

STRUCTURE OF SOLVATED ION PAIRS FROM ELECTRIC DIPOLE MOMENTS

Ernest Grunwald

Department of Chemistry, Brandeis University, Waltham, MA 02154, USA

and Ting-Po I

Central Research, Pfizer Inc., Groton, CT 06340, USA

Abstract - Theory and complications involved in dipole moment measurements in slightly conductive polar solvents are discussed. Experimental results are presented for the following electrolytes in anhydrous acetic acid: LiCl, KCl, KBr, LiTs, KTs, CsTs, TlTs, R_4NNO_3 , BHTs, Ts = *p*-toluenesulfonate; BH = *p*-toluidinium; R_4N = tetra-isoamylammonium.

Except for R_4NNO_3 , the dipole moments indicate that solvation complexes are formed between the respective ion pairs and acetic acid molecules. Comparison of dipole moments of the solvation complexes with intrinsic dipole moments of the ion pairs yields information about the structure of the solvation complexes.

INTRODUCTION

The value of electric dipole moments for elucidating structure and bonding in ion pairs is well known from measurements in the gas phase and in non-polar solvents (Refs. 1-4). However, because of limitations of volatility and solubility, the number of ion pair species that can be studied in this fashion is limited. Measurements in polar solvents offer the advantage of greater solubility and, furthermore, will detect the formation of solvation complexes.

There are formidable difficulties, however. Ion pair dissociation is no longer negligible, and the presence of free ions introduces complications of measurement and interpretation (Ref. 5). For high-precision measurements of solution capacitance at audio-frequencies, the conductivity should be less than about 10^{-6} ohm⁻¹ cm⁻¹ (Ref. 6). High precision is essential because one needs to interpret the small difference $\Delta\epsilon = \epsilon - \epsilon_0$, where ϵ is the dielectric constant of the solution and ϵ_0 that of the solvent. Moreover, the presence of ions complicates the interpretation of the electrical capacitance of the measuring cell, for two reasons: 1) It becomes more difficult to subtract the capacitance due to the electrical double layer at the electrode (Ref. 5). 2) The conducting ions contribute significantly to the capacitance because the ionic current is out of phase with the applied AC voltage (Refs. 7-8). Correcting for this effect unfortunately introduces an adjustable parameter for each electrolyte.

If there is solvent dipole correlation, the introduction of any solute (polar or nonpolar) may interfere with that correlation (Ref. 9). Thus the dielectric constant ascribable to the solvent component may vary with solute concentration. This solute-induced medium effect can be treated rigorously only in rare cases when the molecular interactions are understood in detail. In most cases, the solute-induced medium effect must be evaluated by empirical methods (Ref. 9).

Finally, in polar solvents, basic theory of dielectrics is not as easy to apply. Although the Kirkwood theory in its general form (Refs. 10,11) is

accurate, when the theory is applied to a specific solvent, simplifying assumptions must be made. This is because the general theory is a statistical theory whose application requires detailed microscopic information about the dielectric medium. In the absence of such information, a microscopic model must be assumed to provide the needed link with macroscopic reality. In spite of these difficulties, we hope to show that results of meaningful accuracy can be obtained for ion pair dipole moments in polar solvents.

In the present discussion, we shall be concerned primarily with ion pairs in anhydrous acetic acid. This solvent is of special interest because isomerism between intimate and solvent-separated or "loose" ion pairs was first demonstrated by means of kinetic studies carried out in acetic acid (Ref.12).

EXPERIMENTAL VARIABLES

It is convenient to represent the measuring cell by an equivalent AC circuit consisting of a conductance G in parallel with a capacitance C . The measured complex AC admittance Y^* is equal to $G + j\omega C$, where $\omega = 2\pi f$, $f =$ AC frequency, and $j^2 = -1$. To obtain a quantity that is independent of the dimensions of the measuring cell one next calculates the admittance $y^* = Y^* \cdot \ell/A$. The cell constant ℓ/A is the ratio of the current path length to the cross-sectional area. Eq. (1) represents the admittance in complex notation,

$$y^* = y' + jy'' \quad (1)$$

where y' and y'' denote the respective conductive and capacitive components of y^* ; $y' = G\ell/A$ and $y'' = C\ell/A$.

For a conductive dielectric the admittance is related to the ionic conductivity L^* and the dielectric permittivity ϵ^* via Eq. (2),

$$y^* = L^* + j\omega\epsilon^* \cdot 8.85 \times 10^{-14} \quad (2)$$

in which the constant, 8.85×10^{-14} , denotes the permittivity of empty space in practical cgs units of Farad cm^{-1} . Because there is a phase difference between the AC voltage and the ionic current, L^* can be written in complex notation,

$$L^* = L' + jL'' \quad (3)$$

where L' is the component of L^* that is in phase with the voltage. Similarly, because of dielectric loss, the dielectric permittivity can be written in complex notation,

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (4)$$

Combining (2), (3) and (4) one obtains,

$$y^* = (L' + \omega\epsilon'' \cdot 8.85 \times 10^{-14}) + j(L'' + \omega\epsilon' \cdot 8.85 \times 10^{-14}) \quad (5)$$

Thus the complex component of the admittance after due correction for double-layer capacitance (Ref. 5), links the experimental to theoretical variables via (6).

$$y'' = C\ell/A = 8.85 \cdot 10^{-14} \epsilon' + L''/\omega \quad (6)$$

At audiofrequencies, ϵ' is simply the dielectric constant ϵ . $L''/(8.85 \times 10^{-14} \omega)$ has been called "the effect of the moving ions on the dielectric constant" and denoted by ϵ_T (Refs. 5,7,13).

The component L'' of the ionic conductivity, in solutions containing free ions and ion pairs, is given by the theory of Onsager and Provencher (Ref.7). Under conditions where the free-ion fraction γ of the electrolyte is small, the general expression reduces to the simple form (7) (Ref. 13), which applies to the measurements reported here.

$$\frac{L''}{w} = \frac{6.20 \times 10^{-8} \epsilon_0 I^{\frac{1}{2}} (1 + \alpha[1 + y^2]^{\frac{1}{2}} - [2\alpha R]^{\frac{1}{2}})}{(\epsilon_0 T)^{3/2} [2\alpha R]^{\frac{1}{2}} (\alpha^2 y^2 + [1 - \alpha]^2)} \quad (7)$$

I = ionic strength, γc_2

ϵ_0 = dielectric constant of pure solvent

$\alpha = (1 + 2\beta)/2$; β is a parameter (see below)

$y = 8.85 \times 10^{-14} w \epsilon_0 / (2L'\alpha)$

$R = 1 + (1 + y^2)^{\frac{1}{2}}$

Physically, the parameter β represents the ratio k/A , where k is the actual rate constant for ion pair association, and A is the theoretical rate constant for diffusion-controlled combination of opposite univalent point charges (Refs. 7,8). Because of this, physically plausible values for β lie in the range from 0 to 1.

In the present work it was sufficient to use a uniform value of $\beta = 0.5$ for all electrolytes (Ref. 13). With L''/w thus determined, straightforward application of Eq. (6) to audiofrequency data yielded a value of the dielectric constant $\epsilon' = \epsilon$.

CALCULATION OF DIPOLE MOMENTS

In current practice there are two main approaches to the calculation of molecular dipole moments in polar solvents. One is based on the Kirkwood-Froehlich equation (Ref. 14),

$$\frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} = \frac{4\pi N_0}{9kTV} g\mu^2 \quad (8)$$

Here ϵ_0 is the static dielectric constant, ϵ_∞ is the dielectric constant of induced polarization, N_0 is Avogadro's number, V is the molar volume, g is the Kirkwood correlation factor, and μ is the intrinsic dipole moment of the molecules. For liquids, Eq. (8) is exact if the liquid lattice has cubic symmetry, if the lattice positions are independent of molecular orientations, and if translational fluctuations may be neglected (Ref. 14).

In the present work an alternate approach was used which seemed to be particularly appropriate for dilute solutions. A full derivation has been published elsewhere (Refs. 5,15). For the present, we begin by representing the polarization $f(\epsilon)$ of the solution as a sum of additive terms due to the individual molecular species,

$$f(\epsilon) = (\epsilon - 1)(2\epsilon + 1)/(9\epsilon) = \sum_i c_i P_i \quad (9)$$

where c_i = molar concentration and P_i = molar polarization of the i -th molecular species. Each P_i depends not only on the intrinsic dipole moment μ_i but also on a specific dipole correlation factor g_i (Ref. 15). The final equation for a single solute (subscript 2) in dilute solution in a polar solvent (subscript 1) is (10).

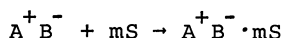
$$\begin{aligned} \mu_2^2 = \frac{9kTh_0^2}{4\pi N_0} & \left\{ \frac{d\epsilon}{dc_2} \left(\frac{2\epsilon_0^2 + 1}{9\epsilon_0^2} - \frac{12\phi_0[f(\epsilon_0) - \phi_0]}{h_0[2\epsilon_0 + 1]^2} \right) \right. \\ & \left. + V_2 f(\epsilon_0) - R_2 - \frac{4[f(\epsilon_0) - \phi_0][R_2 - \phi_0 V_2][\epsilon_0 - 1]}{[2\epsilon_0 + 1]h_0} \right\} \\ & - \left(\mu_2^2 [g_2 - 1] + c_1 \mu_1^2 \frac{dg_1}{dc_2} \right) \quad (10) \end{aligned}$$

$c_1^0 = V_1^{-1}$; $\varphi = (n^2-1)/(n^2+2)$ for the solution; $\varphi_0 = (n_0^2-1)/(n_0^2+2)$ for the pure solvent; $n =$ refractive index; $R_1 = \varphi_0 V_1$ and R_2 denote molar refractions; $h_0 = 1 - 2\varphi_0(\epsilon_0-1)/(2\epsilon_0+1)$.

The first term on the right in (10) can be measured directly and will be denoted by $\mu_{2,app}^2$; the second term involves the unknown quantities g_2 and dg_1/dc_2 . Thus, in the dilute-solution limit ($c_2 \rightarrow 0$),

$$\mu_{2,app}^2 = g_2 \mu_2^2 + c_1^0 \mu_1^2 (dg_1/dc_2)_{c_2=0} \quad (11)$$

In discussing solvated ion pairs, it is reasonable to introduce a chemical model (Ref. 15), i.e. assume that the ion pairs form firm solvation complexes:



Dipole μ_2 μ_1 $\mu_{2,solv}$

We further assume that dipole correlation between $A^+ B^- \cdot mS$ and solvent molecules outside the solvation complexes is negligible, i.e. $g_{2,solv} = 1$. On introducing this model into (11), we obtain

$$\mu_{2,app}^2 = \mu_{2,solv}^2 + c_1^0 \mu_1^2 (dg_1/dc_2)_{c_2=0} \quad (12)$$

It should be noted that, in computing $\mu_{2,app}^2$ from the first term in (10), V_2 and R_2 must be reckoned for $A^+ B^- \cdot mS$ and $\mu_{2,app}^2$ thus depend on the assumed value for the solvation number m . Fortunately, this dependence is slight.

Our aim, of course, is to obtain $\mu_{2,solv}$. Except for a small uncertainty due to the indeterminate solvation number m , $\mu_{2,app}^2$ is known. This leaves one further unknown term, $c_1^0 \mu_1^2 (dg_1/dc_2)$. Because $\mu_{2,app}^2$ (by hypothesis) $g_{2,solv} = 1$, this term can be evaluated by empirical methods (Ref. 9).

Table I lists dielectric data in acetic acid for a series of nonassociating solutes for which g_2 may be assumed to be unity. The results are represented satisfactorily by the empirical equation,

$$\mu_{2,app}^2 - \mu_2^2 = 0.286 \mu_2^2 - 0.0362 V_2 \quad (13)$$

The standard error of fit is $0.77 D^2$, which is within the combined errors of measurement. On introducing this formula into (12), one obtains

$$1.286 \mu_{2,solv}^2 = \mu_{2,app}^2 + 0.0362 V_{2,solv} \quad (14)$$

Table I Data for Nonassociating Solute in Acetic Acid at 25° (Ref.9)

Solute ^a	$d\epsilon/dc_2$ ($l \cdot mol^{-1}$) μ_2 (D)	$\mu_{2,app}^2 - \mu_2^2$ (D^2)
PhNO ₂	1.90	3.93
PhCN	2.02	3.93
PhCl	-0.54	1.58
PhH	-0.82	0.00
DTB	-1.98	0.00
CCl ₄	-1.11	0.00

^a Ph = C₆H₅; DTB = 1,4-di-t-butylbenzene

EXPERIMENTAL RESULTS

Data required for the calculation of electric dipole moments are listed in Table II (Ref. 13). $\mu_{2,app}$ was calculated for $m = 0$ and $m = 1$. Resulting

values of $\mu_{2,\text{solv}}$ (Eq. 14) are listed in Table III (Ref. 13). It can be seen that for each unit increase in solvation number, $\mu_{2,\text{solv}}$ increases by about 0.1 D. Thus any uncertainty owing to lack of knowledge of a precise solvation number is relatively small.

Table II Results for Electrolytes in Acetic Acid at 25°C^a (Ref.13)

Solute ^a	$10^7 K_d^b$	$d\epsilon/dc_2^c$	V_2^d	R_2^d
LiCl	2.5	13.1 ± 0.3	10.4 ^b	9.37
KCl	1.3	12.9 ± 0.8	27.0	13.95
KBr	2.2	15.2 ± 0.6	(34)	(17.6)
LiTs	0.7	11.8 ± 0.7	108.1	42.46
KTs	1.1	12.2 ± 0.5	121.0	46.34
CsTs	(1.5)	12.1 ± 0.5	130.1	50.42
TlTs	(1.0)	11.8 ± 0.5	129.9	50.37
BHTs	0.74	14.6 ± 0.3	218.4	77.83
R ₄ NNO ₃	43 ^f	35.9 ± 3.0	366.6 ^e	(111.9)

^aValues in parentheses are estimates. Ts = *p*-toluenesulfonate, BH = *p*-toluidinium, R₄N = tetraisoamylammonium. ^bConcentrations in mol/l. ^cLiters/mole; $\epsilon (= \epsilon')$ was calculated via Eq. 6. Plots of ϵ vs. c_2 were linear with correlation coefficients averaging about 0.985. ^dMilliliters/mole. ^eMeasured in chlorobenzene. ^f K_d varies with the ion pair concentration: $10^6 K_d = 3.04 + 87(c_2 - 1)$; $c_2 \leq 0.003$.

Table III Dipole Moments of Solvated Ion Pairs in Acetic Acid^a (Ref.13)

Ion Pair	m = 0		m = 1		μ_2^b
	$\mu_{2,\text{app}}$	$\mu_{2,\text{solv}}$	$\mu_{2,\text{app}}$	$\mu_{2,\text{solv}}$	
R ₄ NNO ₃	16.0	14.5	16.1	14.6	14.0 (CB)
LiCl	9.5	8.4	9.6	8.6	7.12 (G), 6.8 (HOct)
KCl	9.4	8.3	9.5	8.5	10.27 (G)
KBr	10.3	9.1	10.4	9.3	10.41 (G)
LiTs	9.1	8.2	9.2	8.4	
KTs	9.3	8.4	9.4	8.6	4.8 (HOct)
CsTs	9.2	8.3	9.3	8.5	
TlTs	9.1	8.2	9.2	8.4	
BHTs	10.2	9.3	10.3	9.5	6.1 (HOct)

^aDipole moments in Debye units. m = assumed solvation number. R₄N = (i-Am)₄N, Ts = *p*-toluenesulfonate, BH = *p*-toluidinium. Data for acetic acid at 25°C: $\epsilon_0 = 6.265$, $n_0 = 1.3699$, $V_1^0 = 57.54$ ml/mol, $R_1(\text{Na-D}) = 13.01$ ml/mol. ^bCB = chlorobenzene, G = gas phase, HOct = octanoic acid, μ_2 for BHTs in HOct estimated from measured μ_2 for *p*-fluoroanilinium *p*-toluenesulfonate.

For most of the ion pairs listed in Table III, intrinsic dipole moments are available from measurements in gas phase, chlorobenzene, or octanoic acid. (Results for LiCl, shown in Table III, suggest that dipole moments in octanoic acid are close to those in gas phase.) For tetra-isoamylammonium nitrate, $\mu_{2,\text{solv}}$ (m = 0) agrees quite well with μ_2 as measured in

chlorobenzene. This ion pair is not expected to form a solvation complex with acetic acid because of the chemical inertness of the cation. Thus the agreement of $\mu_{2,\text{solv}}$ ($m = 0$) with μ_2 tends to confirm the validity of the treatment of the data.

NATURE OF SOLVATION COMPLEXES

For other ion pairs, discrepancies between $\mu_{2,\text{solv}}$ and μ_2 are significant, indicating that the ion pairs form solvation complexes. The differences of $\mu_{2,\text{solv}} - \mu_2$ are positive for LiCl, KTs, and BHTs, and negative for KCl and KBr. Even though the results are not sufficient for suggesting precise structures of the solvation complexes, some unambiguous deductions can be made from the sign of the differences (Ref. 13).

Let us begin by considering some molecular models. In discussing the formation of solvation complexes with acetic acid, it is necessary to consider both the cis and the trans conformation of the carboxyl group (Figure 1) (Ref. 16). The cis conformation has a dipole moment of ~ 1.4 D, which makes an

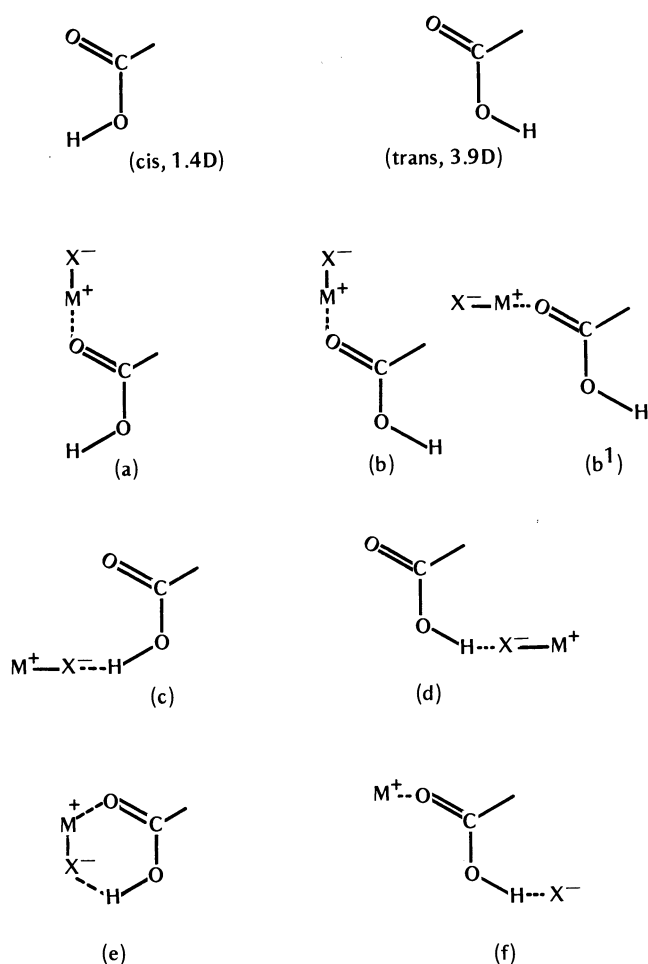


Figure 1. Models for solvation of M^+X^- ion pairs by a molecule of cis or trans-AcOH. For further description, see text.

angle of 112° with respect to the OH-bond direction. The trans conformation has a dipole moment of ~ 3.9 D, which is nearly parallel to the OH-bond direction. The two conformations generate two families of models for the solvation complexes.

The models to be considered will be called monodentate-to-cation (Figures 1a, 1b, and 1b¹), monodentate-to-anion (Figures 1c and 1d), and bidentate (Figures 1e and 1f). In the monodentate-to-cation models, the solvent molecule acts as a ligand. In the monodentate-to-anion models, the solvent molecule acts as a hydrogen-bond donor. In the bidentate model involving cis-AcOH, the structure is cyclic. The bidentate model involving trans-AcOH corresponds to a solvent-separated ion pair.

As for any process involving ring formation, the cyclic bidentate complex involving cis-AcOH will form only if certain geometrical requirements are met. As indicated in Figure 2, the directions of preferred coordination

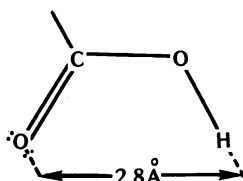


Figure 2. Points of van der Waals contact in cis-AcOH for the formation of a cyclic bidentate solvation complex with M^+X^- .

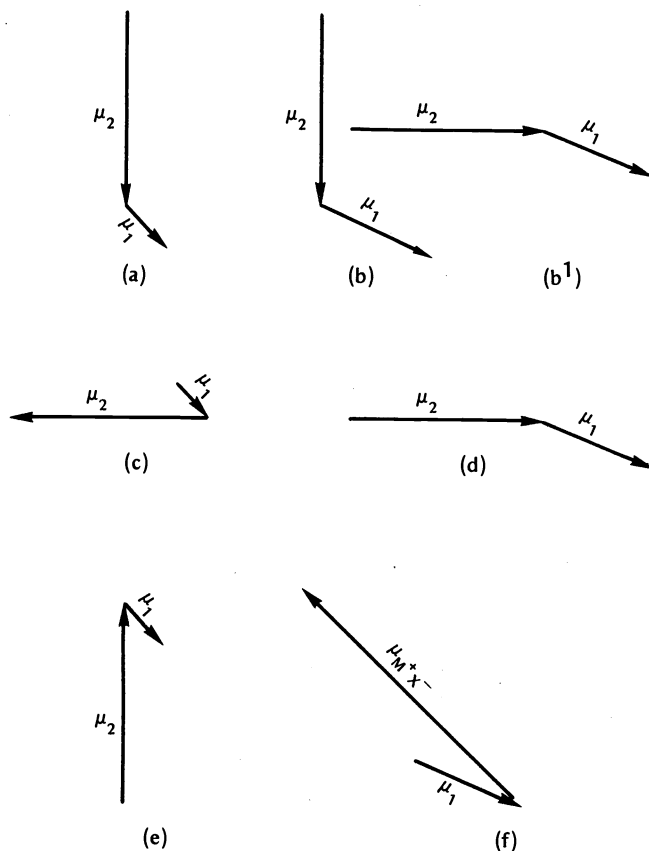


Figure 3. Vector diagrams of dipole orientations of μ_1 and μ_2 for the various models shown in Figure 1.

are roughly parallel, approaching each other only slightly. Hence the distance between the two points of van der Waals contact, $2.8 \pm 0.1 \text{ \AA}$ according to measurements using CPK space-filling molecular models, should match the distance between the binding sites in the ion pairs. For simple ion pairs such as the alkali halides, the latter distance would be essentially equal to the distance between the ionic centers. Hence the geometrical requirements for cyclic bidentate complex formation will be most nearly met if the interionic distance in the alkali halide ion pair is ca. 2.8 \AA .

Vector diagrams of the dipole orientations of μ_1 and μ_2 in the various models are indicated in Figure 3. These diagrams neglect the creation of induced moments by mutual polarization, which would normally reduce the dipole moment of the solvation complex. According to the vector diagrams, we expect $\mu_{2, \text{solv}}$ to be greater than μ_2 for the models in Figures 1a, 1b, and 1d. (See also Figure 1). We expect $\mu_{2, \text{solv}}$ to be less than μ_2 for the models in Figures 1e and (probably) 1c. For the solvent-separated ion pair in Figure 1f, the distance between the ionic centers is greatly increased. Hence a greatly enlarged vector $\mu_{M^+X^-}$ takes the place of μ_2 , and we expect $\mu_{2, \text{solv}}$ to be greater than μ_2 even though the directions of μ_1 and $\mu_{M^+X^-}$ roughly oppose each other.

On the basis of these considerations, if $\mu_{2, \text{solv}} > \mu_2$, there are numerous models that could fit. On the other hand, if $\mu_{2, \text{solv}}$ is about 1-2 D less than μ_2 , then of the models that have been considered, the cyclic bidentate model e is the only one that will fit. If at the same time the geometrical requirements for ring formation are met by the ion pair, then the cyclic bidentate model is strongly indicated.

Specific Ion Pairs. For the alkali halides listed in Table III, interionic distance in the isolated ion pair is 2.02 \AA for LiCl, 2.67 \AA for KCl, and 2.82 \AA for KBr (Ref. 4). The latter values are close to the estimated $2.8 \pm 0.1 \text{ \AA}$ distance that is considered optimum for cyclic bidentate solvation, and we note that $\mu_{2, \text{solv}}$ is appropriately less than μ_2 by 1-2 D. We infer that the solvation complexes of KCl and KBr have structures similar to that modeled in Figure 1e.

On the other hand, for LiCl the interionic distance is too small for strain-free cyclic bidentate solvation. At the same time, the Li^+ ion, owing to its small size and high charge density, is a strong Lewis acid toward oxygen bases. Since $\mu_{2, \text{solv}}$ for LiCl is greater than μ_2 by 1-2 D, we believe that the monodentate-to-cation model 1a is indicated. The model in Figure 1b is less probable, owing to the high μ_1 for $t\text{-AcOH}$.

For unsolvated KTs in previous work (Ref. 17), we considered two kinds of ion-pair structure, shown in Figure 4. The axial structure in Figure 4a has a predicted dipole moment of $\sim 5 \text{ D}$, which is in good agreement with the experimental $\mu_2 = 4.8 \text{ D}$ in octanoic acid (Ref. 17). The corner structure in Figure 4b has a predicted $\mu_2 \sim 10 \text{ D}$. For KTs in acetic acid, as shown in Table III, $\mu_{2, \text{solv}} = 8.6 \text{ D}$ for $m = 1$. This result can be explained by two

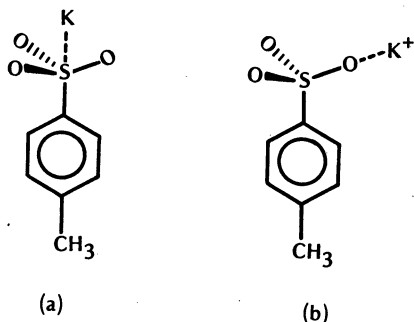


Figure 4. Plausible models of ion pair structure for potassium p-toluenesulfonate: (a) axial structure, (b) corner structure.

different kinds of solvated structure. If the basic axial structure in Figure 4a remains intact (by analogy with Crown complexes of KT's) (Ref. 18), then the large enhancement of μ_2 , owing to solvation requires solvation by trans-AcOH, according to the models in Figures 1b or 1b'. Alternatively, the ion pair could rearrange to the polar corner structure in Figure 4b, which then becomes solvated according to the cyclic bidentate model in Figure 1e. It is relevant in this connection that the nearest-neighbor K^+O^- distance in potassium sulfonate crystals is 2.8-3.2 Å. According to Figure 2, 2.8 ± 0.1 Å would be the optimum distance for bidentate cyclic solvation. It is also relevant that $\mu_{2,solv}$ is 1-2 D less than $\mu_2 \sim 10$ D predicted for the polar corner structure in Figure 4b.

Regarding the structure of solvated p-toluidinium p-toluenesulfonate, it is clear from the large enhancement of the dipole moment that solvation plays a prominent role. In this case the models for cation solvation are different from those of Figure 1 because the cation now can function as hydrogen-bond donor. We prefer not to speculate about detailed structures at this time.

Acknowledgement - The authors thank the American Chemical Society for permission to reproduce some material from reference 13.

REFERENCES

1. A. L. McClellan, "Table of Experimental Dipole Moments" (a) Vol. 1, W. H. Freeman and Company, 1963; (b) Vol. 2, Rahara Enterprises, 1974.
2. K. Bauge and J. W. Smith, J. Chem. Soc., 1964, 244.
3. E. S. Rittner, J. Chem. Phys., 19, 1030 (1951).
4. E. Grunwald, S. Highsmith and T. P. I, "Ions and Ion-Pairs in Organic Reactions," M. Szwarc, ed., Wiley-Interscience, 2, 462 ff. (1974).
5. E. Grunwald and A. Effio, J. Solution Chem., 2, 373 (1973).
6. (a) R. L. Kay, G. A. Vidulich, and K. S. Pribadi, J. Phys. Chem., 73, 445 (1969); (b) G. A. Vidulich, D. F. Evans, and R. L. Kay., ibid., 71, 656 (1967).
7. L. Onsager and S. W. Provencher, J. Amer. Chem. Soc., 90, 3134 (1968).
8. S. Highsmith and E. Grunwald, J. Phys. Chem., 78, 1431 (1974).
9. E. Grunwald, S. P. Anderson, A. Effio, S. E. Gould, and K. C. Pan, J. Phys. Chem., 80, 2935 (1976).
10. (a) J. G. Kirkwood, J. Chem. Phys., 7, 911 (1939); (b) J. G. Kirkwood, Trans. Faraday Soc., A42, (1946).
11. C. F. J. Böttcher, "Theory of Electric Polarization," Elsevier, Amsterdam (1952).
12. (a) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, J. Amer. Chem. Soc., 76, 2597 (1954); (b) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, ibid., 78, 328 (1956).
13. E. Grunwald, M. R. Crampton, A. Effio, and T. P. I, J. Amer. Chem. Soc., 98, 1716 (1976).
14. P. Bordewijk, Physica, 69, 422 (1973).
15. E. Grunwald, and K. C. Pan, J. Phys. Chem., 80, 2929 (1976).
16. C. P. Smyth, "Dielectric Behavior and Structure", McGraw Hill, New York, N.Y., pp 303-309 (1955).
17. T. P. I and E. Grunwald, J. Amer. Chem. Soc., 96, 2387 (1974).
18. T. P. I and E. Grunwald, J. Amer. Chem. Soc., 96, 2879 (1974).