

Calculations on the "Restricted Primitive Model" for 1-1 Electrolyte Solutions

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This paper concerns the "restricted primitive model" of 1-1 aqueous electrolyte solutions at concentrations up to 2.0M. Monte Carlo data are compared with several recent theoretical treatments: those based on the hypernetted-chain (HNC) equation and the Percus-Yevick-Allnatt (PYA) equation, the mean spherical model, and the mode expansion and γ -ordering approaches. Some new theoretical calculations are reported. The hypernetted-chain treatment appears to be the most successful of the integral equation theories. Of particular interest is the observation of charge oscillation in the radial distribution functions in both the HNC and Monte Carlo calculations. It is also noted that the cube-root concentration dependence of the deviation from ideality, previously observed for real systems, occurs also in accurate treatments of the primitive model. When the diameter of the ions is sufficiently large, the thermodynamic properties of the restricted primitive model approach those of the corresponding uncharged system at very moderate concentrations.

I. INTRODUCTION

This article concerns the so-called "restricted primitive model" of a 1-1 electrolyte solution: that is, charged hard spheres of equal size in a continuum dielectric. This is the model on which the Debye-Hückel theory is based, although that theory introduces further serious approximations in calculating thermodynamic properties of the model system. Recently this model and others have been examined using some integral equation methods.¹⁻³ On the basis of tests of internal consistency, Rasaiah and Friedman came to the conclusion that, for a 1-1 aqueous electrolyte at concentrations up to 1.0M, the analog of the hypernetted-chain (HNC) equation is superior to that of the Percus-Yevick equation as derived by Allnatt.⁴ The latter equation shall henceforth be referred to as PYA to emphasize its distinction from the usual PY equation.^{1,2}

Meanwhile the Monte Carlo method has been used to produce thermodynamic data for the restricted primitive model.^{5,6} An "aqueous" perfectly symmetrical 1-1 electrolyte has been examined in some detail. A preliminary comparison⁵ of these data with the HNC and PYA results (which were interpolated to the value of ionic diameter used in the Monte Carlo study) indicated good agreement.

This paper reports a further more detailed discussion of the two different approaches. For this purpose, the HNC and PYA equations were solved anew using the same concentrations and parameters as those of the Monte Carlo (MC) work and were extended in concentration up to 2M to match the MC data. Recently another integral equation, that of the so-called mean spherical model, MSM, has been applied to electrolytes,⁷ and analytical expressions have been obtained for the excess internal energy and osmotic pressure. These expressions are evaluated below using parameters identical to those of the MC study.

Another recent contribution to the field has been the development by Andersen and Chandler⁸ of the so-called "mode expansion" method (MEX) and its application to the restricted primitive model of an electrolyte. This is briefly described later in the paper. Andersen and Chandler have evaluated the osmotic coefficients for the particular parameters used in the Monte Carlo experiments. Stell has discussed the relationship of this theory to a particular graphical expansion scheme (γ ordering) developed by Lebowitz, Stell, and Baer.⁹

The chief methods used in this paper have been described elsewhere.^{1,5} All the ion diameters were taken to be 4.25 Å, and the temperature was 298.0°K. The dielectric constant ϵ was taken as 78.5 to simulate water. It is important to note that the excess energy values U reported here assume that the ionic radii and the dielectric constant of the solvent are independent of temperature. This means that the interionic pair potential is temperature independent. The equations which contain U are also based on this assumption. (The dielectric constant of real water varies with temperature, of course; it is easy to correct the reported energy values U for this effect.^{2,5})

II. MONTE CARLO CALCULATIONS

The basic quantities obtained from the MC calculations are the configurational energy U and values of the radial distribution functions $g_{ij}(r)$. The average configurational energy in the canonical ensemble is given by

$$\langle U \rangle = \frac{\int_{\mathbf{v}} U(\mathbf{q}) \exp[-\beta U(\mathbf{q})] d\mathbf{q}}{\int_{\mathbf{v}} \exp[-\beta U(\mathbf{q})] d\mathbf{q}}, \quad (2.1)$$

where $U(\mathbf{q})$ is the configurational energy of the N -particle configuration \mathbf{q} , with the particles confined

TABLE I. The effect of the range of integration on the thermodynamic properties and moment conditions for 1-1 electrolytes in the HNC approximation. $T=298^\circ\text{K}$, $\epsilon=78.5$, $\partial\epsilon/\partial T=0$.^a

C_2 Moles per liter	ϕ_v		$-U/NkT$		Δ_0		Δ_2	
	$N=512$	1024	512	1024	512	1024	512	1024
0.1	0.9454	0.9453	0.0268	0.0268	0.560	0.301	3.72	0.067
0.5	0.9921	0.9923	0.4505	0.4503	0.311	0.472	-0.431	0.040
1.0	1.0923	1.0926	0.5456	0.5447	0.067	0.558	-3.63	0.138
1.5	1.2155	1.2159	0.6054	0.6043	0.153	0.631	-3.06	0.261
2.0	1.3616	1.3616	0.6488	0.6488	0.776	0.666	3.17	0.367

^a Δ_0 and Δ_2 are defined in Ref. 12. U/NkT corresponds exactly to E^{ex}/ckT of Ref. 12.

to a box of volume V . In Monte Carlo calculations only rather small values of N can be used. The results reported here were obtained from calculations with $N=32$, 64, and 200, afterwards extrapolating against $1/N$ to $1/N=0$. As is usual in MC work, the errors due to the small values of N were reduced by using periodic boundary conditions for the (cubic) box of volume V . Using the method of Metropolis *et al.*,¹⁰ the MC method estimates $\langle U \rangle$ by averaging U over an appropriately distributed chain of configurations. Because of the symmetry of the model chosen, there are only two distinct pair functions,

$$\begin{aligned} g_A(\mathbf{r}) &= g_{++}(\mathbf{r}) = g_{--}(\mathbf{r}), \\ g_B(\mathbf{r}) &= g_{+-}(\mathbf{r}) = g_{-+}(\mathbf{r}). \end{aligned} \quad (2.2)$$

Values of these pair functions may be extrapolated to give the pair functions $g_A(\mathbf{a}+)$, $g_B(\mathbf{a}+)$ at the contact diameter \mathbf{a} of the ions, i.e.,

$$g(\mathbf{a}+) = \lim_{\epsilon \rightarrow 0} g(\mathbf{a}+\epsilon), \quad \epsilon > 0.$$

By applying the virial theorem, one may express the osmotic coefficient in terms of these pair functions. The osmotic coefficient so derived, ϕ_v , may be written

$$\phi_v - 1 = (\langle U \rangle / 3NkT) + \text{CONTACT}, \quad (2.3)$$

where

$$\text{CONTACT} = (\pi N a^3 / 3V) [g_A(\mathbf{a}+) + g_B(\mathbf{a}+)], \quad (2.4)$$

and N is the total number of ions in a volume V at the temperature T . The CONTACT term is again discussed below.

In what follows (Sec. IV) these quantities are compared with the results of the several different recent theoretical treatments of the restricted primitive model (Sec. III). For this purpose the MC data⁵ have been critically re-examined. The chief alteration is that in extrapolating the results to $1/N=0$, the computations with only $N=16$ ions have now been ignored. It appeared that the dubious results for these very small systems were distorting the extrapolations; without them, linear extrapolations appear satisfactory. An error in the earlier analysis of the results was also

corrected. Some new runs have been carried out. These things have in fact not led to any noticeable changes from the results reported previously, but the numbers now reported (in Tables II and III) should be regarded as a refinement of the earlier data.

III. THEORETICAL RESULTS

The MC results are compared with numerical solutions of the HNC and PYA integral equations, with an analytical solution of the MSM integral equation, and with some results of the MEX theory. These theoretical results are first discussed in turn.

A. HNC and PYA Equations

The methods of numerical solution of the HNC and PYA equations have already been described in detail.¹ The calculations were repeated for the parameters used in the MC study. As in the previous work the spacing \hat{r} was $\hat{r}=0.015\kappa^{-1}$, where κ^{-1} is the usual Debye length (i.e., $\kappa^2=4\pi e^2 N/\epsilon kTV$). However, the number, \mathcal{N} , of points used in the numerical procedure was here increased from 512 to 1024 to minimize the contributions of the tails of the pair distribution functions $g_{ij}(\mathbf{r})$.

Because of uncertainties in the asymptotic forms of the pair functions, the effect of the continuation in $g_{ij}(\mathbf{r})$ beyond $r=r_{\max}$ was ignored. To assess the resulting error, the HNC equation has been solved with the same spacing \hat{r} and the same number of iterations, but with $\mathcal{N}=512$ instead of $\mathcal{N}=1024$. The thermodynamic properties ϕ_v and U/NkT (discussed below) and the deviations Δ_0 and Δ_2 from the zeroth and second moment conditions¹¹ are given in Table I, for both values of \mathcal{N} . In each case, contributions to U [cf. Eq. (3.1) below] and to Δ_0 and Δ_2 (defined elsewhere¹²) extended out only to $r_{\max}=0.015\mathcal{N}/\kappa$, rather than to $r \rightarrow \infty$. It can be seen in Table III that the errors due to truncation of the pair functions are small; in particular, they are smaller than the standard error in the MC results.

Since the numerical solution of the integral equations leads to the pair functions, it is convenient to rewrite the excess energy U [cf. Eq. (2.1)] in terms of these

TABLE II. Comparison of MC results for U/NkT and "CONTACT" with results from the HNC, PYA, and MSM theories, with $a = 4.25 \text{ \AA}$, $\epsilon = 78.5$, $\partial\epsilon/\partial T = 0$, $T = 298.0^\circ\text{K}$.

C_2^a Moles per liter	$-U/NkT$				CONTACT			
	MC	HNC	PYA	MSM	MC	HNC	PYA	MSM
0.00911	0.1029±0.0013	0.1014	0.1014	0.0992	0.0044±0.0007	0.0041	0.0041	0.0017
0.10376	0.2739±0.0014	0.2714	0.2712	0.2675	0.0359±0.0011	0.0357	0.0351	0.0203
0.42502	0.4341±0.0017	0.4295	0.4285	0.4264	0.1217±0.0045	0.1228	0.1194	0.0867
1.0001	0.5516±0.0016	0.5447	0.5418	0.5405	0.2777±0.0045	0.2741	0.2595	0.2191
1.9676	0.6511±0.0020	0.6460	0.6376	0.6362	0.5625±0.0088	0.5668	0.5240	0.4878

^a This is the stoichiometric molarity of the electrolyte.

functions,¹³

$$\frac{U}{NkT} = \frac{1}{4}\kappa^2 \int_0^\infty [g_A(r) - g_B(r)] r dr, \quad (3.1)$$

where κ^{-1} is again the Debye length. The CONTACT term and the (virial theorem) osmotic coefficient ϕ_v can again be calculated according to (2.4) and (2.3). The osmotic coefficient can alternatively be calculated using the compressibility equation, as discussed elsewhere^{1,2}; let us call the osmotic coefficient so evaluated, ϕ_c . While ϕ_v and ϕ_c would be identical for an exact solution of the problem, they will differ for approximate treatments. The HNC results, ϕ_v^{HNC} and ϕ_c^{HNC} , and the PYA results, ϕ_v^{PYA} and ϕ_c^{PYA} , are reported in Tables II and III.

B. MSM Equation

The "mean spherical model" leads to an integral equation which, for the restricted primitive model, has been solved by Waisman and Lebowitz.⁷ It is convenient to introduce the abbreviation $x = \kappa a$, and to define a quantity B ,

$$B = -(1/x)[1+x - (1+2x)^{1/2}]. \quad (3.2)$$

In terms of B , the results of the MSM theory may be written

$$U^{\text{MSM}}/NkT = x^2 BV/4\pi a^3 N, \quad (3.3)$$

$$g_A^{\text{MSM}}(a+) = g^0(a+) - (e^2/akT)(1+B),$$

$$g_B^{\text{MSM}}(a+) = g^0(a+) + (e^2/akT)(1+B), \quad (3.4)$$

where $g^0(a+)$ is the corresponding distribution function at "contact" for uncharged hard spheres at the same density. It appears that these results (3.4) are rather unrealistic: In fact the second terms in $g_A(a+)$ and $g_B(a+)$ just cancel each other in (2.4) and so make no contribution to the CONTACT term of ϕ_v (2.3). The CONTACT term is therefore simply that for an uncharged system. Moreover, the energy term U would just vanish for the uncharged system, so that (2.3), (3.3), and (3.4) lead to

$$\phi_v^{\text{MSM}} = \phi_v^0 + (x^2 BV/12\pi a^3 N), \quad (3.5)$$

where ϕ_v^0 is the (virial theorem) osmotic coefficient of the uncharged system.

Waisman and Lebowitz⁷ have also derived osmotic coefficients ϕ_E , in the MSM approximation, from (3.3) by using the thermodynamic relations,

$$\beta(F_{\text{ex}} - F_{\text{ex}}^0) = \int_0^\infty U d\beta, \quad (3.6)$$

$$\phi_E - 1 = \frac{\partial(\beta F_{\text{ex}}/N)}{\partial \ln(N/V)_T}, \quad (3.7)$$

where $\beta = 1/kT$, F_{ex} is the excess Helmholtz free energy, and the superscript zero again refers to the uncharged system. This leads to

$$\phi_E^{\text{MSM}} = \phi^0 + (V/4\pi a^3 N) \times [x + x(1+2x)^{1/2} - \frac{2}{3}(1+2x)^{3/2} + \frac{2}{3}]. \quad (3.8)$$

TABLE III. Comparison of MC results for the osmotic coefficient with the HNC, PYA, MSM, and MEX theoretical treatments. All $a = 4.25 \text{ \AA}$, $\epsilon = 78.5$, $T = 298^\circ\text{K}$.

C_2 Moles per liter	Osmotic coefficient							
	ϕ_v^{MC}	ϕ_v^{HNC}	ϕ_c^{HNC}	ϕ_v^{PYA}	ϕ_c^{PYA}	ϕ_v^{MSM}	ϕ_E^{MSM}	ϕ^{MEX}
0.00911	0.9701±0.0008	0.9703	0.9705	0.9703	0.9705	0.9687	0.9709	0.9707
0.10376	0.9445±0.0012	0.9453	0.9458	0.9452	0.9461	0.9312	0.9454	0.9452
0.42502	0.9774±0.0046	0.9796	0.9800	0.9765	0.9844	0.9446	0.9806	0.9787
1.0001	1.094±0.005	1.0926	1.0906	1.0789	1.1076	1.039	1.097	1.091
1.9676	1.346±0.009	1.3514	1.3404	1.3114	1.386 ^a	1.2757	1.3595	1.342 ^a

^a There is some uncertainty in the last digit.

The Percus-Yevick compressibility equation has been used to calculate a ϕ^0 , and thus ϕ_E^{MSM} .

These results can be used to examine the self-consistency of the MSM results. For the ionic diameter and concentrations studied, the difference between ϕ_v^0 and ϕ_c^0 is small. Hence the difference between ϕ_v and ϕ_E for the restricted primitive model in the MSM approximation is essentially the difference between the second terms on the right of Eqs. (3.5) and (3.8). Expanding these we can write

$$\phi_v^{\text{MSM}} = \phi_v^0 + (V/4\pi a^3 N) \times \left[-\frac{1}{6}x^3 + \frac{1}{6}x^4 - (5/24)x^5 + \dots \right], \quad (3.9)$$

$$\phi_E^{\text{MSM}} = \phi^0 + (V/4\pi a^3 N) \times \left(-\frac{1}{6}x^3 + \frac{1}{4}x^4 - \frac{3}{8}x^5 + \dots \right). \quad (3.10)$$

The x^3 terms give the "limiting law." We see that discrepancies occur already in the first term beyond the limiting law. The compressibility equation for the osmotic pressure in the MSM approximation leads¹⁴ to the same value as it would for uncharged hard spheres, $\phi_c^{\text{MSM}} = \phi_c^0$.

It may be noted that in the MSM theory $\beta(F_{\text{ex}} - F_{\text{ex}}^0)$ depends on temperature and concentration only through $x \equiv \kappa a$ [cf. (3.6) and (3.3)]. It is shown in an Appendix that when this is so,

$$\ln \gamma_{\pm} = \ln \gamma^0 + (U/NkT). \quad (3.11)$$

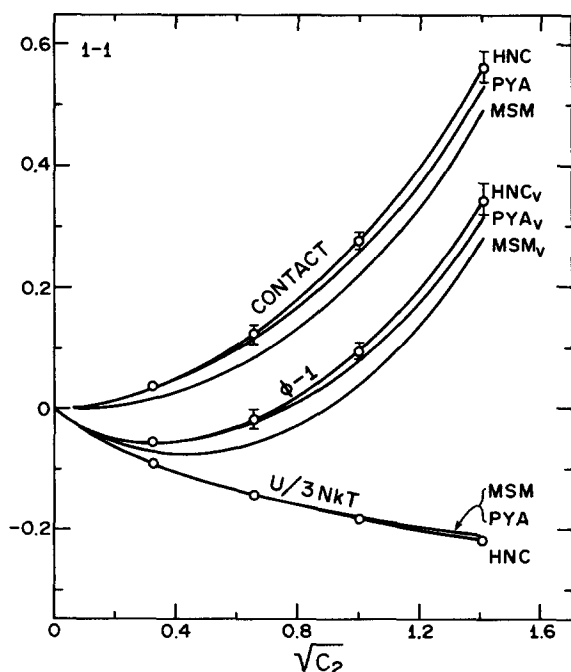


FIG. 1. MC and theoretical values of the configurational energy U , CONTACT [cf. Eqs. (2)-(4)], and the virial theorem osmotic coefficient ϕ . The error bars shown for some of the MC points represent three standard errors; the errors on U are very small on this scale. HNC_v identifies that curve as $\phi_v^{\text{HNC}} - 1$, etc. More detailed comparisons may be found in Figs. 2 and 3. $a = 4.25 \text{ \AA}$; $\epsilon = 78.5$; $T = 298^\circ\text{K}$; \circ , MC.

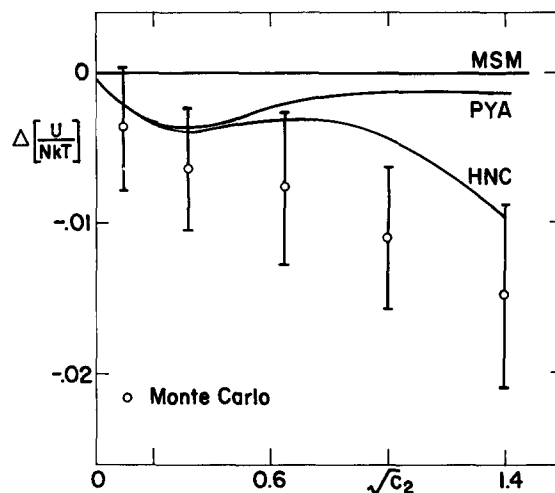


FIG. 2. Excess energy results. The graph shows only differences from the MSM predictions and thus displays, on an enlarged scale, only the differences between the various results. The MC error bars are again ± 3 standard errors.

This provides a convenient route between the activity coefficients and the excess energy U for such systems. The condition on $\beta(F_{\text{ex}} - F_{\text{ex}}^0)$ is *not* met by all theories, however; for example, it doesn't apply to the theory of Stillinger and Lovett.¹¹

C. MEX Theory and γ Ordering

Andersen and Chandler, who developed the "mode expansion" theory^{8a} have applied it to the restricted primitive model.^{8b} In this theory one again considers a reference system which consists of uncharged hard spheres, and the Coulombic interactions are regarded as a perturbation to that reference system. MEX theory expresses the effect of these interactions on the free energy as an infinite series of terms (modes) involving Fourier transforms of the perturbation potential and of correlation functions in the reference system.

The above specification leaves some freedom in the choice of the perturbation potential in the physically inaccessible region where spheres overlap. The choice influences the separate terms of the mode expansion series, however, and in a recent development^{8b} this freedom of choice has been used to "optimize" the convergence of the series. In this version of the theory it turns out that retention (and optimization) of only the first term of the perturbation series for the free energy, and use of the Percus-Yevick approximation for the reference system, leads to the MSM approximation. Andersen and Chandler have carried out calculations which include a second term in the free energy perturbation, and their results are compared here with the MC results.

Stell⁹ has demonstrated the close relationship between MEX and the γ -ordering scheme of Stell and Lebowitz.⁹ The numerical MEX results reported here for a 1-1 electrolyte are identical to the first-order results in the γ -ordered expansion.

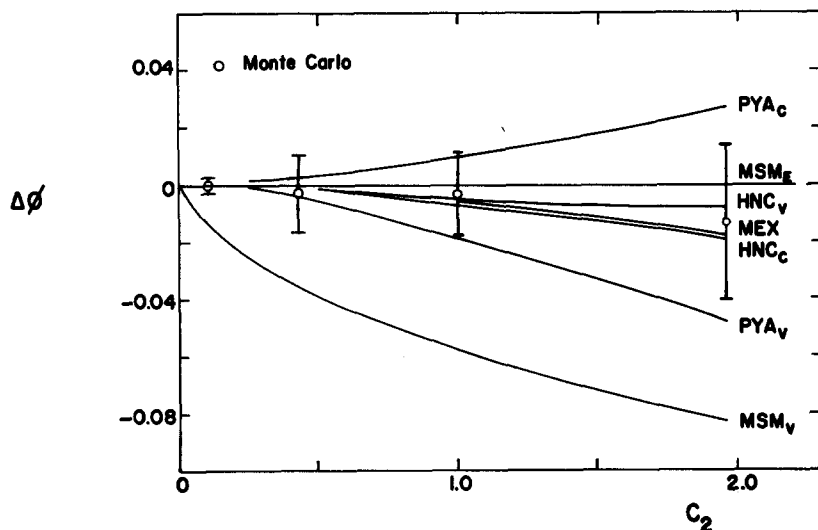


FIG. 3. Osmotic coefficient results compared on enlarged scale, as difference from the ϕ_E^{MSM} result. The MC error bars show three standard errors.

IV. DISCUSSION

The results for the energy U , the CONTACT term (2.4), and the osmotic coefficient ϕ are compared in Tables II and III and Fig. 1, and in greater detail in Figs. 2 and 3. They are discussed below. Then in the remainder of this section and in Figs. 4–6 some other interesting features of the results are discussed.

A. Excess Energy

On the scale of Fig. 1, the various excess energies very nearly coincide. A more detailed comparison is, however, shown in Fig. 2. (In all of these diagrams and tables, C_2 is the molar concentration of the ionic solute.) The MSM results have been used as a convenient base line, and the figure shows the discrepancy of other results from those of the MSM approximation. The error limits on the MC results are *three* standard errors (i.e., a 99.7% confidence limit).

The MSM predictions are not consistent with the MC results. The PYA theory gives reasonable agreement at the lower concentrations but then deviates seriously. The HNC results are definitely closer to the MC results, giving fair agreement over the whole concentration range, but they appear to be systematically higher in energy.

B. Osmotic Coefficient

To obtain the osmotic coefficient from (2.3) one requires, besides the energy, the CONTACT term (2.4) and thus the values $g_A(\mathbf{a}+)$ and $g_B(\mathbf{a}+)$ of the pair functions at ionic contact. The MC values for these were obtained by a least squares extrapolation of $g_A(r)$ and $g_B(r)$ for values of r only slightly greater than \mathbf{a} ; the resulting contact values were subsequently extrapolated to $1/N=0$. The resulting error limits on

CONTACT and ϕ are large compared to those on the energy.¹⁵ The error bars in Figs. 1 and 3 again show 3σ limits.

Figure 3 shows a detailed comparison of the osmotic coefficient results, again using an MSM result as a base line. Both ϕ_v and ϕ_c of the HNC theory agree well with the MC computations over the whole concentration range, and so does the two-mode result of the MEX theory. The PYA and MSM results for ϕ_c

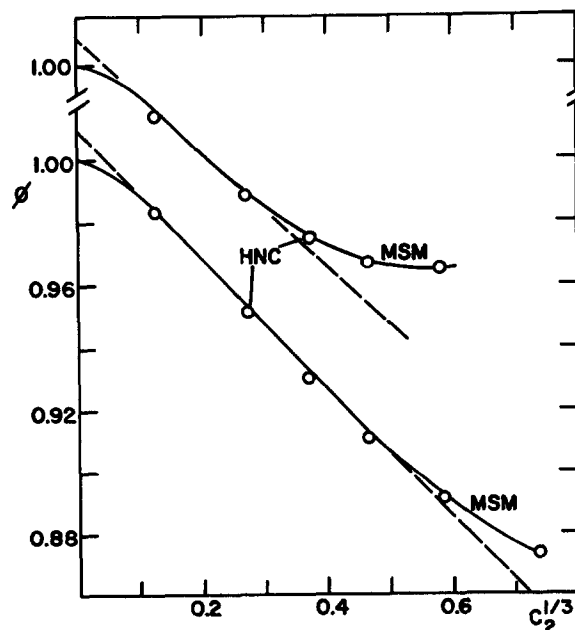


FIG. 4. Cube-root dependence of the osmotic coefficients for the restricted primitive model with diameters $a=3.87 \text{ \AA}$ (upper curve) and $a=2.41 \text{ \AA}$ (lower curve). The ordinates of the upper curve are displaced by 0.03. In this range of concentration the MC, MSM, and HNC results all agree excellently and are presumably accurate results for the restricted primitive model.

agree less well, mainly because the CONTACT term (2.4) is too poorly represented in these theories. We may recall that in the MSM theory only the uncharged hard-sphere pair function $g^0(\mathbf{a}+)$ contributes to CONTACT; such an approximation becomes worse for more highly charged ions or lower dielectric constant, but it improves with increasing ionic size.

The mean ionic activity coefficients γ_{+-} may be obtained from ϕ by integration of the McMillan-Mayer form of the Gibbs-Duhem equation.^{1,5} The deviations of ϕ for the various theories thus reappear in γ_{+-} ; we have therefore not displayed this comparison here.

C. Cube-Root Dependence

It has been pointed out^{16,17} that, at least for 1-1 electrolytes, *experimental* values of $\ln\gamma_{+-}$ are linear in the *cube root* of the concentration over an extensive concentration range. Such behavior extends typically from about 0.001M up to 0.05M or higher. It was suggested by Frank and Thompson¹⁶ that this may correspond to the existence of a "diffuse lattice" structure, rather than a Debye structure, in this concentration range.

The cube-root behavior of $\ln\gamma_{+-}$ implies a similar behavior for the osmotic coefficient ϕ (although over a slightly smaller concentration range). Data on ϕ for the primitive model with two different ionic diameters are plotted against $C_2^{1/3}$ in Fig. 4. In this concentration range the results of the HNC, MSM, MEX, and MC

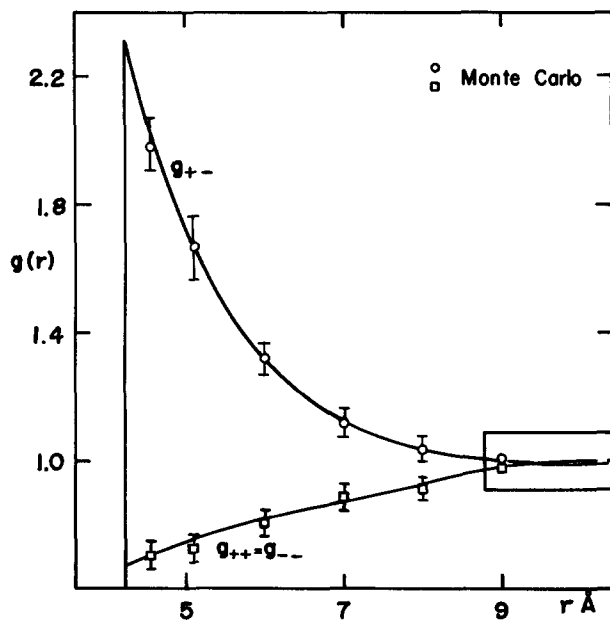


FIG. 5. Like and unlike pair correlation functions at 1.968M. The lines show the HNC prediction. A few of the MC points ($N=200$ ions) are shown for comparison (± 3 standard errors). Note the charge inversion near $r=10$ Å; the boxed section is shown, greatly magnified, in Fig. 6.

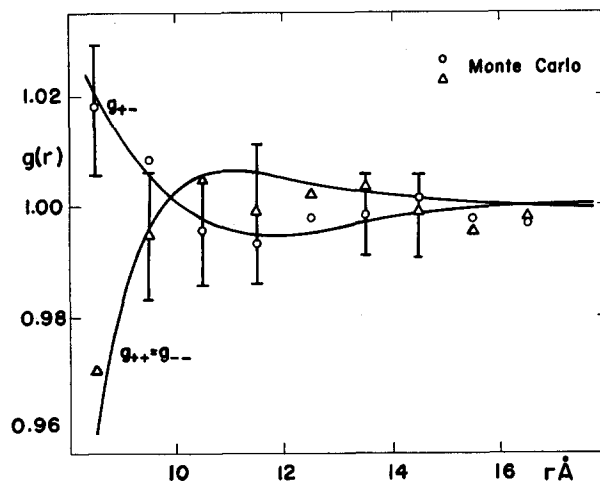


FIG. 6. Charge inversion region of Fig. 5 enlarged, with all the relevant MC points. Some typical error bars are shown, indicating ± 1 standard error.

calculations are in close agreement, so any of them might be used (cf. Fig. 3). The linear regions are evident and occur in the concentration range observed experimentally.

Since these curves arise from an accurate treatment of the *primitive* model, it is clear that no additional forces need to be assumed in order to explain the extensive cube-root behavior. The slopes and intercepts of these curves are slightly larger in magnitude than most of those observed¹⁶ experimentally.

D. Oscillations in the Ion Atmosphere

Figure 5 shows the HNC and some of the MC results for the pair functions at 1.968M. The agreement is excellent.

It is intuitively obvious that the radial charge distribution must become oscillatory at sufficiently high concentration. Stillinger and Lovett¹¹ have derived a "second moment condition" that must be satisfied by the radial charge distribution $g_A(r) - g_B(r)$; they show that for the restricted primitive model the condition can be satisfied only if $g_A(r) - g_B(r)$ changes sign at least once, whenever $\kappa a \geq 6^{1/2}$. This represents an upper concentration limit for the onset of oscillations. Previously, Kirkwood and Poirier¹⁸ had predicted the onset of oscillations at $\kappa a = 1.03$, while Outhwaite¹⁹ gives an estimate of $\kappa a \geq 1.241$ for the presence of oscillations. These estimates are based on approximations of which the accuracy is not known in the concentration range of interest.

The existence of oscillations in the charge density about a given ion has recently been demonstrated for the HNC solutions for the primitive model of 1-1, 2-1, 3-1, and 2-2 electrolytes.¹² For 1-1 electrolytes no oscillatory behavior in the radial charge distribution occurs in the HNC calculations up to 0.5M ($\kappa a = 1.0$)

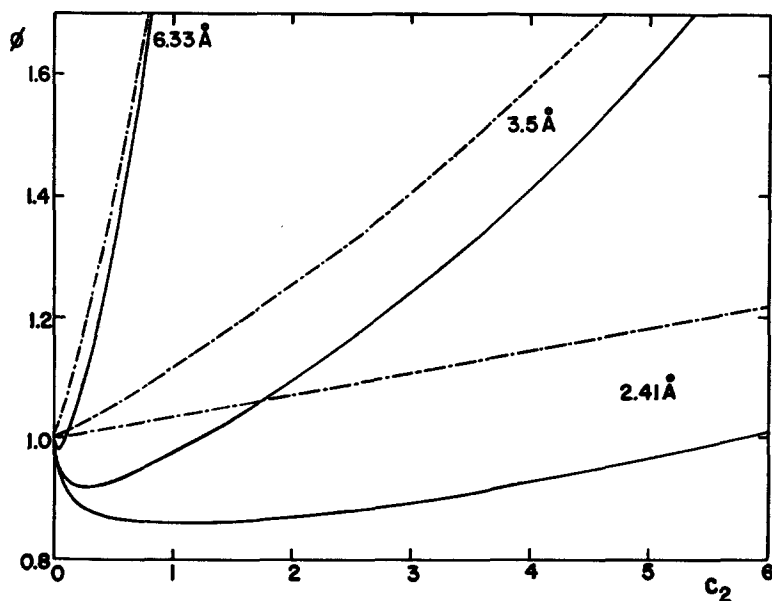


Fig. 7. The MSM osmotic coefficients ϕ_E for the restricted primitive model (solid line) compared with the values ϕ^0 they would have if the charges were removed from the ions (dashed line). The sets of curves are labeled according to the ionic diameters.

with the present parameters. A mild oscillation is noted in the $1.0M$ ($\kappa a = 1.4$) HNC result, but the MC values of $g(r)$ are too imprecise to make comparisons. At $1.968M$ ($\kappa a = 1.98$), the crossing of the HNC pair functions is shown in Fig. 5. In Fig. 6 that part of the pair function curves where charge reversal occurs is looked at in greater detail. The MC points show data from a 200-ion simulation. In spite of the statistical errors in the MC results, the evidence suggests that these "experimental" points do show a charge oscillation, and that it is extraordinarily similar to that predicted by the HNC calculations.

V. CONCLUSION

Hopefully, one may regard the MC calculations as giving a good approximation to experimental results for the primitive model, and if so one can use them to discriminate between the various theoretical treatments. This is rather demanding, since the theoretical predictions don't differ greatly at the low concentrations studied.

Good agreement was noted between the HNC and MC results over the entire concentration range, and it seems likely that they are giving a pretty accurate description of the thermodynamics of the primitive model of electrolytes, at least for 1-1 "aqueous" solutions. Either method could be used in studying the effect of modifications to the interionic force law: the HNC method is much the more economical from the standpoint of computing time.

The mode expansion (MEX) values of the osmotic coefficient leave little to be desired. Unfortunately no energy values are presently available for this theory, so it is difficult to say how its results compare with those of the HNC theory, nor has it been possible for us to

check the self-consistency of the osmotic coefficients.²⁰ The PYA and MSM results definitely agree less well with the MC data, but the MSM equation has the distinct advantage that its results are available in a remarkably simple closed form. Moreover the errors in the thermodynamic properties calculated from the energy equation are small enough to make the theory useful for 1-1 electrolytes at least in a qualitative or semiquantitative sense. The chief drawback is that the MSM results are available only for spheres of equal size. In spite of this the MSM theory can be applied to clarify the roles of some of the competing forces that are present in real solutions. We consider one example of this by calculating ϕ_E for three different model electrolytes with diameters equal to 2.41, 3.5, and 6.6 Å. They correspond roughly to the distances of closest approach of oppositely charged ions in LiCl, CsCl, and Pr_4NCl . In Fig. 7 the osmotic coefficients ϕ_E for the charged systems are compared with the osmotic coefficients ϕ^0 that they would have if the charges were removed. It is apparent that ϕ_E approaches ϕ^0 as the concentration increases and with increasing rapidity as the ionic diameters also increase. In this context we note that F_{ex}^0 forms a strict upper bound on the excess Helmholtz free energy for charged hard spheres of equal size.²¹ What is remarkable, however, is that at a concentration as low as $1M$ the effect of the charges on the osmotic coefficients of the model electrolyte with the biggest ions is almost completely wiped out. We suggest that qualitatively the same conclusions could be drawn about real electrolytes, for example aqueous solutions of some tetraalkyl ammonium halides and other large uni-univalent electrolytes with ions of equal or nearly equal size.

In order to test the range of validity of the various

theoretical approaches, stronger interactions should be studied. Higher valence electrolytes, both symmetrical and unsymmetrical, have been under study by the various techniques,¹⁴ and reports on these studies will appear.

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APPENDIX

We examine $\beta(F_{\text{ex}} - F_{\text{ex}}^0)$ for some approximate solution to the restricted primitive model. We assume that (\mathbf{a} being fixed) this quantity varies only through its dependence on $x = \kappa \mathbf{a}$, as is the case for the MSM approximation,

$$\beta(F_{\text{ex}} - F_{\text{ex}}^0) = f(\kappa), \quad (\text{A1})$$

say. Now providing that the dielectric constant ϵ is independent of temperature,

$$\kappa \propto (\beta C)^{1/2}, \quad (\text{A2})$$

where C is the ionic number density, and it follows that:

$$\begin{aligned} \{\partial[\beta(F_{\text{ex}} - F_{\text{ex}}^0)]/\partial \ln \beta\}_C & \\ &= \{\partial[\beta(F_{\text{ex}} - F_{\text{ex}}^0)]/\partial \ln C\}_\beta \\ &= N(\ln \gamma_{\pm} - \ln \gamma^0). \end{aligned} \quad (\text{A3})$$

However

$$\{\partial[\beta(F_{\text{ex}} - F_{\text{ex}}^0)]/\partial \beta\}_C = \{\partial[\beta F_{\text{ex}}]/\partial \beta\}_C = U, \quad (\text{A4})$$

so that we obtain the desired result

$$\ln \gamma_{\pm} = \ln \gamma^0 + (U/NkT). \quad (\text{A5})$$

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