

where  $\Delta G_i^\circ$  is the free energy of formation of individual reactants and products at 3333 K and  $n_i$  is the stoichiometric coefficient (positive for products and negative for reactants) in the balanced equation. The values used are tabulated in Table VI.

Making use of these values, we arrive at the decomposition reactions and the corresponding  $\log P^*$  values at 3333 K listed

in Table VII.

Registry No.  $\text{Ar}^+$ , 14791-69-6;  $\text{Li}_2\text{WO}_4$ , 13568-45-1;  $\text{Na}_2\text{WO}_4$ , 13472-45-2;  $\text{WO}_2$ , 12036-22-5;  $(\text{NH}_4)_2\text{WO}_4$ , 15855-70-6;  $\text{Na}_2\text{MoO}_4$ , 7631-95-0;  $\text{NaNbO}_3$ , 12034-09-2;  $\text{NaTaO}_3$ , 12034-15-0;  $\text{NaVO}_3$ , 13718-26-8;  $\text{Na}_2\text{CrO}_4$ , 7775-11-3;  $\text{V}_2\text{O}_5$ , 1314-62-1;  $\text{Ag}_2\text{WO}_4$ , 13465-93-5;  $\text{MoO}_2$ , 18868-43-4;  $\text{Cr}_2\text{O}_3$ , 1308-38-9;  $\text{Nb}_2\text{O}_5$ , 1313-96-8.

## Ionic Association in Methanol and Related Solvents: An Extended RISM Analysis

Fumio Hirata\* and Ronald M. Levy\*

Department of Chemistry, Rutgers University, New Brunswick, New Jersey 08903 (Received: July 29, 1986)

Ionic solvation and the interionic potential of mean force between ions in methanol at infinite dilution are examined by the extended RISM theory; the values are compared with those for a simple dipolar solvent for which the molecules have the same dipole moment as methanol but lack sites for hydrogen bonding. A marked qualitative difference is found in the ionic solvation and in the ion-ion potentials of mean force between the two solvents. The magnitude of the ionic association constant is shown to be a sensitive function of the short-range part of the interionic potential of mean force. Furthermore, it is shown that the ionic association constant exhibits a maximum in methanol as the ionic radius is varied, while for the simple dipolar solvent it changes monotonically. The behavior is discussed in terms of the difference in ion-solvent and ion-ion interactions in the two solvents, and results are compared with continuum theory for ionic association in liquids.

### I. Introduction

Alcohols are one of the most widely used solvents for chemical reactions. The simplest alcohol molecule consists of a hydroxyl group and an alkyl group. Although the oxygen atom has three sites (one hydrogen atom and two lone pairs) for hydrogen bonding, alcohols are thought to associate in a linear chain rather than a three-dimensional network which is typically seen in water.<sup>1-3</sup> This has been attributed to the unfavorable steric effect of alkyl groups on hydrogen bonding.<sup>1</sup> Recent computer simulations have explored the existence of other types of association, although the chain-type association is still a dominant component.<sup>3</sup> There have been several theoretical studies of ion-water interactions<sup>4-8</sup> and a few analyses of neat liquid methanol,<sup>2,3</sup> but much less work has been carried out on the structure of ion-alcohol solutions.<sup>5</sup> The ion solvation structure and ion-ion interactions in alcohols are considered to be influenced both by hydrogen bonding and nonpolar packing constraints. Here we examine the effect of hydrogen bonding on ion-solvent and ion-ion interactions in methanol by means of the extended RISM theory.<sup>9-11</sup>

Considerable progress has been made in our understanding of the structure of molecular fluids which are characterized by strong orientational correlations between molecules.<sup>12,13</sup> Two approaches

based on the Ornstein-Zernike (OZ) theory<sup>14</sup> have been developed for studying these liquids. In the linearized hypernetted chain (LHNC) approximation an expansion in angular-dependent functions with radial-dependent coefficients is employed.<sup>7,12,15-17</sup> One of the major achievements of the theory is its successful prediction of the dielectric constant of water when applied to a polarizable model of the liquid.<sup>7</sup> The utility of this method depends upon the rate of convergence of the expansion which becomes slower as molecular anisotropy becomes more significant.<sup>18</sup> The second approach is based upon an interaction site model (ISM).<sup>19-22</sup> The interaction potential between two molecules in the ISM model is expressed as a sum of spherically symmetric functions, each dependent only on the distance between a distinct pair of sites, one in each molecule. The flexibility provided by the ISM model permits the treatment of highly anisotropic interactions between complex molecules in solution. Ornstein-Zernike type equations based on ISM, popularly called RISM,<sup>19,22</sup> have been extended to polar systems.<sup>9</sup> RISM has been used successfully to analyze the short-ranged structure of several polar molecular liquids including hydrogen-bonding species.<sup>2,8,23,24</sup> Furthermore, an integral equation analysis for such systems can provide a reference useful in guiding the development of computer

(1) Franks, F.; Ives, D. J. *Q. Rev. Chem. Soc.* **1966**, *20*, 1.

(2) Pettitt, B. M.; Rossky, P. J. *J. Chem. Phys.* **1983**, *78*, 7296.

(3) Jorgensen, W. L. *J. Am. Chem. Soc.* **1980**, *102*, 543. **1981**, *104*, 341.

(4) Mezei, M.; Beveridge, D. L. *J. Chem. Phys.* **1981**, *74*, 6902. Geiger, A. *Ber. Bunsen-Ges. Phys. Chem.* **1981**, *85*, 52. Bopp, P.; Dietz, W.; Heinzinger, K. *Z. Naturforsch.* **1979**, *34A*, 1424.

(5) Chandrasekhar, J.; Jorgensen, W. L. *J. Chem. Phys.* **1982**, *77*, 15.

(6) Berkowitz, M. L.; Karim, O. A.; Macammon, J. A.; Rossky, P. J. *Chem. Phys. Lett.* **1984**, *105*, 577.

(7) Patey, G. N.; Carnie, S. L. *J. Chem. Phys.* **1983**, *78*, 5183. **1983**, *79*, 4468.

(8) Pettitt, B. M.; Rossky, P. J. *J. Chem. Phys.* **1986**, *84*, 5836.

(9) Hirata, F.; Rossky, P. J. *Chem. Phys. Lett.* **1981**, *83*, 329.

(10) Hirata, F.; Pettitt, B. M.; Rossky, P. J. *J. Chem. Phys.* **1982**, *77*, 509.

(11) Hirata, F.; Rossky, P. J.; Pettitt, B. M. *J. Chem. Phys.* **1983**, *78*, 4133.

(12) Chandler, D. *Annu. Rev. Phys. Chem.* **1978**, *29*, 441. Stell, G.; Patey, G. N.; Hoye, J. S. *Adv. Chem. Phys.* **1981**, *48*, 183.

(13) Rossky, P. J. *Annu. Rev. Phys. Chem.* **1985**, *36*, 321.

(14) Friedman, H. L. *A Course in Statistical Mechanics*; Prentice-Hall: New York, 1985.

(15) Gray, C. G.; Gubbins, K. E. *Theory of Molecular Fluids*; Oxford University: London, 1984.

(16) Carnie, S. L.; Patey, G. N. *Mol. Phys.* **1982**, *47*, 1129.

(17) Levesque, D.; Weis, J. J.; Patey, G. N. *Mol. Phys.* **1984**, *51*, 333.

(18) Haile, J. M.; Gray, C. G. *Chem. Phys. Lett.* **1980**, *76*, 583.

(19) Chandler, D.; Andersen, H. C. *J. Chem. Phys.* **1972**, *57*, 1930.

(20) Ladanyi, B.; Chandler, D. *J. Chem. Phys.* **1975**, *62*, 4308.

(21) Chandler, D.; Pratt, L. R. *J. Chem. Phys.* **1976**, *65*, 2925.

(22) Lowden, L. J.; Chandler, D. *J. Chem. Phys.* **1973**, *59*, 6587. **1974**, *61*, 5228.

(23) Pettitt, B. M.; Rossky, P. J. *J. Chem. Phys.* **1982**, *77*, 1451. Chiles, R. A.; Rossky, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 6867. Zichi, D. A.; Rossky, P. J. *J. Chem. Phys.* **1986**, *84*, 1712.

(24) Pettitt, B. M.; Karplus, M. *J. Chem. Phys.* **1985**, *83*, 781. *Chem. Phys. Lett.* **1985**, *121*, 194.

simulations, from which exact (within the limitations of the potential employed) results can, in principal, be extracted. However, for quantities such as the free energy of ion association, brute force computer simulations are both very time consuming and subject to large sampling errors so that it is very difficult to obtain a complete set of results over a wide enough range of structural or thermodynamic parameters. In this paper extended RISM<sup>9-11</sup> is applied to study the short-range corrections to the continuum theory for the potentials of mean force between ions in methanol. Efforts to improve the RISM theory based upon the physical model<sup>25</sup> and the approximations involved<sup>26-28</sup> are continuing.

The association constant of ions in infinitely dilute solution is one of the fundamental quantities in the study of solution properties.<sup>29,30</sup> Since Bjerrum proposed his famous theory,<sup>31</sup> most theoretical progress in understanding the behavior of ionic association constants has been based on continuum models of electrolyte solutions, in which ions are embedded in a structureless continuum dielectric.<sup>32-34</sup> Although some experimental data have been explained successfully within the context of this simple model, there exists data which the continuum theory completely fails to explain. One such experimental observation is the possibility of very large differences in the association constant for particular salts in various solvents which have approximately the same dielectric constant.<sup>35-39</sup> Since the association constant from the continuum theory depends only upon the ion parameters (ion radii and charges) and the dielectric constant of the solvents, the differences cannot be explained by the continuum model. The continuum theory also fails to explain the ion size dependence of the association constant, especially for hydrogen-bonded solvents. Contrary to the prediction of the continuum theory, the ionic association constants for salts in hydrogen-bonded solvents often increase as ion size increases.<sup>35-37,39</sup> All these observations suggest the utility of studying the effect of solvent structure upon the association constant.

In this article, we analyze ion-solvent and ion-ion interactions in infinitely dilute solutions of NaCl in methanol by the extended RISM theory and compare the results to that obtained for a simple dipolar solvent. The simple dipolar solvent has the same dipole moment as methanol but hydrogen-bonding interactions are excluded. The effect of solvent structure on ionic association is explored. In the following section, the theory is briefly reviewed. In section III, the structure of pure methanol is compared with that of the simple dipolar solvent. In section IV, results concerning ion-solvation structure and the interionic potential of mean force are discussed. Section V is devoted to the discussion of ionic association constants calculated from the interionic potential of mean force.

## II. Theory

The RISM equation generalized to a mixture is written as<sup>11,19</sup>

$$\rho \mathbf{h} \rho = \omega^* \mathbf{c}^* \omega + \omega^* \mathbf{c}^* \rho \mathbf{h} \rho \quad (1)$$

where  $\mathbf{h}$  is the matrix of site-site intermolecular pair correlation

functions,  $\mathbf{c}$  is the matrix of direct correlation functions,  $\rho$  is a diagonal matrix having as elements

$$\rho_{\alpha M \gamma M'} = \delta_{\alpha M \gamma M'} \rho_M \quad (2)$$

where  $\rho_M$  is the number density of the molecular species  $M$  and  $\delta_{\alpha M \gamma M'}$  is a Kronecker delta function. The  $\omega$  is an intramolecular correlation matrix defined as

$$\omega_{\alpha M \gamma M'} = \rho_M \delta_{MM'} \{ \delta_{\alpha M \gamma M} \delta(r_{\alpha M} - r_{\gamma M}) + (1 - \delta_{\alpha M \gamma M}) s_{\alpha M \gamma M} \} \quad (3)$$

where  $s$  is the intramolecular distribution function between site  $\alpha$  and site  $\gamma$  which is a Dirac delta function for a rigid bond. The equations which are suitable for our system, which consists of a molecular solvent and atomic solutes in infinite dilution, are obtained by taking the limit of eq 1 as the solute density approaches zero.<sup>11</sup>

$$\rho \mathbf{h}^{\nu\nu} \rho = \omega^* \mathbf{c}^{\nu\nu} \omega + \omega^* \mathbf{c}^{\nu\nu} \rho \mathbf{h}^{\nu\nu} \rho \quad (4)$$

$$\mathbf{h}^{\nu\nu} \rho = \mathbf{c}^{\nu\nu} \omega + \mathbf{c}^{\nu\nu} \rho \mathbf{h}^{\nu\nu} \rho \quad (5)$$

$$\mathbf{h}^{\mu\mu} = \mathbf{c}^{\mu\mu} + \mathbf{c}^{\mu\nu} \rho \mathbf{h}^{\nu\nu} \quad (6)$$

where superscripts  $u, v$  stand for solute and solvent, respectively, and  $\rho$  and  $\omega$  now refer only to solvent. The HNC-like closure

$$c_{\alpha M \gamma M'}(r) = \exp[-u_{\alpha M \gamma M'}(r)/kT + h_{\alpha M \gamma M'}(r) - c_{\alpha M \gamma M'}(r)] - 1 - (h_{\alpha M \gamma M'}(r) - c_{\alpha M \gamma M'}(r)) \quad (7)$$

has been used throughout this study. In eq 7,  $u_{\alpha M \gamma M'}(r)$  is an interaction potential between two sites, which has the form of

$$u_{\alpha M \gamma M'}(r) = 4\epsilon_{\alpha M \gamma M'} \left\{ \left( \frac{\sigma_{\alpha M \gamma M'}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha M \gamma M'}}{r} \right)^6 \right\} + \frac{q_{\alpha M} q_{\gamma M'}}{r} \quad (8)$$

where  $\epsilon_{\alpha M \gamma M'}$  and  $\sigma_{\alpha M \gamma M'}$  are the Lennard-Jones parameters, and  $q_{\alpha}$  is the charge on site  $\alpha$ . The equations are renormalized for the Coulomb term by a procedure which has been explained previously.<sup>10,11</sup>

In the present study, the first two RISM equations are solved by a standard iterative scheme with Talman's algorithm for the Fourier transform on a logarithmically spaced grid.<sup>40,41</sup> First, eq 4 is solved to get the solvent correlation function,  $\mathbf{h}^{\nu\nu}$ . Then  $\mathbf{h}^{\nu\nu}$  is used to solve eq 5 to obtain  $\mathbf{c}^{\nu\nu}$  and  $\mathbf{h}^{\nu\nu}$ . Using  $\mathbf{c}^{\nu\nu}$  and  $\mathbf{h}^{\nu\nu}$ ,  $(\mathbf{h}^{\mu\mu} - \mathbf{c}^{\mu\mu})$  can be obtained from eq 6 without further iterations for atomic solutes. Alternative methods for solving the RISM equations have also been reported.<sup>42</sup> The potential of mean force is calculated with the HNC closure as

$$W_{ij}^{\mu\nu}/kT = -\ln(\mathbf{h}_{ij}^{\mu\nu} + 1) \quad (9)$$

$$= \mathbf{u}_{ij}^{\mu\nu}/kT - (\mathbf{h}_{ij}^{\mu\nu} - \mathbf{c}_{ij}^{\mu\nu}) \quad (10)$$

The total potential of mean force can be decomposed precisely into two contributions, the Coulomb interaction scaled by the theoretical dielectric constant and the remainder of the potential.<sup>11</sup> That is

$$W_{ij}^{\mu\nu} = q_i q_j / (\epsilon_{\text{RISM}} r_{ij}) + \Delta W' \quad (11)$$

where  $\epsilon_{\text{RISM}}$  is the theoretical dielectric constant of the RISM equation and  $\Delta W'$  is the rest of the contribution which consists of the short-range (Lennard-Jones) part of the gas-phase interaction ( $u^*$ ) and a short-range part of the solvent-mediated potential ( $\Delta W$ ) between two ions. This formal separation of the continuum dielectric contribution to the potential of mean force is necessary because RISM theories do not yield correct long-range dielectric behavior.<sup>43</sup> For methanol,  $\epsilon_{\text{RISM}}$  is much smaller than the cor-

(25) Rosky, P. J. *Mol. Phys.* **1983**, *48*, 615.

(26) Cummings, P. T.; Stell, G. *Mol. Phys.* **1982**, *46*, 383.

(27) Chandler, D.; Silbey, R.; Landanyi, B. *Mol. Phys.* **1982**, *46*, 1335.

(28) Rosky, P. J.; Chiles, R. A. *Mol. Phys.* **1984**, *51*, 661.

(29) Prue, J. E. *J. Chem. Educ.* **1969**, *46*, 12.

(30) Petrucci, S. *Ionic Associations*, Vol. 1, Petrucci, S., Ed.; Academic: New York, 1971.

(31) Bjerrum, N. K. *Dan. Vidensk. Selsk. Mat.-Fys. Medd.* **1926**, *7*, No. 9.

(32) Gilkerson, W. R. *J. Chem. Phys.* **1956**, *25*, 1199.

(33) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.

(34) Ebeling, Von W. *Z. Phys. Chem. (Leipzig)* **1968**, *238*, 400.

(35) Kay, R. L. *J. Am. Chem. Soc.* **1960**, *82*, 2099.

(36) Coplan, M. A.; Fuoss, R. M. *J. Phys. Chem.* **1964**, *68*, 1177.

(37) Graham, J. R.; Kell, G. S.; Gordon, A. R. *J. Am. Chem. Soc.* **1957**, *79*, 2352.

(38) Hawes, J. L.; Kay, R. L. *J. Phys. Chem.* **1965**, *69*, 2420.

(39) Evans, D. F.; Zawoycki, C.; Kay, R. L. *J. Phys. Chem.* **1965**, *69*, 3878. Evans, D. F.; Gardam, P. *Ibid.* **1968**, *72*, 3281.

(40) Talman, J. D. *J. Comp. Phys.* **1978**, *29*, 35.

(41) Rosky, P. J.; Friedman, H. L. *J. Chem. Phys.* **1980**, *72*, 5694.

(42) (a) Gillan, M. J. *Mol. Phys.* **1979**, *38*, 1781. (b) Morriss, G. P.; Macgowan, D. *Mol. Phys.* **1986**, *58*, 745.

TABLE I: Parameters

	$\sigma^a$	$\epsilon^b$	$q^c$
O	3.08	0.175	-0.685 (-0.321) <sup>d</sup>
H	1.00	0.055	0.4
Me	3.86	0.181	0.285 (0.321)
Na <sup>+</sup>	1.897	1.607	1.0
Cl <sup>-</sup>	4.410	0.118	-1.0

<sup>a</sup>Unit in Å. <sup>b</sup>kcal/mol. <sup>c</sup>Unit in electronic charge. <sup>d</sup>Numbers in parentheses are charges for MeO liquid.

responding experimental values. A semiempirical approach has been proposed for which RISM is used to evaluate the short-range part of the potential, while the long-range part is modeled by a phenomenological term<sup>11,13</sup>

$$W_{ij}^{uu} = u^* + q_i q_j / \epsilon r_{ij} + \Delta W \quad (12)$$

where  $\epsilon$  is the phenomenological dielectric constant (methanol,  $\epsilon = 32.62$ .) The approach is based upon the fact that  $\Delta W$  does not include any contribution from terms proportional to  $1/r$ .<sup>11</sup> A recent study of aqueous electrolyte solutions by Pettitt and Rossky, using this approach, shows reasonable agreement with experimental and simulation results, indicating that  $\Delta W$  provides a useful measure of the short-range contribution to the solvent-mediated potential.<sup>8</sup>

The potential parameters which have been employed in the present calculation are the TIPS parameters developed by Jorgensen and co-workers.<sup>3,44</sup> The methyl group (Me) is treated as a united atom as it is in the numerical simulations. The original TIPS potential includes no core repulsion for the interaction associated with the hydrogen sites; this causes a numerical problem when the Mayer  $f$ -function for the oxygen-hydrogen interaction is evaluated. In order to avoid the problem, the potential has been modified to include a core repulsion for the hydrogen sites in a way that does not alter the physical nature of the original TIPS potential. Although the addition of auxiliary sites can alter the RISM correlation functions,<sup>45,46</sup> in the present case the results are not sensitive to the choice of parameters for the auxiliary sites.

The calculations have been carried out for two types of solvent, methanol, which is characterized by hydrogen bonding, and a model nonassociated dipolar liquid (which we call "MeO" solvent). The MeO molecules have the same Lennard-Jones parameters for oxygen and the methyl group as methanol but the site corresponding to the H atom has been removed. The charges on the oxygen atom and the methyl group have been adjusted so that they produce the same dipole moment as methanol.

The MeO solvent provides one possible choice for a reference non-hydrogen-bonded liquid. Since in RISM theory the dielectric constant is determined entirely by the dipole moment,<sup>10,43</sup> the MeO liquid shares those terms corresponding to the primitive model in the potential of mean force for methanol (the first two terms of eq 12). Thus, both the long-range intermolecular potential for MeO and the Lennard-Jones contribution to the short-range packing are the same as for the methanol model employed. The temperature and density of both solvents in the present calculations are 298 K and 0.78664 g/cm<sup>3</sup>, respectively. The parameters which have been employed are shown in Table I.

### III. Solvent Structure

A RISM analysis of the contribution of hydrogen bonding to the structure of liquid methanol has been presented previously by Pettitt and Rossky.<sup>2</sup> The extended RISM results obtained for the pure methanol liquid in the present study are essentially the same as the previous analysis<sup>2</sup> despite small differences in the short-range potential for the hydrogen atom. In the previous study,

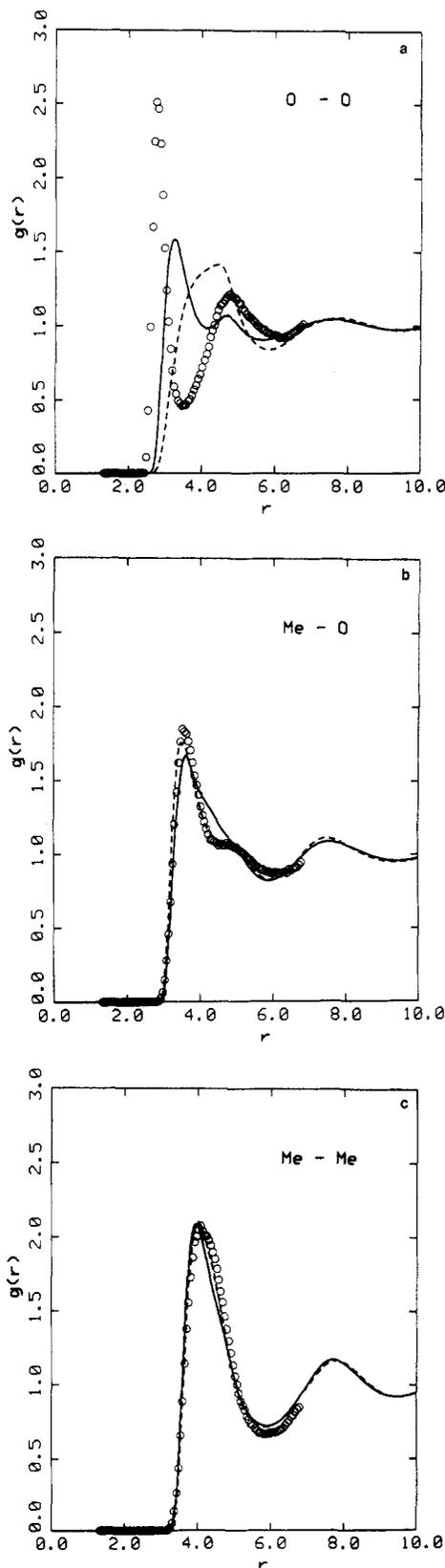


Figure 1. Site-site correlation functions for methanol and the MeO solvent. The circles are the simulation results for methanol by Jorgensen. The solid lines and the dashed lines are the extended RISM calculation for methanol and the MeO solvent, respectively. Only the results for O-O, O-H, and O-Me pairs are shown.

the effect of hydrogen bonding was evaluated by turning on the site charges continuously, so that at zero site charge the nonassociated model has zero dipole moment. This reference system is different from our MeO dipolar liquid which lacks hydrogen bonding but retains the full dipole moment of methanol. In this

(43) Sullivan, D.; Gray, C. G. *Mol. Phys.* **1981**, *42*, 443.

(44) Jorgensen, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 335. Chandrasekhar, J.; Sellmeyer, D. C.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 903.

(45) Cummings, P. T.; Sullivan, D. E.; Gray, C. G. *J. Phys. A* **1981**, *14*, 1483.

(46) Hsu, C. S.; Chandler, D.; Lowden, L. J. *Chem. Phys.* **1976**, *14*, 213.

section we compare the structure of MeO solvent with methanol and the structure of the zero charge reference of Pettitt and Rossky. In Figure 1a-c the extended RISM site-site correlation functions for methanol are compared with the result for MeO solvent. The correlation functions for polar liquids may be explained in terms of two competing effects, the packing effect and polar orientational forces,<sup>10</sup> the ability to hydrogen bond introduces additional orientational constraints. As has been discussed previously,<sup>2</sup> the extended RISM calculation for methanol agrees qualitatively with simulation results but overestimates the size of the first peak of the O-H correlation and underestimates the value for the O-O correlation. The RISM result for the site-site correlation functions of the MeO solvent show similar behavior to methanol except for the O-O pair. This is consistent with the earlier finding for methanol where the RISM correlation functions for the O-Me and the Me-Me pairs were shown to be insensitive to variation in the site charges.<sup>2</sup> This provides additional evidence for the importance of packing in determining the liquid structure. The major difference between methanol and the MeO solvent is seen in the O-O correlation function. In the absence of a site for hydrogen bonding, the O-O distribution function is broadened, the maximum shifts to larger radius (peak at  $\sim 3.85$  Å in methanol,  $\sim 4.5$  Å in MeO), and the second peak in the O-O distribution is removed. It is of interest to compare the O-O distribution function for our dipolar MeO solvent with the zero charge reference results of Pettitt and Rossky.<sup>2</sup> When both the hydrogen-bonding site and the dipole are removed from methanol, the resulting oxygen-oxygen distribution is much broader than the result for the dipolar MeO liquid. Although the hydrogen-bonding site has been removed in our MeO model, the retention of dipolar interactions increases the structure of the liquid with respect to the zero charge reference.

#### IV. Ion-Solvent Interactions and the Interionic Potential of Mean Force

The ion-solvent correlation functions for  $\text{Na}^+$  and  $\text{Cl}^-$  are shown in Figure 2a-f. The solid and dashed curves correspond to the results for methanol and MeO solvent, respectively, while the circles correspond to the simulation of  $\text{Na}^+$  in methanol by Jorgensen and co-workers.<sup>5</sup> As pointed out by these authors,<sup>5</sup> the larger first peaks in the ion-solvent correlation functions for methanol compared to water are due to the differences in the normalization by the solvent density. Comparing the RISM and simulation results for the three  $\text{Na}^+$ -solvent distribution functions ( $\text{Na}^+$ -O,  $\text{Na}^+$ -H,  $\text{Na}^+$ -Me), the position of the first peak is in excellent agreement. The  $\text{Na}^+$ -O distribution is very sharply peaked because of the strong electrostatic attraction and the simulation and RISM results agree quantitatively. The first peak of the  $\text{Na}^+$ -H distribution is also well defined as in the simulation in spite of the fact that  $\text{Na}^+$  and H repel each other by a strong Coulomb interaction. This is a reflection of the intramolecular correlation between O and H. However, the  $\text{Na}^+$ -Me distribution is considerably underestimated.

For  $\text{Cl}^-$ , the strong Coulomb interaction with H is responsible for the very large first peak. Both the  $\text{Cl}^-$ -O and  $\text{Cl}^-$ -Me correlation functions have a smaller and broader peak. They both possess a well-defined second peak at about 7 Å.

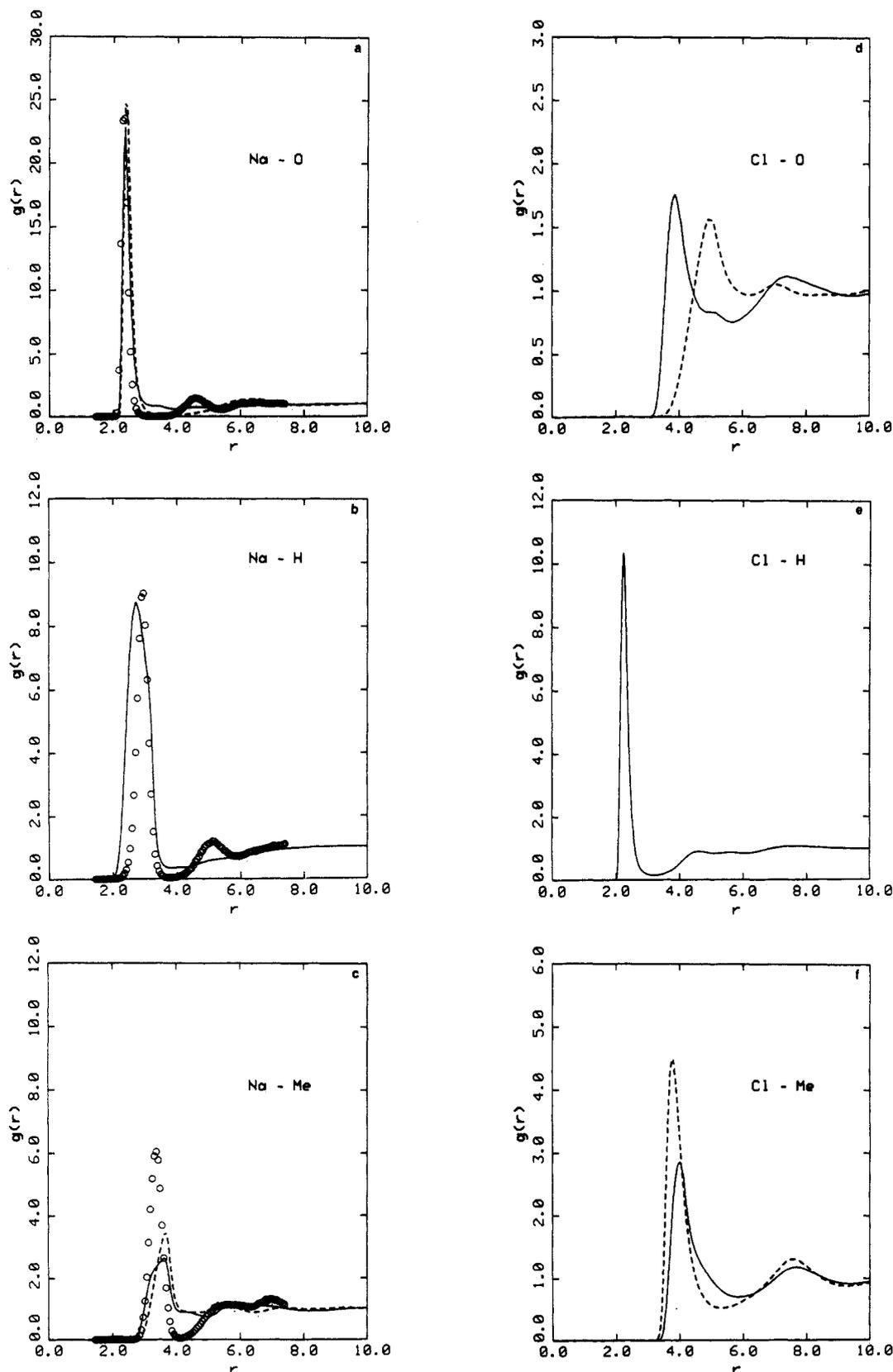
Comparing the methanol results with those for the MeO solvent, the  $\text{Na}^+$ -O distribution curves show quite similar behavior, although small differences are observed in the region beyond the first peak ( $r > 3$  Å). This reflects the difference in the positions of the second nearest neighbors in the two solvents. In methanol, oxygens in the second solvation shell around the  $\text{Na}^+$  ion are bonded through the hydroxyl hydrogen to an oxygen in the first shell while in the MeO solvent there is an intervening methyl group. A similar small difference is seen in the  $\text{Na}^+$ -Me correlation functions, which strongly reflect the effect of the  $\text{Na}^+$ -O correlation. In the MeO solvent the first peak appears at a separation which is typical for a linear  $\text{Na}^+$ -OMe configuration in which the dipole axis is aligned along the Na-O center line. In methanol, the  $\text{Na}^+$ -OMe angle is nonlinear so that the  $\text{Na}^+$ -Me distance is decreased. Although it is not clear from the comparison

of peak positions alone, the curve for methanol shows a shift to shorter separation in accord with the above discussion. Much clearer qualitative differences between the two solvents are observed for the  $\text{Cl}^-$ -O and  $\text{Cl}^-$ -Me distribution functions. In the MeO solvent, the  $\text{Cl}^-$ -Me curve has a large first peak at the  $\text{Cl}^-$ -Me contact distance. That the first peak in the  $\text{Cl}^-$ -O curve is induced by the  $\text{Cl}^-$ -Me correlation through intramolecular correlation may be verified from its position ( $\sim 5$  Å) which is consistent with one in which the  $\text{Cl}^-$  ion is on the MeO dipole axis. In methanol, however, the  $\text{Cl}^-$ -solvent distribution is dominated by the  $\text{Cl}^-$ -H correlation function. That is,  $\text{Cl}^-$  is coordinated by the Me group in the MeO solvent, while it is coordinated primarily by H atoms in methanol. As a consequence, the first peak of the  $\text{Cl}^-$ -O correlation function is displaced toward shorter separations in methanol, and the  $\text{Cl}^-$ -Me correlation function is displaced outward and reduced in height.

The potentials of mean force between ion pairs ( $\text{Na}^+$ - $\text{Na}^+$ ,  $\text{Na}^+$ - $\text{Cl}^-$ ,  $\text{Cl}^-$ - $\text{Cl}^-$ ) in methanol (solid lines) and the MeO solvent (thick dashed lines), calculated from the semiempirical expression (eq 12), are shown in Figure 3a-c. In this figure, curves for the continuum model are also plotted (thin dashed lines). We note there would be a difference of more than a factor of 4 in the absolute values of the continuum electrostatic contribution to the potentials of mean force were the RISM dielectric constant used in place of the phenomenological value. However, since the interionic potentials of mean force for the two solvents share the contribution from the continuum model, the difference between the potentials of mean force in the two solvents is independent of the choice of dielectric. Comparing the potential of mean force in the two solvents, it is clear that electrostatic shielding is greater in methanol than in the dipolar solvent. This effect, which is contained entirely within the short-range  $\Delta W$ , arises from many-body coulomb interactions which decay faster than  $(1/r)$ . In this sense, the differential solvent shielding shown in Figure 3 is a manifestation of dielectric saturation.<sup>47</sup> That there should be greater shielding in methanol than in the dipolar solvent as is observed in Figure 3 makes intuitive sense based on the additional constraints imposed by hydrogen bonding on the liquid structure of methanol. The same effect results in extra destabilization of like charged pairs. The potentials of mean force are discussed more fully below.

(a)  $\text{Na}^+$ - $\text{Cl}^-$ . The potential of mean force for the  $\text{Na}^+$ - $\text{Cl}^-$  ion pair in the dipolar solvent, MeO, contains a double well. The potential has a deep minimum around the contact separation (about 2.8 Å), followed by a shallow minimum at (about 8 Å) corresponding to a configuration in which the two ions are separated by a solvent molecule with the solvent dipole axis aligned along the ion-ion center line. The two minima are separated by a potential barrier of about 5 kcal/mol. The potential of mean force for  $\text{Na}^+$ - $\text{Cl}^-$  in methanol is qualitatively different. The well depth of the first minimum is drastically reduced; this extra shielding reflects the competition between opposing orientational forces on the solvent molecule; one produced by the electric field of the ions and the other by the hydrogen bonding among the solvent molecules. The curve is flattened in the region following the first minimum, indicating essentially no preferential configuration between the ions in that region, although there is a small local minimum at a separation, of 4.5 Å. The minimum may be attributed to a solvent-mediated configuration between the two ions in which  $\text{Cl}^-$  ion is attached to the hydrogen site and  $\text{Na}^+$  ion to the oxygen site in a way as to minimize the repulsion between the  $\text{Na}^+$  and the Me sites. Such a configuration is likely considering the well-defined first peaks in the  $\text{Na}^+$ -O and  $\text{Cl}^-$ -H correlation functions. In contrast, the potential of mean force for  $\text{Na}^+$ - $\text{Cl}^-$  in water calculated from RISM<sup>8</sup> and from simulations<sup>6</sup> is quite different. In water, the potential of mean force between the  $\text{Na}^+$ - $\text{Cl}^-$  pair features a well-resolved double well, the first minimum being attributed to the contact configuration and the second one to the solvent separated structure which changes

(47) Bottcher, C. J. F. *Theory of Electric Polarization*, Vol. 1; Elsevier: Amsterdam, 1973.

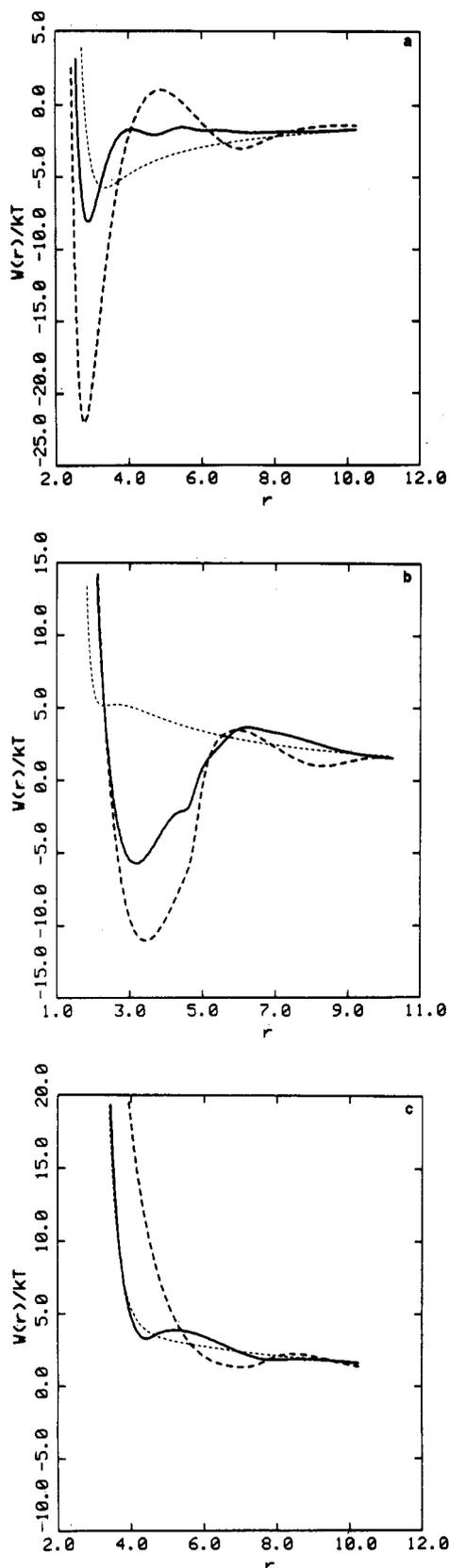


**Figure 2.** The ion-solvent correlation functions. The circles are the simulation results for Na<sup>+</sup>-methanol pairs by Jorgensen. The solid and the dashed lines are the extended RISM calculation for the ion-methanol and the ion-MeO solvent, respectively: (a) Na<sup>+</sup>-O, (b) Na<sup>+</sup>-H, (c) Na<sup>+</sup>-Me, (d) Cl<sup>-</sup>-O, (e) Cl<sup>-</sup>-H, (f) Cl<sup>-</sup>-Me.

continuously from a bridged structure to one with a dipole oriented intervening solvent molecule.<sup>6,8</sup> The solvent-separated structure may be more stable in water, because the intervening solvent molecule in the bridged structure does not interfere with the hydrogen-bonding coordination in water as much as in methanol. In methanol, the formation of a bridged structure largely prevents

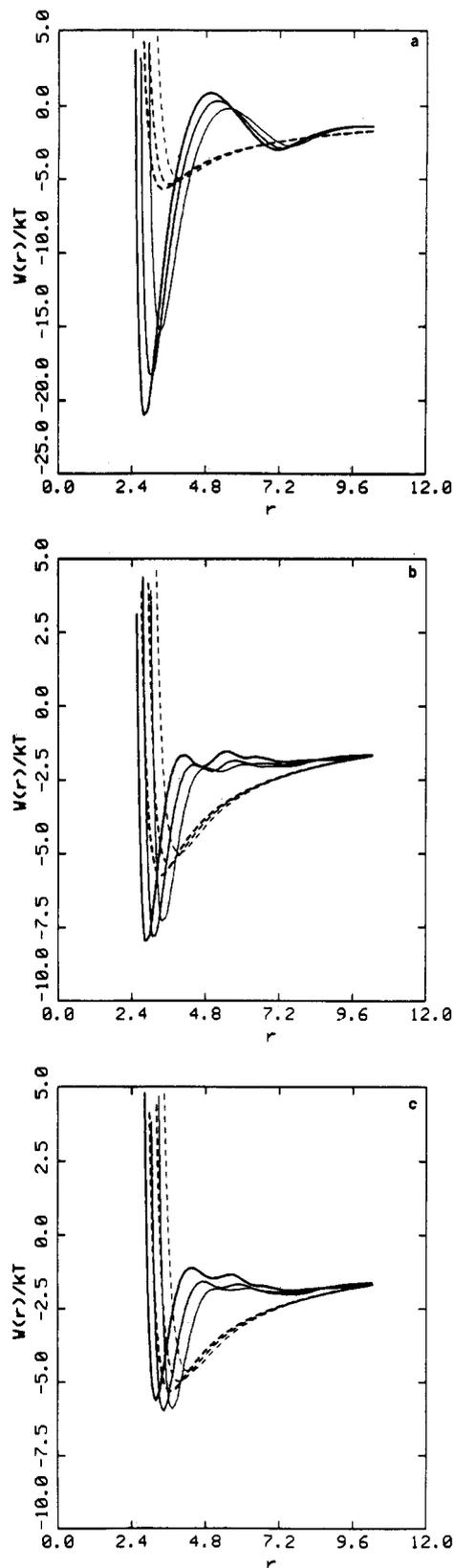
the intervening solvent molecule from hydrogen bonding due to the lack of an additional hydrogen bond donor and the bulky nature of the methyl group which prevents the hydroxyl oxygen from accepting a second hydrogen bond.

In Figure 4, the dependence of the potential of mean force upon cation size is plotted. The extended RISM results (solid lines)



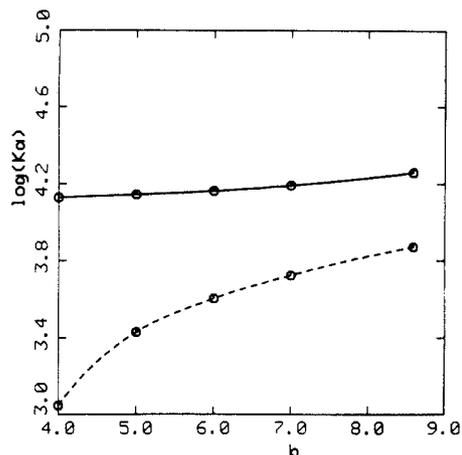
**Figure 3.** The interionic potential of mean force. The solid lines and the thick dashed lines are those in methanol and the MeO solvent, respectively. The thin dashed lines correspond to the continuum model: (a)  $\text{Na}^+-\text{Cl}^-$ , (b)  $\text{Na}^+-\text{Na}^+$ , (c)  $\text{Cl}^--\text{Cl}^-$ .

are compared with those for the continuum model (dashed lines). In the curve for the dipolar MeO solvent, Figure 4a, a rise in the first and second potential minima is observed; the potential barrier separating the two minima is lowered as the cation size increases. The rise in the first minimum is much more rapid than that



**Figure 4.** The dependence of the potential of mean force upon the cation radius: solid lines, extended RISM; dashed lines, continuum model. Various lines correspond to cation radius of 0.948, 1.2, and 1.5 in the order of thicker to thinner: (a) solvent, MeO; anion radius, 2.205 Å; (b) solvent, methanol; anion radius, 2.205 Å; (c) solvent, methanol; anion radius, 2.5 Å.

corresponding to the continuum model. Figure 4b shows corresponding plots for methanol, in which the first minimum calculated from RISM rises more slowly than the continuum. The second minimum, which corresponds to the bridged structure, is also



**Figure 5.** The association constant as a function of cutoff distance: dashed line, the continuum model; solid line, the RISM potential of mean force.

reduced. In Figure 4c results calculated for a slightly larger anion ( $r = 2.5 \text{ \AA}$ ) are shown; the contact minimum deepens as the cation size increases. The results reflect a balance among competing forces as the cation size increases: (1) a decrease in the continuum contribution to the potential, (2) a decrease in dielectric saturation, and (3) a loosening of the first solvation shell for the isolated species. The first two effects act in the same direction and produce a weaker contact minimum with increasing ionic radius. The third effect acts in the opposite direction; the displacement of more weakly bound solvent molecules associated with the larger cations deepens the contact minimum. In the dipolar MeO solvent the first two effects dominate. In methanol, the balance is more delicate, and the third effect begins to dominate as the anion radius increases (see Figure 4c). A similar but even stronger trend has been reported for the RISM potentials of mean force for the alkali chlorides in water.<sup>8</sup>

(b)  $\text{Na}^+ - \text{Na}^+$ . As seen in Figure 4b, the potential of mean force for the  $\text{Na}^+ - \text{Na}^+$  pair shows a net stabilization at short separation, which is puzzling based on an intuitive understanding of the interaction between two like-charged ions in a dipolar solvent. A similar result has been reported for  $\text{Cl}^- - \text{Cl}^-$  and  $\text{F}^- - \text{F}^-$  interactions in water.<sup>8</sup> Although relatively large LJ interactions between the  $\text{Na}^+ - \text{Na}^+$  ion pair, which contribute about  $-1 \text{ kcal/mol}$  to  $W(r)$  at separations  $r \approx 3.0 \text{ \AA}$ , will cancel part of the Coulomb repulsion between the ions, most of the stabilization comes from the solvent mediated (indirect) part of the potential. It has been pointed out in a previous paper that there is a relatively stable position for a like-charged pair at a distance in between the contact separation and one in which the ions are separated by a solvent molecule.<sup>11</sup> These configurations correspond to ones for which one of the ionic solute partners partially penetrates the solvation layer of the other. The effect, however, seems to be larger than expected, which suggests the existence of specific favorable configurations which include a  $\text{Na}^+$  pair and one or more methanol molecules. A more detailed study of this effect by computer simulation would be of interest.

### V. Ionic Association Constant and the Dependence on Ion Radii

Since Bjerrum introduced the concept of ionic association as a way to extend the Debye-Huckel theory to concentrated solutions, the theory has been developed by many authors and numerous improvements of the theory have been proposed. In its most general form, the ionic association constant is written as<sup>48</sup>

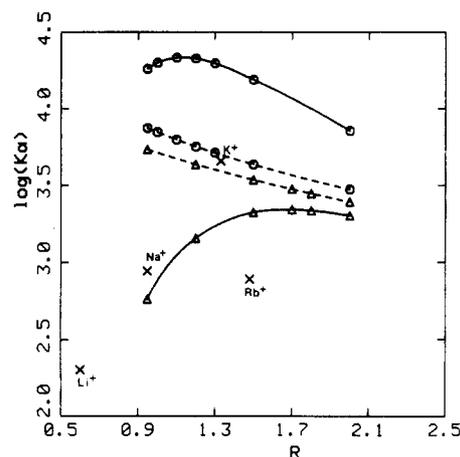
$$K_a = (4\pi N_A / 1000) \int_0^b \exp\{-W_{+-}(r) / kT\} r^2 dr \quad (13)$$

where  $W_{+-}(r)$  is the interionic potential of mean force,  $N_A$  is Avogadro's number, and  $b$  is a cutoff parameter which must be

**TABLE II: Experimental Association Constants of Alkali-Metal Salts in Various Solvents**

	MeOH ( $\epsilon = 32.62$ )	EtOH ( $\epsilon = 24.33$ )	$\text{C}_6\text{H}_5\text{NO}_2$ ( $\epsilon = 34.82$ )	$(\text{CH}_3)_2\text{CO}_2$ ( $\epsilon = 20.56$ )
LiPi			$1.7 \times 10^{7e}$	819 <sup>e</sup>
NaPi	0 <sup>a</sup>		$3.6 \times 10^{4e}$	680 <sup>e</sup>
KPi	9.9~15.4 <sup>a</sup>		$1.46 \times 10^{3e}$	244 <sup>e</sup>
LiNO <sub>3</sub>	10 <sup>b</sup>			
NaNO <sub>3</sub>	19 <sup>b</sup>			
KNO <sub>3</sub>	39 <sup>b</sup>			
RbNO <sub>3</sub>	18 <sup>b</sup>			
LiCl		27 <sup>b,c</sup>		
NaCl		44 <sup>b,c</sup>		
KCl		95 <sup>b,c</sup>		
CsCl		158 <sup>d</sup>		

<sup>a</sup>Reference 36. <sup>b</sup>Reference 35. <sup>c</sup>Reference 37. <sup>d</sup>Reference 38. <sup>e</sup>Reference 39.



**Figure 6.** The dependence of the association constant of cation-anion upon the cation radius in methanol.  $R$  in  $\text{\AA}$ . The circles and the triangles label different anion radii: circles, 2.205; triangles, 2.5. The dashed lines are corresponding association constants for the continuum model. Experimental data for  $\text{XNO}_3$  ( $X = \text{Li, Na, K, and Rb}$ ) in methanol is also plotted against crystal radii of cations.

determined from the definition of the association. The equation reduces to the Bjerrum theory if  $W_{+-}(r)$  is replaced by a primitive model potential

$$W_{+-}(r) = u_d(r) + q_+q_- / \epsilon r \quad (14)$$

where  $u_d(r)$  is the hard-sphere potential and  $b$  by  $q^2 / 2\epsilon kT$ . The choice of the upper bound of the integral implies that a pair of ions is considered associated if their interaction energy is larger than twice the thermal energy. Since the continuum model potential decays like  $1/r$  with  $r$ , this choice of cutoff is somewhat arbitrary. It is easy to see the association constant calculated from the Bjerrum equation decreases monotonically with increasing hard-sphere diameter. Two questions naturally arise for the Bjerrum theory: is the choice of cutoff reasonable, and is the primitive model realistic enough to represent the interionic potential of mean force in solvent? In Figure 5, the ionic association constants for the continuum model are plotted as a function of the cutoff distance (dashed line). The solid line in the same figure shows a corresponding result for the potential of mean force which is obtained by the RISM calculation in the preceding section. As is clear from the picture, the dependence of  $K_a$  on the cutoff distance is much weaker for the RISM potential of mean force than for the continuum model. In Table II, experimental data for association constants of some alkali-metal salts in various solvents are shown.<sup>35-39</sup> One interesting feature of the data is the large difference in  $K_a$  for the same salt (e.g. lithium picrate) among various solvents which have similar dielectric constants. The difference is clearly much larger than the one predicted from differences in dielectric constants by the continuum theory. Another point concerns the ion size dependence of  $K_a$ . A very sharp decrease with increase in ion size has been observed for

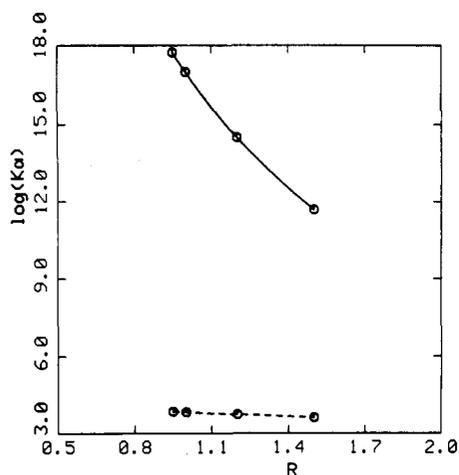


Figure 7. The association constant of cation-anion in MeO solvent labeled as in Figure 6.

alkali-metal picrates in nitrobenzene, while either a monotonic increase or a maximum has been observed for hydrogen-bonded solvents. With respect to the adequacy of the primitive model, it should be noted that the continuum potential of mean force fails to explain, even qualitatively, the ion size dependence of  $K_a$  for hydrogen-bonded solvents.

In the present study, we calculate  $K_a$  from eq 13 using eq 12 for  $W_+(r)$ . For the cutoff distance,  $b$ , the Bjerrum critical distance is employed. If the third term in the exponent is ignored, then  $K_a$  is the Bjerrum association constant. In Figure 6, the ionic association constants in methanol calculated from eq 13 have been plotted against  $R$ , where  $R$  is the Lennard-Jones diameter of the cation divided by two. (The anion radii are kept constant. Note the natural logarithm of the association constants are plotted.) The curve for the dipolar solvent is plotted in Figure 7. The large difference in the magnitude of  $K_a$  between the two solvents is a result of the difference in the short-range part of the interionic potential of mean force. Concerning the RISM results for the cation size dependence,  $K_a$  exhibits a maximum in methanol while in the dipolar solvent there is a sharp (monotonic) decrease in the association constant with increasing cation radius. The results may be interpreted in terms of the dependence of the potential of mean force upon ion size. In the case of the dipolar MeO solvent, both the rapid decrease in the dielectric saturation (not included in the continuum theory) and the decrease in the coulomb interaction as the cation size increases act in the same direction and cause the sharp and monotonic decrease in  $K_a$ . In contrast for methanol, these effects are balanced against the weaker solvation of the larger ion and this competition produces a maximum in the association constant as the cation size increases. It should be noted that the continuum model does not have the ability to produce such behavior. In Figure 6, we include experimental results for  $XNO_3$  in methanol<sup>35</sup> where X stands for the cation series Li, Na, K, and Rb. We are not yet able to make a quantitative comparison between the extended RISM predictions for  $K_a$  and experimental values. There are several reasons for this including the difficulty encountered in the interpretation of experimental data in terms of molecular parameters. Most experiments concerning ionic association make use of conductivity measurements.<sup>49</sup> The association constants extracted from the measurements largely depend on the models employed to analyze

the experiments. Although Fuoss-Onsager type equations<sup>50</sup> are well established for the primitive model of electrolytes, they can lead to inconsistent results for molecular parameters such as ion radii when applied to structured solvents.<sup>35</sup> Despite these difficulties, the general trend concerning the dependence of  $K_a$  on  $R$ , which is characterized by the existence of a maximum agrees with the predictions of the extended RISM theory.

## VI. Conclusions

Ionic solvation and the interionic potential of mean force of ions in methanol at infinite dilution have been examined by the extended RISM theory; the results have been compared with those for a dipolar solvent in which molecules have the same dipole moment as methanol but lack sites for hydrogen bonding. It has been shown that there is a qualitative difference in the ion solvation and in the ion potentials of mean force between the two solvents. Of particular interest is the large difference in the magnitude of the interionic potential of mean force at short separation, which clearly demonstrates additional screening in methanol due to the competition between different orientational forces acting on the solvent; the forces due to the ionic field and ones due to hydrogen bonding. A marked difference has been observed in the dependence of the potential of mean force upon the cation size between the two solvents; a sharp rise in the first minimum with increasing cation size for the dipolar MeO solvent due to decreasing dielectric saturation and a small rise or lowering in the minimum for methanol depending on the anion size, which results from the more delicate balance among the competing orientational effects.

Many experiments on ionic association in hydrogen-bonding liquids have established trends opposite to those predicted by the Bjerrum theory. The data have been interpreted in terms of an increase in the effective ionic radii due to solvation as the bare ionic radii decrease. The explanation coincides with the present analysis of the association constant in the sense that both attribute the behavior to the loosening of the solvation shell as the ionic radius is increased. However, it is obvious that the specificity of the ion-solvent interaction cannot be incorporated in a Bjerrum-type theory because the solvent is treated as a continuum dielectric at all interionic distances. The present results further emphasize the importance of properly accounting for the effects of solvent molecular shape and solute-solvent interactions at short range in the analysis of electrostatic effects in solution. The RISM theory<sup>12,13</sup> has now been used to analyze structural and thermodynamic aspects of a variety of solute-solvent systems in which the solutes are very small polyatomic molecules. An extension of the theory is needed to treat electrostatic effects of large molecules in solution, e.g., biopolymers. One approach involves the application of a superposition approximation.<sup>24</sup> Alternatively, we have employed a RISM equation applicable to solvated polymers which possess periodicity (e.g. DNA). The extension of the theory to polymeric molecules is presented in a separate communication.<sup>51</sup>

**Acknowledgment.** This work has been supported in part by grants from the NIH (GM-30580), the National Science Foundation Office of Advanced Scientific Computing, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. R.M.L. is the recipient of a NIH Research Career Development Award. We thank Dr. William Jorgensen for sending us the results of the simulations of methanol and a sodium ion in methanol.

**Registry No.** MeOH, 67-56-1.

(49) See General Discussion in *Faraday Discuss. Chem. Soc.* **1977**, No. 64.

(50) Fuoss, R. M.; Accasina, F. *Electrolyte Conductance*; Interscience: New York, 1959.

(51) Hirata, F.; Levy, R. M. *Chem. Phys. Lett.* **1987**, *136*, 267.