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Equilibrium Properties of Ionic Solutions; The Primitive Model and its Modification for Aqueous Solutions of the Alkali Halides at 25°C

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The hypernetted-chain (HNC) equation, which is accurate up to concentrations of $1M$, is applied to test the validity of some models that have been used previously to describe ionic solutions. The osmotic coefficient (ϕ) calculated for the primitive model, with the distances of closest approach (a_{ij}) chosen to fit the experimental data at low concentrations ($<0.1M$), is too large in comparison with experiment at $1M$. This contradicts the basic assumption in several hydration theories that have appeared, in which the primitive model contributions to ϕ are assumed, on the basis of approximate theories, to be too small at high concentrations. When the a_{ij} parameters are the sums of the Pauling radii, the characteristic order of the experimental osmotic coefficients of the alkali halides is preserved even when the primitive model contributions have been subtracted out. It is shown that the residual short-range effects necessary to obtain qualitative agreement with the experimental osmotic coefficients and heats of dilution can be represented by a square well, and that the sign and magnitude of the well depth and its temperature coefficient seem to reflect the nature of the overlap contributions of the cospheres around each ion.

I. INTRODUCTION

The numerical solution of Allnatt's integral equations for the correlation functions in ionic systems,[1] from which the equilibrium properties may be obtained, have been described in two recent publications.[2,3] The most extensive computations have been restricted to the primitive model (charged hard spheres),[3] while some preliminary work has also been described for the square-well (or mound) model.[4] All of these calculations, together with several tests for the consistency and accuracy of the results, point to the excellence of the HNC approximation[1] for concentrations up to $1M$ for model parameters suitable for the description of aqueous 1–1 electrolytes at 25°C. In this paper we make a detailed comparison of the results for the primitive model with some of the thermodynamic properties of these electrolytes and conclude that the discrepancies that arise are due to deficiencies in the model rather than deficiencies in the statistical treatment of these systems. The relevance of the square-mound potential to real systems is then discussed, and comparisons between theory and experiment for the excess free energy and excess energy are presented for aqueous solutions of the alkali halides. The success of this modification of the primitive model suggests that it may be a useful description of aqueous electrolyte solutions and that the model parameters reflect the real structural attributes of the environment around an ion.

II. GENERAL CONSIDERATIONS OF MODEL PARAMETERS FOR AQUEOUS IONIC SYSTEMS

The integral equations and methods of solution are applicable to a model system in which (a) the direct potential of an assembly of ions is pairwise additive and (b) the pair component $u_{ij}(r)$ between ions i and j at distance r apart has the general form

$$u_{ij}(r)=e_ie_j/\epsilon r+u_{ij}^*(r), \qquad (2.1)$$

where e_i and e_j are the ionic charges, ϵ the dielectric constant of the solvent, and $u_{ij}^*(r)$ is the short-range potential. Unlike the Debye–Hückel theory, and certain other developments, the short-range interactions do not have to be described in terms of a single cut-off distance, and in principle the present formalism which originated with Mayer[5] is sufficiently powerful to deal with almost any functional form for $u_{ij}^*(r)$ that experiment or theory may suggest. In particular it can be used to discuss many of the short-range effects that

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[1] A. R. Allnatt, Mol. Phys. **8**, 533 (1964).

[2] J. C. Rasaiah and H. L. Friedman, J. Chem. Phys. **48**, 2742 (1968).

[3] J. C. Rasaiah and H. L. Friedman, J. Chem. Phys. **50**, 3965 (1969).

[4] (a) J. C. Rasaiah and H. L. Friedman, J. Phys. Chem. **72**, 3352 (1968). (b) We list here several other computations for these two models for single electrolytes in which theories not directly based on the original Debye–Hückel formalism have been compared with experiment. The Debye–Hückel limiting law plus second virial coefficient (DHLL+S_2) approximation in the Mayer theory applied to the primitive model has been discussed by J. C. Poirier [J. Chem. Phys. **21**, 965, 972 (1953)], E. Haga [J. Phys. Soc. Japan **8**, 714 (1953)], and G. C. Benson [Can. J. Chem. **32**, 802 (1954)]. The collective coordinate treatment of the long-range interactions with a cluster expansion of the short-range effects is described by G. Kelbg [Ann. Physik **9**, 159, 168 (1962)]. For a review see G. Kelbg in *Chemical Physics of Ionic Solutions*, B. E. Conway and R. G. Barradas, Eds. (John Wiley & Sons, Inc., New York, 1966). The lowest-order terms for the thermodynamic properties can be shown to be identical with the DHLL+S_2 approximation in Mayer's theory. At this level of approximation the theory for the square-well model has been compared with experiment for aqeuous solutions of $N(C_3H_7)_4NCl$ at 0°C. The collective coordinate treatment has also been applied by K. B. Eisenthal and W. G. McMillan [J. Chem. Phys. **42**, 11 (1965); **44**, 2542 (1966)] to a model different from those discussed in this paper. Another treatment in which an integral equation for the distribution functions is used with a superposition approximation is discussed by G. Kelbg in a series of papers [Z. Physik. Chem. (Leipzig) **214**, 8, 26, 141, 153 (1960)]. The numerical results for parameters in the square-well model for the tetralkyl ammonium halides (R_4NX) and the primitive model for the alkali nitrates (MNO_3) are comparable to those obtained from the DHLL+S_2 approximation in Mayer's theory. The Born–Green equation with the superposition approximation and certain other assumptions has been solved for the primitive model by U. Möller [Z. Physik. Chem. (Leipzig) **208**, 220, (1958)]. For a review which includes comparison with experiment see H. Falkenhagen and G. Kelbg in *Modern Aspects of Electrochemistry*, J. O'M. Bockris, Ed. (Academic Press Inc., New York, 1969), No. 2.

[5] J. E. Mayer, J. Chem. Phys. **18**, 1426 (1950).

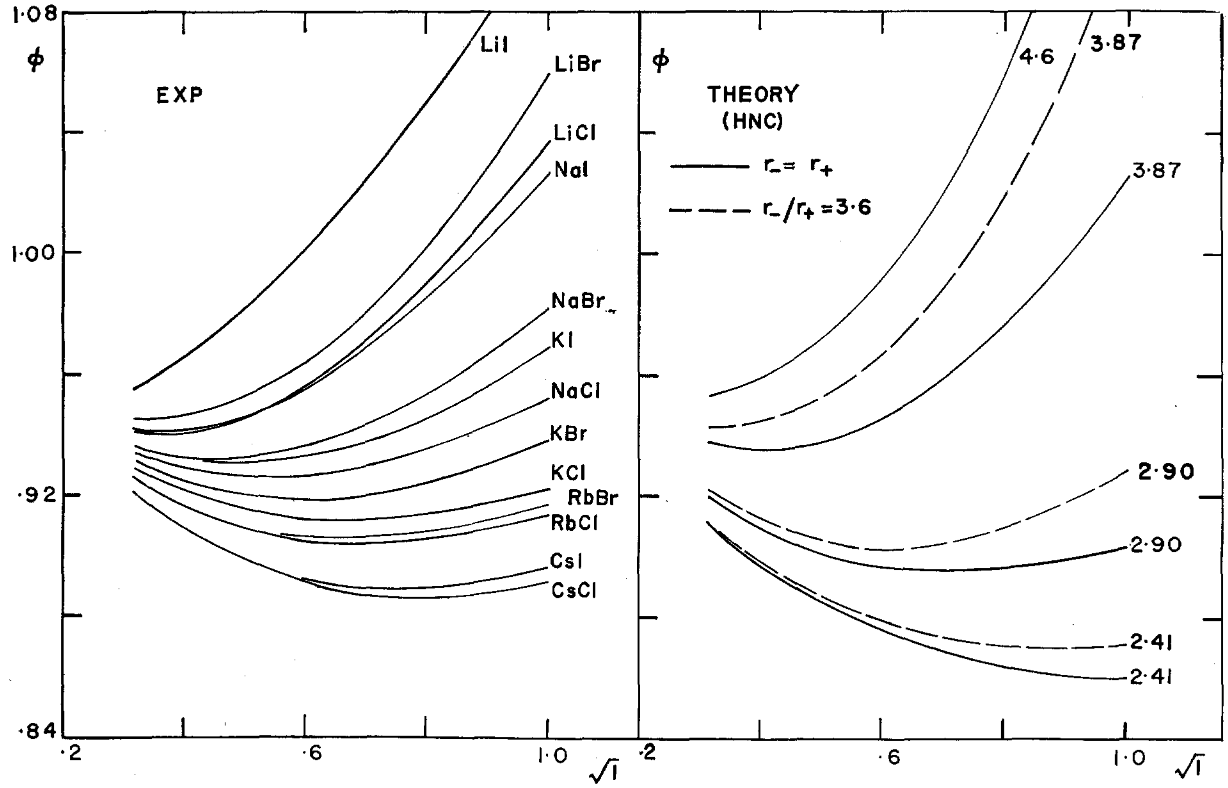

FIG. 1. The theoretical (HNC) osmotic coefficients (ϕ) for a range of a_{ij} parameters in the primitive model compared with the experimental results for aqueous solutions of alkali halides at 25°C. The a_{ij} parameters are the sums of ionic radii (r_i, r_j) which are assumed to be either equal or in the ratio 3·6:1 for oppositely charged ions. The value assumed for a_{+-} is given next to each theoretical curve. I is the ionic strength.

have been proposed to account for the peculiarities of aqueous electrolyte solutions.[6] The chief limitation is that the potential must be pairwise additive. We also note that the calculations pertain to systems at constant temperature T and chemical potential μ_w of the solvent (the McMillan–Mayer system[7]) and that the experimental results, usually obtained at constant temperature and total external pressure, have to be corrected to these states before they can be compared with theory.[8] All of the experimental and theoretical results in this paper are for McMillan–Mayer standard states.

The potential $u_{ij}(r)$ is the free energy required to move a pair of ions i and j through the solvent medium from infinite separation to a distance r apart under isothermal conditions, while $\partial[\beta u_{ij}(r)]/\partial\beta$, where $\beta = 1/kT$ and $-\partial u_{ij}(r)/\partial T$ are the corresponding changes in energy and entropy, respectively, for the process described. In a given state defined by the variables T, μ_w, and $\mathbf{c}$, where $\mathbf{c}$ is the concentration set $(c_1 \cdots c_i \cdots c_\sigma)$ of the σ ionic species in solution, the distribution functions $g_{ij}(r, \mathbf{c})$ are functionals only of $u_{ij}(r)$. The excess free energy per unit volume F^{ex}, the excess pressure P^{ex}, the osmotic coefficient ϕ, and activity coefficient $\gamma_\pm$ are all completely determined by the potential $u_{ij}(r)$. For example, the virial equation for P^{ex} is

$$P^{ex} = -\tfrac{1}{6}\sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma} c_i c_j \int_0^\infty \frac{\partial[u_{ij}(r)]}{\partial \ln r}\, g_{ij}(r)\, 4\pi r^2 dr. \quad (2.2)$$

The osmotic coefficient and the excess free energy are available from P^{ex} through the defining relations

$$\phi - 1 \equiv P^{ex}/ckT, \quad (2.3)$$

$$F^{ex} \equiv ckT \int_0^c (\phi - 1)\, d\ln c', \quad (2.4)$$

where

$$c = \sum_{i=1}^{\sigma} c_i. \quad (2.5)$$

The activity coefficient $\gamma_\pm$ can be obtained from ϕ by integration of the differential relation

$$d[c(1-\phi)] + cd\ln\gamma_\pm = 0 \quad (2.6)$$

which is applicable to systems at constant T and μ_w. It can also be obtained independently from the compressibility equation.[2]

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[6] For a review see H. S. Frank, Z. Physik. Chem. (Leipzig) **228**, 364 (1965).

[7] W. G. McMillan and J. E. Mayer, J. Chem. Phys. **13**, 276 (1945).

[8] (a) J. C. Poirier, J. Chem. Phys. **21**, 965 (1953). (b) H. L. Friedman, J. Chem. Phys. **32**, 1351 (1960).

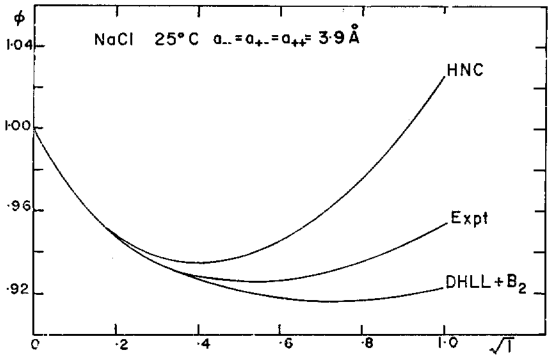

FIG. 2. ϕ for the primitive model compared with experimental results for NaCl in H_2O at 25°C. The a_{+-} parameter has been chosen to fit the experimental data below $0.05M$. $DHLL+S_2$ is the limiting law plus the second virial coefficient in the Mayer theory and is known to fall quite closely to the extended form of the Debye–Hückel theory.

In computing the excess energy per unit volume E^{ex} however, the temperature coefficient of $u_{ij}(r)$ is also required[3]:

$$E^{\text{ex}}=\tfrac{1}{2}\sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma}c_ic_j\int_0^{\infty}\frac{\partial[\beta u_{ij}(r)]}{\partial\beta}g_{ij}(r)\,4\pi r^2dr. \qquad (2.7)$$

Since

$$\frac{\partial(\beta u_{ij})}{\partial\beta}=\frac{e_ie_j}{\epsilon r}\left[1+\frac{\partial\ln\epsilon}{\partial\ln T}\right]+\frac{\partial[\beta u_{ij}^*(r)]}{\partial\beta}, \qquad (2.8)$$

and ϵ and $\partial\ln\epsilon/\partial\ln T$ are, respectively, 78.358 and -1.3679 for water at 25°C,[9] the long-range contributions to the excess energy of aqueous solutions are radically altered by the temperature dependence of the dielectric constant. We will see later that the temperature coefficient of the short-range potential appears to make an equally important contribution to the E^{ex} functions of aqueous ionic solutions.

TABLE I. Comparison of osmotic coefficients of $1M$ aqueous alkali halides with the HNC calculation for primitive model, assuming $r_+=r_-$. For each salt the a_{+-} parameter[a] gives agreement between experiment and the Debye–Hückel theory up to $0.05M$.

		$10^3(\phi-1)$				
		Li⁺	Na⁺	K⁺	Rb⁺	Cs⁺
Cl^-	HNC	91	47	15	−13	−84
	Exp	37	−47	−77	−85	−108
	Diff	54	94	92	72	24
Br^-		102	64	21	−20	−92
		61	−18	−61	−83	−109
		41	82	82	63	17
I^-		289	82	37	−27	−97
		119	27	−31	−76	−104
		170	55	68	49	7
Uncharged hard spheres						
$r_+=r_-=2.3$ Å		HNC	288			
$r_+=1.8$ A, $r_-=2.8$Å		HNC	314			

[a] Harned and Owen, *The Physical Chemistry of Electrolyte Solutions* (Reinhold Publ. Corp. New York, 1957), 3rd ed., Eq. (12-5-2) and Table (12-5-2).

The pressure coefficient of $u_{ij}(r)$ is necessary in the computation of the excess volume V^{ex}:

$$V^{\text{ex}}=\tfrac{1}{2}\sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma}c_ic_j\int_0^{\infty}\frac{\partial[u_{ij}(r)]}{\partial P_0}g_{ij}(r)\,4\pi r^2dr, \qquad (2.9)$$

where

$$\frac{\partial[u_{ij}(r)]}{\partial P_0}=-\frac{e_ie_j}{\epsilon r}\frac{\partial\ln\epsilon}{\partial P_0}+\frac{\partial[u_{ij}^*(r)]}{\partial P_0}, \qquad (2.10)$$

P_0 is the external pressure on the solvent, and $\partial\ln\epsilon/d\ln P_0$ is 47.1×10^{-6} for water at 25°C.[9]

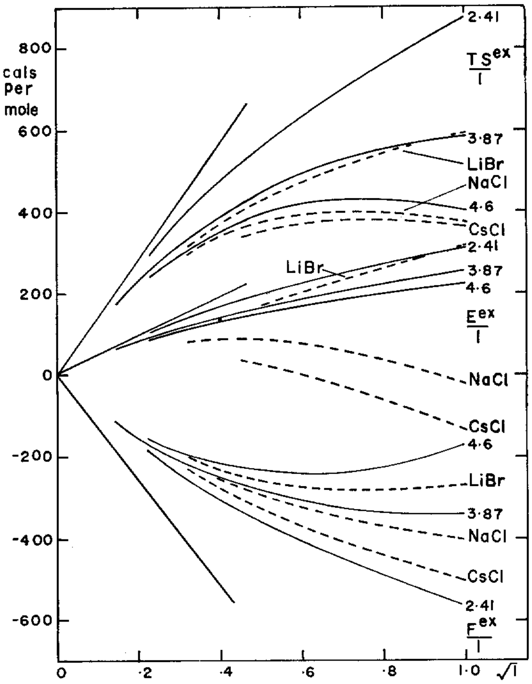

FIG. 3. The thermodynamic functions F^{ex}/I, E^{ex}/I, TS^{ex}/I for the primitive model assuming $r_+=r_-$ compared with the experimental results for aqueous LiBr, NaCl, CsCl. The straight lines represent the Debye–Hückel limiting law for each of the thermodynamic functions considered.

The specification of $u_{ij}^*(r)$ enables the correlation functions $g_{ij}(r)$ that correspond to the analogs of the hypernetted chain (HNC) and Percus–Yevick (PY) equations for ionic systems[1] to be computed with only minor modifications in the numerical procedures described earlier for charged hard spheres.[2] Due to indications of its superior accuracy,[3] only the HNC approximation is considered here. Also the thermodynamic properties reported in this paper are restricted to the

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[9] B. B. Owen, R. C. Miller, C. E. Milnes, and H. L. Cogan, J. Phys. Chem. **65**, 2065 (1961).

osmotic coefficients (or equivalently the excess free energies) and the excess energies of the systems studied. For the latter, the functions $\partial[\beta u_{ij}^*(r)]/\partial\beta$ or $-\partial u_{ij}^*(r)/\partial T$ must also be specified.

Information about the nature of some of the short-range effects may be gained by passing from water to heavy water as solvent. ϵ and $\partial \ln\epsilon/\partial \ln T$ are almost the same in these two solvents, and the small differences observed by Kerwin[10] for the excess free energy of the same alkali halide in water and heavy water solution imply that the $u_{ij}^*(r)$ functions must be very nearly the same in the two media. The sign and magnitude of the differences in the E^{ex}/I functions observed by Wu and Friedman[11] (I is the ionic strength) however point to significant changes in $\partial[\beta u_{ij}^*(r)]/\partial\beta$ on passing from H_2O to D_2O. Since

$$\partial[\beta u_{ij}^*(r)]/\partial\beta = u_{ij}^*(r) - T\partial[u_{ij}^*(r)]/\partial T, \qquad (2.11)$$

the differences in E^{ex}/I could be interpreted in terms of the entropy functions $-\partial u_{ij}^*(r)/\partial T$.

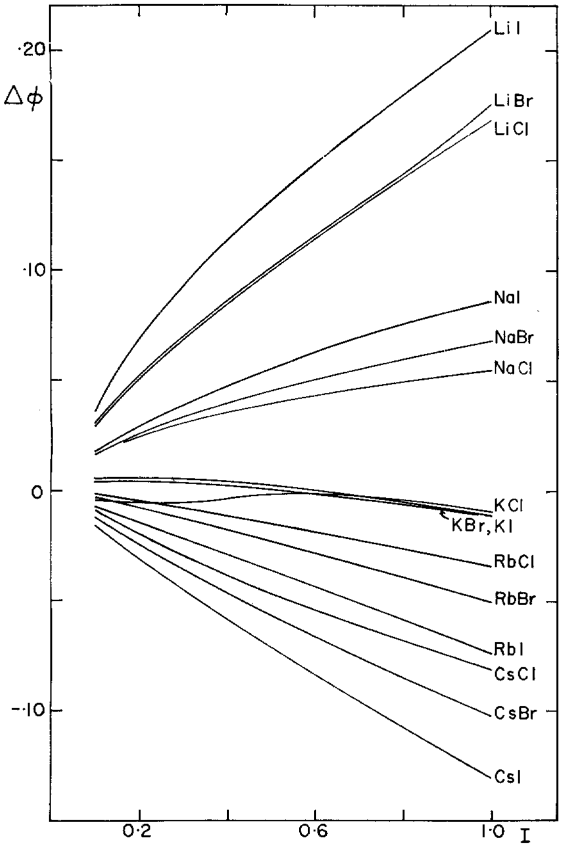

FIG. 4. $\Delta\phi$ as a function of the ionic strength (I) at 25°C, where $\Delta\phi = \phi(\text{Exp}) - \phi(\text{Pauling})$ and $\phi(\text{Pauling})$ is the theoretical osmotic coefficient in the primitive model with the ion radii equal to the Pauling radii.

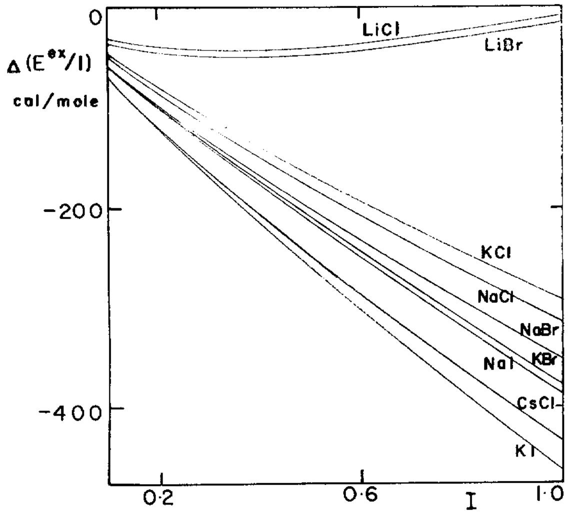

FIG. 5. $\Delta E^{ex}/I$ as a function of I at 25°C, where $\Delta E^{ex} = E^{ex}(\text{Exp}) - E^{ex}(\text{Pauling})$ and $E^{ex}/I(\text{Pauling})$ is the theoretical heat of dilution in the primitive model with ion radii equal to the Pauling radii and independent of temperature.

Since $u_{ij}^*(r)$ is a free energy averaged over the solvent coordinates,[7] $u_{ij}^*(r)$ and its derivatives have contributions from changes in the coordinates of the solvent molecules when two ions approach each other. These include the effects of overlap of the structurally altered zones (cospheres) in the solvent around two adjacent ions[12] in addition to the more familiar conse-

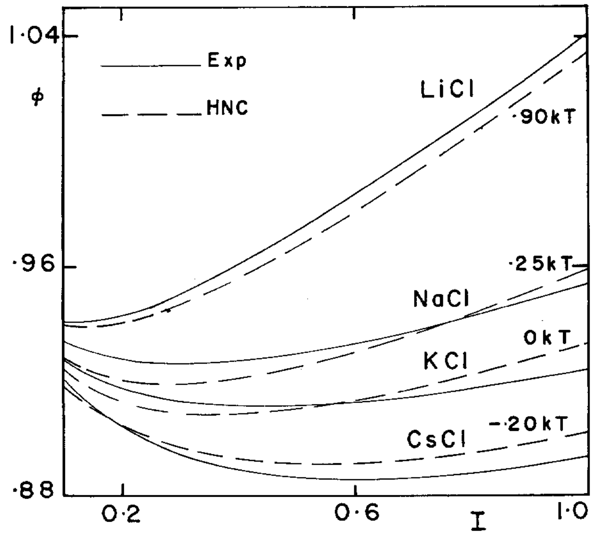

FIG. 6. Theoretical (HNC) osmotic coefficients for the square model compared with experimental values for aqueous solutions of Li, Na, K, and Cs chlorides at 25°C. The parameters assumed for this model are $a_{ij} = r_i(\text{Pauling}) + r_j(\text{Pauling})$, $d_{++} = d_{--} = 0$ and d_{+-} indicated in the figure.

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[10] R. Kerwin, Ph.D. thesis, University of Pittsburgh, 1964.

[11] Y. C. Wu and H. L. Friedman, J. Phys. Chem. **70**, 166 (1966). These results have recently been extended by R. H. Wood, R. A. Rooney, and J. N. Braddock, J. Phys. Chem. **73**, 1673 (1969).

[12] H. S. Frank and M. W. Evans, J. Chem. Phys. **13**, 507 (1945).

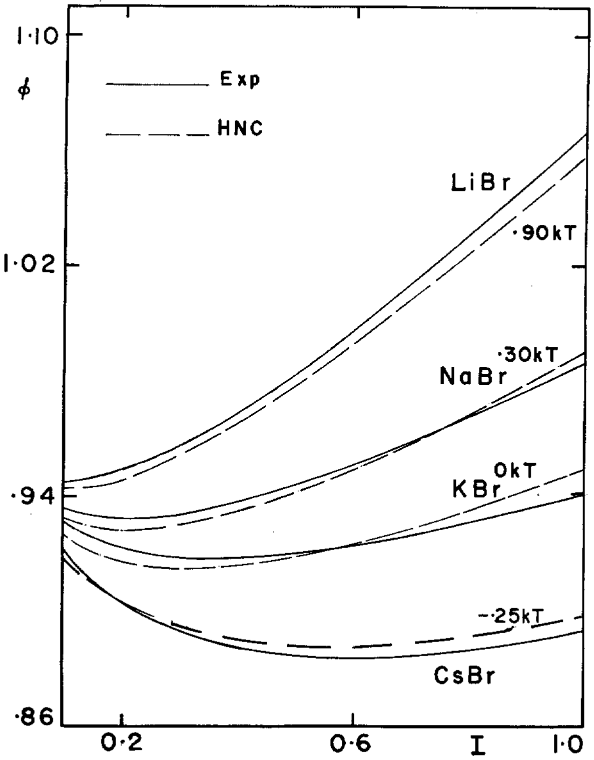

FIG. 7. Theoretical (HNC) osmotic coefficients for the square-well model compared with experimental values for aqueous solutions of Li, Na, K, and Cs bromides at 25°C. The parameters assumed for this model are described below Fig. 6.

quences of electron repulsion and polarizabilities of the ions that are present even in gases and plasmas. As noted by Gurney,[13] the overlap contributions can be attractive or repulsive depending on the extent of overlap and the mutual compatibility of these regions. If the free energy of a system containing two ions at infinite separation in a medium is increased by structural alteration of the solvent immediately around the ions, the overlap of these regions at short distances of separation between the ions will decrease the free energy of the system, producing an attractive component to the short-range potential $u_{ij}^*(r)$. A repulsive contribution to $u_{ij}^*(r)$ can arise from the overlap of the structurally altered zones which decrease the free energy of the system by their presence around the ions at large r.

Since no accurate *a priori* calculations of $u_{ij}^*(r)$ which include all of the detailed features of the short-range potential is available, it seems practical as an interim measure to represent it by a simple functional form, which simulates some of the effects discussed above. An example is the step function described in Sec. III, for which the constants and their derivatives with respect to T and P_0 are adjustable parameters that are subject to molecular interpretation and correlation within a group of electrolytes, such as the alkali halides. While it is necessary to proceed more or less empirically at first to determine the relative importance of each parameter for a particular model, it appears that the more important aspects of the equilibrium properties are determined by only a few of them.

The different contributions which the long-range and short-range components of $u_{ij}(r)$ make to F^{ex}, E^{ex}, and V^{ex} provide a useful tool in the evaluation of various models for ionic solutions. It is conceivable for example that an assumed functional form for $u_{ij}^*(r)$ gives good agreement with experiment for F^{ex} at a single temperature and that the $u_{ij}^*(r)$ functions are readily understood in terms of molecular interactions in solution. It may turn out however that the molecular interpretation of the functions $\partial[\beta u_{ij}^*(r)]/\partial\beta$ necessary in the same model to obtain a fit for E^{ex} contradict or are partly inconsistent with our understanding of molecular interactions derived from $u_{ij}^*(r)$. Then our ideas about the behavior of ionic solutions at a molecular level and our assumptions about the correct functional form for $u_{ij}^*(r)$ and its derivatives will have to be revised. We find that when these arguments are applied to the charged square-well model, the model has to be revised in a way that would not have been obvious from con-

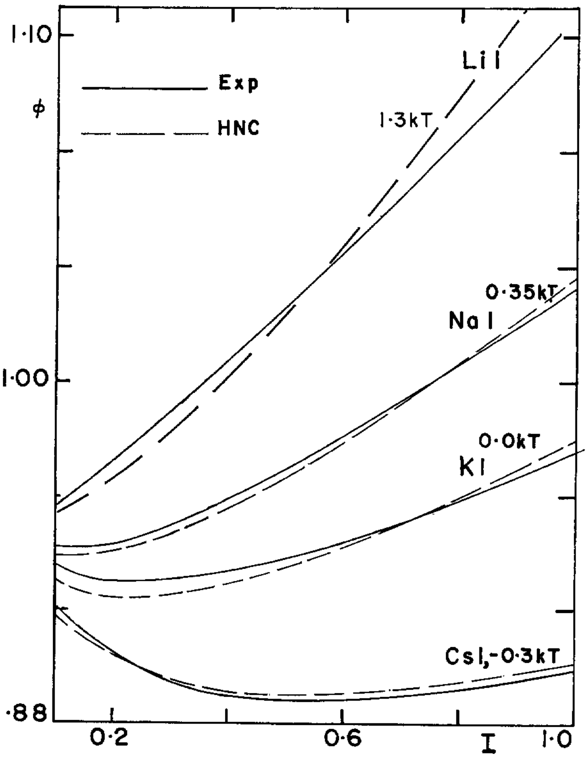

FIG. 8. Theoretical (HNC) osmotic coefficients for the square-well model compared with experimental values for aqueous solutions of Li, Na, K, and Cs iodides at 25°C. The parameters assumed for this model are described below Fig. 6.

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[13] R. W. Gurney, *Ionic Processes in Solution* (Dover Publications, Inc., New York, 1963).

siderations of F^{ex} alone. Models that give agreement with experiment for F^{ex} at a single temperature can be very misleading.

III. COMPARISON OF THE PRIMITIVE MODEL WITH EXPERIMENT

The simplest model that is relevant to ionic solutions, is the primitive model, described by Eq. (2.1) with

$$\begin{aligned} u_{ij}^*(r) &= \infty, \quad \text{if} \quad r<a_{ij}, \\ &=0, \quad \text{if} \quad r>a_{ij}, \end{aligned} \tag{3.1}$$

where a_{ij} parameters are the distances of closest approach between the ions i and j. We assume for the present that they are additive and equal to the sum of arbitrary ionic radii r_i and r_j.

For this model the osmotic coefficient ϕ [Eq. (2.2)] and excess energy per unit volume E^{ex} [Eq. (2.7)] are given by

$$\phi = 1+(6\epsilon kTc)^{-1}\sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma} c_ic_je_ie_jT_{ij} + \frac{2\pi}{3c}\sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma} c_ic_jg_{ij}(a_{ij}+)a_{ij}^3, \tag{3.2}$$

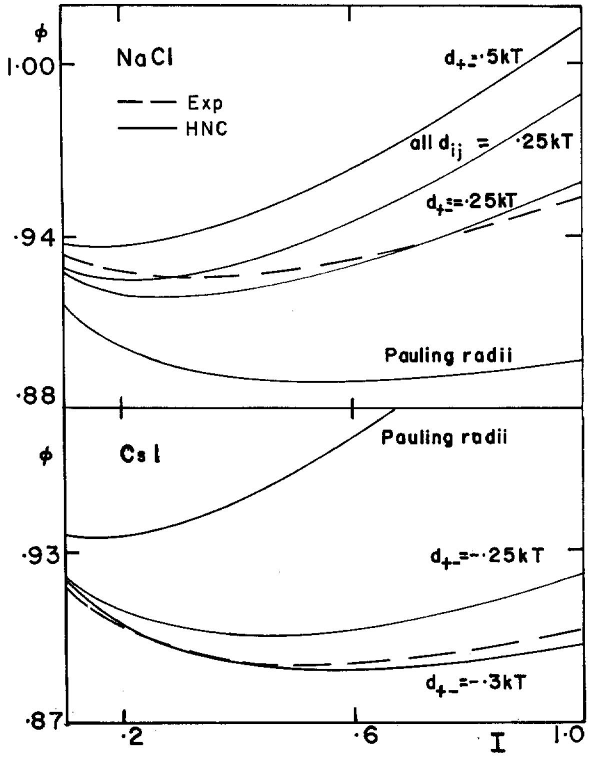

FIG. 9. The effect of changes in d_{ij} on the square-well model computations which give qualitative agreement with the osmotic coefficients of NaCl and CsI in aqueous solution at 25 C. (See Figs. 6 and 7.) $d_{++}=d_{--}=0$ unless specified otherwise. All $d_{ij}=0$ for Pauling radii computations.

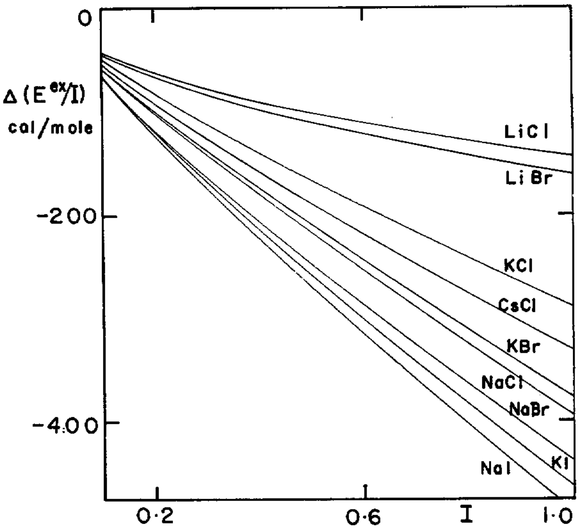

FIG. 10. $\Delta E^{ex}/I = E^{ex}/I(\text{Exp}) - E^{ex}/I(\text{square well})$ as a function of I, for several alkali halides. The parameters for the square-well model are the same as those used in Figs. 6–8 with the assumption that $k^{-1}(\partial d_{ij}/\partial T)=0$.

and

$$E^{ex} = \frac{(1+\partial\ln\epsilon/\partial\ln T)}{2\epsilon}\sum_{i=1}^{\sigma}\sum_{i=j}^{\sigma} c_ic_je_ie_jT_{ij}, \tag{3.3}$$

where

$$T_{ij} = \int_0^\infty [g_{ij}(r)-1]4\pi r dr \tag{3.4}$$

and $g_{ij}(a_{ij}+)$ is the distribution function immediately outside the discontinuity in the short-range potential.

The accuracy of the HNC approximation for a certain range of parameters in this model has been shown,[2,3] and it is also clear from Fig. 1 that this range is adequate to cover the experimental data for the excess free energy (or osmotic or activity coefficients) of aqueous solutions of alkali halides at 25°C up to $1M$. We also note that the osmotic coefficients for example have qualitatively the correct shape and that only a single parameter a_{+-} determines the nature of the first deviations from the Debye–Hückel limiting law. With increasing concentration, the deviations become more pronounced partly under the influence of nonelectrostatic contributions to the excess free energy such as the excluded volume. It is not surprising then to observe that these deviations are greater in systems with the same a_{+-} but with $r_+\neq r_-$; qualitatively the same difference between the symmetrical and asymmetrical systems is also observed when the particles are not charged.[3] The supplementary effects due to the asymmetrical nature of the hard cores become important at about $0.4M$. It is still correct however to state that the main characteristics of the osmotic coefficients are determined by a_{+-} for the a_{ij} parameters used in computing the curves shown in Fig. 1.

TABLE II. Comparison of E^{ex}/I [a] for aqueous solutions of alkali halides at 25°C with the HNC results for the square-well model.

		LiCl	LiBr	NaCl	NaBr	NaI	KCl	KBr	KI	CsCl
	$k^{-1}T^{-1}d_{+-}$	0.90	0.90	0.25	0.30	0.35	0	0	0	−0.20
Molarity	$k^{-1}(\partial d_{+-}/\partial T)$	1.57	1.39	1.03	1.22	1.28	0.65	0.81	0.88	0.60
0.1	Exp[b]	100	108	84	75	72	80	67	57	55
	HNC	100	108	84	75	72	80	67	57	55
	Diff	0	0	0	0	0	0	0	0	0
0.4		183	193	69	49	32	67	31	−11	−8
		130	152	78	51	43	66	22	−6	−6
		53	41	−9	2	−11	1	9	−5	−2
0.7		239	250	26	−5	−33	27	−33	−98	−87
		148	163	46	4	−10	26	−40	−88	−94
		91	87	−20	−9	−23	1	7	−10	−7
1.0		284	300	−28	−64	−105	−20	−110	−184	−172
		118	165	8	−50	−68	−19	−109	−171	−180
		166	135	−36	−14	−37	−1	−1	−12	8

[a] This is the heat of dilution in the McMillan–Mayer system, in units of calories per mole.

[b] The experimental value at each molarity was interpolated from the heats of dilution compiled by V. B. Parker (U. S. National Bureau of Standards, Washington, D. C. 1965), NJRDS-NBS 2.

When the parameter a_{+-} is chosen to fit the activity or osmotic coefficients of a particular alkali halide electrolyte below $0.05M$, the computed curves for each of these functions, assuming $r_+=r_-$, lie above the experimental ones at higher concentrations. One example of this (LiBr) appeared in a previous paper.[2] We show one more (NaCl) over the whole concentration range up to $1M$ in Fig. 2 and make the comparison with experiment for many alkali halides at a single concentration ($1M$) in Table I. This comparison contradicts the assumption made in several hydration theories that have appeared, in which the primitive model contributions to the excess free energy are assumed on the basis of less exact theories to be too small at high concentrations. While the repulsion exhibited by this model is too large at the high-concentration end, it is too great also at low concentrations when the a_{+-} parameters required to obtain agreement with experiment are larger than the sum of the Pauling radii. This is often interpreted as an increase in ion size due to hydration, but the assumed infinite positive potential at the point of contact of two hydrated ions neglects consideration of all effects associated with the interpenetration of the hydration shells. We will see in Sec. III that these effects are not negligible for the square-well model, which persuades us to believe that they exert a major influence on the thermodynamic properties of real systems.

It is instructive to extend the comparison with experiment to other thermodynamic properties as well, especially the excess energy and excess entropy functions, using the same a_{ij} parameters discussed in the previous paragraph. This has been done for a few selected cases in Fig. 3, where E^{ex}/I and S^{ex}/I have been calculated on the assumption that the a_{ij} parameters are temperature independent. These computations also show no agreement with the experimental results, and no simple correlation exists between the deviations in F^{ex}/I and E^{ex}/I. It is also not clear how the adjustment of parameters (additive or not) and the introduction of temperature dependent a_{ij}'s could improve the results simultaneously for all of these thermodynamic functions. It appears more likely that the short-range forces have been too poorly represented in the primitive model with the a_{+-} parameters chosen to fit the experimental results in the low concentration range below $0.05M$.

There is another set of the primitive model calculations which may be of importance to real systems and which provides useful reference systems against which the experimental results may be judged. When the distances of closest approach between the ions are equal to the sum of the Pauling radii, we obtain the results shown in Fig. 4 for the differences ($\Delta\phi$) between the experimental and theoretical osmotic coefficients. In Fig. 5 we have the corresponding differences in the E^{ex}/I functions. It is striking that almost the same order found for the experimental osmotic coefficients in the McMillan–Mayer system (Fig. 1) is preserved when the primitive model contributions of the "Pauling ions" have been subtracted from them. Since all classifications of the ionic radii based on crystallographic measurements agree on the various r_++r_- sums, and since the principle nonideal contributions to the osmotic coefficients are determined by just this quantity (a_{+-}), the order obtained here for the osmotic coefficients will not be changed by the use of other sets of ionic radii, for example the set proposed by Gourary and Adrian.[14]

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[14] B. S. Gourary and F. J. Adrian, Solid State Phys. **10**, 127 (1960).

TABLE III. Identification of the systems in Fig. 11.

	d_{++}/kT	d_{--}/kT	d_{+-}/kT	$k^{-1}(\partial d_{++}/\partial T)$	$k^{-1}(\partial d_{--}/\partial T)$	$k^{-1}(\partial d_{+-}/\partial T)$
A	0	0	0	0	0	0
B	0	0	0.25	0	0	0
C	0	0	0.25	0	0	1.03
D	0	0	0.25	0	0	1.3
E	0.25	0.25	0.25	0	0	0
F	0.25	0.25	0.25	1.03	1.03	1.03

The magnitude and sign of the difference between experiment and theory will also not be altered very much with the possible exception of borderline cases like the potassium halides for which the deviations may change sign but would still lie close to zero.[15]

Gurney[13] interpreted the observed sequence in the activity (or osmotic) coefficients of a family of electrolytes by proposing that the order in which they decrease at a given concentration is also the order in which the cospheres around oppositely charged ions change from dissimilar to similar character.[16] This correlation can now be extended to the residual effects that remain when the primitive model contributions have been subtracted out as described (Fig. 4).

The modifications that are required in the model (using the Pauling radii) to obtain agreement with experiment are obvious; an additional over-all repulsive contribution to the short-range potential u_{ij}^* would be required when ϕ(exptl) $>$ ϕ(Pauling) and an over-all attractive contribution is necessary when ϕ(exptl) $<$ ϕ(Pauling). These conclusions are subject to revision (which can easily be carried out) if there is convincing evidence in favor of substantially different values for a_{+-} from the sum of the Pauling radii. Accepting for the present the Pauling radii as the basis for further discussion, we note that the sign of the change in $u_{ij}^*(r)$ is positive (repulsive) when the ions of opposite sign are dissimilar in the structural sense and negative (attractive) when they are structurally alike.[16] It is plausible that at least part of this change in u_{ij}^* is due to the overlap of the cospheres around the ions. Gurney[13] discussed this within the framework of the only available theory, namely the Debye–Hückel primitive model, by considering the effect of overlap on the apparent distance of closest approach. We exploit instead the accuracy of the hypernetted chain equation, use the Pauling radii to represent the hard-core repulsions and account for the remaining contributions to $u_{ij}^*(r)$ by adding a square well or mound. In doing so we are able to consider the possibility of a more complex environment around an ion, as suggested by Frank and Evans.[12]

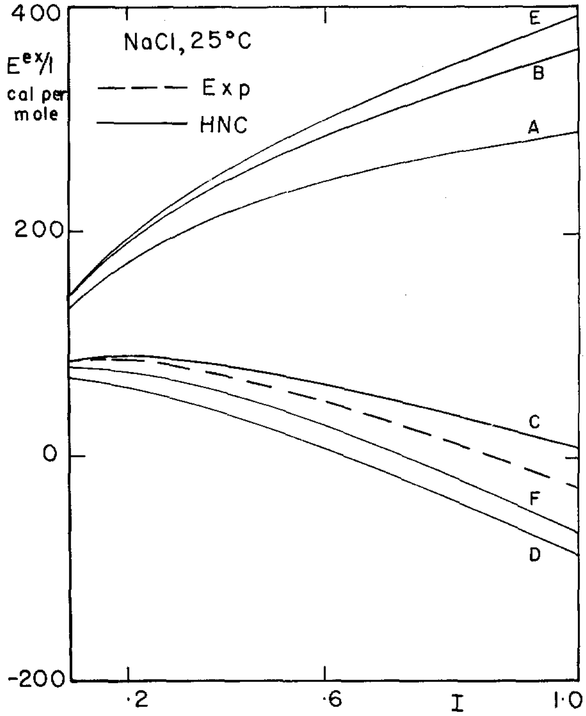

FIG. 11. E^{ex}/I as a function of I for several choices of d_{ij} and $k^{-1}(\partial d_{ij}/\partial T)$ in the square-well model, assuming ion radii equal to the Pauling radii for Na^+ and Cl^-. The systems are identified in Table III.

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[15] There is also the possibility that the a_{+-} parameters in aqueous solutions are not equal to the sums of the crystallographic radii. When $r_+ + r_-$ obtained from microwave measurements on alkali halides in the gas phase is plotted against $r_+ + r_-$ (Pauling), all the representative points for the alkali halides lie on the same straight line, except for the Cesium salts which appear on a line with a slightly different slope. Hence the order obtained in Fig. 4 will not be changed if we substitute a set of additive microwave radii for the Pauling radii. The order will also be the same if the $(r_+ + r_-)$ distances obtained from microwave or crystallographic data are increased or decreased by a constant factor; the sign and magnitude of the difference between theory and experiment however will differ in every case.

[16] Structural disruption or enhancement of the solvent by ions in aqueous media has been invoked in attempts to rationalize several different experimental observations. For examples see (a) J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933). (b) W. M. Cox and J. H. Wolfenden, Proc. Roy. Soc. (London) **A145**, 486 (1934). (c) H. S. Frank and M. W. Evans, Ref. 12. (d) R. W. Gurney, Ref. 13, p. 166 and 289. (e) H. S. Frank and W. Y. Wen, Discussions Faraday Soc. **24**, 133 (1957). *Structural similarity* and *structural dissimilarity* used in this paper are to be interpreted in terms of the usual classification of ions into structure breakers and structure makers. See for example Ref. 6 for a detailed classification.

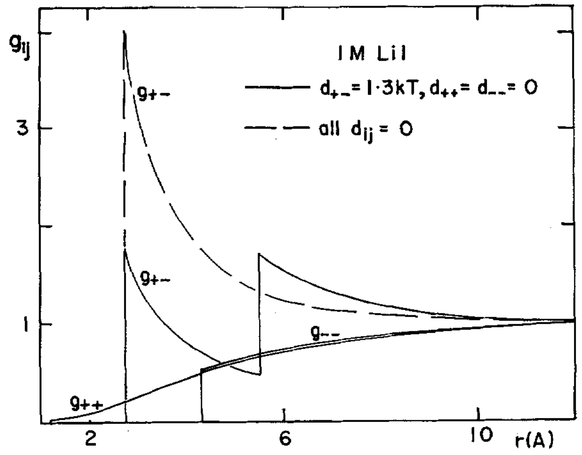

FIG. 12. The pair correlation function for square-well model with parameters chosen to correspond to LiI. When all $d_{ij}=0$ the pair correlation functions are for the Pauling ions.

IV. THE CHARGED SQUARE-WELL MODEL

This model is defined by Eq. (2.1) together with

$$\begin{aligned} u_{ij}^*(r) &= \infty, & \text{if } & r<a_{ij}, \\ &= d_{ij}, & \text{if } & a_{ij}<r<b_{ij}, \\ &= 0, & \text{if } & r>b_{ij}. \end{aligned} \tag{4.1}$$

We take a_{ij} as the sum of the Pauling radii for the ions i and j and $(b_{ij}-a_{ij})$ as the width of one water molecule. For F^{ex}, ϕ, and $\gamma_\pm$ the only adjustable parameters left in this model are the d_{ij} free energy functions; each d_{ij} is negative for a well and positive for a mound. The osmotic coefficient from the virial equation takes the form

$$\phi=1+(6\epsilon kTc)^{-1}\sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma}c_ic_je_ie_jT_{ij}+\frac{2\pi}{3c}\sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma}c_ic_j \times\{a_{ij}^3g_{ij}(a_{ij}+)+b_{ij}^3g_{ij}(b_{ij}+)[1-\exp(-d_{ij}/kT)]\}, \tag{4.2}$$

where T_{ij} is defined in Eq. (3.4), and $g_{ij}(a_{ij}+)$ and $g_{ij}(b_{ij}+)$ are the correlation functions immediately outside the discontinuities in the short-range potential. The excess energy per unit volume is given by

$$E^{\text{ex}}=E_L+E_S, \tag{4.3}$$

$$E_L=\frac{(1+\partial\ln\epsilon/\partial\ln T)}{2\epsilon}\sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma}c_ic_je_ie_jT_{ij}, \tag{4.4}$$

$$E_S=\tfrac{1}{2}\sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma}c_ic_j\frac{d_{ij}-T\partial d_{ij}}{\partial T}\int_{a_{ij}}^{b_{ij}}g_{ij}(r)4\pi r^2dr, \tag{4.5}$$

in which the new parameters, $\partial d_{ij}/\partial T$ appear. We note that the long-range part E_L is positive for aqueous solutions, while E_S (short range) has the same sign when the set of d_{ij} functions are positive and their temperature coefficients are negligible or zero. But E_S is not a monotonic function of the variables d_{ij}. As any one of the d_{ij} parameters increases, the ionic population within the corresponding mound[17] decreases and the short-range contribution to the excess energy E_S passes through a maximum and finally descends to zero when $d_{ij}\to\infty$. In this limit the mound takes on the appearance of a hard core with a discontinuity at $r=b_{ij}$. Thus E^{ex}/I as a function of d_{ij} has a maximum in the domain $d_{ij}>0$. It has a minimum in the domain $d_{ij}<0$ due to the balance between the long-range term which is positive and the short-range term which is negative. This description of the general behavior of E^{ex} is correct only when $\partial d_{ij}/\partial T$ is negligible or zero.

The osmotic coefficients ϕ computed by the HNC equation for this model, with parameters chosen to correspond to all the halides except fluoride of Li, Na, K, and Cs, are shown in Figs. 6–8. For these electrolytes we have used d_{+-} as the only adjustable parameter and assumed d_{++} and d_{--} to be zero. In Fig. 9 we have the results for NaCl and CsI with additional computations to show the sensitivity of the osmotic coefficients to changes in d_{+-} and also to show the consequences of discarding the assumption about d_{++} and d_{--} described above. We remark that d_{+-} is either small or zero for all of the potassium halides since $\phi(\text{Pauling})\sim\phi(\text{exptl})$ in this case.

Although no special effort has been made to obtain

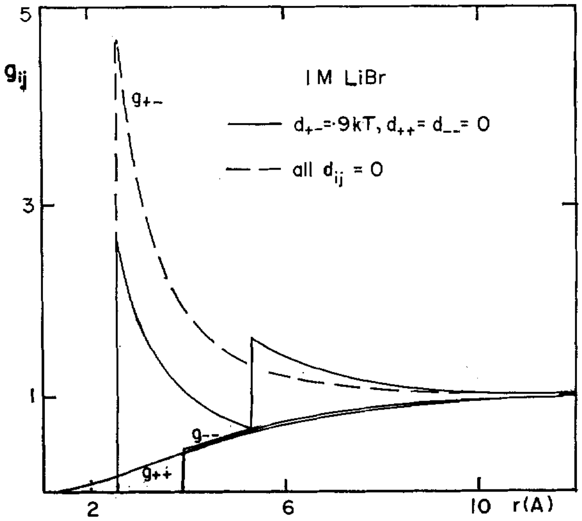

FIG. 13. The pair correlation functions for the square-well model with parameters chosen to correspond to LiBr.

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[17] The population of j ions in the mound around the ith central ion is proportional to the integral between the limits a_{ij} and b_{ij} in Eq. (4.5).

the best possible set of d_{ij} parameters for each salt, respectable and in some instances excellent agreement with the experimental results for ϕ is obtained with rather small values for d_{+-}. It is also apparent that for NaCl, for example, this agreement will not be radically changed when d_{++} and d_{--} are of magnitudes comparable to d_{+-}. The fit could be improved by altering the width and shape of the mound (or well), but it seems unlikely that the qualitative conclusions will be affected. While we expect that refinements, especially to the nature of the short-range interactions between charges of the same sign, will come from the study of mixed electrolytes, we may conclude that, for this model, the dominant contributions to the excess free energy functions for the alkali halides up to $1M$ apparently depend on the magnitudes of $e_+e_-/\epsilon kT$ and a_{+-}, which are predetermined, and the single parameter d_{+-}.

For most alkali halides, d_{+-} is small enough when positive to ensure that E^{ex}/I at $1M$ lies before the extremum of E^{ex}/I as a function of d_{+-}. This point is relevant to the HNC results in Fig. 10, where the difference between the experimental and computed E^{ex}/I functions for several salts are shown. In every case the theoretical values have been obtained with the d_{+-} parameters used to fit the osmotic coefficients but with the assumption that all of the d_{ij} parameters are independent of temperature. Comparison with the corresponding figure for the Pauling radii (Fig. 5) shows that the differences between experiment and theory for all the alkali halides are now spread over a narrower range, but the computed values are still too positive. It follows from Eq. (4.5) that the observed trends of the excess energy functions can be reproduced only if

$$\sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma} c_ic_jT\frac{\partial d_{ij}}{\partial T}\int_{a_{ij}}^{b_{ij}} g_{ij}(r)4\pi r^2dr$$

is positive.

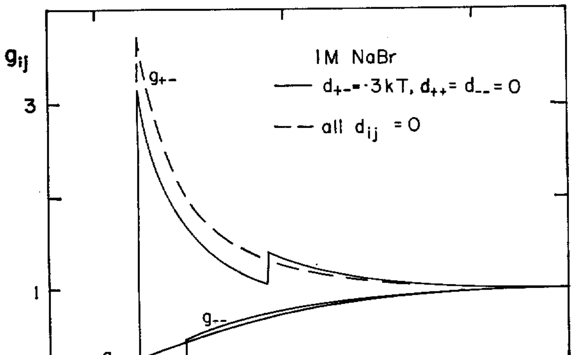

FIG. 14. The pair correlation function for the square-well model with parameters chosen to correspond to NaBr.

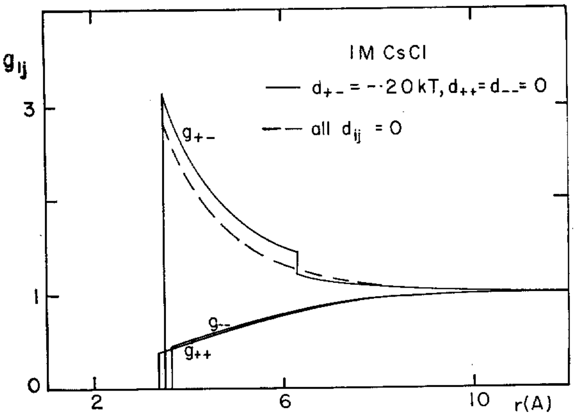

FIG. 15. The pair correlation function for the square-well model with parameters chosen to correspond to CsI.

When $\partial d_{+-}/\partial T$ is used as the only additional parameter, we obtain the HNC results for E^{ex}/I given in Table II. Except for the lithium and sodium salts, the agreement with experiment is good if not excellent in terms of the absolute error in E^{ex}/I. This agreement could be improved by taking an average value for $\partial d_{+-}/\partial T$ over the whole concentration range instead of the value necessary to make the fit perfect at $0.1M$. For NaCl, for example, the discrepancy between experiment and theory could be reduced below 10 cal/mole over the range from $0.1M$ to $1M$ by choosing $\partial d_{+-}/\partial T=1.1k$. For the lithium salts however it is not possible to improve the results substantially by a similar adjustment of $\partial d_{+-}/\partial T$.

In Fig. 11 we compare the experimental E^{ex}/I functions for NaCl with several HNC results to show the sensitivity of the results to changes in $\partial d_{+-}/\partial T$ and also to clarify the effect of assuming additional interactions between charges of the same sign. We note in particular that when d_{++}, d_{--}, and their temperature coefficients are of the same order of magnitude as d_{+-} and $\partial d_{+-}/\partial T$, E^{ex}/I changes by only 5 cal/mole at $0.1M$ and by about 75 cal/mole at $1M$. It is apparent from the magnitude of these changes that $\partial d_{+-}/\partial T$ together with d_{+-} dominate the picture for the E^{ex}/I functions in the high-concentration range up to $1M$ and that within the framework of this model, $\partial d_{+-}/\partial T$ is positive for all of the alkali halides in aqueous solution.

The distribution functions at $1M$ computed by the HNC equation for parameters chosen to correspond to LiI, LiBr, NaBr, and CsCl are shown in Figs. 12–15. They are representative of the distribution functions obtained for the alkali metal chlorides, bromides, and iodides. The large changes in g_{+-} due to the mounds for the lithium salts are of particular interest in contrast to the rather small distortions for the sodium salts. A similar effect but in the opposite sense is observed in the correlation functions of the cesium salts.

The excess probability due to molecular interactions

TABLE IV. The excess probabilities of pair formation at 1.0M calculated by the HNC equation for the parameters in the charged square-well model used to interpret the osmotic coefficients of the alkali halides in H_2O at 25°C.

Salt	d_{+-}/kT	a_{+-}[a]	$g_{+-}(a_{+-})$	$P_{+-}(a_{+-})$	b_{+-}[a]	$g_{+-}(b_{+-})$	$P_{+-}(b_{+-})$
LiCl	0.90	2.41	3.080	151.8	5.18	1.639	215.7
LiBr	0.90	2.55	2.725	140.5	5.32	1.619	220.7
LiI	1.30	2.76	1.749	71.7	5.52	1.702	301.8
NaCl	0.25	2.76	3.536	242.7	5.52	1.408	156.2
NaBr	0.30	2.90	3.139	226.0	5.66	1.408	164.2
NaI	0.35	3.11	2.715	208.4	5.85	1.408	175.5
KCl	0	3.14	3.283	282.8	5.91	1.292	127.7
KBr	0	3.28	3.075	280.5	6.05	1.292	127.7
KI	0	3.49	3.825	279.3	6.25	1.264	129.6
CsCl	−0.20	3.50	3.138	329.1	6.27	1.200	98.9
CsBr	−0.25	3.64	3.063	343.5	6.41	1.173	98.9
CsI	−0.30	3.85	2.943	361.9	6.60	1.144	78.8

[a] $a_{+-}=r_+(\text{Pauling})+r_-(\text{Pauling})$. $b_{+-}\simeq a_{+-}+2.76$ Å.

$P_{ij}(r')dr$ of finding two ions i and j, respectively, at a distance between r' and $r'+dr$ apart is given by

$$P_{ij}(r')dr \equiv 4\pi r'^2[g_{ij}(r')-1]dr. \qquad (4.6)$$

In Table IV we have collected these probabilities of pair formation between oppositely charged ions for two different configurations, one corresponding to contact ($r=a_{+-}$) and the other representing a solvent separated pair with only one water molecule between the positive and negative ions. In contrast to the cesium salts, the lithium halides show a preference for pair formation through a water molecule in qualitative agreement with data obtained from the scattering of x rays.[18] It is not surprising, however, that solvent separated ion pairs have not been detected as yet in ultrasonic relaxation experiments on aqueous solutions of lithium halides; the barriers that we have calculated for these systems are probably too small to produce a step in the kinetic sequence of events in contact pair formation which is sufficiently slow to be detected by these experimental techniques.[19] We expect that when these calculations are extended to higher valence electrolytes, different conclusions will be reached about the heights of barriers against contact pair formation in agreement with the detection of solvent separated ion pairs for example in aqueous $MnSO_4$.[20]

V. DISCUSSION

At this stage it is worthwhile to recall the assumption made in the theory of the integral equations that the direct potential is pairwise additive. This assumption cannot be strictly correct even for a set of charged particles whose centers of mass are fixed without any restrictions on the orientations of the induced dipoles and multipoles of each molecule.[21] Doubts have also been expressed as to whether interactions which occur through changes in water structure can be pairwise additive.[6] If these effects contribute significantly to the direct potential, they could introduce some concentration dependence into the pair potentials when the direct potential is treated as though it were pairwise additive. In the square-well model, these deficiencies as well as others due to changes in ϵ with r and the simple form assumed for $u_{ij}^*(r)$ may have been absorbed by the parameters of the step function. When more information is available on the detailed contributions of the higher component potentials to the direct potential, their effect on the thermodynamic properties of the system could possibly be calculated as a perturbation to the results of a strictly pairwise additive potential,[22] or they may be incorporated more directly into the integral equations by methods similar to those suggested by Rushbrooke and Silbert[23] and by Rowlinson.[24] We proceed to a discussion of our results assuming that the effects that have been neglected or absorbed by the parameters of the model do not dominate the properties of aqueous solutions.

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[18] (a) R. M. Lawrence and R. F. Kruh, J. Chem. Phys. **47**, 4758 (1967). (b) G. Brady, J. Chem. Phys. **28**, 464 (1958). (c) M. A. Strauss, thesis, University of Cincinnati, 1960.

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[20] G. Kurtze and K. Tamm, Acustica **3**, 33 (1953).

[21] H. Marganau and J. Stamper, Advan. Quantum Chem. **3**, 129 (1969).

[22] For an example of such a calculation for a different system see: J. A. Barker, D. Henderson, and W. R. Smith, J. Phys. Soc. Japan suppl. **26**, 284 (1969). (Proceedings of the International Conference on Statistical Mechanics, Kyoto, 1968).

[23] G. S. Rushbrooke and M. Silbert, Mol. Phys. **12**, 505 (1967).

[24] J. Rowlinson, Mol. Phys. **12**, 513 (1967).

We begin with the interpretation of the parameters d_{+-} and $\partial d_{+-}/\partial T$ at a molecular level. A positive d_{+-} signifies strong hydration for at least one of the ions, and its magnitude reflects the work necessary to replace the water of hydration by an ion. This is apparently the same for LiCl and LiBr, an idea consistent with the notion that only one water molecule separates the ions at the onset of the barrier posed by hydration. A likely configuration for this water molecule is one in which Li^+ lies next to the oxygen atom with the halide ion on the same side as the hydrogen atoms but on the axis bisecting the HOH angle—the water dipole is here favorably oriented to form a link between Li^+ and X^-. For LiI, the strong structure breaking property of the I^- could make more water readily available for alignment by Li^+ outside the primary hydration sheath when an I^- appears nearby, contributing to an additional barrier that has to be surmounted before the ions can make contact. A negative d_{+-}, such as for the Cs salts, may be due to polarization or due to the overlap of the structure broken regions around the ions of opposite sign.

The positive sign for $\partial d_{+-}/\partial T$ is more difficult to interpret; it reflects a negative contribution to the entropy of the system as oppositely charged ions pass through the hydration shell to make contact. This is the opposite of the changes expected in the entropy due to the expulsion of the water of hydration into the bulk solvent, assuming that the bulk solvent is less ordered than the hydrated regions next to an ion.

A possible explanation is that, $\partial d_{+-}/\partial T$ is determined by an outer cosphere on each ion, which is neglected in this model and which makes a strong positive contribution to $\partial u_{+-}^*/\partial T$. This corresponds to a negative contribution to S^{ex}, which would arise from the overlap of the structure broken regions in these outer cospheres which must be large enough to outweigh the increase in entropy from the overlap of the inner cospheres. The picture due to Frank and Evans[8] of two concentric regions of "frozen" and "melted" water around an ion is implicit in the above explanation of the sign of $\partial d_{+-}/\partial T$ for systems in which $d_{+-}>0$. For these systems also it is implied that the effect of the structure broken regions is much more noticeable in the S^{ex} and E^{ex} functions than in the F^{ex} functions. For the cesium salts, for which $d_{+-}<0$ and $\partial d_{+-}/\partial T>0$, the presence of structure broken regions is apparent in all of the thermodynamic functions studied here, but there is no strong evidence for the existence of an innermost frozen region next to Cs^+.

The detailed implications of introducing structural features into the model have yet to be worked out. Only the gross aspects of the environment around an ion have been accounted for in the overlap calculations based on the square-well model presented here, and presumably, apart from the contributions of the higher component potentials, this is partly why there remain detailed differences in shape between the experimental curves, both for ϕ and E^{ex}/I, and the calculated curves of this paper. The success that we have achieved so far with this simple model and the apparent need for structural concepts in interpreting the results should make it worthwhile to include the refinements of the two-zone model for these simple electrolytes and also to extend these computations to more complicated systems.

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