

Lattice theory of solvation and dissociation in macromolecular fluids.

II. Quasichemical approximation

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(Received 20 January 1994; accepted 24 March 1994)

Solvation and association of ions in polymer solvents used for polymer electrolytes is studied in the framework of the Guggenheim quasichemical approximation using a lattice model. The pure solvent is described using the mean-field approximation of Sanchez and Lacombe. The model accounts for the short range part of the ion-polymer interaction, in particular at specific interaction sites (such as the cation-oxygen attraction in polymer hosts), while long range dielectric effects are added as in the Born theory of solvation. We obtain expressions which relate thermodynamic quantities of solvation (free energy, entropy, enthalpy, and volume) to properties of the pure solvent. From these, the equilibrium constant for the ion pairing can be obtained as a function of temperature, pressure, and solvent properties. A consistent fit to the experimental data in poly(propylene oxide) (PPO) can be obtained if specific interaction sites for the cations are assumed. Dependence of the solvation and the equilibrium constant on the polymer chain length which is seen in the short chain limit saturates and disappears beyond a few monomer sizes. The relative roles of short range and of dielectric interactions is discussed.

I. INTRODUCTION

The increasing activity in studies of solid ionic conductors, and more recently in polymeric ionic conductors, has renewed the interest on the long studied problems of ion dissociation-association equilibrium and ion mobility in electrolyte solutions. Polymeric ionic conductors are essentially solutions of salt in polymeric hosts. The conductivity and equilibrium properties of such systems are determined, as in other electrolyte solutions, by the ion-host and ion-ion interactions.

This paper is a continuation of a previous work,¹ referred to as paper I. Our studies were motivated by the recent series of papers of Torell and co-workers²⁻⁴ in which ion association and mobility in polymer-salt complexes based on poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) were studied for several salts as functions of temperature, pressure, and molecular weight of the polymer. The following observations are relevant to our work:

- (1) Ion association increases with temperature, above the glass transition temperature of the system, for perchlorate and triflate salts of Li^+ and Na^+ in PEO and PPO. The temperature dependence is affected by the strength of the ion-ion and ion-host interactions. For example, ion association decreases with increasing temperature for complexes containing Nd^{3+} cations.
- (2) Detailed thermodynamic analysis by Schantz⁵ of the ion association equilibrium in the NaCF_3SO_3 -PPO and LiClO_4 -PPO systems indicate that ion association in such systems is accompanied by a large positive entropy change ($T\Delta S^0 = 30 \pm 12$ and 36 ± 12 kJ/mol, respectively). This suggests that linking of the dissociated ions to the host matrix has a strong ordering effect on the system.

- (3) Ion association strongly depends on the pressure in these systems. For the LiCF_3SO_3 -PPO complex (O:M=32:1) the number of unpaired ions doubled when P increased from 1 atm to 3 kbar. This is in accordance with the expectation that the volume change ΔV associated with the $\text{M}^+ + \text{A}^- \rightarrow \text{MA}$ reaction in a dielectric solvent is positive because of the electrostriction effect which accompanies ion solvation.⁶
- (4) The association constant $K_{\text{Assoc}} = ([\text{MA}]/[\text{M}^+][\text{A}^-])$ depends on the molecular weight of the host polymer. In the recent studies with "endcapped chains"— CH_3 terminated PEO, K_{Assoc} decreases with increasing size between 4 and 8 repeat units. The coordination of the cation to the electronegative oxygens is the main driving force for the dissociation reaction. At the same time cation-oxygens bonding may lead to transient crosslinks in the system, which will reduce the local flexibility of the host matrix. Such additional entropic effects may become important for longer chains and may alter the behavior of the association equilibrium in such systems. Indeed K_{Assoc} increases with increasing molecular weight for NaCF_3SO_3 in polypropylene glycol (PPG) (PPO terminated with OH groups). Unfortunately no results are available for long endcapped chain solvents.

More details about the experimental observations are summarized in paper I. The observed increase in the concentration of associated ion-pairs in the monovalent salt-polymer systems with increasing T are observed in many electrolyte solutions.⁷⁻¹⁰ In paper I we review some continuum dielectric theories of ion pairing¹¹⁻¹³ and note that any theory that assumes that the free energy of the association reaction is negative and proportional to the inverse dielectric constant D^{-1} , i.e., $\Delta G = -\kappa/D$, ($\kappa > 0$), results in a change in enthalpy $\Delta H = \Delta G + T\Delta S = \Delta G - T(\partial \Delta G / \partial T)$

$= -(\kappa/D)[1 + T(\partial \ln D/\partial T)]$ which is positive if the inequality $T(\partial \ln D/\partial T) < -1$ holds. For amorphous high molecular weight PPO where $D \approx 5$ and $-(dD/dT) \approx 0.016$ (Ref. 14) we have argued in paper I that the temperature dependence of the dielectric constant is not enough to explain the observed ionic association behavior.

In the present study we develop a description of the equilibrium that includes the influence of the molecular size of the host solvent and the details of the ion-solvent interactions. We are particularly interested in the influence of the macromolecular structure of the solvent in the association-dissociation ionic equilibrium.

Ionic equilibrium in solution can be discussed in terms of appropriate thermodynamic quantities. In particular, Gilkerson¹⁵ has divided the free energy of the ion association reaction $M^+ + A^- \rightarrow MA$ into two main contributions, the electrostatic part $\Delta G_{EL} = -\kappa/D$, where κ is a constant which depends on the ion charge and size, and a part which accounts for specific ion-solvent short range interactions, (ΔG_{SH}). The enthalpy change, ΔH_{EL} , and the entropy change, ΔS_{EL} , associated with the electrostatic part are calculated as described above. The present paper, as paper I before, focuses on the enthalpy, ΔH_{SH} , the entropy, ΔS_{SH} , and the free energy $\Delta G_{SH} = \Delta H_{SH} - T\Delta S_{SH}$ associated with the short range part of the solute-solvent interaction. This short range interaction is important in polyether salt complexes because of the strong selective binding of the cations to the ether oxygens. As mentioned above, the long range electrostatic interactions which incorporate the dielectric response of the solvent cannot account by themselves for the experimental observations.

In paper I we have described a lattice model for ionic equilibrium in polymer hosts that focuses on the short range ion-solvent interaction. The model is characterized by the following features: (a) The system is described by a lattice of coordination number z , in which each component of type i occupies r_i lattice sites. The size of a lattice site is a constant, independent of the composition of the mixture. (b) Only site exclusion and nearest-neighbor interactions between the components of the mixture are considered. (c) The lattice contains empty sites. These vacancies "interact" with the other components only by site exclusion. The amount of empty sites is determined such that the system is at equilibrium for the given pressure.

In paper I the thermodynamic quantities ΔG , ΔH , ΔS , and ΔV were obtained for the ion solvation and association process using the Sanchez-Lacombe mean-field theory. This approach, which can successfully account for the thermodynamic properties of the pure polymer solvents as well as for polymer mixtures, is questionable for the present application where the solvent-solute interactions can be much stronger than kT . Indeed, using this approach to analyze the experimental results of Schantz⁵ for the dependence of ionic association equilibrium in polymer solvents on the temperature, pressure, and molecular size have revealed serious flaws, which were attributed to the mean-field assumptions, even though it manages to reproduce the general trends of the system.

In the present paper we continue our study of this model.

Here the mean-field approximation (MFA) is replaced by the more realistic quasichemical approximation (QCA).¹⁶ The latter accounts better than the MFA for correlations between the positions of interacting particles and has been used by Marcus^{8,17} to calculate the standard Gibbs free energy of transfer of an ion between different solvents or solvent mixtures. In our present application we describe the pure solvent at the MFA level of Sanchez and Lacombe and introduce the QCA to account for the strong solvent-solute interactions. Using the QCA, the standard free energy of solvation (at infinite dilution), which involves only short-range contributions, is calculated and is used to evaluate the other thermodynamic quantities associated with ion solvation and association in polymer hosts. In addition we reassess the effect of the long range dielectric interactions on the association-dissociation equilibrium.

In the following section the quasichemical formalism is described in detail, and is used to calculate the standard free energy of solvation at infinite dilution, within the lattice model described above.

II. QUASICHEMICAL APPROXIMATION

In the MFA the probability of finding solvent molecules on the sites nearest neighbor to the solute is taken identical to its value in the pure solvent. This assumption becomes questionable when the solvent-solute interaction energy is large (in absolute value) relative to kT . Indeed, the MFA adopted in paper I could not account for all observations made on ionic equilibrium in polymer hosts in a consistent way. In this section we use the Guggenheim's QCA approach^{18,16} for a mixture of chain molecules of arbitrary sizes in an attempt to correct this problem.

The model is the same as that used in paper I and described in the previous section. In what follows we first review the QCA for a general mixture and then apply it to our particular problem. The system considered consists of a mixture of N_i molecules of type i , ($i=0, \dots, k$), where i denotes a particular component of the $(k+1)$ -component mixture and $i=0$ refers to the empty sites. Each molecule in the mixture is made of r_i identical "beads," each occupying one site on a lattice of coordination number z . By definition $r_0=1$. The volume of the system is expressed by $V = Mv^*$, where $M = \sum_{i=0}^k r_i N_i$ is the total number of sites and v^* is the average volume of a lattice site in the mixture. In general v^* is a function of the lattice site volumes $\{v_i^*\}$ of the pure components i , but in this simplified approach we take $v_i^* = v^*$, independent of i . Using a closed-packed volume, defined as $V^* = v^* \sum_{i=1}^k r_i N_i$, the reduced volume \tilde{v} and the reduced density ρ are defined as $\tilde{v} = V/V^* = 1/\rho$. The density of component i is defined as $\rho_i = r_i N_i / M$. ρ_i is the average probability that a site is occupied by a segment of a molecule of type i . The correspondent density in a closed packed mixture is given by $\phi_i = \rho_i / \rho$.

Let N_{ij} be the number of nearest neighbor pairs of beads of types i and j ($N_{ij} = N_{ji}$) in the system with N_i molecules of types i . The number, Ω , of configurations of the chains in the lattice for given sets $\{N_i\}$ and $\{N_{ij}\}$ is given by Guggenheim¹⁸ by the expression¹⁹

$$\begin{aligned} \ln \Omega(\{N_{ij}\}, \{N_{ij}\}) &= - \sum_{i=0}^k \ln N_i! - \left(\frac{1}{2}z-1\right) \ln M! + \sum_{i=0}^k N_i \ln \frac{\delta_i}{\sigma_i} \\ &\quad - \sum_{i=0}^k \ln N_{ii}! - \sum_{i=0}^k \sum_{j>i} \ln N_{ij}! + \sum_{i=0}^k \sum_{j>i} N_{ij} \ln 2 \\ &\quad + \sum_{i=0}^k z \ln(q_i N_i)! + \frac{z}{2} N_q \ln \frac{z}{2}. \end{aligned} \quad (1)$$

The parameter q_i is defined by

$$q_i = [r_i(z-2) + 2]/z. \quad (2)$$

For an unbranched chain $q_i z$ is the number of nonbonded nearest neighbors to a molecule of type i .¹⁸ Note that for empty sites $q_0 = 1$. The total number of nonbonded pairs $(z/2)N_q$ is defined as $(z/2)N_q = (z/2)\sum_{i=0}^k q_i N_i$.

Also in Eq. (1), the parameter δ_i is defined as the number of ways that a chain that occupies r_i consecutive sites can be arranged in the lattice after one of its monomers is fixed at a certain lattice site.¹⁸ It is usually associated with the flexibility of the chain. The parameter σ_i is the symmetry number of the corresponding molecules. These two parameters are related to the intrinsic configurational entropy of the chain molecules of kind i .

The energy of the system, considering only nearest neighbor interactions, is given by

$$E(\{N_{ij}\}, \{N_{ij}\}) = - \sum_{i=0}^k \sum_{j \geq i} N_{ij} \epsilon_{ij}, \quad (3)$$

where $-\epsilon_{ij}$ ($\epsilon_{ij} > 0$) is the (attractive) interaction energy between particles (i.e., molecular beads) of types i and j . The interaction parameters $\{\epsilon_{ij}\}$ are constant parameters of this theory. The interactions involving empty sites ($\{\epsilon_{i0}\}$) are taken zero. The quantities N_i and N_{ij} are related by¹⁸

$$2N_{ii} + \sum_{j(\neq i)} N_{ij} = q_i z N_i. \quad (4)$$

Using Eq. (4), Eq. (3) can be rewritten in the form

$$E(\{N_{ij}\}, \{N_{ij}\}) = -\frac{1}{2} \sum_{i=0}^k q_i z N_i \epsilon_{ii} + \frac{1}{2} \sum_{i=0}^k \sum_{j>i} \Delta \epsilon_{ij} N_{ij}, \quad (5)$$

where $\Delta \epsilon_{ij} \equiv (\epsilon_{ii} + \epsilon_{jj} - 2\epsilon_{ij})$.

The average equilibrium values of the number of pairs $\{N_{ij}\}$ and the number of vacancies N_0 , at given values of N_i ($i=1, \dots, k$), and of P and T are obtained by minimizing the free energy $G(\{N_{ij}\}, \{N_{ij}\}) = E(\{N_{ij}\}, \{N_{ij}\}) - kT \times \ln \Omega(\{N_{ij}\}, \{N_{ij}\}) + PV(\{N_{ij}\})$ with respect to these parameters, as well as with respect to the total volume

$$\left[\frac{\partial G(\{N_{ij}\}, \{N_{ij}\})}{\partial N_{ij}} \right]_{T, P, \{N_i\}, \{N_{km}\} \neq ij} = 0, \quad (6)$$

$$\left[\frac{\partial G(\{N_{ij}\}, \{N_{ij}\})}{\partial V} \right]_{T, P, \{N_i\} \neq 0, \{N_{ij}\}} = 0. \quad (7)$$

Equation (6) leads to the well known quasichemical relations

$$4N_{ii}N_{jj} = e^{\Delta \epsilon_{ij}/kT} N_{ij}^2. \quad (8)$$

Equation (7) is in fact a derivative with respect to the number of vacancies N_0 and leads to

$$Pv^* + kT \left[\ln \frac{N_0}{M} + \frac{z}{2} \left(\ln \frac{2N_{00}M}{zN_0^2} \right) \right] = 0. \quad (9)$$

Equation (9) is the QCA equation of state. It can be shown (see Appendix B) that it is reduced to the MFA equation of state of Sanchez and Lacombe [Eq. (32) below] in the limit $z \rightarrow \infty$, $\{\epsilon_{ij}\} \rightarrow 0$ with $\{z\epsilon_{ij}\} \rightarrow \text{constants}$.

Note that using the set of Eqs. (4), (8), and (9) the values of the amount of pairs $\{N_{ij}\}$ can be determined in terms of the temperature T , the pressure P , the amount of each component $\{N_i\}$ ($i \neq 0$) and the energy parameters $\{\Delta \epsilon_{ij}\}$. It is useful for the calculations that follow to scale the amount of pairs N_{ij} by the total number of pairs $(z/2)N_q$, and the amount of binding sites of each kind $q_i N_i$ by the total number of binding sites in the mixture N_q . In terms of the scaled variables $\{\chi_{ij}\}$ and $\{\varphi_i\}$, defined by

$$\chi_{ii} \equiv \frac{N_{ii}}{(z/2)N_q}, \quad \chi_{ij} \equiv \frac{1}{2} \frac{N_{ij}}{(z/2)N_q}, \quad \varphi_i \equiv \frac{q_i N_i}{N_q}, \quad (10)$$

Eqs. (4), (8), and (9) become

$$\varphi_i = \chi_{ii} + \sum_{j(\neq i)} \chi_{ij}, \quad (11)$$

$$\chi_{ii}\chi_{jj} = e^{\Delta \epsilon_{ij}/kT} \chi_{ij}^2, \quad (12)$$

$$Pv^* = -kT \left[\ln \varphi_0 + \left(\frac{z}{2} - 1 \right) \ln \frac{M}{N_q} + \frac{z}{2} \ln \frac{\chi_{00}}{\varphi_0^2} \right]. \quad (13)$$

These quantities satisfy $\sum_{i=0}^k \varphi_i = 1$, $M/N_q = \sum_{i=0}^k (r_i/q_i) \times \varphi_i = (\sum_{i=0}^k (q_i/r_i)\varphi_i)^{-1}$. In the random mixing limit, $\{\Delta \epsilon_{ij}/kT\} = 0$, Eqs. (11) and (12) above can be solved exactly in terms of $\{\varphi_i\}$, yielding $\chi_{ij} = \varphi_i \varphi_j$ for any i and j . φ_0 is then determined from Eq. (13) in terms of Pv^*/kT , $\{r_i\}$, z and $\{\varphi_i\}_{i \neq 0}$. In general this set of equations has to be solved numerically and the relevant solution is the one in the range $0 \leq \varphi_0, \{\chi_{ij}\} < 1$.

The chemical potential of molecules of kind i ($i \neq 0$) is obtained from the derivative of the free energy with respect to the amount of component i . This can be written in the form

$$\begin{aligned} \mu_i &= \left(\frac{\partial G}{\partial N_i} \right)_{T,P,\{N_j\} \neq 0,i} \\ &= \left(\frac{\partial G}{\partial N_i} \right)_{T,P,\{N_j\} \neq i,\{N_{ij}\}} + \sum_{i=0}^k \sum_{j>i} \left(\frac{\partial G}{\partial N_{ij}} \right)_{T,P,\{N_j\},\{N_{km}\} \neq ij} \\ &\quad \cdot \left(\frac{\partial N_{ij}}{\partial N_i} \right)_{T,P,\{N_j\} \neq i,\{N_{km}\} \neq ij} + \left(\frac{\partial G}{\partial N_0} \right)_{T,P,\{N_j\} \neq 0,\{N_{ij}\}} \\ &\quad \cdot \left(\frac{\partial N_0}{\partial N_i} \right)_{T,P,\{N_j\} \neq 0,i,\{N_{ij}\}}. \end{aligned} \quad (14)$$

From Eqs. (6) and (7), the second and third terms on the right-hand side of Eq. (14) are zero at equilibrium. The derivative of the remaining first term yields

$$\begin{aligned} \mu_i &= -\frac{z}{2} q_i \epsilon_{ii} + kT \left[\ln \frac{N_i}{M} - \ln \frac{\delta_i}{\sigma_i} + \frac{z}{2} q_i \ln \left[\frac{2N_{ii}M}{z(q_i N_i)^2} \right] \right] \\ &\quad + P_V^* r_i. \end{aligned} \quad (15)$$

In terms of the scaled variables defined by Eq. (10) this takes the form

$$\begin{aligned} \mu_i &= kT \ln \frac{N_i}{M} - kT \ln \frac{\delta_i}{\sigma_i} - \frac{z}{2} q_i \epsilon_{ii} + \frac{z}{2} q_i kT \\ &\quad \times \left(\ln \frac{M}{N_q} + \ln \frac{\chi_{ii}}{\varphi_i^2} \right) + P_V^* r_i. \end{aligned} \quad (16)$$

Our goal is to obtain the standard free energy of solvation, ΔG_a , of a molecule of type a in the given mixture of the other components. This can be identified as the infinite dilution limit, $\varphi_a \rightarrow 0$, of the change in free energy associated with transferring a molecule a from an otherwise empty lattice to the lattice containing the solvent mixture. The first two terms in Eq. (16) do not contribute to this difference²⁰ and we get

$$\begin{aligned} \Delta G_a &= -\frac{z}{2} q_a \epsilon_{aa} + \frac{z}{2} q_a kT \left(\ln \frac{M^0}{N_q^0} + \lim_{\varphi_a \rightarrow 0} \ln \frac{\chi_{aa}}{\varphi_a^2} \right) \\ &\quad + P_V^* r_a, \end{aligned} \quad (17)$$

where the superscript 0 indicates quantities calculated for the pure solvent, i.e., with $\varphi_a = 0$ (while subscript 0 indicates properties evaluated for the "vacancy species"). We are left with the task of calculating the limit appearing in Eq. (17) in the presence of solvent. This limit can be calculated from Eqs. (11) and (12) using a generalization of the calculation of Hagemark²¹ for a binary mixture with no empty sites. The detailed calculation is presented in Appendix A. The final result is

$$\lim_{\varphi_a \rightarrow 0} \ln \frac{\chi_{aa}}{\varphi_a^2} = -2 \ln \left(\sum_{i=0}^k e^{-(1/2)\Delta \epsilon_{ai}/kT} \sqrt{\chi_{ii}^0} \right), \quad (18)$$

where \sum_i' denotes summation over all $i \neq a$. Substituting Eq. (18) back in Eq. (17), one gets

$$\begin{aligned} \Delta G_a &= \frac{z}{2} q_a kT \left\{ \ln \frac{M^0}{N_q^0} - 2 \ln \left[\sum_{i=0}^k e^{(2\epsilon_{ai} - \epsilon_{ii})/2kT} \sqrt{\chi_{ii}^0} \right] \right\} \\ &\quad + P_V^* r_a. \end{aligned} \quad (19)$$

Note that for a molecule a in an empty lattice (i.e., in the absence of solvent) $P = 0$, $N_q^0 = N_0^0 = M^0$ and $\chi_{00} = 1$ so, since $\epsilon_{a0} = \epsilon_{00} = 0$, $\Delta G_a = 0$ as should be. Equation (19) can be further simplified using that $\chi_{ii} \exp(-\epsilon_{ii}/kT) = \chi_{0i}^2 / \chi_{00}$ [cf. Eq. (12)] together with Eq. (13) for the pressure. The final result is

$$\begin{aligned} \Delta G_a &= \frac{z}{2} q_a kT \left[\ln \frac{M^0}{N_q^0} - 2 \ln \left(\sum_{i=0}^k e^{\epsilon_{ai}/kT} \chi_{0i}^0 \right) + \ln \chi_{00}^0 \right] \\ &\quad + P_V^* r_a = -kT \left[q_a \ln(1 - \rho^0) + z q_a \right. \\ &\quad \times \left. \ln \left(\sum_{i=0}^k e^{\epsilon_{ai}/kT} \frac{\chi_{0i}^0}{\varphi_0^0} \right) \right] + P_V^* (r_a - q_a). \end{aligned} \quad (20)$$

The values of ρ^0 , $\{\chi_{0i}^0\}$, and φ_0^0 are functions of the pure solvent compositions $\{\varphi_i^0\}$ ($i \neq 0$), interaction energies $\{\Delta \epsilon_{ij}\}$, pressure, and temperature. This can be easily seen for a single component solvent s which is described by a binary mixture of solvent particles and of vacancies. For this system the QCA equations

$$\chi_{ss} + \chi_{0s} = \varphi_s, \quad (21a)$$

$$\chi_{00} + \chi_{0s} = \varphi_0, \quad (21b)$$

$$\chi_{ss} \chi_{00} = e^{\epsilon_{ss}/kT} \chi_{0s}, \quad (21c)$$

$$\varphi_0 + \varphi_s = 1, \quad (21d)$$

are easily solved, yielding

$$\frac{\chi_{0s}}{\varphi_0} = \frac{2\varphi_s}{1 + \sqrt{1 - 4\varphi_0\varphi_s(1 - e^{\epsilon_{ss}/kT})}}. \quad (22)$$

Equation (20), which for this case takes the form [using Eq. (21b)],

$$\begin{aligned} \Delta G_a &= -kT \left\{ q_a \ln(1 - \rho_s) + z q_a \right. \\ &\quad \times \left. \ln \left[1 + (e^{\epsilon_{as}/kT} - 1) \frac{\chi_{0s}^0}{\varphi_0^0} \right] \right\} + P_V^* (r_a - q_a), \end{aligned} \quad (23)$$

can now be evaluated using Eq. (22) for χ_{0s}/φ_0 .

Two more observations can be made concerning the result (20). First, it is straightforward to show that it is reduced to the mean-field result [Eq. (59) of paper I] by taking $\{\epsilon_{ij}/kT\} \rightarrow 0$ and $z \rightarrow \infty$, using also $\chi_{0i} \rightarrow \varphi_0 \varphi_i$, $q_i \rightarrow r_i$, $\varphi_i^0 \rightarrow \rho_i^0$, while keeping the products $\{z\epsilon_{ai}\}$ constant. Secondly, in the limit $\epsilon_{ai}/kT \rightarrow 0$ for all $i \neq a$, Eq. (11) implies that the second term of Eq. (20) vanishes. Consequently, the remaining terms can be identified as the free energy of cavity formation, of the size needed to accommodate the impurity, in the solvent. The term that vanishes for $\epsilon_{ai} = 0$ (all $i \neq a$) is

then the free energy associated with the impurity interaction with the solvent. Note that this is the additional interaction, on the top of that responsible for the site exclusion.

Equation (23) gives the free energy of solvation of the impurity a in a single component solvent. In a general many component solvent a numerical solution of Eqs. (11)–(13) and (20) has to be used. If we make the reasonable assumption that the solvent–solvent interactions, ϵ_{ij} ($i, j \neq a$), are weak relative to kT we can evaluate the quantity χ_{0i}^0/φ_0^0 needed in Eq. (20) as an expansion in the small parameters $\{\epsilon_{ij}/kT\}$ (see Appendix B). This procedure leads to

$$kT z q_a \ln \left(\sum_{i=0}^k e^{\epsilon_{ai}/kT} \frac{\chi_{0i}^0}{\varphi_0^0} \right) \approx kT z q_a \ln \left(\sum_{i=0}^k e^{\epsilon_{ai}/kT} \varphi_i^0 \right) + q_a \left[\sum_{i(\neq 0)}' \sum_{j(\neq 0)}' z \epsilon_{ij} \varphi_i^0 \varphi_j^0 - \frac{\sum_{i(\neq 0)}' \sum_{j(\neq 0)}' e^{\epsilon_{ai}/kT} z \epsilon_{ij} \varphi_i^0 \varphi_j^0}{\sum_{i=0}^{k'} e^{\epsilon_{ai}/kT} \varphi_i^0} \right]. \quad (24)$$

Note that the first term on the right-hand side corresponds to the simplest (mean-field) approximation $\chi_{0i}^0 = \varphi_0^0 \varphi_i^0$. The other terms are corrections associated with the solvent–solvent interactions. Using Eq. (24), Eq. (20) becomes

$$\Delta G_a = \Delta G_a' + \Delta G_a'', \quad (25)$$

$$\Delta G_a' = -q_a kT \ln(1 - \rho^0) - q_a \left[\sum_{i(\neq 0)}' \sum_{j(\neq 0)}' z \epsilon_{ij} \varphi_i^0 \varphi_j^0 - \frac{\sum_{i(\neq 0)}' \sum_{j(\neq 0)}' e^{\epsilon_{ai}/kT} z \epsilon_{ij} \varphi_i^0 \varphi_j^0}{\sum_{i=0}^{k'} e^{\epsilon_{ai}/kT} \varphi_i^0} \right] + P v^* (r_a - q_a), \quad (26)$$

$$\Delta G_a'' = -z q_a kT \ln \left(\sum_{i=0}^k e^{\epsilon_{ai}/kT} \varphi_i^0 \right). \quad (27)$$

Expression (27) for $\Delta G_a''$ is similar to the result [Eq. (12) of paper I] for the free energy of solvation in a solvent represented by a noninteracting lattice gas. This result was obtained in paper I using the ansatz that the solvent concentration at sites nearest to the solute is proportional to $\rho_i \exp(\epsilon_{ai}/kT)$. Here the result is obtained from the QCA formalism without further assumptions.

For normal pressures and temperatures, of the order of 1 atm and 300 K, and for typical values for v^* [e.g., 20 cm³/mol (Ref. 22)], one gets that $P v^*/kT \approx 8 \times 10^{-4}$, which is much smaller than the solvent–solvent interactions [typically of the order of $(z/2)\epsilon/kT \approx 1.0$ (Ref. 22)]. Since the experimental data available are for these conditions, we disregard the term containing pressure in the following equations.

Equations (25)–(27) have to be supplemented by the equation of state (13) which determine the equilibrium number of vacant sites, hence the volume M of the lattice. To first order in ϵ_{ij}/kT , ($i, j \neq a$), we get (see Appendix B),

$$\frac{\chi_{00}^0}{\varphi_0^0} = 1 + \sum_{i(\neq 0)} \sum_{j(\neq 0)} \frac{\epsilon_{ij}}{kT} \varphi_i \varphi_j. \quad (28)$$

Using this in Eq. (13) results in the equation of state

$$P v^* + kT \left[\ln \varphi_0 + \left(\frac{z}{2} - 1 \right) \ln \left(\sum_{i=0}^k \frac{r_i}{q_i} \varphi_i \right) \right] + \frac{z}{2} \sum_{i(\neq 0)} \sum_{j(\neq 0)} \epsilon_{ij} \varphi_i \varphi_j = 0. \quad (29)$$

We now follow Sanchez and Lacombe (and Flory) in taking the large z limit of Eqs. (26)–(29), i.e., $z \rightarrow \infty$, $q \rightarrow r$, $\varphi_i \rightarrow \rho_i = \phi_i \rho$, with $\{z \epsilon_{ij}\}$ kept constant. In this limit there is a large body of data for the parameters $(z/2)\epsilon$, v^* , and r obtained by Sanchez and Lacombe²² by fitting PVT behavior of pure solvents to the equation of state (32) below (a similar procedure was used in paper I to determine these parameters for PEO and PPO). In this limit Eqs. (26) (without the term containing P) and (27) become

$$\Delta G_a' = -q_a \left[kT \ln(1 - \rho^0) + \sum_{i(\neq 0)}' \sum_{j(\neq 0)}' z \epsilon_{ij} \rho_i^0 \rho_j^0 - \frac{\sum_{i(\neq 0)}' \sum_{j(\neq 0)}' e^{\epsilon_{ai}/kT} z \epsilon_{ij} \rho_i^0 \rho_j^0}{\sum_{i=0}^{k'} e^{\epsilon_{ai}/kT} \rho_i^0} \right] \quad (30)$$

$$\Delta G_a'' = -z q_a kT \ln \left[1 - \rho^0 + \rho^0 \sum_{i(\neq 0)}' e^{\epsilon_{ai}/kT} \phi_i \right] \quad (31)$$

while Eq. (29) takes the form

$$P v^* + kT \left[\ln \rho_0 + \sum_{i=0}^k \frac{r_i - 1}{r_i} \rho_i \right] + \frac{z}{2} \sum_{i(\neq 0)} \sum_{j(\neq 0)} \epsilon_{ij} \rho_i \rho_j = P v^* + kT \left[\ln(1 - \rho) + \left(1 - \frac{1}{r} \right) \rho \right] + \epsilon^* \rho^2 = 0. \quad (32)$$

where $\epsilon^* \equiv (z/2) \sum_{i(\neq 0)} \sum_{j(\neq 0)} \epsilon_{ij} \phi_i \phi_j$ and $(1/r) \equiv \sum_{i(\neq 0)} (\phi_i/r_i)$. Note that in our application Eq. (32) is to be used in the zero impurity concentration limit, $\varphi_a \rightarrow 0$.

Further simplification is achieved for a single component solvent s . In this case Eqs. (30) and (31) become

$$\Delta G_a' = -q_a \left[kT \ln(1 - \rho_s) + z \epsilon_{ss} \rho_s^2 \frac{(1 - \rho_s)(1 - e^{\epsilon_{as}/kT})}{1 - \rho_s + e^{\epsilon_{as}/kT} \rho_s} \right], \quad (33)$$

$$\Delta G_a'' = -z q_a kT \ln(1 - \rho_s + \rho_s e^{\epsilon_{as}/kT}). \quad (34)$$

Here and henceforth we drop the superscript 0, keeping in mind that all quantities correspond to pure solvent. The changes in the other thermodynamic functions (e.g., entropy, enthalpy, and volume of solvation) can be readily obtained from the corresponding derivatives of the free energy,

$$\Delta H_a = -T^2 \left[\frac{\partial(\Delta G_a/T)}{\partial T} \right]_P; \quad \Delta S_a = - \left(\frac{\partial \Delta G_a}{\partial T} \right)_P; \quad \Delta V_a = \left(\frac{\partial \Delta G_a}{\partial V} \right)_T. \quad (35)$$

Equations (33), (34), and (35) constitute the final results for the thermodynamic quantities of solvation of species a in solvent s . Note that the derivatives in Eq. (35) involve the temperature and pressure derivatives of ρ_s , namely, the isobaric expansivity α_s and the isothermal compressibility β_s of the pure solvent, obtained from Eq. (32) in the forms^{22,23}

$$\alpha_s = -\frac{1}{\rho_s} \left(\frac{\partial \rho_s}{\partial T} \right)_P = \frac{1}{T} \left[\frac{\epsilon^* \rho_s^2 + P v^*}{k T \rho_s \left(\frac{\rho_s}{1-\rho_s} + \frac{1}{r_s} \right) - 2 \epsilon^* \rho_s^2} \right], \quad (36)$$

$$\beta = \frac{1}{\rho_s} \left(\frac{\partial \rho_s}{\partial P} \right)_T = \frac{v^*}{k T \rho_s \left(\frac{\rho_s}{1-\rho_s} + \frac{1}{r_s} \right) - 2 \epsilon^* \rho_s^2}. \quad (37)$$

Simpler expressions are obtained if further approximations are made. In the limit $\epsilon_{as}/kT \gg 1$ Eqs. (33)–(35) lead to

$$\Delta G_a^\infty = -l_a [\epsilon_{as} - \epsilon_{ss} \rho_s (1 - \rho_s)] - kT [l_a \ln \rho_s + q_a \ln(1 - \rho_s)], \quad (38)$$

$$\Delta H_a^\infty = -l_a [\epsilon_{as} - \epsilon_{ss} \rho_s (1 - \rho_s) - \epsilon_{ss} T \alpha_s (\rho_s - 2\rho_s^2)] - kT^2 \alpha_s \left(l_a - q_a \frac{\rho_s}{1 - \rho_s} \right), \quad (39)$$

$$\Delta S_a^\infty = l_a \epsilon_{ss} (\rho_s - 2\rho_s^2) \alpha_s - kT \alpha_s \left(l_a - q_a \frac{\rho_s}{1 - \rho_s} \right) + k [l_a \ln \rho_s + q_a \ln(1 - \rho_s)], \quad (40)$$

$$\Delta V_a^\infty = \beta_s \left[l_a \epsilon_{ss} (\rho_s - 2\rho_s^2) - kT \left(l_a - q_a \frac{\rho_s}{1 - \rho_s} \right) \right], \quad (41)$$

where the superscript ∞ refers to this limit and where $l_a \equiv z q_a$. The limit $\epsilon_{as}/kT \gg 1$ is relevant for ion solvation. Note that Eqs. (40) and (41) for the entropy and volume changes do not depend on ϵ_{as} . The reason for this is that for $\epsilon_{as}/kT \gg 1$ the occupation probability of sites nearest neighbor to the solute is 1. In this saturation limit, in the present model of only nearest neighbor interactions, the volume and entropy changes associated with the solvation are independent of ϵ_{as} and depend only on the solvent properties and on the amount of available sites.

It should be emphasized again that the model used to obtain the thermodynamic quantities of solvation, Eqs. (38)–(41), does not take into account long range electrostatic interactions. These can be accounted for, in principle, by considering the solvation of a species which includes the ion and its first solvation shell in a continuum solvent characterized by the dielectric response of the polymer host. In what follows we include the contribution of such terms parametrically in the calculation of the free energy of ionic association reaction.

Consider now the ionic dissociation–association equilibrium at infinite dilution. The equilibrium constant for the association reaction $a + b \rightleftharpoons ab$ is given by

$$K_{\text{Assoc}} = \exp \left(\frac{-\Delta G_{\text{Assoc}}}{kT} \right), \quad (42)$$

where $\Delta G_{\text{Assoc}} = \Delta G_{\text{SH}} + \Delta G_{\text{ED}} = \Delta G_{ab} - \Delta G_a - \Delta G_b + \Delta G_{\text{EL}}$. In a system with only nearest-neighbor solute–solvent interactions ΔG_{EL} is the (negative) free energy of the association reaction in vacuum. In a realistic system ΔG_{EL} contains also the contributions from long range solute–solvent interactions. In what follows we use ΔG_{EL} as a parameter of the theory, and do not dwell on its exact nature. In the limit of strong solute–solvent interactions we get, using Eq. (38),

$$\begin{aligned} \Delta G_{\text{Assoc}}^\infty = & \Delta G_{\text{EL}} - (l_{ab} \epsilon_{ab-s} - l_a \epsilon_{as} - l_b \epsilon_{bs}) + (l_{ab} - l_b \\ & - l_a) \epsilon_{ss} (\rho_s - \rho_s^2) - kT [(l_{ab} - l_a - l_b) \ln \rho_s \\ & + (q_{ab} - q_a - q_b) \ln(1 - \rho_s)]. \end{aligned} \quad (43)$$

The first three terms in this equation are energetic. In particular, the combination $-(l_{ab} \epsilon_{ab-s} - l_a \epsilon_{as} - l_b \epsilon_{bs})$ correspond to the change in the interaction energy between the solutes and nearest neighbor solvent molecules due to the association reaction (recall that in this strong solute–solvent coupling limit all sites nearest neighbor to the solutes are occupied by solvent molecules). Together with ΔG_{EL} these terms account for the energy change associated with the reaction in vacuum and with the solute–solvent interactions (dielectric and short range). The term containing ϵ_{ss} correspond to the change in the solvent–solvent interaction energy associated with the change in the solvent packing near the solutes resulting from the difference in their effective sizes (given by $l_{ab} - l_a - l_b$). The other terms, proportional to kT are entropic in origin. For large z the dominant one is $(l_{ab} - l_a - l_b) \ln \rho_s$, provided that ρ_s is not too close to 1. (For PPO at $T=295$ K and $P=1$ atm we have found that $\rho_s=0.92$.) For association, $(l_{ab} - l_a - l_b)$ is expected to be negative and, since $\ln \rho_s < 0$, this entropic term contribution is negative, encouraging association at higher temperature, in accordance with an argument given by de Gennes.²⁴

In what follows we disregard ϵ_{ss} , the solvent–solvent interaction term in ΔG_{Assoc} , assuming that the ion–solvent interaction energies are much larger. We also neglect the entropic term containing q_i relative to that containing l_i ($i=a, b, ab$). The final equations for the thermodynamic functions of the association reaction become

$$\begin{aligned} \Delta G_{\text{Assoc}}^\infty = & \Delta G_{\text{EL}} - (l_{ab} \epsilon_{ab-s} - l_a \epsilon_{as} - l_b \epsilon_{bs}) \\ & - kT (l_{ab} - l_a - l_b) \ln \rho_s, \end{aligned} \quad (44)$$

$$\begin{aligned} \Delta H_{\text{Assoc}}^\infty = & \Delta H_{\text{EL}} - (l_{ab} \epsilon_{ab-s} - l_a \epsilon_{as} - l_b \epsilon_{bs}) \\ & - kT^2 \alpha_s (l_{ab} - l_a - l_b), \end{aligned} \quad (45)$$

$$\Delta S_{\text{Assoc}}^\infty = \Delta S_{\text{EL}} + k (l_{ab} - l_a - l_b) (\ln \rho_s - T \alpha_s), \quad (46)$$

$$\Delta V_{\text{Assoc}}^\infty = -kT \beta_s (l_{ab} - l_a - l_b), \quad (47)$$

where ΔH_{EL} and ΔS_{EL} are obtained from ΔG_{EL} using Eq. (35). If $\Delta G_{\text{EL}} = -\kappa/D$, where D is the dielectric response function and κ is a temperature independent constant, then $\Delta S_{\text{EL}} = -(\kappa/D)(\partial \ln D / \partial T)$ and $\Delta H_{\text{EL}} = \Delta G_{\text{EL}} + T \Delta S_{\text{EL}}$. In Eq. (47) we have neglected the corresponding contribution to the electrostriction. Note that we have assumed that the in-

teraction energies ϵ_{ab} , ϵ_a , ϵ_b and the numbers of nearest neighbors l_a , l_b , and l_{ab} are temperature independent constants.

Equations (44)–(47) can be written in terms of three parameters, $\delta E = -\Delta G_{EL} + \epsilon_{ab}l_{ab} - \epsilon_a l_a - \epsilon_b l_b$, the change in the reaction energy, $\delta l = l_{ab} - l_a - l_b$, the change in the number of nearest neighbor of the reactants and κ , which measures the strength of the long range interactions. These values will be used as fitting parameters, to be determined from the experimental values of ΔH_{Assoc} and ΔS_{Assoc} , via Eqs. (45) and (46).

III. IMPLICATIONS FOR POLYETHER ELECTROLYTES

For pure long chain polymers (i.e., very large r_s), the equation of state (32) depends only on the parameters $(z/2)\epsilon_{ss}$ and v^* . These parameters are obtained²² from a nonlinear fit of the thermodynamic properties of the polymer to those inferred from the equation of state. Here we take $(z/2)\epsilon_{ss} = 1.127$ kcal/mol and $v^* = 11.41$ cm³/mol, the parameters calculated in paper I for PPO. Using these parameters, in the limit of large chain molecules ($1/r_s \sim 0$), one gets from Eqs. (32), (36), and (37) the values of ρ_s , α_s , and β_s , respectively, for given temperature and pressure.

Not enough is known about the molecular parameters to make the theory fully predictive. In the analysis of the experimental results of Schantz,⁵ we assume that the coordination number z is large, so that Eqs. (45) and (46) are used. We are then left with two unknown parameters, δE and δl defined above, which can be fitted to the experimentally available ΔH_{Assoc} and ΔS_{Assoc} . In what follows we compare the behavior of the model with experimental observations, in order to see whether a reasonable choice of parameters yields consistent results.

In order to use the data for ΔH_{Assoc} and ΔS_{Assoc} provided by Schantz⁵ we note (see also paper I) that these values were calculated from $\Delta G_{Assoc} = -kT \ln \bar{K}_{Assoc}$, with \bar{K}_{Assoc} calculated in units of ℓ /mol. K_{Assoc} , Eq. (42), is dimensionless and is related to \bar{K}_{Assoc} by $\bar{K}_{Assoc} = v^* K_{Assoc}$. Therefore a term $-kT \ln v^*$ should be added to ΔG_{Assoc} and a term $k \ln v^*$ should be added to ΔS_{Assoc} in order to correspond to Schantz's data, with v^* , the volume per site, expressed in ℓ /mol. In what follows we denote $\Delta G_{Assoc} = \Delta G_{Assoc} - kT \ln v^* = \Delta H_{Assoc} - T\Delta S_{Assoc}$.

In what follows we first disregard the temperature dependence of ΔG_{EL} in Eqs. (44)–(46), as was done in paper I. In this case $\Delta S_{EL} = 0$ and $\Delta H_{EL} = \Delta G_{EL}$ so Eqs. (44)–(47) become

$$\Delta G_{Assoc}^\infty = -\delta E - kT \delta l \ln \rho_s, \quad (48)$$

$$\Delta H_{Assoc}^\infty = -\delta E - kT^2 \alpha_s \delta l, \quad (49)$$

$$\Delta S_{Assoc}^\infty = k \delta l (\ln \rho_s - T \alpha_s), \quad (50)$$

$$\Delta V_{Assoc}^\infty = -kT \beta_s \delta l. \quad (51)$$

Here, the thermodynamic quantities of solvation are expressed in terms of two free parameters, δE and δl , which can be fitted to the experimental results. Using Schantz's data,⁵ $\Delta H_{Assoc} = 4$ kJ/mol and $\Delta S_{Assoc} = 101.7$ J/(K mol) for

NaCF₃SO₃-PPO at 295 K together with $\rho_s = 0.9223$, $\alpha_s = 7.205 \times 10^{-4}$ K⁻¹, $\beta_s = 6.122 \times 10^{-5}$ atm⁻¹ [obtained from Eqs. (32), (36), and (37), respectively, using the parameters listed above and $r = 10\,000$] and $v^* = 11.41 \times 10^{-3}$ ℓ /mol, Eqs. (45) and (46) yield $\delta E = 25.68$ kJ/mol and $\delta l = -56.9$ for this system. A similar analysis for LiClO₄-PPO where, at 295 K, $\Delta H_{Assoc} = 13$ kJ/mol and $\Delta S_{Assoc} = 122.0$ J/(K mol) (Ref. 5) leads to $\delta E = 21.04$ kJ/mol and $\delta l = -65.3$. It is immediately clear that these values of δl are unphysically large.

There are three questionable features in the model considered above. (a) All solvent sites were assumed to interact equally (with interaction energy ϵ_{as}) with the solute. (b) The temperature dependence of ΔG_{EL} was disregarded. (c) The use of the QCA does not account properly for the effect of ions on the polymer structure, specifically for the formation of ion mediated crosslinks. The latter approximation cannot be relaxed in the present treatment. In what follows we consider the possible effects of the first two approximations.

Consider first the consequences of a generalization of the QCA that accounts for distinct interactions between different parts of the molecules in the mixture. As shown by Barker,²⁵ the equations obtained from the QCA for the number of pairs of molecules of each kind [cf. Eqs. (11) and (12)] can be generalized to treat specific interactions between different molecular segments. Such a model with site specific interactions seems to be particularly proper for solvents like polyethers where only the oxygen sites interact strongly with the dissolved cations.

The idea behind this version of the QCA is to treat each type of segment, characterized by specific interactions, as a separate entity i , with q_i being the fraction of nonbonded neighbors associated with it. When treating the solvent in this picture the QCA is modified in an essential way because Eq. (2) has to be replaced by a proper generalization.²⁵ However since in the present application we adopt the simple mean-field description of the pure solvent, this fact has no consequences with regard to our treatment. All the quantities associated with the pure solvent therefore retain their former meaning when the pure solvent is considered, however the solute sees two kinds of solvents with different interactions. Denoting by ϕ_x the fraction of solvent sites which strongly interact with the solute, assuming these interactions are much larger than kT and neglecting the other interactions, leads to

$$\Delta G_a^\infty = -l_a \epsilon_{ax} - kT l_a \ln(\phi_x \rho_s), \quad (52)$$

where ρ_s is the total density of the solvent which is calculated from the equation of state (32) with the appropriate solvent-solvent interactions, and where we have also anticipated the other approximations that led to Eqs. (44)–(47) (namely large z and small ϵ_{ss}) by disregarding the contribution (26) to ΔG_a , keeping only the term equivalent to Eq. (27). The enthalpy, entropy, and volume changes of solvation derived from the free energy (52) are given by (assuming that ϕ_x is temperature independent)

$$\Delta H_a^\infty = -l_a \epsilon_{ax} - kT^2 \alpha_s l_a, \quad (53)$$

$$\Delta S_a^\infty = kl_a[\ln(\phi_x \rho_s) - T\alpha_s], \quad (54)$$

$$\Delta V_a^\infty = -kT\beta_s l_a. \quad (55)$$

As before these expressions do not contain contributions from the long range part of the electrostatic solvent–host interaction. These contributions are included (in the δE parameter) in the expressions for the thermodynamic quantities of association which are now given, in analogy to Eqs. (48)–(51), by

$$\Delta G_{\text{Assoc}}^\infty = -\delta E - kT\delta l \ln(\phi_x \rho_s), \quad (56)$$

$$\Delta H_{\text{Assoc}}^\infty = -\delta E - kT^2\alpha_s \delta l, \quad (57)$$

$$\Delta S_{\text{Assoc}}^\infty = k\delta l[\ln(\phi_x \rho_s) - T\alpha_s], \quad (58)$$

$$\Delta V_{\text{Assoc}}^\infty = -kT\beta_s \delta l. \quad (59)$$

Again the temperature dependence of ΔG_{EL} was disregarded in obtaining Eqs. (53)–(54). Comparing these equations with Eqs. (48)–(51), it is seen that the new parameter ϕ_x appears only in the entropic part of the free energy. The equations for the changes in enthalpy and the volume remains unchanged in this limit of strong solute–solvent interactions, because in this limit the sites nearest to the solute are saturated, namely fully occupied by the specific solvent binding sites x . Note that δE now refers to interactions with this specific site.

Repeating now the procedure of fitting these expressions to the experimental results of Schantz⁵ we keep the parameters obtained for the pure PPO as before namely, $(z/2)\epsilon_{ss} = 1.127$ kcal/mol and $v^* = 11.41$ cm³/mol. For the experimental values of $P = 1$ atm, $T = 295$ K, and $r_s = 10\,000$, these imply $\rho_s = 0.9223$, $\alpha_s = 7.205 \times 10^{-4}$ K⁻¹, and $\beta = 6.122 \times 10^{-5}$ atm⁻¹. Taking $\phi_x = 1$ in Eqs. (56)–(59) lead to Eqs. (48)–(51) above. In what follows we use also $\phi_x = 0.25$, corresponding to the ratio of oxygens to methylic groups (1:3) in the PPO molecule, in order to assess the effect of this parameter. Then using the Schantz's data for ΔH and ΔS for NaCF₃SO₃–PPO we get from Eqs. (57) and (58) $\delta E = 1.18$ kJ/mol and $\delta l = -9.9$, while for LiClO₄–PPO, $\delta E = -7.11$ kJ/mol and $\delta l = -11.3$ are obtained. Note that the δl values obtained now for changes in the number of sites around the reactants and products are more reasonable than those obtained for the choice $\phi_x = 1$. This estimate for δl still looks large. The value of ϕ_x that yields a more reasonable value $\delta l = -4$ for the NaCF₃SO₃–PPO system is found to be $\phi_x = 0.02$, seemingly too small.²⁶ Obviously further modifications to the model are possible, e.g., taking the strong solvent–solute coupling limit only for the solvent–cation interaction but not for the solvent–anion or solvent–pair interactions.

Next consider the temperature dependence of ΔG_{EL} , assumed to result from the temperature dependence of the solvent dielectric function D . In order to estimate the corresponding effect on the thermodynamic quantities of association we replace Eqs. (57)–(58) by

$$\Delta H_{\text{Assoc}}^\infty = -\delta \tilde{E} - kT^2\alpha_s \delta l, \quad (60)$$

$$\Delta S_{\text{Assoc}}^\infty = k\delta l[\ln(\phi_x \rho_s) - T\alpha_s] + \Delta S_x, \quad (61)$$

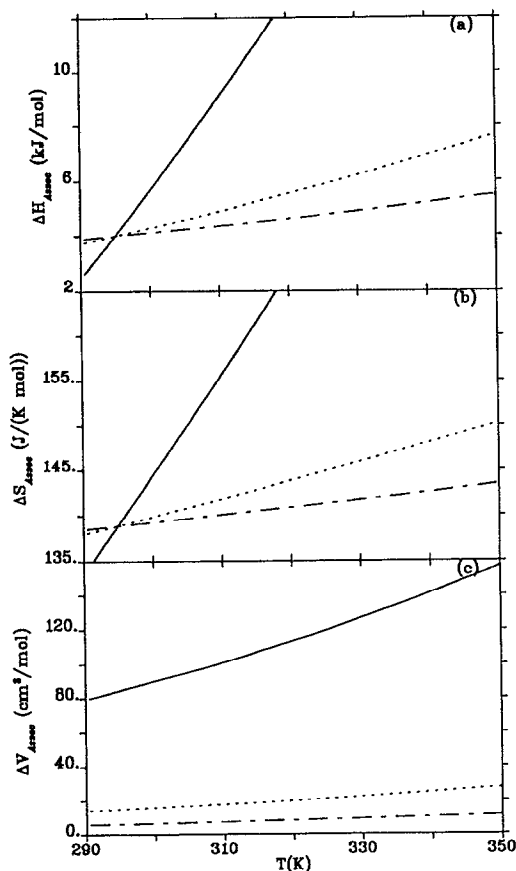


FIG. 1. Temperature dependence of the thermodynamic functions (enthalpy, entropy, and volume) of the association reaction, for constant r pressure ($P = 1$ atm) and solvent molecular size ($r_s = 10\,000$). The solid and dotted lines correspond to $\phi_x = 1$ and $\phi_x = 0.25$, respectively. The dashed-dotted lines correspond to $\phi_x = 0.25$ and $\delta l = -4$.

where $\delta \tilde{E} = \delta E - T\Delta S_x$ and with Eqs. (56) and (59) unchanged. ΔS_x can be identified with the electrostatic contribution $\Delta S_{\text{EL}} = -(\kappa/D)(\partial \ln D/\partial T)$ but we can also view it more generally as “any additional entropy change not accounted for by the original model.” For simplicity we assume that $\delta \tilde{E}$ and ΔS_x are constant parameters. Together with δl and ϕ_x we now have four free parameters. Obviously with such a large number of free parameters getting a reasonable fit cannot be considered a success of the theory but only, at most, a test for its consistency. For example, the choice $\delta l = -4$ and $\phi_x = 0.25$ gives, by fitting to the experimental ΔH and ΔS for the NaCF₃SO₃–PPO system, $\delta \tilde{E} = -1.917$ kJ/mol and $\Delta S_x = 83.04$ J/(K mol). If we assume that all this “missing entropy” originates from the electrostatic term, then from $\Delta S_x = -(\kappa/D)(\partial \ln D/\partial T)$ together with $D \approx 5$ and $dD/dT \approx -0.016$ (Ref. 14) we get $\kappa = 129.75$ kJ/mol. If we further take $\kappa = q^2/R$ and chose q to be one electron charge we obtain $R = 10.7$ Å, a possibly reasonable number for the effective separation within a contact ion-pair in this system. Obviously, this exercise in parameter choice should not be taken too seriously; it may indicate the origin of possible flaws in the present model, however any attempt to use it in a quantitative manner would

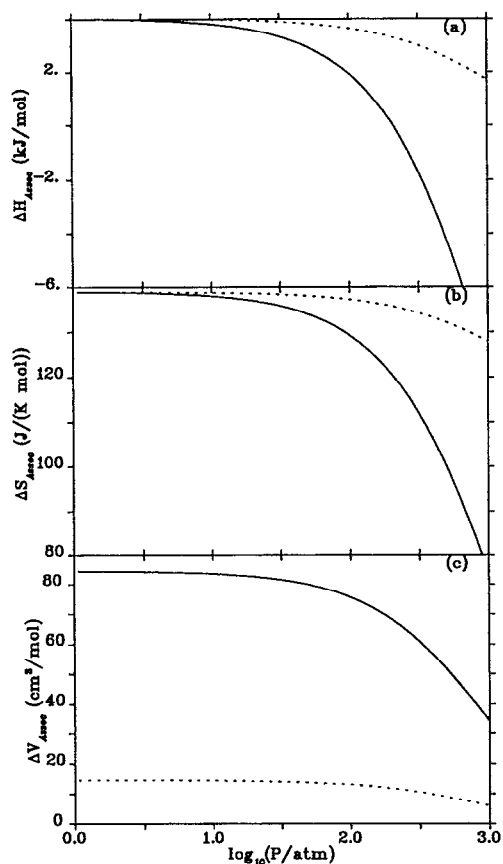


FIG. 2. Pressure dependence of the thermodynamic functions of the association reaction, for constant temperature ($T=295$ K) and solvent molecular size ($r_s=10\ 000$). The solid and dotted lines correspond to $\phi_x=1$ and $\phi_x=0.25$, respectively.

require a better theory for ΔS_x , including its dependence on temperature, pressure, and solvent chain length.

Next we consider the implications of our model with the values of $\phi_x=1$ and $\phi_x=0.25$ for the temperature, pressure and solvent molecular size dependence of the thermodynamic functions of the association reaction. Figures 1, 2, and 3 show the change in enthalpy, entropy, and volume per association-mole as functions of T , P , and r_s , respectively,²⁷ using the results for $\phi_x=1$ ($\delta E=25.68$ kJ/mol and $\delta l=-56.9$), solid line, $\phi_x=0.25$ ($\delta E=1.18$ kJ/mol and $\delta l=-9.9$), dotted line. The dashed-dotted lines in Figs. 1(a)–(c) (and in Fig. 4) correspond to the model of Eqs. (60) and (61) with $\phi_x=0.25$, $\delta l=-4$, $\delta \bar{E}=-1.917$ kJ/mol, and $\Delta S_x=83.04$ J/(K mol). Figures 4 and 5 show the temperature dependence of the association constant at constant pressure and at constant volume respectively for a solvent of large molecular weight ($r_s=10\ 000$). Note that these figures (as well as Figs. 6 and 7) show $\bar{K}_{\text{Assoc}}=v^*K_{\text{Assoc}}$. The pressure dependence of \bar{K}_{Assoc} is displayed for the same r_s in Fig. 6. Finally, Fig. 7 shows the r_s dependence of \bar{K}_{Assoc} at standard temperature and pressure. It should be emphasized that r_s , the number of “chain units,” does not necessarily represent the number of real ether monomers in the chain. It is however proportional to this number.

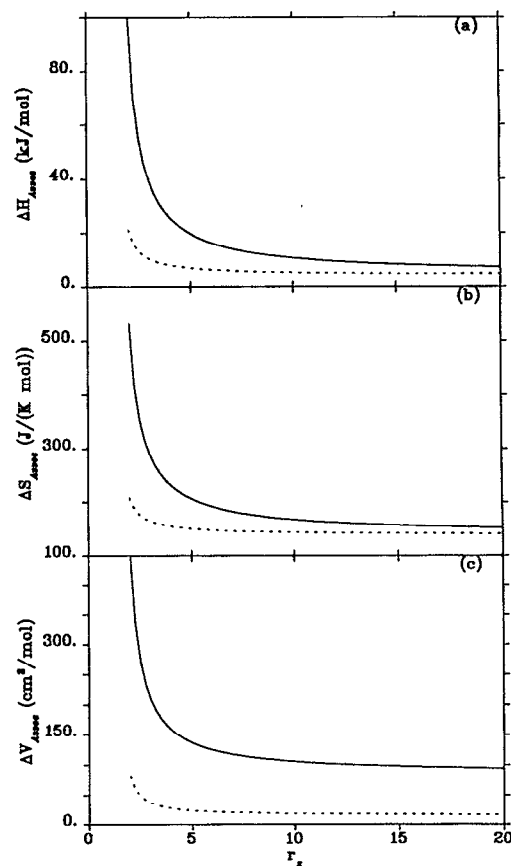


FIG. 3. The dependence of the thermodynamic functions of the association reaction on the solvent size expressed by r_s . The temperature and the pressure are $T=295$ K and $P=1$ atm. The solid and dotted lines correspond to $\phi_x=1$ and $\phi_x=0.25$, respectively.

From the results displayed in Figs. 1–7 the following conclusions can be drawn:

- (a) The dependence on temperature, pressure, and solvent

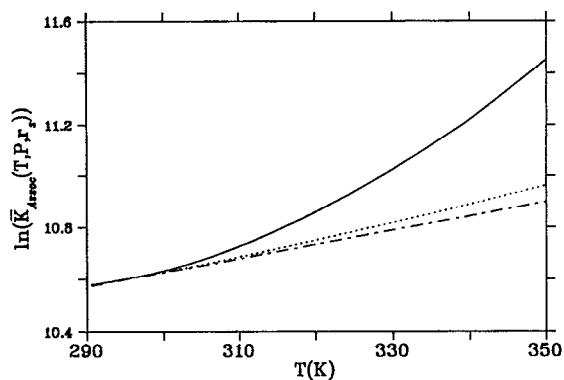


FIG. 4. Temperature dependence of the association equilibrium constant at constant pressure, $P=1$ atm, $r_s=10\ 000$. The solid and dotted lines correspond to $\phi_x=1$ and $\phi_x=0.25$, respectively. The dashed-dotted line corresponds to $\phi_x=0.25$ and $\delta l=-4$.

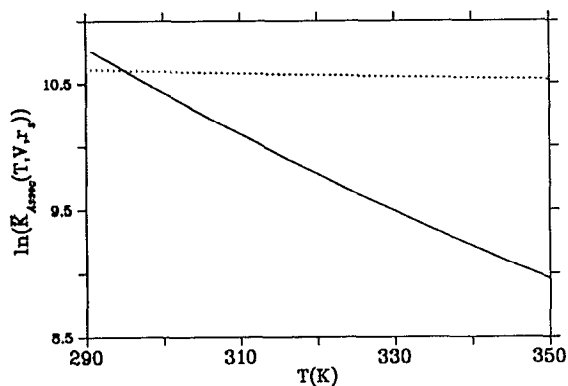


FIG. 5. Temperature dependence of the association equilibrium constant at constant volume (i.e., constant solvent density). The value of ρ_s used is $\rho_s = 0.92$, which is the density calculated from Eq. (56) at $P = 1$ atm and $T = 295$ K. Solvent size is $r_s = 10\,000$. The solid and dotted lines correspond to $\phi_x = 1$ and $\phi_x = 0.25$, respectively.

molecular size calculated in the QCA show the same qualitative trends obtained from the mean-field treatment of paper I.

- (b) The enthalpy and entropy of the association reaction vary in a reasonable range with temperature and pressure. The variations obtained for $\phi_x = 1$ are stronger than for $\phi_x = 0.25$. It is interesting to note that for $\phi_x = 1$, ΔH_{Assoc} changes sign with increasing pressure. This change in sign does not appear for $\phi_x = 0.25$.
- (c) The volume change ΔV is smaller for smaller values of ϕ_x . The results obtained for $\phi_x = 0.25$ are closer to the typical values expected for the volume changes of an ionic association reaction, which is of the order of $10\text{ cm}^3/\text{mol}$.
- (d) The dependence of the thermodynamic functions of association on the solvent molecular size and in particular the decrease of \bar{K}_{Assoc} with r_s shown in Fig. 7, is consistent with the observation of Torell and co-workers⁴ on short (4–8) chain methyl capped PPO, but not with the observation of the opposite effect in

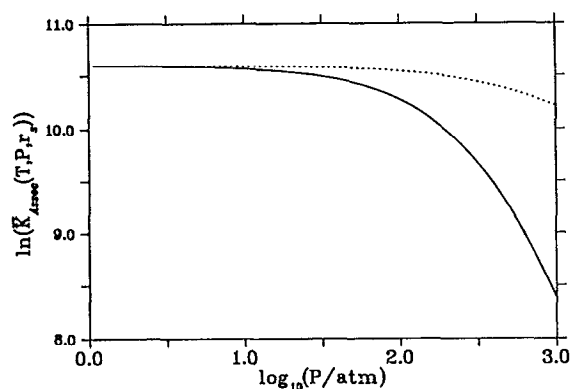


FIG. 6. Pressure dependence of the association equilibrium constant at $T = 295$ K, for $r_s = 10\,000$. The solid and dotted lines correspond to $\phi_x = 1$ and $\phi_x = 0.25$, respectively.

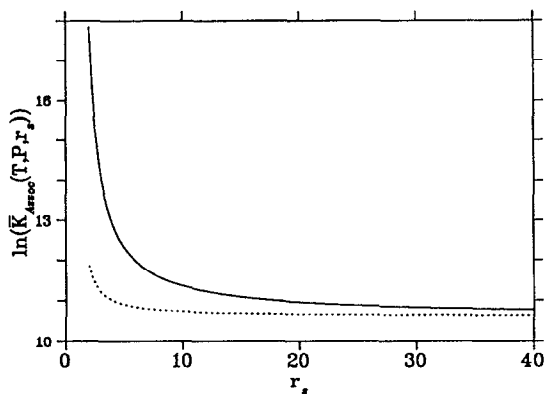


FIG. 7. Solvent size dependence of the association equilibrium constant at $P = 1$ atm and $T = 295$ K. The solid and dotted lines correspond to $\phi_x = 1$ and $\phi_x = 0.25$, respectively.

longer chain PPG.³ Unfortunately there is no overlap between the size range of these two groups of experiments and the results of Fig. 7 suggest that the trend observed in PPG is due to chain-end effect as discussed in Ref. 4.

- (e) The somewhat larger than expected value obtained for the change δl in the total solvent coordination associated with the ion-association reaction may be related to a possible underestimate, in the present model, of the entropy of association. The source of this “additional entropy change” may be related to dielectric effects or to crosslink formation as discussed above. Obviously, using a smaller δl with an additional constant entropy change ΔS_x and associated enthalpy change δE will weaken the T , P , and r_s dependencies of the thermodynamic quantities of solvation and of the association equilibrium constant (as seen in Figs. 1 and 4). This simply reflects the choice of constant ΔS_x and does not necessarily have any physical significance.

IV. SUMMARY AND CONCLUSIONS

In this paper we have investigated the solvation of ionic species in polymer hosts such as polyethers, in a framework which distinguishes between the long range dielectric effect and between short range interactions of the ions with nearest neighbor specific solvent sites (such as the cation–oxygen interactions in polyether electrolytes). In particular we have focused on the effects of short range interactions using the quasichemical approximation within a lattice model.

The model is obviously too simplified to be fully predictive. It does provide a parametrized description of the thermodynamic quantities (energy, volume, enthalpy, entropy, and free energy) which makes it possible to use a selected set of experimental data in order to predict or interpret other experimental quantities. Thus we have found that available experimental results on the NaCF_3SO_3 –PPO and LiClO_4 –PPO systems could not be accounted for in a consistent way unless the idea of selective cation-binding sites was included in the model. Furthermore the model calculations clearly indicate that solvent molecular chain-length de-

pendence of the association-dissociation equilibrium saturates at a relatively low solvent molecular weight, so that the observation of such dependence³ must have resulted from chain-end effects as has already been anticipated in Ref. 4.

We have not done an exhaustive search of parameter space in order to find the best possible description of our systems. Thus, the parameters used to describe the polyether solvent were derived from data available for the pure high molecular weight polymers and was used as constants for all r_s values.²⁸ We expect that better fits could be obtained by using experimental input from both low and high molecular weight polymers. Similarly, dielectric data for these solvents (e.g., dielectric response as function of chain length) is needed in order to assess the role played by the long range part of the solute-solvent interaction.

Even on the level of our present effort it appears that the model can account consistently for qualitative features in the behavior of the association-dissociation equilibrium in polyether-salt systems. Thus once the parameters of the pure solvent were determined from the dependence of the pure solvent density on temperature¹ and once energetic parameters associated with the solvation were fitted to the temperature dependence data, correct trends and orders of magnitude (as compared to experiments⁴) were obtained for the pressure (Fig. 6) and chain length (Fig. 7) dependencies of the association equilibrium constant.

Our model leaves open the possible role played by the cross-linking effect of the ions. Ion mediated transient crosslinks between solvent chains show themselves in the profound effect of added salt on the solvent viscosity and mobility. Their possible contribution to the thermodynamics of the solvation cannot be accounted for on the level of the QCA. We are currently studying this issue using lattice Monte Carlo simulations.

ACKNOWLEDGMENTS

This research was supported by the Israel National Science Foundation and by the Kurt Lion Fund. A. N. thanks Professors M. Ratner and L. M. Torell for useful discussions.

APPENDIX A: CALCULATIONS OF THE INFINITE DILUTION LIMIT IN THE QCA

Substituting $\varphi_i = \chi_{ii} + \sum_{j(\neq i)} \chi_{ij}$ [Eq. (11)] in Eq. (12) leads to the the following equations for $\{\chi_{ij}\}$ ($i \neq j$):

$$e^{\Delta\epsilon_{ij}/kT} \chi_{ij}^2 = \left[\varphi_i - \sum_{k(\neq i)} \chi_{ik} \right] \cdot \left[\varphi_j - \sum_{m(\neq j)} \chi_{jm} \right] - \chi_{ij} \left[\varphi_i + \varphi_j - \sum_{k(\neq i,j)} \chi_{ik} - \sum_{m(\neq i,j)} \chi_{jm} \right] = 0 \quad (\text{A1})$$

which can be rewritten as

$$(1 - e^{\Delta\epsilon_{ij}/kT}) \chi_{ij}^2 + \left[\varphi_i - \sum_{k(\neq i,j)} \chi_{ik} \right] \cdot \left[\varphi_j - \sum_{m(\neq i,j)} \chi_{jm} \right] - \chi_{ij} \left[\varphi_i + \varphi_j - \sum_{k(\neq i,j)} \chi_{ik} - \sum_{m(\neq i,j)} \chi_{jm} \right] = 0 \quad (\text{A2})$$

Note that in the case of a binary mixture the set of Eqs. (A2) is reduced to a single quadratic equation for χ_{ij} , with solution given by Eq. (22).

It is useful to note that performing the limit $\varphi_a \rightarrow 0$ in Eq. (A2), for an arbitrary component a , the remaining non-zero terms yield the relation

$$\left[\sum_{i(\neq a)} \frac{\chi_{ai}}{\varphi_a} \right]_{\varphi_a=0} = 1 \quad (\text{A3})$$

Another useful expression that can be obtained in a similar way from Eq. (A1), is given by

$$\left\{ \frac{1}{\varphi_a} \left[1 - \sum_{j(\neq a)} \frac{\chi_{aj}}{\varphi_a} \right] \right\}_{\varphi_a=0} = \left(\frac{\chi_{aa}}{\varphi_a} \right)_{\varphi_a=0}^2 \cdot \left[\frac{e^{\Delta\epsilon_{ai}/kT}}{\varphi_i^0 - \sum_{j(\neq a,i)} \chi_{ij}^0} \right] \quad (\text{A4})$$

which is valid for any i . Note that the left-hand side is, from Eq. (11), just $(\chi_{aa}/\varphi_a^2)_{\varphi_a=0}$. In the expression above the superscript 0 indicates a mixture with $\varphi_a=0$. Finally Eq. (A4) can be rewritten in the form

$$\left(\frac{\chi_{ai}}{\varphi_a} \right)_{\varphi_a=0} = \left\{ \left(\frac{\chi_{aa}}{\varphi_a} \right)_{\varphi_a=0} \cdot e^{-\Delta\epsilon_{ai}/kT} \left[\varphi_i^0 - \sum_{j(\neq a,i)} \chi_{ij}^0 \right] \right\}^{1/2} \quad (\text{A5})$$

Summing Eq. (A5) for the different values of $j(\neq a)$ and using the identity (A3), one gets

$$\left(\frac{\chi_{aa}}{\varphi_a} \right)_{\varphi_a=0} = \left[\sum_{i(\neq a)} e^{-(1/2)\Delta\epsilon_{ai}/kT} \sqrt{\varphi_i^0 - \sum_{j(\neq a,i)} \chi_{ij}^0} \right]^{-2} \quad (\text{A6})$$

$$\left(\frac{\chi_{ai}}{\varphi_a} \right)_{\varphi_a=0} = \frac{e^{-(1/2)\Delta\epsilon_{ai}/kT} \sqrt{\varphi_i^0 - \sum_{j(\neq a,i)} \chi_{ij}^0}}{\sum_{j(\neq a)} e^{-(1/2)\Delta\epsilon_{aj}/kT} \sqrt{\varphi_j^0 - \sum_{k(\neq a,j)} \chi_{jk}^0}} \quad (\text{A7})$$

Substituting Eq. (11) in Eq. (A6), Eq. (18) is finally obtained.

APPENDIX B: EQUATION OF STATE IN THE WEAK INTERACTIONS LIMIT

In order to obtain the limit of weak interactions of the equation of state (13), it is necessary to expand the scaled number of pairs χ_{00} in terms of powers of the energy parameters $\{\epsilon_{ij}\}$. It is straightforward to show that Eq. (12) can be rewritten in the form

$$\chi_{ii}\chi_{jk} = e^{[(1/kT)(\epsilon_{ii} + \epsilon_{jk} - \epsilon_{ij} - \epsilon_{ik})]} \chi_{ij}\chi_{ik} \quad (\text{B1})$$

which for $i=0$, it is simplified to $(\epsilon_{0j}=0, \text{ for any } j)$,

$$\chi_{00}\chi_{jk} = e^{(\epsilon_{jk}/kT)} \chi_{0j}\chi_{0k} \quad (\text{B2})$$

Expanding to the first order in the energy ϵ_{jk} , Eq. (B2) becomes

$$\chi_{00}\chi_{jk} = \left(1 + \frac{\epsilon_{jk}}{kT}\right) \chi_{0j}\chi_{0k}. \quad (\text{B3})$$

Summing up Eqs. (B3) above for all values of the indices k and j and using Eq. (11), it simplifies to

$$\chi_{00} = \varphi_0^2 + \sum_{j(\neq 0)} \sum_{k(\neq 0)} \frac{\epsilon_{jk}}{kT} \chi_{0j}\chi_{0k}. \quad (\text{B4})$$

Now we assume that the same kind of expansion (B4) is valid for any pair, that is, χ_{0k} can be written for, weak interactions, as $\chi_{0k} = \varphi_0\varphi_k + O(\{\epsilon_{lm}\})$, where the first term on the right-hand side is the solution of Eqs. (11) and (12) for zero interaction energies, and the second term is some expansion in powers of the energies. Using this assumption in Eq. (B4) and keeping only terms that are first order in energy, we finally get Eq. (28).

An explicit form for χ_{0j} can be obtained by summing Eqs. (B3) for all values of the index k and substituting the value of χ_{00} given by Eq. (28). The final result to first order in the energies is given by expression

$$\chi_{0j} = \varphi_0\varphi_j \left[1 + \sum_{l(\neq 0)} \sum_{k(\neq 0)} \frac{\epsilon_{lk}}{kT} \varphi_l\varphi_k - \sum_{k(\neq 0)} \frac{\epsilon_{jk}}{kT} \varphi_k \right]. \quad (\text{B5})$$

If one considers also the limit of large coordination of the lattice (i.e., $z \rightarrow \infty$), we have

$$\frac{z}{2} \ln \left(\sum_{i=0}^k \frac{r_i}{q_i} \varphi_i \right) = -\frac{z}{2} \ln \left(\sum_{i=0}^k \frac{q_i}{r_i} \rho_i \right) \approx \sum_{i=0}^k \frac{r_i - 1}{r_i} \rho_i, \quad (\text{B6})$$

where Eq. (2) was used for the fraction q_i/r_i in the equation above. Therefore, substituting the above limit in Eq. (29), neglecting terms of order $1/z$ and using $\{(z/2)\epsilon_{jk}\}$ as constants, we get the mean-field equation of Sanchez and Lacombe,²³ Eq. (32).

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²⁰We assume that δ_i and σ_i are not changed by the solvation process.

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²⁶The value of δE obtained for this fit is -1.91 kJ/mol, opposite in sign to that obtained for $\phi_x = 0.25$.

²⁷Note that the r_s dependence is shown for $r_s \geq 2$. For $r_s = 1$ the pure solvent appears to be a gas at $P = 1$ atm and at the temperature range considered, as is evidenced from the much lower density obtained. In any case $r_s < 4$ is not physically consistent with our choice of $\phi_x = 0.25$ which originates from the carbon-oxygen ratio of PPO.

²⁸Fitting experimental data [cf. J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds* (American Elsevier, New York, 1950), Vol. 1] of a corresponding monomer fluid, ethyl methyl ether, to the mean field theory prediction at the gas-liquid coexistence equilibrium, using the procedure described in Ref. 22, yields $\epsilon^* = 0.814$ kcal/mol and $v^* = 8.51$ cm³/mol (also $r_s = 8$) while the parameters used in the present paper are $\epsilon^* = 1.13$ kcal/mol and $v^* = 11.4$ cm³/mol, obtained (Ref. 1) using properties of the high molecular weight PPO.