nu_3|(M_{12}/\eta_2)) \\
(M_{12}/\nu_1)|(M_{23} - [\nu_3/\nu_1]M_{12})/\eta_3)
\end{bmatrix}
\begin{bmatrix}
d\mu_{13}/kT \\
d\mu_{23}/kT
\end{bmatrix}
$$

$$
= \begin{bmatrix}
\nu_1 d\varrho_{13} \\
\eta_2 d\varrho_{23}
\end{bmatrix}
\tag{47}
$$

We note the perfect symmetry in the two salts. From eqn. (47), the variations in salt activities caused by the variations in salt concentrations are easily found:

$$
\begin{bmatrix}
d\mu_{13}/kT \\
d\mu_{23}/kT
\end{bmatrix}
$$

$$
= \begin{bmatrix}
\nu_1\nu_3(M_{23} - [\nu_3/\nu_1]M_{12})/\Delta \mid -\nu_3\eta_3 M_{12}/\Delta \\
-\nu_3\eta_3 M_{12}/\Delta \mid \eta_2\eta_3(M_{13} - [\eta_3/\eta_2]M_{12})/\Delta
\end{bmatrix}
\begin{bmatrix}
d\varrho_{13} \\
d\varrho_{23}
\end{bmatrix}
\tag{48}
$$

with

$$
\Delta \equiv M_{13}M_{23} - [\nu_3/\nu_1]M_{13}M_{12} - [\eta_3/\eta_2]M_{12}M_{23}.
\tag{49}
$$

Clearly, the eqn. (48) exhibit *Maxwell symmetry* as they should, since the off-diagonal elements in the coefficient matrix are equal.

Comparison with experimental results for KCl + KF solutions

In preparation for the comparison with experimental results, we reformulate eqn. (48) in terms of mean ionic activities for the two salts and in terms of the salt fraction (X_{23}) of salt 23 in the mixed solution. It should be remembered that the elements of the matrix **M** are functions of the ionic concentrations. The salt fractions are defined as:

$$
X_{23} = 1 - X_{13} = \varrho_{23}/(\varrho_{13} + \varrho_{23}).
\tag{50}
$$

For a mixture of two 1:1 electrolytes ($\nu_1 = \nu_3 = \eta_2 = \eta_3 = 1$) we obtain after rearrangements:

$$
\frac{d\ln y_\pm(13)}{d\varrho_{tot}} = \frac{1}{(\varrho_{tot})^2 G_{13}\{1 + \beta_{13}X_{23}\}} - \frac{1}{\varrho_{tot}}
\tag{51a}
$$

$$
\frac{d\ln y_\pm(23)}{d\varrho_{tot}} = \frac{1}{(\varrho_{tot})^2 G_{23}\{1 + \beta_{23}X_{13}\}} - \frac{1}{\varrho_{tot}}
\tag{51b}
$$

$$
\beta_{13} = [G_{12}/(G_{23} - G_{12})]\{1 - [G_{23}/G_{13}]\}
\tag{52a}
$$

$$
\beta_{23} = [G_{12}/(G_{13} - G_{12})]\{1 - [G_{13}/G_{23}]\}.
\tag{52b}
$$

It is evident that for $X_{23} = 0$ we obtain from eqn. (51a):

$$
\frac{d\ln a_\pm(13)}{d\varrho_{tot}} = \frac{1}{(\varrho_{tot})^2 G_{13}} - \frac{1}{\varrho_{tot}}.
\tag{53}
$$

This equation is identical to eqn. (38) for a solution of pure salt (replacing ion No. 2 by ion No. 3). Similarly for eqn. (51b) with $X_{13} = 0$. In some cases we may have the following conditions fulfilled:

$$
\beta_{13} \ll 1 \quad \beta_{23} \ll 1.
\tag{54}
$$

From eqns. (52a) and (52b) it is apparent that this is the case when the two salts are quite similar ($G_{13} \approx G_{23}$) and when the "interaction term" between the two ions of similar charge is small ($|G_{12}| \ll |G_{13}|$ and $|G_{23}|$). In that case, the activity of the salts in a mixture will be equal to the activities in a pure solution of a concentration equal to the total concentration in the mixed solution, if we have *pairwise autonomy of the radial distribution functions* (G_{13} and G_{23} in eqns. (51a–b) should be equal in mixed and pure solutions). Not even the trace activities will be different from the pure salt activities. This seems to be the case with KF/KCl mixtures.

In the case of hard-core potentials we have:

$$
G_{ab} = 4\pi a^3[i_{ab} - (1/3)d_{ab}^3].
\tag{55}
$$

Finally, when the GDHX model is assumed to be a valid approximation, the integrals i_{ab} given by eqn. (25) may be calculated explicitly by numerical integration using the radial distribution functions given by eqn. (6). It has proven sufficient to use 6-point Gauss quadrature (Ref. 13) in 40 intervals, each of a length equal to one half the Debye–Hückel length. The i_{ab} integrals in particular necessitate integration extending far out, because of the weighing with the square of the distance in eqn. (25).

In the following, we present mean ionic activity coefficients calculated in three different manners from the GDHX assumption:

(1) By means of osmotic coefficients and Gibbs–Duhem integration.

(2) By direct solution of (inversion of) the Kirkwood–Buff equations. This latter approach is possible since the GDHX does not satisfy electroneutrality. The changes in the "single ionic activities" have no meaning by themselves, but they may be combined to give mean ionic activities.

(3) By using the electroneutrality condition together with the Kirkwood–Buff equations and a subset of the GDHX radial distribution functions. In all cases, the second integration (over concentrations) is performed using 6-point Gauss quadrature in intervals of the

square root of the ionic strength corresponding to 0.1 $\sqrt{}$(mol dm^{-3}). No difference was found when smaller concentration intervals were used. The starting point was solutions containing 10^{-8} mol dm^{-3} salt. In such solutions, $\ln y_\pm$ may safely be set equal to E (ex, const. ε)/kT according to the Debye–Hückel limiting laws.

For uni-univalent salts in water at 25 °C we may write:

$$\varrho_s^* = (C_s/\text{mol dm}^{-3}) \cdot (a_{12}/\text{Å})^3/830.22 \tag{56}$$

$$B = 7.1356/(a_{12}/\text{Å}). \tag{57}$$

Therefore, the calculated curves of $\ln y_\pm$ vs. $\sqrt{I}$ for a single salt in solution are determined by only one variable parameter, the contact distance $a = a_{12}$, if the radii of the two
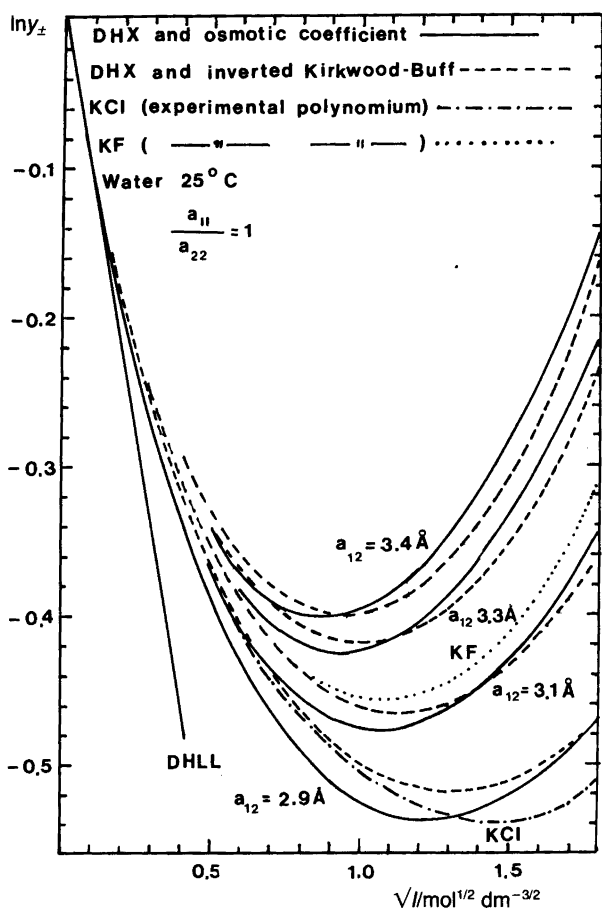
Fig. 6. The natural logarithm of the mean ionic activity coefficient as a function of the square-root of the ionic strength in water at 25 °C, as calculated from the DHX model (GDHX with equal ionic diameters). The ionic diameter in Å is used as the single adjustable parameter. The values calculated from osmotic coefficients and the Gibbs–Duhem equation (solid curves) are in reasonable agreement with the values calculated by inversion of the Kirkwood–Buff equations (dashed curves). The best-fitting polynomials for the experimental data obtained in Ref. 1 for KCl and KF are also shown (pooled values for pure solutions and 1:1 mixtures). DHLL stands for "Debye–Hückel Limiting Law".
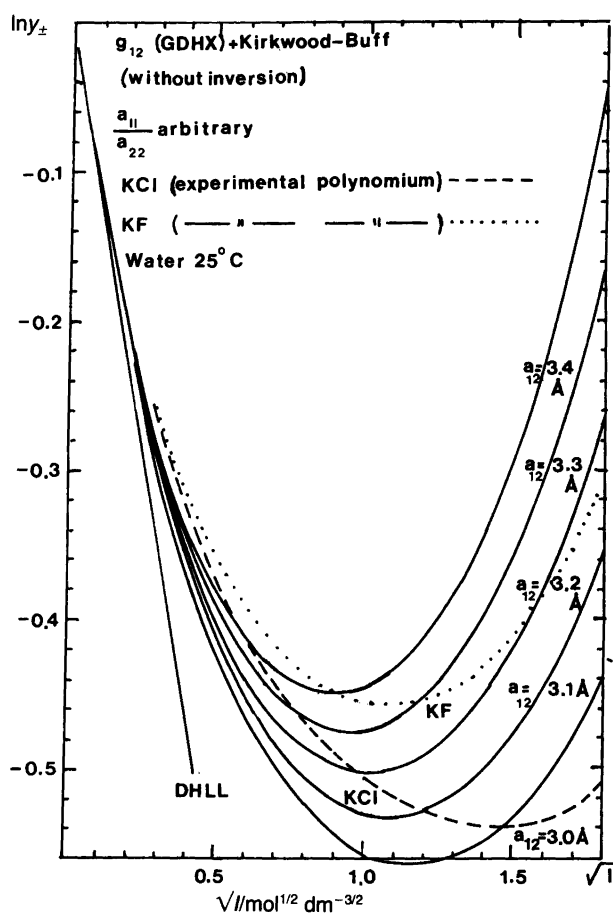

Fig. 7. The natural logarithm of the mean ionic activity coefficient as a function of the square-root of the ionic strength in water at 25 °C, as calculated from the GDHX model for $g_{+-}(s)$ from the Kirkwood–Buff equations plus electroneutrality. The contact distance between cation and anion is the single adjustable parameter, since the ratio of the cationic to the anionic radius may be chosen arbitrarily in this case. The polynomials of the experimental values for KCl cross the curves of equal contact distance.

ions are set equal to each other. Fig. 6 shows a family of such curves calculated from osmotic coefficients and from inversion of the Kirkwood–Buff equations. The two methods yield quite consistent results in spite of the different types of integrals involved (e-integrals and i-integrals, respectively). The polynomals that best fit the experimental data for pure and mixed solutions of KCl and KF obtained previously are (Ref. 1):

$$\ln y_\pm(\text{KCl}) = 0.117x^4 - 0.547x^3 + 1.101x^2 - 1.175x \tag{58}$$

$$\ln y_\pm(\text{KF}) = 0.098x^4 - 0.446x^3 + 1.011x^2 - 1.118x \tag{59}$$

$$x = \sqrt{I}. \tag{60}$$

These experimental curves are also drawn in Fig. 6. The form of the curves fits well with the GDHX values, and it seems possible to fit the KCl data with a contact distance
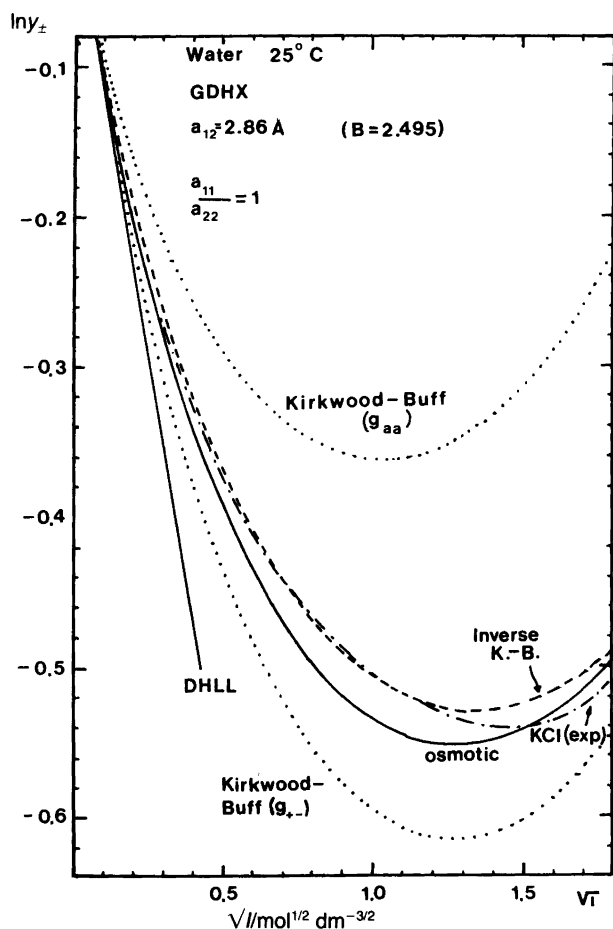
Iny±

Fig. 8. The Iny± vs. √I curves in water at 25 °C for a contact distance between cations and anions equal to 2.86 Å calculated in various ways from the GDHX model: (a) From osmotic coefficients with $a_{++}/a_{--} = 1$ (solid curve). (b) From the inverse Kirkwood–Buff equations with $a_{++}/a_{--} = 1$ (dashed curve).
(c) From Kirkwood–Buff plus electroneutrality plus g_{+-}(GDHX), arbitrary ratio a_{++}/a_{--} (lower dotted curve). (d) From Kirkwood–Buff plus electroneutrality plus g_{aa}(GDHX) with $a_{++}/a_{--} = 1$ (upper dotted curve). The models (a) and (b) fit the experimental polynomial for KCl within experimental error.

slightly lower than 2.9 Å, and the KF data with a contact distance slightly above 3.1 Å. Fig. 7 shows that everything is not as perfect as it looks, however. The family of GDHX curves drawn in this figure is calculated from the Kirkwood–Buff equations using electroneutrality and the GDHX expression for g_{+-}. In this calculation, the ratio between the cationic and the anionic diameters does not matter, only the contact distance a_{+-} being of importance. However, it does not seem to be possible to fix the value of this contact distance for any of the two salts. The best than can be said is that the contact distance is between 3.2 and 3.5 Å for KF and between 2.9 and 3.5 Å for KCl. We postpone the discussion of these findings to the last section.

The inconsistency of the GDHX also shows up in Figs. 8 and 9. In Fig. 8, the KCl data are shown together with theoretically calculated values for a contact distance of 2.86 Å and a ratio of ionic diameters of 1. The fit to the

inverse Kirkwood–Buff values and the values obtained from the osmotic coefficients is virtually perfect. The values calculated using electroneutrality and GDHX for g_{+-} are somewhat too low, and the values obtained similarly from $g_{++} = g_{--}$ are very much too high. The values obtained from osmotic coefficients and from the inverse Kirkwood–Buff values seem to strike a sensible balance between the two extremes obtained from Kirkwood–Buff together with electroneutrality. The same seems true in Fig. 9, where the data for KF are fitted to a contact distance of 3.16 Å (equal radii) when the osmotic values or the inverse Kirkwood–Buff values are used.

In the case with three ions we choose a radius for K⁺ and Cl⁻ of 2.86/2 = 1.43 Å. For the F⁻ ion we then have a radius of 3.16 − 1.43 = 1.73 Å. For KF, we should then have chosen $a_{++}/a_{--} = 0.826$. However, the influence of the slightly unequal radii on the activity coefficients is quite small in the case of a pure solution of KF. The precise values of the radii of the three ions will only be important for the conclusions in the case of a three-ion system.

Fig. 10 shows the quantities β_{13} and β_{23} as functions of the square-root of the ionic strength. It is seen that they
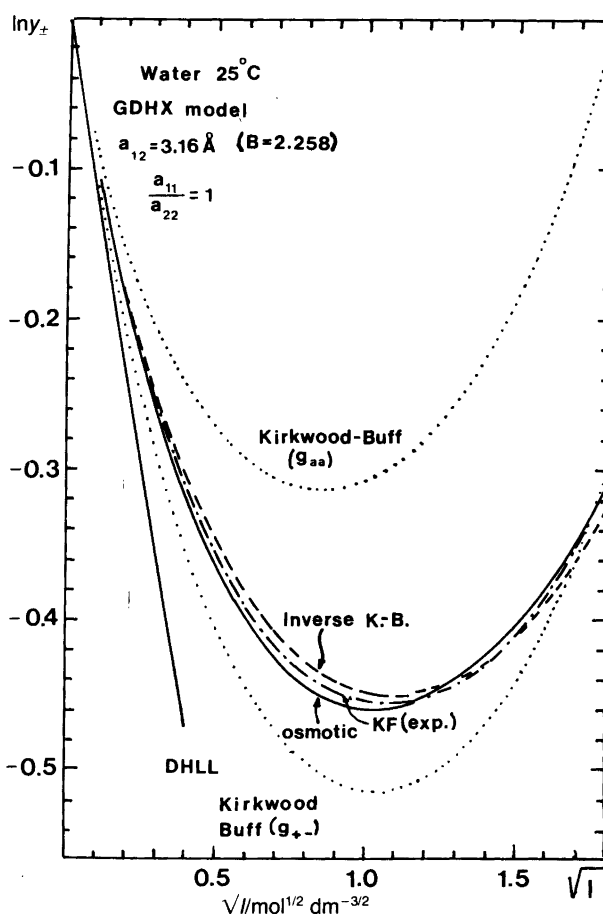

Fig. 9. The samt plots as in Fig. 8, but with $a_{+-} = 3.16$ Å. The values from osmotic coefficients and the values from inverse Kirkwood-Buff fit the experiments for KF within experimental error.
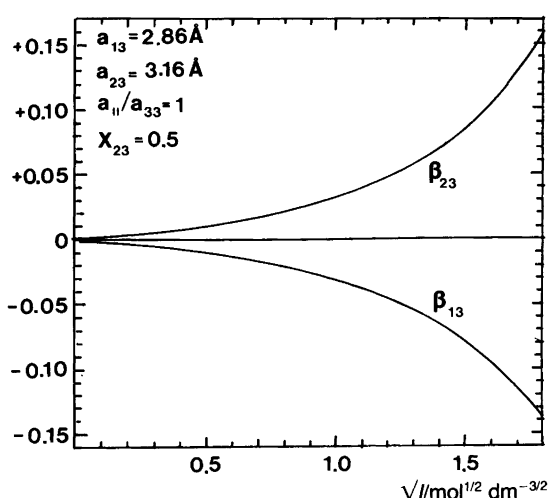
Fig. 10. The interaction coefficients β_{13} and β_{23} in a ternary mixture of two salts (13 and 23) with the salt fraction $X_{23} = 0.5$, i.e. a 1:1 mixture, calculated from Kirkwood–Buff plus electroneutrality plus g_{12}(GDHX), g_{13}(GDHX) and g_{23}(GDHX) [eqns. (52a–b)]. Since the absolute values of the interaction coefficients are mostly $\ll 1$, it is difficult to distinguish between $\ln \gamma_{\pm}$ in solutions of pure salts and in mixed solutions with the same total ionic strength. The contact distances correspond roughly to a mixture of KCl and KF in water at 25 °C.

are both much smaller than unity for most of the concentrations considered. Thus, it is not strange that it was not possible to distinguish experimentally between KF and KCl in pure and in mixed solutions.

Comparison between Monte Carlo results and GDHX calculations

As we have seen, the activity coefficients are highly sensitive to small variations in the manner in which the GDHX assumption is applied. Thus, the case is somewhat weak concerning the validity of the GDHX model at higher concentrations. One piece of supporting evidence is that the values obtained from osmotic coefficients are almost equal to the values obtained from Kirkwood–Buff inversion. However, the support is somewhat destroyed when one considers that it is in principle wrong to invert the Kirkwood–Buff equations! More direct evidence for the usefulness of the GDHX approximation would be desirable, and such evidence will be given here in the form of direct comparison with Monte Carlo (MC) simulations.

The conditions corresponding to the MC simulations shown in Figs. 3 and 4 ($B = 2.272$, $a_{++}/a_{--} = 0.858$ and ϱ_{tot}^* $= 8.39 \cdot 10^{-2}$) seem to be quite close to the conditions prevailing in an aqueous KF solution of ca. 2 mol dm^{-3} at 25 °C (see the previous section; Fig. 9). The excess energy has been calculated directly by the Metropolis method for $N = 216$ and 512 ions. The values of the radial distribution functions at contact and the volume term (VOL) in the osmotic coefficients can be found by polynomial extrapola-

tion. In Table 1, a comparison is given between excess osmotic coefficients calculated from Monte Carlo simulations and from the GDHX model. The deviation is 4 %, so at least in this case the GDHX osmotic coefficient is a fair approximation. In Table 1 we also give values of the excess energy and the osmotic coefficient calculated alternatively from direct integration of the best polynomial approximation of the Monte Carlo results for the radial distribution functions. For $N = 512$ and 235,000 configurations these are given by:

$$g_{+-}(s) = 2.71637 - 4.7014s + 5.81284s^2 - 4.06930s^3$$
$$+ 1.65400s^4 - 0.36116s^5 + 0.0325409s^6 \qquad (61)$$

$$g_{++}(s) = 0.303885 + 0.879493s - 0.37201s^2$$
$$+ 0.052000s^3 \qquad (62)$$

$$g_{--}(s) = 0.445579 + 0.824623s - 0.47199s^2$$
$$+ 0.123428s^3 - 0.012539s^4. \qquad (63)$$

Eqns. (61)–(63) are all valid only in the range from $s = 0$ (contact) to $s = 3$. However, all Monte Carlo radial distribution functions seem to deviate less than 1 % from unity at $s = 3$, so the e-integrals may well be truncated at this value. It is very important to retain all the decimals in the polynomial coefficients in the analytical formulae for the integrals, since the net results appear as a small difference between almost cancelling positive and negative values. We obtain:

$$e_{++} = -0.6162675$$
$$e_{--} = -0.4900236$$
$$e_{+-} = +0.7389816. \qquad (64)$$

From these values, the excess energy in the second row of Table 1 has been found. It deviates only 1.5 % from the Metropolis value.

Table 1. Dimensionless excess energy, corrected excluded volume (VOL) and excess osmotic coefficient ($\varphi - 1$) calculated by three methods for $B = 2.272$, $\varrho_{tot}^* = 8.39 \cdot 10^{-2}$.

Method	E_{ex}/NkT	VOL	$\varphi - 1$
Monte Carlo (Metropolis) 216 ions	−0.7851		
512 ions	−0.7840	0.276	+0.0147
From Monte Carlo $g_{ab}(r)$ for 512 ions up to 4 contact distances	−0.776	0.276	+0.0173
From GDHX $g_{ab}(r)$	−0.7129	0.2517	+0.01410

Cases of mixtures with almost equal trace activities

The KCl–KF case is quite peculiar. In the introductory section we mentioned that we more often experience cases of electrolyte mixtures in which the two trace activity coefficients are almost equal at the same ionic strength, e.g. the HCl–NaCl system. This peculiarity is clearly exhibited also by the GDHX model in a variety of other situations (Figs. 11, 12 and 13). For simplicity, all calculations are made with the *uninverted* Kirkwood–Buff equations plus electroneutrality, i.e. eqn. (48) have been used. Thus, the GDHX model has room for a qualitative explanation of seemingly paradoxical experimental findings.

Conclusions

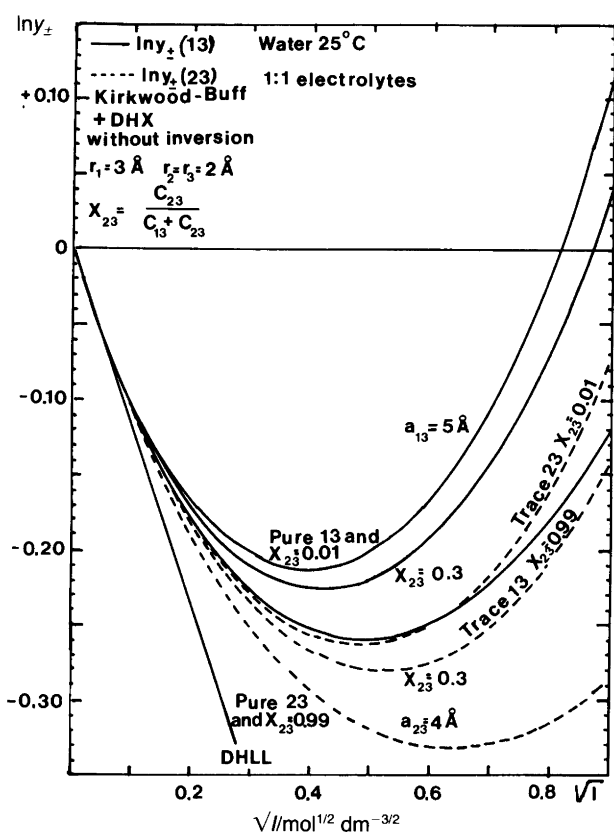From the considerations described above we may draw the following conclusions:

Fig. 11. The $\ln y_\pm$ vs. $\sqrt{I}$ curves in water at 25 °C for mixtures of two salts 13 and 23 with contact distances $a_{13} = 5\,\text{Å}$ and $a_{23} = 4\,\text{Å}$, and with ionic radii: $r_1 = 3\,\text{Å}$ and $r_2 = r_3 = 2\,\text{Å}$. In mixtures, the mean ionic activity coefficients for the two salts approach each other. The activity coefficient of a *trace* of 13 in a great excess of 23 is *almost* equal to the activity coefficient of a *trace* of 23 in a great excess of 13. Such cases are often found experimentally (Ref. 4, Chap. 15, p. 434). The calculations are based on GDHX plus Kirkwood–Buff plus electroneutrality.
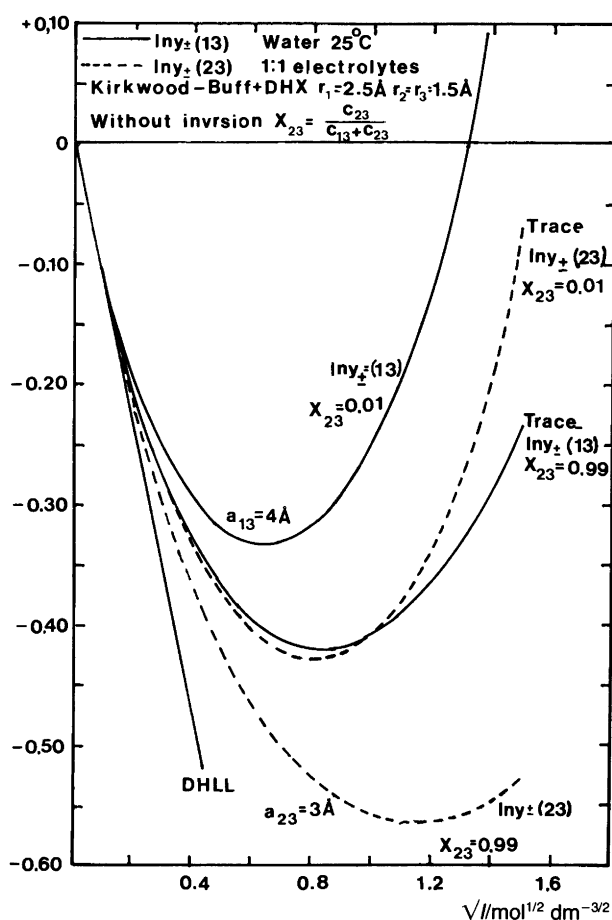
Fig. 12. Curves as in Fig. 11, but with $r_1 = 2.5\,\text{Å}$ and $r_2 = r_3 = 1.5\,\text{Å}$. The positions of the curves are lower than in Fig. 11, but the trace activity coefficients are almost equal for the two salts, as in Fig. 11.

(1) The GDHX expressions for the radial distribution functions are quite exact at low concentrations. At higher concentrations, the expressions constitute a fair approximation, although the agreement is at most semi-quantitative in mixed electrolytic solutions.

(2) At Bjerrum parameter values around 2, values of $\ln y_\pm$ calculated from GDHX osmotic coefficients and from the inverted Kirkwood–Buff equations are quite consistent.

(3) Inversion of the GDHX Kirkwood–Buff equations is only possible because electroneutrality is not strictly satisfied by the GDHX radial distribution functions.

(4) Values of $\ln y_\pm$ calculated from Kirkwood–Buff equations without inversion using electroneutrality differ widely according to which radial distribution functions we calculate from the GDHX expressions. The values obtained from GDHX osmotic coefficients or from inversion seem to strike a compromise between the two extremes.
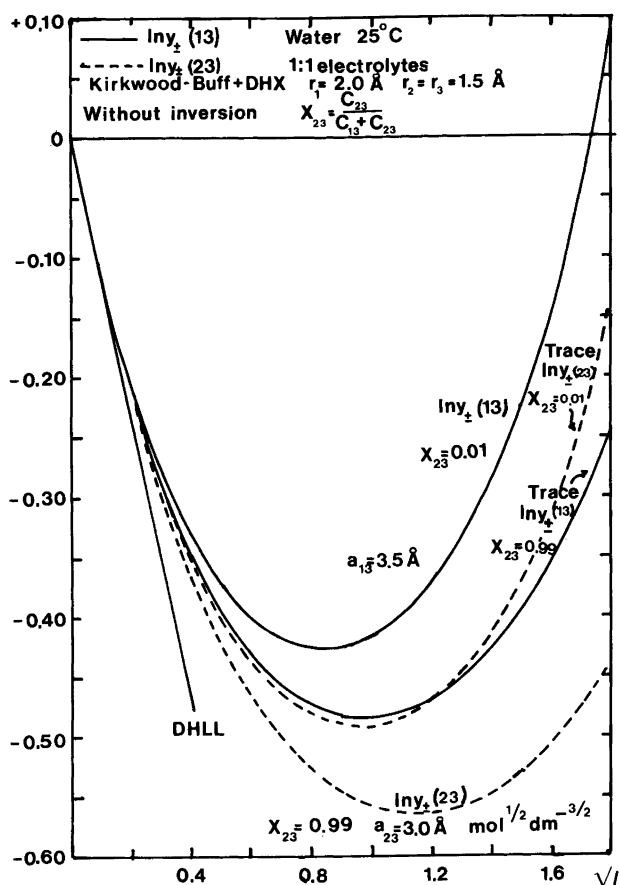
Fig. 13. Curves as in Fig. 11, but with $r_1 = 2.0$ Å and $r_2 = r_3 = 1.5$ Å. The positions of the curves are lower than in Fig. 12, and we are quite close to the KF/KCl situation. Nevertheless, the trace activity coefficients are still almost equal. Figs. 11–13 suggest that the KF/KCl situation (where the trace activity coefficients are equal to the activity coefficients of the pure salts) is very atypical.

(5) The osmotic coefficients calculated from GDHX seem reasonable compared to Monte Carlo results.

(6) The contact distance in KF solutions at 25 °C seems to be around 3.15 ± 0.10 Å when experimental $\ln y_\pm$ values for aqueous solutions of KF are compared to values obtained from the GDHX model and osmotic coefficients or from inverted Kirkwood–Buff equations. Similarly, a contact distance of 2.85 ± 0.10 Å is obtained for KCl solutions. From such comparisons, it is not possible to tell what the ratio of the ionic radii should be in the two salts.

(7) From the Kirkwood–Buff equations and electroneutrality (using the GDHX assumption for g_{+-}) it is not possible to fit a definite contact distance for KCl or for KF. One obtains contact distances which decrease with increasing concentration from 3.5 to 3.2 Å for KF and from 3.5 to 2.9 Å for KCl.

(8) Assuming radii of 1.43 Å for K^+ and Cl^-, and 1.73 Å for F^-, we find from the GDHX model that there is almost no difference between the activity coefficients of each of the two salts in pure solutions and in mixed solutions at the same ionic strength. Even the trace activity of one salt in a great excess of the other is almost equal to the activity of the solution of the same pure salt at comparable ionic strengths.

(9) More typically, GDHX calculations on ternary mixtures using the Kirkwood–Buff equations and electroneutrality lead to the result that the $\ln y_\pm$ of each salt vary with the salt fraction. The two $\ln y_\pm$ curves meet in almost identical values of the trace activity coefficients of the two salts in a great excess of the other.

The range of contact distances found (conclusions 6 and 7) is not at all surprising. Adams[14] has given a survey over ion hard-sphere dimensions estimated in various ways in solid-state structural chemistry. The best values are probably those determined from electron density maps for ionic crystals obtained by X-ray diffraction. The best estimate for the radius of the K^+ ion is 1.49 Å, and for the Cl^- ion 1.64 Å (Ref. 14, Chap. 2 and Table 6). When the two ions are not hydrated, the resulting contact is 3.13 Å. However, it is reasonable to assume that the ionic separations would be slightly larger in a crystal than for an ion-pair in solution, since the electrostatic attraction between ions of opposite charge is less oriented in the crystal. The F^- ion has a radius of only 1.16 Å as judged from electron density maps (Ref. 14, Chap. 2 and Table 6). The unhydrated contact distance is then only 2.65 Å for KF. On the contrary, we find a larger contact distance for KF than for KCl. One obvious explanation would be that the small (and hydrogen-bonding) F^- ion is hydrated so as to have a radius larger than the radius of Cl^-.

The hydration of ions in aqueous solution is a controversial issue, since widely different values for the hydration numbers are found by different methods (see, for example, the review by Hinton and Amis[15]). However, it is most often assumed that large ions such as K^+ or Cl^- are not hydrated to any great extent, whereas small ions such as Li^+ or F^- are strongly hydrated. It is also worth mentioning that Onsager and Fuoss have determined the contact distance of KCl in water at 25 °C to be 3.07 Å by comparison of conductance data with their theoretical formula (Ref. 16, p. 451). This is very close to the value found here from activity coefficients. This is somewhat in conflict with the theory of Möller, from which one obtains rather a contact distance equal to about 2 Å for KCl in water at 0 °C by comparison with the measured osmotic coefficients (Ref. 16, p. 417 and Fig. 115).

Should we therefore conclude that the $\ln y_\pm$ values calculated from GDHX osmotic coefficients or by inversion of the Kirkwood–Buff equations are better than the values calculated from the Kirkwood–Buff equations plus electroneutrality and g_{+-}(GDHX), because the latter values can-

not fit the experimental data with one fixed value of the contact distance? No. This is not at all a safe conclusion! First of all, it is very risky under any circumstances to interpret the thermodynamic properties of more concentrated solutions by means of such a crude tool as the primitive model, so we cannot expect an exact fit using a fixed contact distance. Having said this we try anyway, since we are left with no choice in the case of the KF–KCl system. In the latter system we have to go to quite high concentrations to see any differences at all between the two mean ionic activity coefficients. However, even within the framework of the primitive model, many reasons could be given for an observed *decrease* of the contact distance with increasing ionic strength:

(a) First of all it should be noted that the activity coefficients calculated refer to MacMillan–Mayer conditions (pressure equal to osmotic pressure) rather than to the usual Lewis and Randal conditions (atmospheric pressure). In a 1 mol dm^{-3} solution one has to subtract ca. 0.02 from the calculated $\ln y_{\pm}$ values (Ref. 16, p. 414 and Table 77). This would deflect the GDHX curves in Fig. 7 in the right direction, whereas the calculated curves in Fig. 6 would deviate from the experimental curves.

(b) Secondly, the hydration of the ions should naturally decrease with decreasing concentration of water. However, for KCl this explanation cannot be used, since none of the ions seem to by hydrated to any measurable extent.

(c) Thirdly, an apparent decrease in the contact distance is really an increase in the Bjerrum parameter. The Bjerrum parameter is inversely proportional to the dielectric constant of the medium [eqn. (7)]. However, it has long been known that the macroscopic dielectric constant of aqueous solutions decreases considerably with increasing salt concentration for many salts. For example, for salts such as LiCl, NaCl and KCl, Hasted *et al.* found a decrease from 78 to around 60 for the dielectric constant when the concentration increased from zero to 1.5 mol dm^{-3} (25 °C).[17,18] The explanation proposed by Hasted[19] was that because of the reorientation of the dipole moment of water molecules in the neighbourhood of the ions, the local dielectric constant may drop to a value of from 4 to 6 within a distance of about 2 Å from the ion.

A decrease in the dielectric constant with increasing concentration would lead to a considerable downward deflection of the calculated curves for the activity coefficients. However, it should be remembered that the effect on the activity coefficient is cumulative over the lower concentrations, so the effect is not as large as it may first seem. Furthermore, when the concentration is around 1–2 mol dm^{-3} the value of $\varkappa a$ is around unity. This means that most of the dielectric phenomena are taking place in the immediate neighbourhood of the ion according to the GDHX model. Since the local dielectric constant is very low here,

the "local Bjerrum parameter" is very high, and many complications may appear which are not accounted for by the primitive model.

Nevertheless, the reasonable values of the contact distances found, as well as the semi-quantitative agreement with measurements in electrolyte mixtures, lend some credibility to the straightforward use of the primitive model and to the GDHX assumption, even in the quite concentrated solutions considered here. The present work is meant as a first step towards more exact theories in which we may adjust the GDHX radial distribution functions in order to achieve complete thermodynamic consistence. This programme seems to be promising in view of the extreme sensitivity, demonstrated above, of the $\ln y_{\pm}$ vs. $\sqrt{I}$ curves to the method of calculation.

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