On the Transition from the Lattice-like Structure of Electrolytes to the Debye–Hückel Limit

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Charge densities around a central ion are calculated with the assumption of a slightly distorted normal distribution of point-charge ions around regular lattice sites. The conditions under which this charge distribution approaches that of the Debye–Hückel theory at infinite dilution are discussed. The lattice model in this form predicts oscillations in the charge cloud at any finite concentration, but these oscillations are very far from the central ion in dilute systems. Pair correlation functions are also reported for concentrated solutions. The shift of the first-neighbour maxima follows a concentration dependence steeper than the cube-root law for oppositely-charged pairs and less steep for like-charged pairs. The excess energy has been calculated and is in very good agreement with the HNC and MSA theory for low concentrations.

1. INTRODUCTION

Most of the theories of electrolyte solutions use the following route in treating ionic solutions: (*a*) assume a mathematical function for the description of the interactions between ions, (*b*) use a statistical theory to calculate the pair correlation functions and (*c*) from these calculate the thermodynamic properties of the system. In order to reduce the difficulties in step (*b*), the usual assumption for the interactions is a simple Coulomb law combined with hard-sphere repulsion (primitive model). In more sophisticated approximations the so-called Gurney co-sphere repulsion[1] and cavity terms are also considered. The various theories differ mainly in the applied statistical-mechanical tools, the most important of which are the Debye–Hückel theory and its extensions,[2] the HNC theory,[3] the mean spherical model,[4] the ion-pair theory[5] and the applications of the Monte Carlo method.[6] It has been proved[2b] that all of these theories lead to the same result when the electrolyte concentration tends to zero, *viz.* to the limiting laws of the Debye–Hückel theory. In this case the pair potentials are additive.

At higher concentrations, however, the effect of the other ions on the pair potentials is not negligible and leads to very complicated many-body problems.

Recently, some authors[7] have reversed the above logic of the theoretical calculations in order to obtain more realistic interaction potentials: they (*a*) assume many-particle correlation functions which have some symmetry properties which allow (*b*) the calculation of the interaction between ions in a more sophisticated way; they then (*c*) calculate the thermodynamic properties. It is evident that many-body problems are very much simplified if the possible distances between particles can be generated by a few simple rules such as the symmetry operations for regular lattices. In such a way, a continuous function for the interionic distance could be given for

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ionic interactions which also accounts for the repulsion originating from the non-linear dielectric behaviour of the solvent in the vicinity of ions.[7b,d] On qualitative grounds, this model can be expected to give a good description of electrolytes at high concentrations, when repulsive forces are commensurate with attractive ones or even predominate, but a rigorous lattice-like structure cannot yield the statistically correct DH limiting laws, because all thermodynamic properties would depend on $c^{n/3}$ instead of $c^{n/2}$.

However, if the ions are allowed to scatter randomly around the regular lattice points, the radial charge distribution can, in principle, be spread out in such a way that the desired limiting cases are obtained. This has been qualitatively implied in all lattice theories known so far,[7] but it has never actually been shown how increasing disorder can produce the transition to the DH limit. In the present paper we describe one possible approach to this problem.

2. RADIAL CHARGE DISTRIBUTION IN A RANDOMLY DISTORTED CUBIC LATTICE

Let us consider a positive ion in a regular cubic lattice. The angle-averaged charge density, ρ_i, originating from the ith layer of ions around it can be given as:

$$\rho_i = z_i \delta(r, r_i)/4\pi r^2 \qquad i = 1, 2, \ldots \tag{1}$$

where r is the distance from the central ion, r_i is the ith distance where lattice sites occur, z_i is the charge at a distance r_i (with positive or negative sign depending on the charge of the ions occupying these sites) and δ denotes the Dirac delta-function.

For example, in the case of a body-centred cubic lattice:

$$r_j^+ = r_0\sqrt{h^2 + k^2 + l^2} \tag{2}$$

and

$$r_j^- = r_0\sqrt{(h + \tfrac{1}{2})^2 + (k + \tfrac{1}{2})^2 + (l + \tfrac{1}{2})^2} \tag{3}$$

where r_0 is a scaling parameter, the $+$ and $-$ superscripts correspond to the sign of the charge on the ions at those distances and h, k and l are non-negative integers. The numbers of ions at r_j is:

$$z_j = \pm \frac{2^n 3!}{m!} \tag{4}$$

where n is the number of non-zero terms and m the number of identical terms among the three terms under the square-root sign in eqn (2)–(3). [For instance, if $h = 1$, $k = l = 0$, then z_j is either $+6$, or, since with the addition of $\tfrac{1}{2}$ there are never zero terms in eqn (3), it is -24.]

Since the same r_j may be obtained with different sets of h, k and l, all identical distances can be unified into one set labelled by i:

$$z_i = \sum_{\substack{j \\ r_j = r_i}} z_j. \tag{5}$$

For instance, the distance $2.598r_0$ can be obtained using values of 1, 1, 1 and 2, 0, 0 for the indices in eqn (3). The corresponding charges are -8 and -24, thus $z_i = -32$.

Fig. 1 shows the surface charge density around a positive ion in a body-centred cubic crystal. This is obtained by replacing the Dirac δ-function with the Kronecker
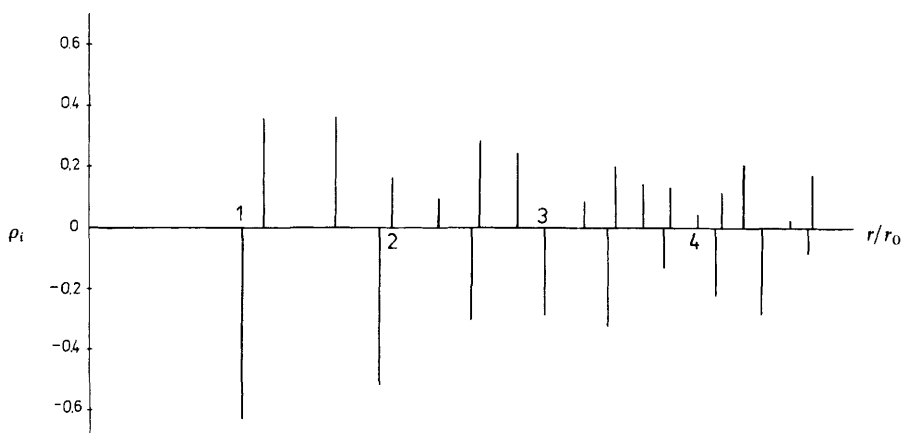
FIG. 1—Charge distribution in a rigorous body-centred cubic lattice.

δ-function to avoid the difficulty of showing infinitely high volume densities (whose integral over r is, however, finite and equal to z_i).

Now let us allow the ions to scatter radially and randomly around r_i. With a high concentration of ions the repulsion terms, which are independent of the sign of the charges, predominate. Therefore we can assume that the shell of ions at r_i is repulsed by both the inner and outer shells with almost the same force, so that this scatter would be well-approximated by a symmetrical distribution. With the justification postponed to section 3, we chose a slightly distorted normal distribution to replace the Dirac delta-function in eqn (1):

$$\rho_i = (A_i/4\pi r^2)\{\exp[-q_i(r-r_i)^2] - \exp[-q_i(r+r_i)^2]\} \tag{6}$$

which can be transcribed into:

$$\rho_i = (A_i/2\pi r^2)\exp[-q_i(r^2+r_i^2)]\sinh(2q_ir_ir) \tag{7}$$

where q_i determines the scattering and A_i is the normalizing factor.

It can be easily seen that eqn (6) becomes the normal distribution when q_i tends to infinity.

The total charge on the spherical surface at r around a positive central ion is thus:

$$\rho' = 4\pi r^2 \sum_i \rho_i = \sum_i \rho_i' \tag{8}$$

where $\rho_i' = 4\pi r^2 \rho_i$ and the normalizing factors can be obtained from:

$$z_i = \int_0^\infty \rho_i'\, \mathrm{d}r \tag{9}$$

which, when summed over all i, yields -1:*

$$A_i = z_i \sqrt{\frac{q_i}{\pi}} \frac{1}{\mathrm{erf}\,(r_i\sqrt{q_i})} \tag{10}$$

* The normalization is different when a hard-core diameter a is taken into account. We plan to discuss such cases in a separate paper. Here we deal with point-like charges only, which, however, does not mean that there are no repulsion forces, since their existence is implied in the assumption of the almost normal distribution function.

where

$$\text{erf } x = \frac{2}{\sqrt{\pi}} \int_0^x \exp{(-t^2)} \, dt. \tag{11}$$

The scatter parameter q_i is labelled by i to indicate that it may depend on r_i, since one would expect that the chance of finding an ion outside its lattice point is higher the farther it is from the central ion. The actual form of this r_i-dependence is to be determined later.

The concentration dependence of the charge distribution is influenced by both r_i and q_i. The former quantities depend on concentration via eqn (2) and (3) in which the distance between oppositely charged ions in the elementary cell is:

$$r_0 = r^\circ / c^{1/3} \tag{12}$$

where r° is a constant depending only on the actual geometry.

3. TRANSITION TO INFINITE DILUTION

One possible way to provide proof that the charge distribution of a lattice distorted randomly in the above manner goes over into the DH charge distribution (for $1:1$ electrolytes to which we restrict the present treatment) would be to show analytically that:

$$\lim_{\substack{q_i \to 0 \\ r_0 \to \infty}} \sum_i \rho_i' = \lim_{\kappa \to 0} -\kappa^2 \frac{\exp{\kappa a}}{1 + \kappa a} r \exp{(-\kappa r)} \tag{13}$$

where κ is the inverse Debye length and a the hard-core diameter of ions. Unfortunately, the form of $z_i(r)$ is analytically untractable [see eqn (4)], thus we were unable to follow this path.

Another proof could be based on the theorem that two distributions are equal, if the total set of their moments is identical (the uniqueness of moments).

The kth moment of the DH charge density function given on the right-hand side of eqn (13) is:

$$\mu_k^{DH} = -\frac{(k+1)!}{\kappa^k} \tag{14}$$

whereas that of the distorted lattice-like distribution is to be calculated from the following equation:

$$\begin{aligned}
\mu_k &= \sum_i \lim_{q_i \to 0} \int_0^\infty r^k \rho_i' \, dr \\
&= 2 \sum_i z_i q_i \int_0^\infty r^{k+1} \exp{(-q_i r^2)} \, dr \\
&= \frac{k}{2} \Gamma\left(\frac{k}{2}\right) \sum_i z_i q_i^{-k/2}.
\end{aligned} \tag{15}$$

All of these moments are finite if $k \geqslant -1$, like those of the DH distribution in eqn (14). This is one argument justifying the use of eqn (7), since if undistorted normal distribution had been chosen, the order in r would have been less by one than in the present case which would result in the non-existence of the "minus first moment."

By equating eqn (14) with eqn (15) and using some known relationships for the factorials and Γ functions,[8] we have:

$$-\kappa^k \sum_i z_i q_i^{-k/2} = \Gamma\left(\frac{k+3}{2}\right)\frac{2^{k+1}}{\sqrt{\pi}}. \tag{16}$$

On the other hand, we can select, say, the "minus first moment" to eliminate κ from eqn (16):

$$\kappa = -\sqrt{\pi}\sum_i z_i q_i^{1/2} \tag{17}$$

which, when inserted into eqn (16), yields:

$$\left(\sum_i z_i q_i^{1/2}\right)^k \left(\sum_i z_i q_i^{-k/2}\right) = \Gamma\left(\frac{k+3}{2}\right)\left(-\frac{2}{\sqrt{\pi}}\right)^{k+1}. \tag{18}$$

By taking $k = 1, 2, 3, \ldots$, this is an infinite set of non-linear equations with an infinite number of unknown q_i. The structure of these equations is such that, if a series of q_i satisfies them, then any values of q_i multiplied by a constant will also satisfy them. Thus, the solutions of eqn (18) must depend only on the geometry of the actual lattice chosen, i.e. q_i can be written in the form:

$$q_i = (b/r_0^2)Q_i(R_i) \tag{19}$$

where $R_i = r_i/r_0$ and b can be determined from, say, eqn (17):

$$b = \kappa^2 r_0^2 / \pi \left(\sum_i z_i Q_i^{1/2}\right)^2. \tag{20}$$

If we succeed in finding the series of positive real q_i that satisfy the set of eqn (18) and (20), we can substitute them into eqn (7) and (8) and the thus calculated charge density function will be identical with that of the Debye–Hückel theory.

For body-centred cubic geometry r_0 is:

$$r_0 = \frac{\sqrt{3}}{2}\left(\frac{1000}{Nc}\right)^{1/3} \tag{21}$$

where N is the Avogadro number and c the molar concentration. Thus:

$$b = 6e^2(Nc)^{1/3}/\varepsilon kT\left(\sum_i z_i Q_i^{1/2}\right)^2. \tag{22}$$

An approximate solution of the set of eqn (18) was found in the following way: We tried out some elementary functions for the dependence of Q_i on R_i for $k = 1, 2, 3$ and 4, i.e. for the first four moments. The best, though still not satisfactory, results were obtained with $\sqrt{Q_i} = 1 + \sin(\pi/2R_i^{5/2})$. The relative errors in the four moments were $-8.3, -7.3, -0.4$ and $+6.5\%$, respectively. Then with an iteration procedure we fitted the values of Q_2 to Q_6 (fixing $\sqrt{Q_1} = 2$) so that the $k = 1$ to 4 cases in eqn (18) are satisfied while the "tail" of the sums was still approximated by the sine formula up to $h, k, l = 12$. (This latter summation was made with the Evjen method[9] to hold the partial sums over z_i always at -1, as required by the electroneutrality condition.) Table 1 shows the results. With these values, the equality is statisfied to errors of $+3.6, +1.9, -1.2$ and -0.2% for $k = 1, 2, 3$ and 4, respectively.

TABLE 1.—SCATTERING PARAMETERS FOR THE FIRST SIX NEIGHBOURS IN A BODY-CENTRED CUBIC LATTICE

i	R_i	z_i	$\sqrt{Q_i}$
1	1.000	−8	2.
2	1.1547	6	1.922 88
3	1.6330	12	1.472 58
4	1.9148	−24	1.364 25
5	2.0000	8	1.287 73
6	2.3094	6	1.326 18

Thus we could calculate also the sum in eqn (22):

$$\sum_i z_i Q_i^{1/2} = -2.057\,29 \tag{23}$$

which, when inserted into eqn (22), yields:

$$b = 0.8550\,c^{1/3} \tag{24}$$

for water at 25 °C.

4. CALCULATION OF CHARGE DISTRIBUTION

With the aid of the above treatment we obtained an equation for the charge distribution around a central ion in electrolyte solutions, in the form of eqn (8), (7) and (10), which fulfils two limiting cases: (1) at infinite dilution it goes over into the statistically correct Debye–Hückel distribution and (2) at very high concentrations it yields a lattice-like charge distribution. It is plausible to assume that the same equation can also be used for the description of electrolyte solutions at moderately high concentrations. However, it is not justified to retain the same series of Q_i and to assume the concentration dependence of b to be the same as at infinite dilution. If we still do so, we must be aware of the possibility that this sort of interpolation between the two extreme cases may only be the first approximation.

Charge densities were calculated in a summation over all lattice sites within $R \leqslant 19.8663$, whereby the total charge of the system is -1, i.e. the central charge is overcompensated by only one charge at a very large distance. The results are shown in fig. 2.

Oscillations in the charge cloud occur at all concentrations studied, however dilute the system is, but these oscillations are very far from the central ion if $c < 0.1$ mol dm^{-3}. The location of the first change in the sign of the charge cloud is shown in table 2 as a function of concentration.

This result is different' from that calculated on the basis of the primitive model,[2b−e,5b−c] viz. the first oscillation appears in concentrations of ca. 1 to 1.7 mol dm^{-3}. Instead of having a monotonously decaying oppositely charged ionic atmosphere at low concentrations which develops an oscillation at a short distance from the central ion at a definite concentration, our model predicts oscillations at any finite concentration which creep closer to the central ion as the concentration increases. Since the assumption of almost normal distribution around the lattice sites implies the assumption of smooth repulsion in the pair potentials which are longer range than the hard-core repulsion in the primitive model, and since it is known that
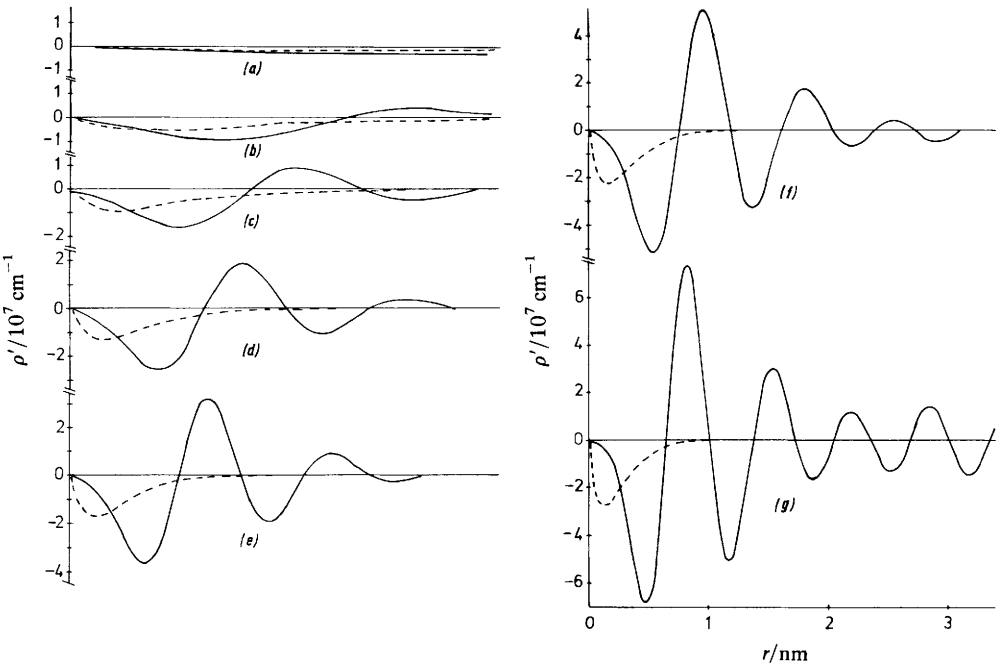
FIG. 2—Charge densities around a positive ion in different concentrations of a 1 : 1 electrolyte (the dotted curves are the DH charge distributions for comparison). $c =$ (a) 0.025, (b) 0.20, (c) 0.55, (d) 1.17, (e) 2.13, (f) 3.52 and (g) 5.40 mol dm^{-3}.

TABLE 2.—LOCATION OF THE FIRST CHANGE IN THE SIGN OF THE CHARGE CLOUD AND THE RELATIVE AMPLITUDE OF THE FIRST OPPOSITE WAVE AS A FUNCTION OF CONCENTRATION

$c/\text{mol dm}^{-3}$	r_{osc}/nm	A_{rel} (%)
0.000 003 13	>1051	—
0.000 0250	179	3.76
0.000 0844	95.8	6.36
0.000 200	61.3	7.88
0.001 60	21.9	12.8
0.005 40	12.3	16.6
0.012 8	8.33	20.0
0.025 0	5.96	23.3
0.043 2	4.67	26.3
0.200	2.45	41.5
0.549	1.63	58.6
1.17	1.17	74.8
2.13	0.956	86.6
3.52	0.809	98.3
5.40	0.701	107.6
7.86	0.619	115.4
11.0	0.553	122.2

any lattice-like structure is built up when repulsion forces start to affect the distribution of particles, this result does not seem unreasonable.

A consequence of these ever-present oscillations is also shown in the second moment of the distorted lattice-like distribution. At any finite concentration it is:

$$\mu_2 = \frac{2}{\sqrt{\pi}} \sum_i \frac{z_i \sqrt{q_i} \exp(-q_i r_i^2)}{\mathrm{erf}(r_i \sqrt{q_i})} \int_0^\infty r^2 \exp(-q_i r^2) \sinh(2q_i r_i r) \, \mathrm{d}r$$

$$= \sum_i z_i \left(r_i^2 + \frac{1}{2q_i} + \frac{r_i \exp(-q_i r_i^2)}{\sqrt{\pi q_i} \, \mathrm{erf}(r_i \sqrt{q_i})} \right) \tag{25}$$

which does not exist, except in the limit $q_i \to 0$, since the $z_i r_i^2$ terms are alternating and divergent. Thus, the second-moment criterion, obtained by Stillinger and Lovett[5b-c] for the primitive model, does not hold in our case. Eqn (25) is, at the same time, a proof that the oscillations observed in the numerical calculations are not a consequence of some errors in Q_i or due to the cut-off of the infinite series.

This divergent behaviour of the large-r tail of the second moment, however, has no practical consequence whatsoever in the properties of electrolyte solutions, since the interaction potentials and the spherical charge density function itself are always convergent.

5. PAIR CORRELATION FUNCTION

In the previous treatment criteria were given for the total charge density function whereby the conditions of the transition to the DH charge density at infinite dilution could be obtained. The separation of the total charge at a given distance into the pair correlation functions, $g_{++}(= g_{--})$ and g_{+-}, is uncertain with respect to an additive function of r:

$$g_{++} = \frac{\rho_+}{\rho_0} + F(r) \tag{26}$$

and

$$g_{+-} = -\frac{\rho_-}{\rho_0} + F(r) \tag{27}$$

where ρ_0 is the particle density at very large r, since with any $F(r)$ we have:

$$\rho = \rho_0(g_{++} - g_{+-}) = \rho_+ + \rho_- \tag{28}$$

where ρ_+ and ρ_- are the sum of the terms in eqn (7) over all positive or negative z_i, respectively.

Both ρ_+ and ρ_- tend to plus and minus infinity, respectively, as r tends to zero. Since we known that g_{++} must be zero at $r = 0$, one criterion for $F(r)$ is that it must contain at least those terms which compensate the divergence of ρ_+ at small r:

$$F(r) = \frac{-1}{\rho_0 \pi^{3/2} r} \sum_i^+ z_i q_i^{3/2} r_i \frac{\exp(-q_i r_i^2)}{\mathrm{erf}(r_i \sqrt{q_i})} + f(r) \tag{29}$$

where the + superscript of the sum means that the summation must be made only over positive z_i: $f(r)$ is an unknown function, but numerical results obtained with the assumption $f(r) = 0$ suggest that it is negligible at higher concentrations.
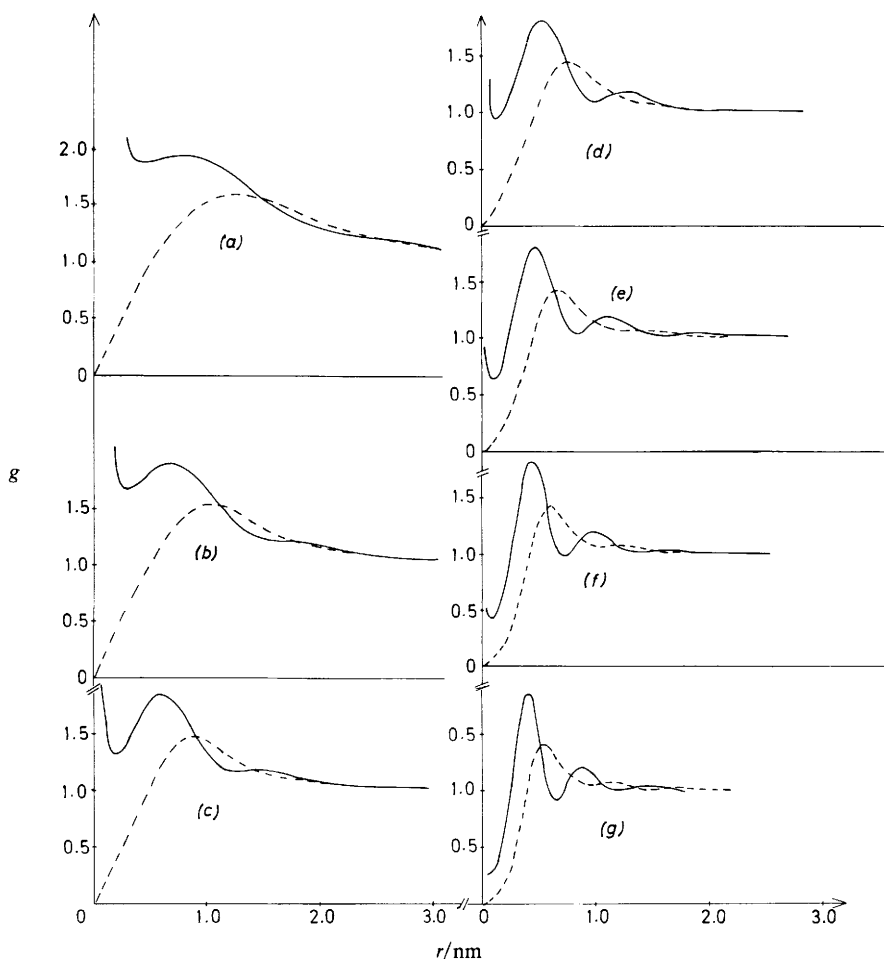
FIG. 3—Pair correlation functions for a 1 : 1 electrolyte in different concentrations (full curve: oppositely-charged pairs; dotted curve: like-charged pairs). $c = $ (a) 0.55, (b) 1.17, (c) 2.13, (d) 3.52, (e) 5.40, (f) 7.86 and (g) 11.0 mol dm^{-3}.

The pair correlation functions calculated in this way are shown in fig. 3. They predict, on the one hand, that it is impossible to detect any crystal-like structure in aqueous solutions of 1 : 1 electrolytes by diffraction methods below a concentration of *ca.* 2 mol dm^{-3}. On the other hand, the shift of the maxima with concentration is not strictly in accordance with a cube-root law as might be expected for a regular lattice (fig. 4). In accordance with the discussion of Pálinkás and Kálmán[10] on a non-lattice-like case, the location of the diffraction intensity peak should be shifted with a power of c higher or lower than 1/3 depending on whether the scattering particles are unlike- or like-charged, respectively.

A more detailed study of these pair correlation functions and their comparison with experiments will be reported in another paper.
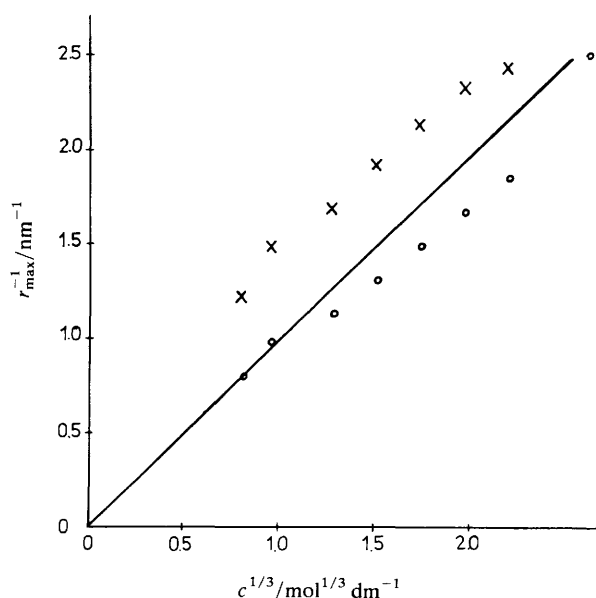
FIG. 4—Concentration dependence of the peak position of pair correlation functions corresponding to first-neighbour pairs (circles: like-charged pairs; crosses: oppositely-charged pairs).

6. EXCESS ENERGY

In order to provide a further illustration of the transition of a lattice-like arrangement of ions into the DH distribution, we present only a comparison of the excess energy of dilute solutions calculated by this model and by other theories.

For dilute solutions, the pair potential between two ions can be approximated by the Coulomb law. This being symmetrical for like- and unlike-charged pairs, the excess energy of a positive central ion is:

$$E^{ex} = \frac{e^2}{\varepsilon} \int_0^\infty \frac{1}{r} \rho' \, dr$$

$$= \frac{e^2}{\varepsilon} \frac{2}{\sqrt{\pi}} \sum_i \frac{z_i \sqrt{q_i}}{\text{erf}\,(r_i \sqrt{q_i})} \int_0^\infty \frac{\exp\,[-q_i(r^2 + r_i^2)]}{r} \sinh\,(2q_i r_i r) \, dr \qquad (30)$$

which can be integrated, after expending the sinh term, to yield:

$$E^{ex} = \frac{2e^2}{\varepsilon \sqrt{\pi}} \sum_i \frac{z_i q_i r_i \exp\,(-q_i r_i^2)}{\text{erf}\,(r_i \sqrt{q_i})} \sum_{j=0}^\infty \frac{(q_i r_i^2)^j}{(2j+1)(j)!}. \qquad (31)$$

Substituting $t_i^2 = q_i r_i^2$, one can see that eqn (31) takes the form:

$$E^{ex} = \frac{e^2}{\varepsilon} \sum_i \frac{z_i}{r_i} \frac{2t_i^2}{\sqrt{\pi} \, \text{erf}\,(t_i)} \sum_{j=0}^\infty \frac{t_i^{2j}}{(2j+1)(j)!}$$

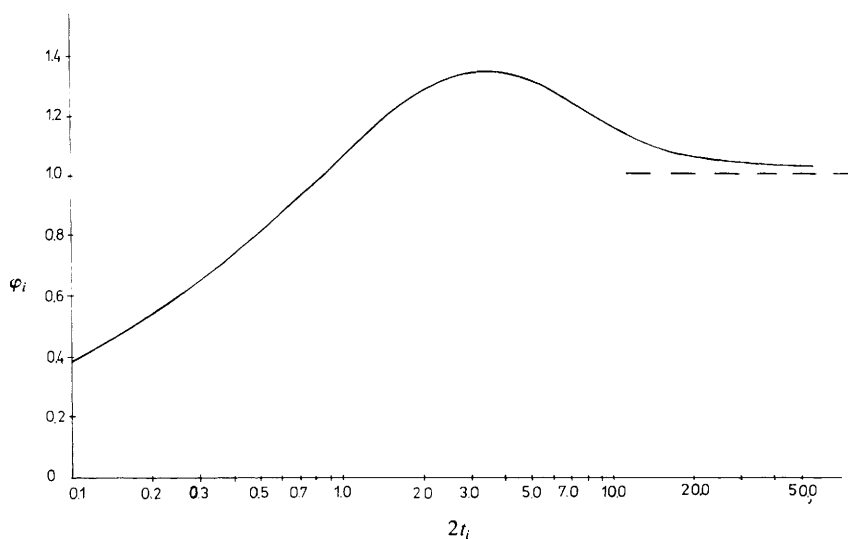$$= -\frac{e^2}{\varepsilon} \sum_i \frac{z_i}{r_i} \varphi_i. \qquad (32)$$

FIG. 5—φ_i function involved in the concentration dependence of $M(b)$ [see eqn (32)].

The φ_i function is given in fig. 5. It is seen that at large values of t_i it tends to unity, *i.e.* for large b the sum of the right-hand side of eqn (32) tends to M/r_0, where M is the Madelung constant. For smaller b the Madelung constant will depend on b, *i.e.* on the concentration. This dependence is shown in fig. 6.

In table 3 a comparison is given between the excess energy calculated by the HNC and MSA theories and the present lattice model. The agreement between them is excellent for dilute solutions in spite of the fundamental differences in the assumptions. The deviation at higher concentration is expected to be due both to the lack of any hard-core repulsion in the lattice model and to the neglect of repulsion terms in
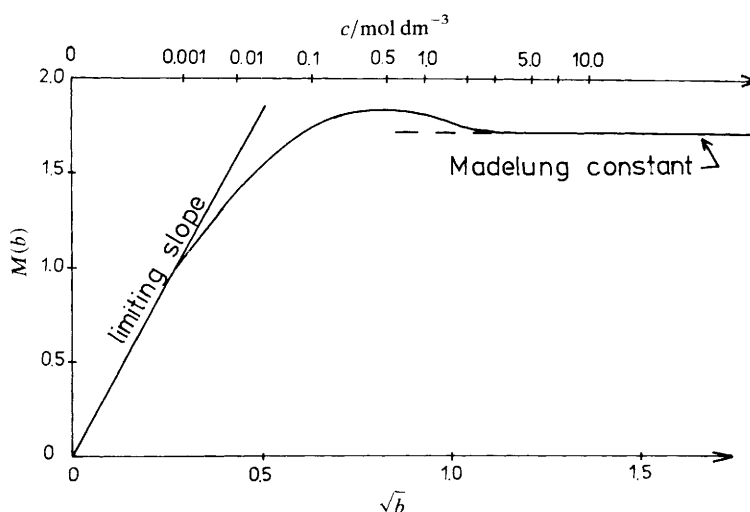

FIG. 6—Concentration dependence of the Mandelung constant of a distorted body-centred cubic lattice.

TABLE 3.—COMPARISON OF THE EXCESS ENERGY OF 1:1 ELECTROLYTES CALCULATED BY DIFFERENT THEORIES

	$-E^{ex}/\mathrm{J\ mol^{-1}\ dm^{-3}}$		
$c/\mathrm{mol\ dm^{-3}}$	HNC$^\alpha$ ($a = 0.46$ nm)	MSA$^\alpha$ ($a = 0.46$ nm)	this work ($a = 0$)
0.002	246	245	246
0.02	694	685	698
0.2	1632	1625	1823
1	2601	2581	3126

^{a} See ref. (4b).

eqn (30). Both deficiencies can be eliminated with not too great difficulties by refining the lattice model, which we plan to do in the future.

Qualitatively it is evident that, while the concentration dependence of thermo-dynamic quantities follows square-root laws in dilute solutions due to the common effect of the concentration dependence of $M(b)$ and r_0, at higher concentrations it will go over into cube-root laws, since $M(b)$ becomes independent of concentration and the cube-root dependence of r_0 will predominate.

There are some arguments in the literature [see *e.g.* ref. (3c)] which conclude that the cube-root concentration dependence of some thermodynamic parameters of electrolytes, observed in many cases within a broad concentration range, should not be interpreted as a sign of a lattice-like distribution of ions, since it may equally well be a consequence of hard-core effects even in the primitive model. However, making allowance for this possibility, the present results on both the oscillations in the charge cloud and the concentration dependence of the excess energy support the opinion that the cube-root concentration dependence is a manifestation of the development of lattice-like structures.

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