

ION SOLVATION AND ASSOCIATION IN COMPLEX SOLVENTS: THEORETICAL CONSIDERATIONS

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Abstract—We discuss some theoretical issues concerning ion association in complex hosts. In particular the effect of temperature and pressure on ion pairing is discussed in relation to recent experimental observations in polymer ionic conductors.

Key words: ion solvation, complex solvents, polymer electrolytes, lattice gas, size effects.

INTRODUCTION

The effect of ion-ion and ion-host interactions on ionic transport in polymer ionic conductors has been the focus of many studies in the last few years[1-3]. Ion matrix interaction plays the dominant role in determining the ion mobility. Interionic coupling is important both because it affects the ion mobility and because it affects, via ion association, the concentration of free carriers. Ion association is of course a subject of major importance in the general chemistry of electrolyte solutions[4-9].

Recent experimental results[10-15] have shown that ion-ion interactions in general, and ion association in particular are strongly affected by the polymer matrix environment. Greenbaum and co-workers[10-12] have observed salt precipitation out of poly(propylene oxide) (PPO) as the temperature increased. Torrel and co-workers[13-15] have observed an increase of ion pairing at higher temperature also in PPO salt systems. These observations stand in contrast to previous intuitive expectations[16] that salts in polymer hosts behave as weak electrolytes with ionic dissociation increasing with temperature.

Let ξ denote the reaction coordinate of the dissociation reaction $MA \rightarrow M^+ + A^-$, so that $1 - \xi$ denotes the fraction of MA molecules which remain associated. The Bjerrum theory[17] of ion association predicts

$$1 - \xi \propto r_{\min}^3 \int_{a/r_{\min}}^1 dx x^2 e^{2/x}, \quad (1)$$

where a is the distance of the closest approach of the ions (*ie* sum of their radii) and where

$r_{\min} = |z_A z_M| q^2 / 2DkT$ (q is the electron charge, z_A and z_M (taken for specificity to be ± 1 in the following discussion) are the dimensionless charges on the ions, D is the solvent dielectric constant, T is the temperature and k is the Boltzmann constant) is the distance of minimum probability for the ion pair separation. According to equation (1) association decreases with increasing T if the temperature dependence of D is disregarded. The Bjerrum theory and its generalizations[18] describe relatively loose ion pairs whose motion is correlated but their influence on the solvent may be similar to that of the individual ions. For tight ion pairs Fuoss[19] and Denison and Ramsey[20] predict $1 - \xi \propto \exp(|z_A z_M| q^2 / DkT)$ which again decreases as T increases if D is assumed constant.* Thus these theories of ion pairing are in accord with our intuitive expectations.

While these kinds of considerations have proven useful in analysing several aspects, in particular the dependence on the dielectric constant D , of ion association, we are not familiar with critical studies of the predicted temperature dependence. In fact there are many ionic dissociation reactions which are characterized by negative standard (at infinite dilution) enthalpies (*eg* ΔH^0 for the dissociation of $MgSO_4$, $PbCl_2$ and $CaSO_4$ in water are -4.84 , -4.38 and -1.65 kcal mol $^{-1}$, respectively[4]) implying increase in association with increasing temperature. We may expect positive standard enthalpies in non-aqueous solvent where the contribution of ion solvation energies is smaller, still it appears that disregarding aspects of the solvent structure in the traditional theories of ion association leads to incorrect estimates of the temperature dependence of the effect.

In what follows, we describe and analyse an extremely simple model of ion solvation and pairing. This is a lattice gas model which for (unrealistic) simple choices of interaction potentials can be solved exactly. We use this model to study the factors that may be involved in the pressure and temperature dependence of ion association in complex fluids. Before doing so, we discuss some implication of general thermodynamics theory on our problem.

*In fact the temperature dependence of the dielectric constant D may be important in these considerations. Experimental results for PPO (see Ref. [21], Fig. 1) may be approximately represented above T_g by $D \approx 9 - [T(K)/70]$ which indicates that the product DT decreases when T increases beyond ~ 310 K. The experimental results of Refs [13-15] however show increasing association for $T \geq T \approx 220$ K and the temperature dependence of D cannot explain this trend.

THERMODYNAMICS OF (IONIC) DISSOCIATION REACTIONS

Consider the equilibrium system solute/solvent where the solute undergoes a simple chemical reaction $MA \rightleftharpoons M^+ + A^-$. For a fixed solvent/solute ratio the equilibrium state of the system is characterized by the temperature T and the pressure P . In particular T and P determine the equilibrium value of ξ , $\xi = \xi(P, T)$. Usually the analysis of the dependence of ξ (or of the equilibrium constant $K \approx \xi^2/(1-\xi)$) on T proceeds by considering $K = e^{-\Delta G^0/RT}$, where $\Delta G^0 = \Delta H^0 - T \Delta S^0$ is the difference between the standard molar Gibbs free energies of reactants and products, so that $d \ln K/dT = \Delta H^0/RT^2$, implying that K increases or decreases with T according to whether ΔH^0 is positive or negative. Note that the exact expression for K involves the activities and not the concentrations, so a given temperature dependence of K implies the temperature dependence of ξ only for dilute solutions. On the other hand, the thermodynamic expression of the Le Chatelier principle

$$\left(\frac{\partial \xi}{\partial T}\right)_P = \frac{1}{G''} \left(\frac{\partial S}{\partial \xi}\right)_{P,T} = \frac{1}{TG''} \left(\frac{\partial H}{\partial \xi}\right)_{P,T}, \quad (2)$$

is exact, where all quantities are evaluated at equilibrium and where $G'' = (\partial^2 G/\partial \xi^2)_{P,T} > 0$. Thus the derivative with respect to temperature of the reaction coordinate ξ (at constant pressure) has the same sign as $(\partial H/\partial \xi)_{P,T}$. Note that in contrast to ΔH^0 (which is the enthalpy change per mole for the dissociation reaction at infinite dilution), $(\partial H/\partial \xi)_{P,T}$ here refers to the variation with ξ of the actual enthalpy in the present equilibrium state.

Equation (2) is derived by considering the variations of thermodynamic functions along the chemical equilibrium line using T, P as independent variables. A similar procedure with T and the volume V as independent parameters results in another realization of the Le Chatelier principle

$$\left(\frac{\partial \xi}{\partial T}\right)_V = \frac{1}{A''} \left(\frac{\partial S}{\partial \xi}\right)_{V,T} = \frac{1}{TA''} \left(\frac{\partial E}{\partial \xi}\right)_{V,T}, \quad (3)$$

with $A'' = (\partial^2 A/\partial \xi^2)_{V,T} > 0$, so $(\partial \xi/\partial T)_V$ has the same sign as $(\partial E/\partial \xi)_{V,T}$. Thus the direction of the temperature dependence of the reaction coordinate is determined at constant pressure by $(\partial H/\partial \xi)_{P,T}$ and at constant volume by $(\partial E/\partial \xi)_{V,T}$. General thermodynamic relations also yield

$$\begin{aligned} \left(\frac{\partial H}{\partial \xi}\right)_{P,T} &= \left(\frac{\partial E}{\partial \xi}\right)_{V,T} + T \left(\frac{\partial P}{\partial T}\right)_{\xi,V} \left(\frac{\partial V}{\partial \xi}\right)_{P,T} \\ &= \left(\frac{\partial E}{\partial \xi}\right)_{V,T} + T \frac{\alpha}{\beta} \left(\frac{\partial V}{\partial \xi}\right)_{P,T}, \end{aligned} \quad (4)$$

where $\alpha = V^{-1}(\partial V/\partial T)_P$ and $\beta = -V^{-1}(\partial V/\partial P)_T$ are the isobaric thermal expansion coefficient and the isothermal compressibility, respectively. Since in general $\alpha, \beta > 0$ we see that it is possible to have $(\partial E/\partial \xi)_{V,T} > 0$ and $(\partial H/\partial \xi)_{P,T} < 0$ if $(\partial V/\partial \xi)_{P,T}$ is sufficiently large and negative. In this case, the temperature dependence of the reaction coordinate will be qualitatively different in constant volume and in constant pressure experiments: ξ will increase with T

in the former situation, and decrease with T in the latter one. This can indeed be the situation in realistic systems of interest because for solvents of low dielectric constant we expect that the energy change associated with the reaction $MA \rightarrow M^+ + A^-$ is positive, namely the energy cost for the charge separation is larger than the energy gain due to ion solvation. However the change in volume in this reaction is expected to be negative (electrostriction) so it is possible to have $\Delta H = \Delta E + P \Delta V < 0$ even if $\Delta E > 0$. (For any extensive thermodynamic quantity X , $\Delta X = (\partial X/\partial \xi) \Delta \xi$ where $\Delta \xi$ corresponds to one mole-reaction.) We investigate this possibility next with a simple lattice gas model.

MODEL AND RESULTS

In our model the solvent is a non-interacting lattice gas (NILG) where each molecule occupies one site and multiple site occupation is forbidden. The solute can be in one of two forms: either a neutral molecule (ion pair) which does not interact with the solvent (except of site blocking) or as two separated ions. The anion lattice interaction is again neglected (except of site blocking), while the cation lattice interaction is taken to be $\epsilon (< 0)$ for nearest neighbors and zero otherwise. The dissociation energy ($MA \rightarrow M^+ + A^-$) is taken as $E_r (> 0)$. Different MA, M^+ and A^- species do not interact with each other.

This model is exactly soluble. So are simple generalizations (eg longer range ion-lattice interaction and non-zero anion-lattice interaction) but this simplest model is sufficient for our purpose. Note that neglecting the anion lattice interaction reflects the observation that in polyethers (where "inverse" temperature dependence of ξ was found)[10-15], cations interact more strongly with the host matrix (via the oxygen sites) than anions. Taking only nearest neighbor cation-host interactions is consistent with the fact that oxygen sites which are not nearest to the cation are relatively far from it.

For the model defined, the changes in the enthalpy energy and volume which accompany the reaction $MA \rightarrow M^+ + A^-$ are the same as that associated with the reaction $M \rightarrow M^+$ if the energy of the corresponding gas phase reaction is taken as E_r . The grand partition function (GPF) for the system is

$$\Xi = (1 + e^{\beta \mu})^{N-2} (1 + e^{-\beta \epsilon} e^{\beta \mu})^l e^{-\beta E_r \xi}, \quad (5)$$

where l is the solute coordination number, μ is the solvent chemical potential, $N + 2$ is the number of sites (ie the volume) of the lattice and $\beta = 1/kT$. The case $\xi = 0$ represents the case of neutral M undissociated MA while $\xi = 1$ corresponds to M^+ . From the $\xi = 0$ case, the chemical potential and pressure P are obtained in terms of T and of density $\rho = n/N$ of solvent particles

$$\begin{aligned} \mu &= kT \ln \frac{\rho}{1-\rho} \\ P &= -kT \ln(1-\rho). \end{aligned}$$

Therefore, keeping P and T constant for this system implies that μ and ρ are also constants. The variations $(\partial E/\partial \xi)_{N,T}$ and $(\partial n/\partial \xi)_{N,T}$ in the energy and

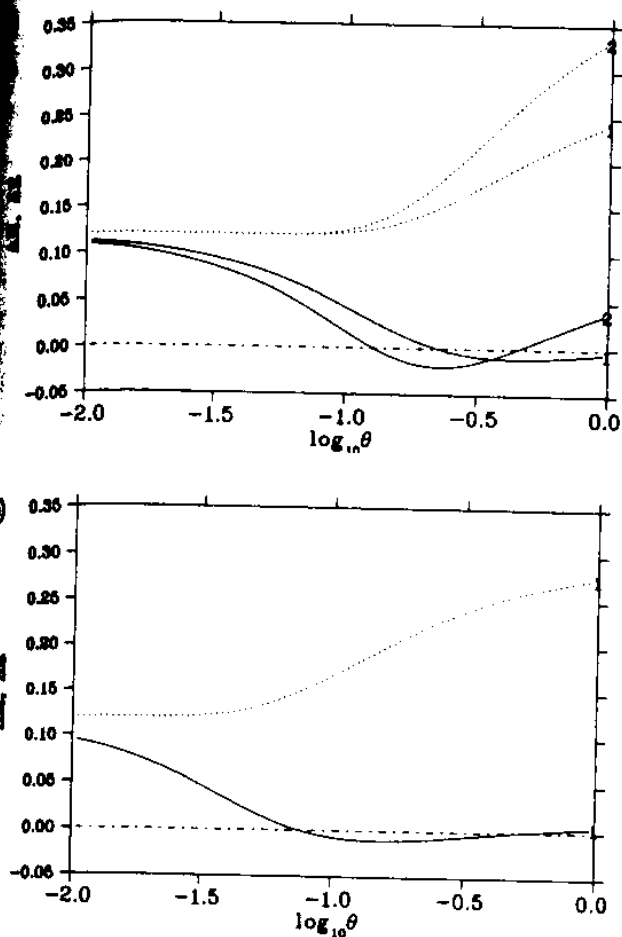


Fig. 1. (a) The enthalpy (full lines) and the energy (dotted lines) of the ionization reaction $M \rightarrow M^+$ as a function of temperature in the 1-D ($l = 2$) lattice gas model. The curves marked 1 are for a "monoatomic" solvent (each molecule occupies one lattice site) and those marked 2 are for a "diatomic" solvent (each molecule occupies two lattice sites). The horizontal line is drawn to help the distinction between the positive and negative ΔH regions. (b) As for (a), but for a "monoatomic" solvent in a cubic ($l = 6$) lattice gas model.

ditions a change in volume ($N - N'$) of the exterior subsystem,

$$\left(\frac{\partial N}{\partial \xi}\right)_{P,T} = -\frac{1}{\rho} \left(\frac{\partial n}{\partial \xi}\right)_{N,T} = -l \frac{(1-\rho)(e^{-\beta\epsilon} - 1)}{1 - \rho + \rho e^{-\beta\epsilon}} \quad (10)$$

Inserting equations (7), (8) and (10) into

$$\left(\frac{\partial H}{\partial \xi}\right)_{P,T} = \left(\frac{\partial E}{\partial \xi}\right)_{P,T} + P \left(\frac{\partial N}{\partial \xi}\right)_{P,T} \quad (11)$$

we finally get

$$\left(\frac{\partial H}{\partial \xi}\right)_{P,T} = E_R + \frac{\rho l \epsilon e^{-\beta\epsilon}}{1 - \rho + \rho e^{-\beta\epsilon}} + l k T (1 - \rho) \ln(1 - \rho) \frac{e^{-\beta\epsilon} - 1}{1 - \rho + \rho e^{-\beta\epsilon}} \quad (12)$$

The first two terms on the right hand side of equation (12) represent $(\partial E / \partial \xi)_{P,T}$ [it is easy to show that for the present model this is equal to $(\partial E / \partial \xi)_{N,T}$ given by equation (8)]. As stated above we expect that for the system considered $\epsilon < 0$ but $E_R + l\epsilon > 0$ ($|l\epsilon|$ is the maximal "solvation energy" for this model) so an increase in T at constant volume will cause the "intuitively expected" increase in dissociation. However for $\epsilon < 0$ the last term in equation (12) is negative, which may lead to $(\partial H / \partial \xi)_{P,T} < 0$ and a "counter-intuitive" temperature dependence for constant pressure experiments.

number of solvent particles with respect to the reaction coordinate are obtained in terms of N , μ and T from the usual thermodynamic derivatives of the GPF

$$\left(\frac{\partial E}{\partial \xi}\right)_{N,T} = E_r + \frac{\rho l \epsilon e^{-\beta\epsilon}}{1 - \rho + \rho e^{-\beta\epsilon}} \quad (8)$$

$$\left(\frac{\partial n}{\partial \xi}\right)_{N,T} = l \rho \frac{(1 - \rho)(e^{-\beta\epsilon} - 1)}{1 - \rho + \rho e^{-\beta\epsilon}} \quad (9)$$

Equation (9) expresses (for $\epsilon < 0$) the increase in the number of solvent molecules in a system of given N and T , due to accumulation of solvent particles near the charged solute. If we replace the constant N (volume) constraint by a constant P constraint this accumulation implies a decrease in N . This can be seen by regarding our system as made of two subsystems in contact: an interior one of constant volume N' which surrounds the reaction center [in which the number of solvent particles changes according to equation (9)] and an exterior one surrounded by impermeable wells in which pure solvent is kept at constant T , P , μ and ρ . The accumulation of particles in the interior subsystem implies under these con-

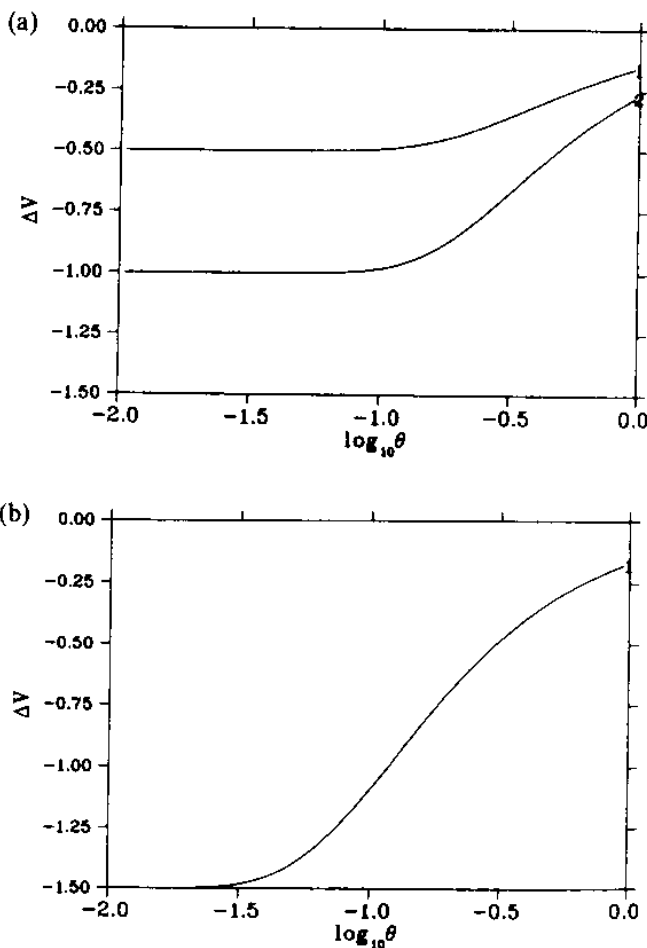


Fig. 2. (a) The volume change ΔV for the $M \rightarrow M^+$ reaction as a function of temperature in the 1-D lattice gas model ($l = 2$). The curves marked 1 and 2 are for "monoatomic" and "diatomic" solvents respectively. (b) As for (a), but for a 3-D "monoatomic" solvent ($l = 6$).

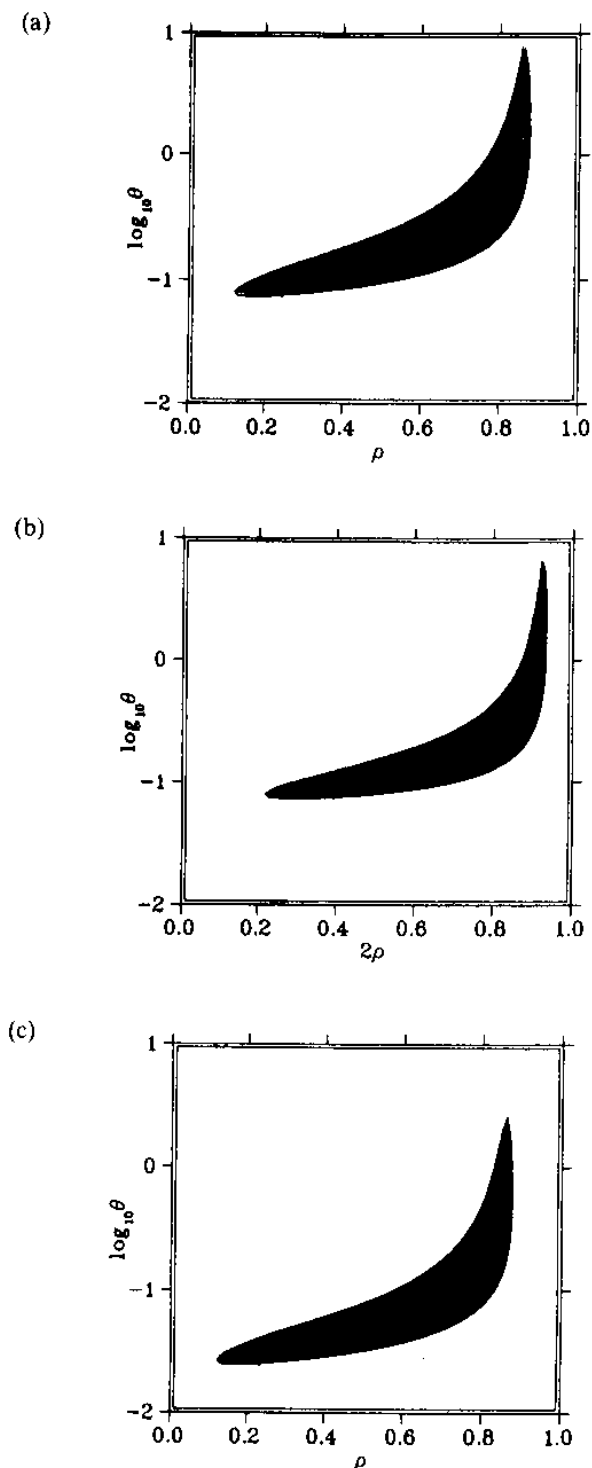


Fig. 3. Contour plots showing ΔH in the temperature-density plane. The shaded areas are regions where $\Delta H < 0$. (a) 1-D "monoatomic" solvent; (b) 1-D "diatomic" solvent; (c) 3-D monoatomic solvent ($l = 6$).

This negative contribution to ΔH has been traced to the negative ΔV associated with the ionic dissociation reaction. The magnitude of this effect depends on the size and shape of the solvent molecules. To demonstrate this we have considered another exactly solvable model. This is a one-dimensional lattice gas in which the reaction center is the same as before, but the solvent molecules are now larger, each occupying s lattice sites ($s = 1$ corresponds to the previous case). Here we shall present some results for the case $s = 2$. Details of the solution and generalization to large values of s will be presented elsewhere. We shall refer to this solvent as "diatomic" and the former solvent where each mol-

ecule occupies one lattice site will be referred to as "monoatomic". This case of $s = 2$ in one dimension can be mapped onto a special limit of the 1-D interacting lattice gas model, described by the Hamiltonian

$$H = \eta \sum_{k=1}^N P_k P_{k+1} - \mu \sum_{k=1}^N P_k, \quad (P_k = 0 \text{ or } 1) \quad (13)$$

where η is the nearest neighbor interaction. The GPF for the model (13) can be calculated by the transfer matrix method. A system of non-interacting diatomic species (*ie* $s = 2$) corresponds to the $\eta \rightarrow \infty$ limit of this model. The corresponding GPF is

$$\Xi = \lambda_+^N + \lambda_-^N \quad (14a)$$

$$\lambda_{\pm} = \frac{1}{2}(1 \pm \sqrt{1 + 4e^{\beta\eta}}). \quad (14b)$$

For $N \rightarrow \infty$ the λ_- term in equation (14a) may be disregarded. In the presence of an impurity which occupies one lattice site and interacts with solvent molecules when they occupy nearest neighbor sites (with interaction energy ϵ) the transfer matrix formalism yields

$$\Xi = \frac{\lambda_+^{N-2}}{\lambda_+ - \lambda_-} (1 - \lambda_- e^{-\beta\epsilon})^2. \quad (15)$$

Taking thermodynamic derivatives as in the previous case, equations (14) and (15) yield the excess thermodynamic quantities (in particular ΔE , ΔH and ΔV associated with the ionic dissociation reaction within this model). Results for this case are shown in the following figures together with the results for the monoatomic solvents.

Figure 1a shows the dependence of ΔH and ΔV associated with the $M \rightarrow M^+$ reaction on the temperature, for a one-dimensional lattice gas ($l = 2$) with monoatomic and diatomic solvents. Figure 1b shows similar results for a three-dimensional monoatomic solvent in ($l = 6$). In these figures ΔH and ΔE are in units of E_r and θ is the temperature in units of E_r/k . In these and other figures ϵ/E_r is taken equal to $-0.88/l$ so $E_r + l\epsilon > 0$ and $\Delta E > 0$ for all T as seen in the figures. ΔH can however be negative. This results from the negative ΔV for the reaction seen in Fig. 2a for 1-D monoatomic and diatomic solvents ($l = 2$) and Fig. 2b for a 3-D monoatomic solvent ($l = 6$). The region in the θ - ρ plane where $\Delta H < 0$ is shown in Fig. 3a (1-D monoatomic solvent), Fig. 3b (1-D diatomic solvent) and Fig. 3c (3-D monoatomic solvent with $l = 6$). These figures show marked regions of negative enthalpies of reaction, where $\xi(T)$ is predicted to decrease (*ie* more association) with increasing temperature at constant pressure.

DISCUSSION AND CONCLUSION

These results clearly demonstrate the main message of this paper: negative, "counter-intuitive" temperature dependence of ionization reactions can be observed in systems where the reaction is accompanied by a large negative volume change, even though energetic considerations would have suggested "normal, intuitive" behaviour. The effect is observed at relatively high temperatures and low densities.

However the observed dependence on the solvent size shows a shift of the region where this behavior exists to higher densities and lower temperatures for the larger solvent. This may suggest that solvents of larger molecular size will show the effect at physically realistic temperatures and densities, however we should not draw firm conclusions on these issues from the present unrealistic one-dimensional model.

While the results given earlier are general, the model described is far from the reality of polymer electrolytes. We should point out that some of the simplifying assumptions made can be relaxed: interactions between the host and the anions and/or the ion-pairs can be included at the cost of a somewhat more complicated formalism. This is not expected to change the qualitative behavior of the model.

Previous discussions of the "inverse temperature dependence" have referred to "entropic" or to "free volume" effects [13-15, 22]. It should be pointed out (cf. equation (2)) that these are not separable effects. This is particularly true for the system studied here. The negative contribution to ΔH comes from the negative ΔV of the reaction. In the present model (as in the ideal gas), the solvent energy at constant temperature is independent of its volume and $P(\Delta V)_{P,T}$ reflects a change in the solvent entropy.

The fact that negative ΔH for the ionic dissociation originates from the negative ΔV of the reaction suggests that solvent compressibility may be a factor in the occurrence of the effect. Indeed, larger negative ΔV values are observed for dissociative ionization reactions in methyl alcohol than in water [5], in accord with the fact that the compressibility of the former is ca. 2.5 times larger. However, the complexity of this issue is seen from the structure of the last term in equation (4): whether α or β plays the major role in determining the magnitude of this term depends on the PVT equation of state of the host, as well as on the (unknown) relation between the local volume changes which determine $\partial V/\partial \xi$ and the macroscopic compressibility.

A macroscopic theory of solvation depends on the host matrix through the dielectric constant D . We have already pointed out that the temperature dependence of D cannot be the only source of the effect observed in PPO cf. footnote on p. 1505. Another factor which was disregarded in our discussion is the effect, for finite salt concentration, of ion-ion interactions. Within the Debye-Huckel picture the solvation energy of an ion increases due to its interaction with the background ionic atmosphere, and temperature dependence will enter via the Debye screening length. This will make a negative contribution to $\partial E/\partial \xi$ in equation (4), namely an additional driving force (which in principle depends on the free ion concentration) for increasing association at larger T .

Finally, we should keep in mind that ion solvation in polymer ionic conductors such as polyethers are associated with considerable dynamical and structural changes whose role in the present context is yet to be clarified.

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