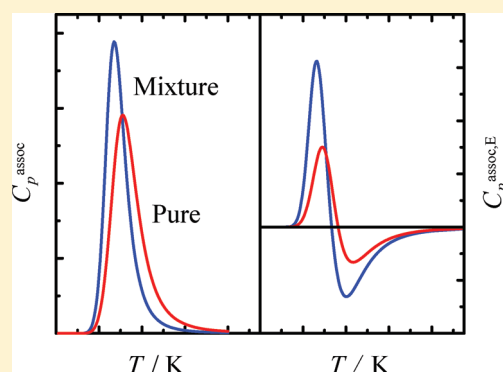


# Energetic, Entropic, and Volumetric Effects in Nonaqueous Associated Solutions

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S Supporting Information

**ABSTRACT:** On the basis of a simple two-state association model (TSAM), a comprehensive study of thermodynamic response functions for nonaqueous associated solutions is presented. The excess isobaric heat capacities  $C_p^E(T)$  and excess thermal expansivities  $V_p^E \equiv (\partial V^E/\partial T)_p$  for a number of alcohol–alkane, amine–alkane, alcohol–ether, and alcohol–alcohol mixtures have been experimentally determined at atmospheric pressure within 278.15–338.15 K for  $C_p^E$  and 283.15–333.15 K for  $V_p^E(T)$ . A rich variety (in some cases unreported) of temperature dependences for  $C_p^E(T)$  but also for  $V_p^E(T)$  curves has been observed. This thermodynamic information has been rationalized with the TSAM, which is found to qualitatively account for all observations. Specifically, the model provides a detailed dissection of the energetic and entropic effects of association that are reflected on  $C_p^E(T)$ , and of the volumetric effects that are echoed on  $V_p^E(T)$ . The latter, almost unexplored to date, are found to be opposite to what is currently being conjectured for “low-temperature water”, and they stimulate further experimental studies on aqueous solutions of nonelectrolytes.



## 1. INTRODUCTION

Statistical mechanics provides a link between thermodynamic response functions—also referred to as second-order derivatives or thermodynamic derivatives—and fluctuations. Among other relations,<sup>1</sup> one has

$$C_p = \frac{1}{k_B T^2} \langle (\delta H)^2 \rangle \quad (1)$$

$$\alpha_p = \frac{1}{\langle V \rangle k_B T^2} \langle \delta V \delta H \rangle \quad (2)$$

$$\kappa_T = \frac{1}{\langle V \rangle k_B T^2} \langle (\delta V)^2 \rangle \quad (3)$$

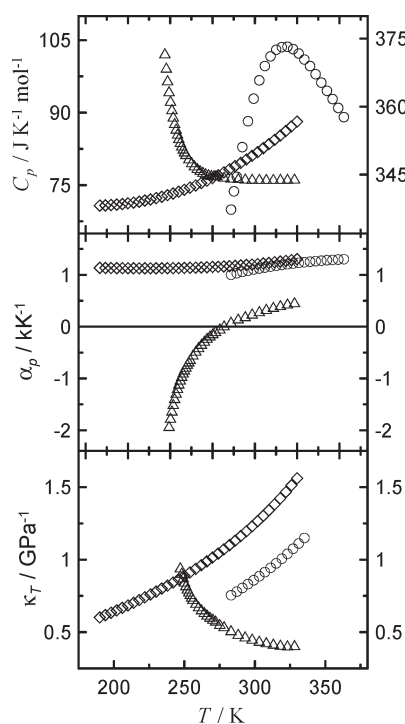
That is, the isobaric heat capacity  $C_p$  and the isothermal compressibility  $\kappa_T$  are a measure of enthalpy ( $\langle (\delta H)^2 \rangle$ ) and volume ( $\langle (\delta V)^2 \rangle$ ) fluctuations, respectively, while the isobaric thermal expansivity  $\alpha_p$  quantifies the correlation between them ( $\langle \delta H \delta V \rangle$ ). ( $k_B$  is the Boltzmann constant.) Naturally, eqs 1–3 are consistent with the second law of thermodynamics, which implies that  $C_p > 0$  and  $\kappa_T > 0$  while  $\alpha_p$  is unrestricted in sign.

The local energetic, entropic, and volumetric effects associated with intermolecular interactions must manifest in the above response functions, with hydrogen bonding being an example.<sup>2,3</sup> Indeed, the formation/disruption of hydrogen bonds in the

liquid state is accompanied by local changes in energy, entropy, and volume that contribute to  $\delta H$  and  $\delta V$  in eqs 1–3. Let us illustrate this for water. The enhanced “quality” of its three-dimensional hydrogen-bond network as temperature is decreased—especially down to the deeply supercooled region—is accompanied by a decrease in local enthalpy, entropy, and density,<sup>4</sup> so contributing positively to  $C_p$  and  $\kappa_T$  and negatively to  $\alpha_p$  (Figure 1). At sufficiently higher temperatures, a fraction of hydrogen bonds are broken so that monomers, dimers, and larger multimers are present. At such temperatures the fluid resides in a low-density state, implying that formation of hydrogen bonds when O and H atoms concur in space decreases the enthalpy and entropy of the system but results in a local density increase. On the other hand, while energetic and entropic effects of H-bonding are also important in other associated liquids such as alcohols (see, e.g., refs 2, 3, 11, and 13–18), experimental data give no indication of negative  $\langle \delta H \delta V \rangle$  (Figure 1). Since the enhancement of H-bond structure as the temperature is lowered results, as for water, in an enthalpy decrease, one may infer—from eq 2—that volumetric effects are at both high and low temperatures like those for “high-temperature” water. Clearly, that an alkyl chain (that is, a number of nonpolar chemical units) is bonded to the

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**Figure 1.** Isobaric heat capacity  $C_p$ , isobaric thermal expansivity  $\alpha_p$ , and isothermal compressibility  $\kappa_T$  of water ( $\Delta$ ), methanol ( $\Diamond$ ), and 3-ethyl-3-pentanol ( $\circ$ ) as a function of temperature  $T$  at atmospheric pressure. The left y-axes set the scales for water and methanol, and the right ones correspond to 3-ethyl-3-pentanol. Data for water were taken from refs 5 ( $C_p$ ), 6 ( $\alpha_p$ ), and 7 ( $\kappa_T$ ); those for methanol were taken from refs 8 ( $C_p$ ), 9 ( $\alpha_p$ ), and 10 ( $\kappa_T$ ); and those for 3-ethyl-3-pentanol were taken from refs 11 ( $C_p$ ) and 12 ( $\alpha_p$  and  $\kappa_T$ ).

hydroxyl group of the alcohol causes this markedly different behavior.

The study of response functions for liquid solutions opens a number of avenues to examine the features of association because the excess isobaric heat capacity  $C_p^E(T)$  is basically driven by its associational part.<sup>11,19–28</sup> This has been exploited in previous works<sup>11,25</sup> to analyze  $C_p^E(T)$  for alcohol solutions, thereby enabling the identification and characterization of various interesting features of that property for inert and noninert solvents (here, noninert solvents refer to nonassociated liquids that are proton acceptors and thus capable of H-bonding with alcohols). Such a task was accomplished with the aid of a two-state association model (TSAM).<sup>11,13,25</sup>

To provide a fuller account of association effects in non-aqueous associated systems, we present here a comprehensive set of  $C_p^E(T)$  measurements (at atmospheric pressure) for three types of binary liquid mixtures, namely, associated–inert, associated–noninert, and associated–associated. In addition, data for the temperature derivative of the excess volume or excess thermal expansivity  $V_p^E \equiv (\partial V^E / \partial T)_p$ , for which very little information and knowledge have been accumulated, are provided. All this information is discussed and qualitatively analyzed by use of the TSAM. Although the model allows obtaining information at a quantitative level when applied to the  $C_p$  of pure associated liquids,<sup>11,13</sup> such a study does not seem pertinent for the case of binary mixtures: excess properties are small in magnitude so that their behavior cannot be quantitatively captured without a proper accounting of subtle phenomena (e.g., H-bond cooperativity),

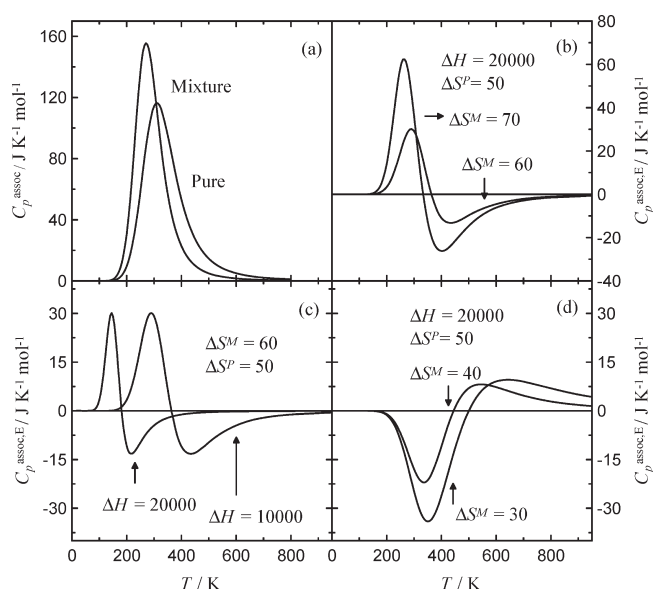
which escape from the basic nature of the model. Nevertheless, as will be shown, a qualitative analysis provides useful insights into energetic, entropic, and volumetric effects associated with H-bonding. The paper is organized as follows. In section 2 we describe the experiments. The discussion of the results and the corresponding analysis of energetic, entropic, and volumetric effects in terms of the model—which is described in the Appendix—are contained in section 3. Section 4 includes some concluding remarks.

## 2. EXPERIMENTAL METHODS

**2.1. Studied Systems.** Experiments were planned using the following criteria: (i) in order to avoid the effect of orientational order between segments of linear alkyl chains of neighboring molecules,<sup>29–31</sup> liquids (self-associated and solvent) with branched alkyl chains have been selected; (ii) one alcohol and one amine were employed as self-associated liquids with a view to analyze the effect of the strength of H-bonding; and (iii) branched alkanes and mono- and polyethers were employed as inert and noninert solvents, respectively. The studied systems (with the number of measured compositions specified in parentheses) are 3M3P–br-C<sub>8</sub> (9), 3M3P–br-C<sub>12</sub> (6), 3M3P–br-C<sub>16</sub> (9), C<sub>6</sub>NH<sub>2</sub>–br-C<sub>16</sub> (12), 3M3P–diglyme (3), 3M3P–triglyme (3), 3M3P–tetraglyme (3), 3M3P–DBE (3), and 3M3P–1-propanol (10). The meanings of the abbreviated compound names are as follows: 3M3P  $\equiv$  3-methyl-3-pentanol; br-C<sub>8</sub>  $\equiv$  2,3,4-trimethylpentane; br-C<sub>12</sub>  $\equiv$  2,2,4,6,6-pentamethylheptane; br-C<sub>16</sub>  $\equiv$  2,2,4,4,6,8,8-heptamethylnonane; C<sub>6</sub>NH<sub>2</sub>  $\equiv$  cyclohexylamine; DBE  $\equiv$  dibutyl ether.

**2.2. Materials.** The employed liquids were purchased from Fluka [*n*-heptane\* (99.8%), toluene\* (99.8%), water\* (99.9%), and br-C<sub>12</sub> (99%)] and from Aldrich [*n*-decane\* (99%), cyclohexane\* (99.9%), 1-propanol (99.4%), 1-butanol\* (99.7%), 2-butanol\* (99.4%), br-C<sub>8</sub> (98%), br-C<sub>16</sub> (98%), 3M3P (99%), C<sub>6</sub>NH<sub>2</sub> (99%), diglyme (99%), triglyme (99%), tetraglyme (99%), and DBE (99%)]. The stated purities are expressed on a molar basis, and the liquids marked with an asterisk were used as calibrating substances. Polar liquids, namely, water, 1-butanol, 2-butanol, 3M3P, C<sub>6</sub>NH<sub>2</sub>, diglyme, triglyme, tetraglyme, and DBE, were dried using Fluka 4 nm molecular sieves. All liquids were degassed prior to preparation of mixtures, which were made by weighing using a Mettler AE-240 balance. The estimated accuracy in the mole fraction is  $\pm 0.0001$ .

**2.3. Instrumentation and Procedures.** Data for the excess heat capacity  $C_p^E$  were obtained by combining heat capacities per unit volume  $C_p V^{-1}$  and densities  $\rho$  for pure liquids and mixtures ( $C_p^E \equiv C_p - x_1 C_p^1 - x_2 C_p^2$ , with superscripts “1” and “2” referring to the pure liquids). Densities were measured with an Anton-Paar vibrating-tube densimeter, which was calibrated by using *n*-heptane, cyclohexane, toluene, and Milli-Q water as density standards. Heat capacities per unit volume were determined with a Micro DSCII calorimeter from Setaram. This apparatus and the experimental technique have been described previously.<sup>32,33</sup> *n*-Heptane, *n*-decane, 1-butanol, and 2-butanol were employed as calibrating liquids, and their  $C_p$  values were taken from the literature.<sup>8</sup> Working in an up-scan mode at a 0.25 K·min<sup>−1</sup> rate, the uncertainty in  $C_p^E$  data was found to be  $\pm 0.1$  J·mol<sup>−1</sup>·K<sup>−1</sup> (see ref 33 for a detailed explanation). The determination of excess thermal expansivities  $V_p^E$  entails, first, that of  $V_p \equiv (\partial V / \partial T)_p$  for pure liquids and mixtures from  $\rho(T)$  data. Such a task was accomplished by means



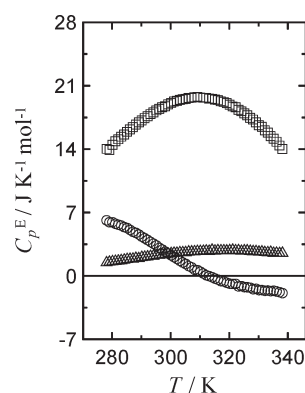
**Figure 2.** (a) Temperature dependence of the associational part of the isobaric heat capacity  $C_p^{\text{assoc},E}(T)$  as obtained from eq A.15. The associational excess isobaric heat capacities  $C_p^{\text{assoc},E}(T)$  in panels b–d result from two such peaks (pure and mixture), as eq A.17 indicates. Values for  $\Delta H \equiv \Delta H^M = \Delta H^P$  and  $\Delta S$  are given in  $\text{J} \cdot \text{mol}^{-1}$  and  $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , respectively.

of an incremental procedure described in detail elsewhere.<sup>34</sup> Then,  $V_p^E \equiv V_p - x_1 V_p^1 - x_2 V_p^2$  was computed; its uncertainty was  $\pm 0.1 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ .<sup>34</sup> Data were obtained with a step of 1 K within 278.15–338.15 K for  $C_p^E$  and 283.15–333.15 K for  $V_p^E$ . They have been deposited as Supporting Information.

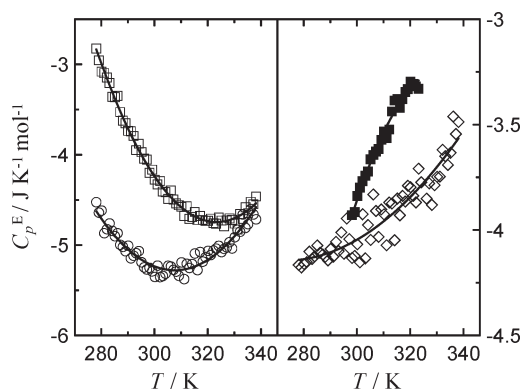
### 3. RESULTS AND DISCUSSION

**3.1. Qualitative Model Predictions.** Figure 2 illustrates the model predictions—a detailed description of the model can be found in the Appendix—for the associational part of  $C_p^E$  (i.e., the second term in the right-hand side of eq A.18). As Figure 2a indicates,  $C_p^{\text{assoc},E}(T)$  results from the balance of two association peaks corresponding to  $C_p^{\text{assoc},M}(T)$  and  $C_p^{\text{assoc},P}(T)$ . Curves shown in Figure 2b–d correspond to particular sets of parameters, which, as we shall see, have been chosen for convenience. By comparing eqs A.18–A.20, one infers an analogous qualitative picture for  $V_p^{\text{assoc},E}(T)$  and  $V_T^{\text{assoc},E}(T)$ . The magnitude of association effects is modulated by the prefactors  $\Delta H^2$ ,  $\Delta H \Delta V$ , and  $\Delta V^2$ . As defined in the Appendix,  $\Delta H$  and  $\Delta V$  are the (molar) enthalpy of dissociation and (molar) volume of dissociation, respectively. Such quantities are closely related to the association energies and to the volume changes resulting from association. They are the crucial model parameters together with the dissociation entropy  $\Delta S$ , obviously a measure of entropic effects involved in association processes. We will assume (see the Appendix) that  $\Delta H$ ,  $\Delta S$ , and  $\Delta V$  do not depend on temperature and pressure. Moreover, the nature of the nonassociated liquid (especially if noninert) and composition may affect the capability of a given molecule to H-bond with its neighbors as well as the hydrogen-bond energy and volume themselves, so that  $\Delta H^M(x) \neq \Delta H^P$ ,  $\Delta S^M(x) \neq \Delta S^P$ , and  $\Delta V^M(x) \neq \Delta V^P$ .

In what follows, we will show experimental data of associated–inert liquid mixtures, associated–noninert liquid mixtures,



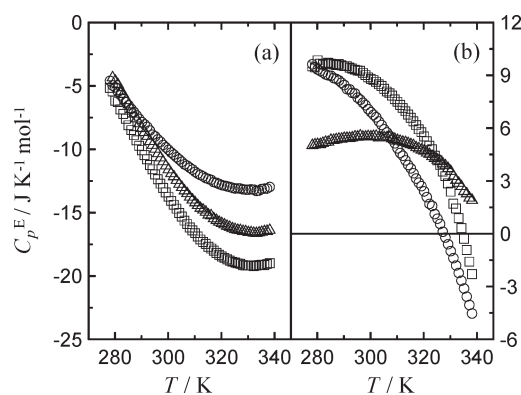
**Figure 3.** Excess isobaric heat capacities  $C_p^E$  as a function of temperature  $T$  for  $x3\text{M3P}-(1-x)\text{br-C}_{12}$ . (○)  $x = 0.0241$ ; (□)  $x = 0.4745$ ; (△)  $x = 0.9487$ .



**Figure 4.** Excess isobaric heat capacities  $C_p^E$  as a function of temperature  $T$  for  $x\text{C}_6\text{H}_{11}\text{NH}_2-(1-x)\text{br-C}_{16}$ . (○)  $x = 0.2927$ ; (□)  $x = 0.4960$ ; (◇)  $x = 0.4960$ . Filled squares are literature data<sup>34</sup> for  $x(n\text{-dodecane})-(1-x)\text{cyclohexane}$  with  $x = 0.4662$ . Lines are only intended to guide the eye.

and associated–associated liquid mixtures. Such information will be compared qualitatively to that given in Figure 2. The justification and usefulness of such an approach have been provided at the end of the Introduction.

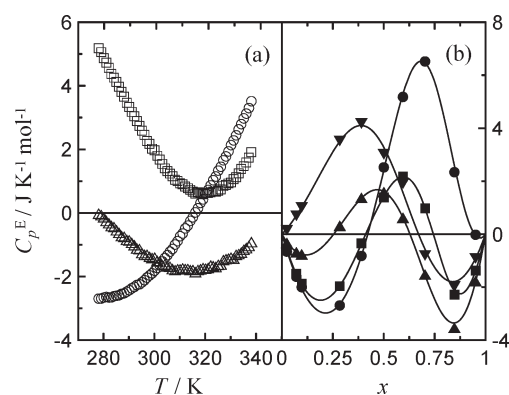
**3.2. Energetic and Entropic Effects for Associated–Inert Liquid Mixtures.** For associated–inert liquid mixtures one may expect that  $\Delta H^M \approx \Delta H^P \equiv \Delta H$  is a good approximation. On the other hand, since self-association in the mixture implies bringing molecules together over longer distances than for the pure associated liquid,  $\Delta S^M(x) > \Delta S^P$  (i.e.,  $d\Delta S^M/dx < 0$ ). Assuming that  $C_p^E(T)$  is dominated by its associational contribution (which is fairly justified<sup>11</sup>), the TSAM then predicts that  $C_p^E(T)$  will vary with  $T$  as shown in Figure 2b,c. Concretely, for a given  $\Delta H$  value, the observed  $C_p^E(T)$  within the fixed experimental temperature window must be seen to be displaced to the right as  $\Delta S^M(x)$  is increased (see Figure 2b). These predictions are corroborated by data for 3M3P–alkane mixtures; the data for mixtures containing br-C<sub>12</sub> shown in Figure 3 are a representative example of the behavior for the remaining systems. To our knowledge, experimental evidence of associated–inert liquid mixtures whose  $C_p^E(T)$  displays a minimum, such as those corresponding to the high-temperature region in Figure 2c, has not been previously reported. From Figure 2c, one infers that  $C_p^E(T)$  curves are displaced toward lower temperatures as the  $\Delta H$  value is



**Figure 5.** Excess isobaric heat capacities  $C_p^E$  as a function of temperature  $T$  for (a)  $x$ 3M3P–(1– $x$ )diglyme [(○)  $x = 0.2649$ ; (□)  $x = 0.5189$ ; (△)  $x = 0.7519$ ] and (b)  $x$ 3M3P–(1– $x$ )DBE [(○)  $x = 0.2525$ ; (□)  $x = 0.4747$ ; (△)  $x = 0.7438$ ].

decreased. To corroborate this TSAM prediction, it is then important to examine mixtures containing primary amines since they are characterized by a lower self-association energy ( $\approx 10 \text{ kJ} \cdot \text{mol}^{-1}$ )<sup>35</sup> than that for alcohols ( $\approx 20 \text{ kJ} \cdot \text{mol}^{-1}$ ).<sup>36</sup> Figure 4 shows that  $C_x\text{NH}_2$ – $\text{br-C}_{16}$  mixtures display the predicted behavior. Beyond that, it is interesting to note that amines fall in between alcohols and long-chain normal alkanes. For the latter, it has been shown that heat capacities are sensitive to the orientation of chain segments between neighboring molecules.<sup>29–31</sup> Since orientational order embodies small energies (as compared, for instance, to self-association energy in alcohols), it seems natural that  $C_p^E(T)$  covers the very-high-temperature limit of the curves of Figure 2b,c. Figure 4 shows that this is indeed the case for a  $n$ -dodecane–cyclohexane mixture.

**3.3. Energetic and Entropic Effects for Associated–Noninert Liquid Mixtures.** When an alcohol is mixed with a liquid that cannot self-associate but acts as a proton acceptor, say a noninert liquid, hydrogen bonding between alcohol molecules competes with alcohol–noninert cross association. For an equimolar mixture, cross association may dominate when the fraction of association sites in the proton acceptor is sufficiently larger than that in the alcohol, with this effect being amplified as the proton acceptor mole fraction is increased. In the limiting case where the concentration of proton acceptor groups is so large that most alcohol molecules are H-bonded to one such group,  $\Delta H^M$  must take on the characteristic value of the cross H-bond, and since more proton acceptor sites to hydroxyl groups are available in the mixture than in the pure fluid, one may have  $\Delta S^M < \Delta S^P$ . In fact, this behavior has been found previously for alcohol–ester solutions.<sup>11</sup> For the 3M3P–glyme mixtures studied in this work we may suppose<sup>37</sup>  $\Delta H^M \approx \Delta H^P$  while  $\Delta S^M < \Delta S^P$ , with the latter assumption being supported by the values for the fraction of proton acceptor groups in each molecule<sup>38</sup> (namely,  $\phi_{PA} = 1/3$  for glymes and  $\phi_{PA}^* = 1/7$  for 3M3P). It is on this basis that qualitative predictions of the TSAM for  $C_p^{\text{assoc},E}(T)$  are depicted in Figure 2d, and they are verified by the experimental  $C_p^E(T)$  data in Figure 5a. (We only show data for 3M3P–diglyme mixtures; the behavior displayed by mixtures with triglyme and tetraglyme is fully analogous mainly because these three glymes are characterized by  $\phi_{PA} = 1/3$ .) On the other hand, for the 3M3P–DBE binary system the above rationale indicates that  $C_p^E(T)$  may approach the “alcohol–inert-like” behavior since  $\phi_{PA} = 1/9$  for DBE. This is what is actually observed in Figure 5b.

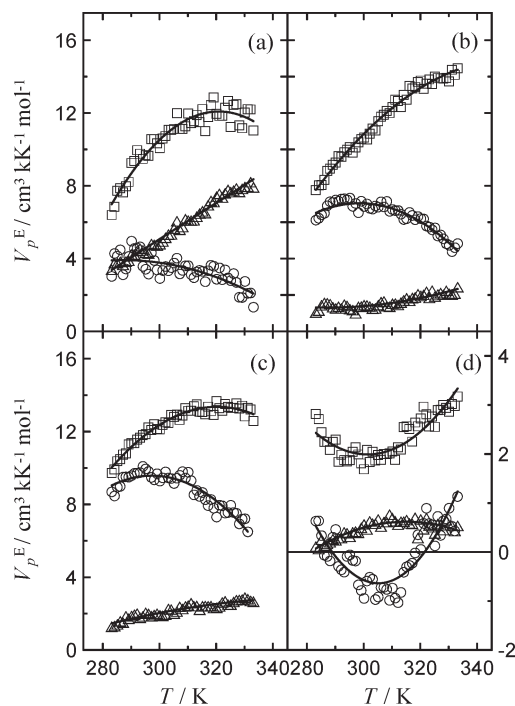


**Figure 6.** Excess isobaric heat capacities  $C_p^E$  as a function of (a) temperature  $T$  and (b) composition  $x$  for  $x$ 3M3P–(1– $x$ )1-propanol. Compositions in (a) are (○)  $x = 0.2841$ , (□)  $x = 0.5944$ , and (△)  $x = 0.9510$ . Temperatures in (b) are (●) 278.15 K, (■) 298.15 K, (▲) 318.15 K, and (▼) 338.15 K. Solid lines in (b), which are intended to guide the eye, are the fitted values to the Redlich–Kister-type equation  $C_p^E = x(1-x)\sum_{i=1}^n A_i(2x-1)^{i-1}/\sum_{i=1}^m B_i(2x-1)^i$ .

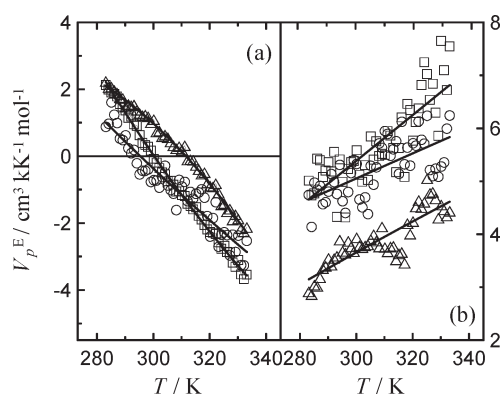
**3.4. Energetic and Entropic Effects for Associated–Associated Liquid Mixtures.** Another interesting type of mixtures would be that where the noninert or proton acceptor is also a self-associated liquid (e.g., alcohol–alcohol mixtures). Since  $C_p^{\text{assoc},E}(T)$  results from three association peaks (see Appendix), the expected phenomenology is more diverse. Figure 6a evidences this fact for 3M3P–1-propanol mixtures at three concentrations. Standing out is the unusual, previously unseen, minimum with  $C_p^E > 0$  that is encountered for one of them. Furthermore, the crossing between the various  $C_p^E$  vs  $x$  curves of Figure 6b indicates that the type of temperature dependence changes from one composition to another, thus revealing that the balance among the various relevant contributions to  $C_p^E$  is a delicate one. As observed for other alcohol–alcohol mixtures,<sup>24</sup>  $C_p^E$  vs  $x$  curves are W-shaped. Such behavior has been frequently observed—and extensively discussed—for mixtures containing a polar (nonassociated) liquid and a nonpolar one (usually an alkane). The general consensus<sup>39,40</sup> is that they mark the prelude of liquid–liquid demixing at lower temperatures, with concentration fluctuations at intermediate compositions being responsible for the positive part of the  $C_p^E$  increase at intermediate compositions. This is unlikely to be a plausible picture for alcohol–alcohol mixtures. Instead, the W-shape arises from the above-noted delicate balance between associational contributions to  $C_p^E$ . Therefore, no liquid–liquid phase transition is expected at lower temperatures, all the more so because both liquids are of quite similar physicochemical nature.

**3.5. Volumetric Effects.** In Figure 7, which shows  $V_p^E(T)$  for associated–inert liquid mixtures, it is seen that trends are quite similar to those encountered for  $C_p^E(T)$ : specifically, various portions of the curves of Figure 2a,b are covered, with basically the same evolution of  $V_p^{\text{E,assoc}}(T)$  with  $x$ . That is consistent, in the context of the TSAM, with  $\Delta V^M \approx \Delta V^P \equiv \Delta V > 0$  (see eq A.19). Overall, for  $V_p^E(T)$  the temperature dependence is smoother than for  $C_p^{\text{E,assoc}}(T)$ , implying that contributions arising from non-specific interactions and packing effects (see, e.g., ref 41) play a significant role. In fact, previous estimations for alcohol solutions indicate that  $\Delta V$  is a small positive parameter on the order of a few  $\text{cm}^3 \text{mol}^{-1}$ .<sup>11,42</sup> On choosing  $\Delta V = 5 \text{ cm}^3 \text{mol}^{-1}$ , one obtains



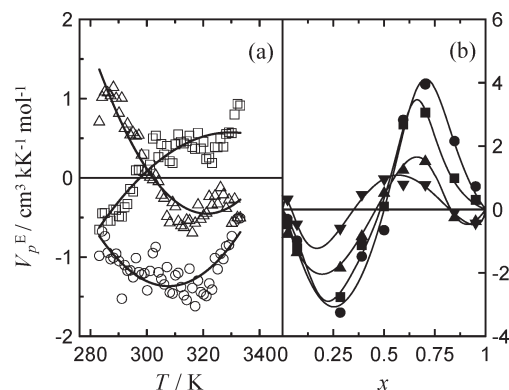


**Figure 7.** Excess isobaric thermal expansivities  $V_p^E$  as a function of temperature  $T$  for (a)  $x$ 3M3P–(1– $x$ )br–C<sub>8</sub> [(○)  $x$  = 0.0506; (□)  $x$  = 0.2959; (△)  $x$  = 0.7442], (b)  $x$ 3M3P–(1– $x$ )br–C<sub>12</sub> [(○)  $x$  = 0.1074; (□)  $x$  = 0.5010; (△)  $x$  = 0.9504], (c)  $x$ 3M3P–(1– $x$ )br–C<sub>16</sub> [(○)  $x$  = 0.1495; (□)  $x$  = 0.2994; (△)  $x$  = 0.9502], and (d)  $x$ C<sub>8</sub>NH<sub>2</sub>–(1– $x$ )br–C<sub>16</sub> [(○)  $x$  = 0.0909; (□)  $x$  = 0.4960; (△)  $x$  = 0.9525]. Lines are only intended to guide the eye.



**Figure 8.** Excess isobaric thermal expansivities  $V_p^E$  as a function of temperature  $T$  for (a)  $x$ 3M3P–(1– $x$ )diglyme [(○)  $x$  = 0.2649; (□)  $x$  = 0.5189; (△)  $x$  = 0.7519] and (b)  $x$ 3M3P–(1– $x$ )DBE [(○)  $x$  = 0.2525; (□)  $x$  = 0.4747; (△)  $x$  = 0.7438]. Lines are only intended to guide the eye.

from eq A.19 typical values for  $V_p^{\text{assoc},E}$  ranging from  $-5$  to  $10 \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$ , which are reasonably consistent with experimental observations (see Figure 7). On the other hand, the small  $\Delta V$  value results in negligible  $V_T^{\text{assoc},E}$ ; i.e., by setting  $\Delta V = 5 \text{ cm}^3 \text{ mol}^{-1}$  in eq A.20, one finds that the association contribution is 0.1% of  $V_T^E$  (for which typical values range around a few  $\text{cm}^3 \text{ mol}^{-1} \text{ GPa}^{-1}$ <sup>12</sup>). Data for alcohol–noninert and alcohol–alcohol mixtures (Figures 8 and 9) reinforce the above conclusions; namely, they are consistent with  $\Delta V > 0$  and



**Figure 9.** Excess isobaric thermal expansivities  $V_p^E$  as a function of (a) temperature  $T$  and (b) composition  $x$  for  $x$ 3M3P–(1– $x$ )1-propanol. Compositions in (a) are (○)  $x$  = 0.0708, (□)  $x$  = 0.5002, and (△)  $x$  = 0.9510. Temperatures in (b) are (●) 283.15, (■) 298.15, (▲) 318.15, and (▼) 333.15 K. Lines are only intended to guide the eye; in (b) they correspond to the fitted values to the Redlich–Kister-type equation  $V_p^E = x(1-x)\sum_{i=1}^n A_i(2x-1)^{i-1}/\sum_{i=1}^m B_i(2x-1)^i$ .

small, so that the temperature dependence is smoother than that of  $C_p^E$ . In summary, we have found that  $V_p^E(T)$  is sensitive to association. Remarkably, the result  $\Delta V > 0$  indicates that the formation of H-bonds in these mixtures is accompanied by a local volume decrease. Such volumetric effects are similar to those for pure alcohols, and hence they are different from those described in the Introduction for low-temperature water.

#### 4. CONCLUSION AND OUTLOOK

The study of thermodynamic response functions for non-aqueous associated solutions of nonelectrolytes was initiated in the 1980s at McGill University under the guidance of Donald Patterson (see refs 19–24). The present work culminates a series of papers on this topic, in which the “two-state” idea, originally envisioned in ref 20, has been exploited. Here, we have restricted ourselves to a qualitative treatment. A quantitative analysis would need more refined models and detailed simulations (see ref 17) that should provide a proper connection between structure and response functions.

The implications of this work for aqueous solutions of nonelectrolytes might be important. Much theoretical knowledge on water and aqueous solutions has been gained during past decades.<sup>43</sup> Particularly, progress toward elucidating intricate phenomena such as hydrophobicity and amphiphilic self-assembly<sup>44</sup> as well as water’s anomalous thermodynamics<sup>4</sup> has been achieved. On the other hand, existing experimental studies of response functions for aqueous solutions are rather incomplete in that they cover narrow temperature ranges (usually, data at a single temperature are reported, but see, e.g., ref 45 for early work and ref 46 for a recent account). It turns out that further experiments on the temperature and, perhaps, pressure dependence of thermodynamic response functions for aqueous solutions could enhance the actual understanding on the structure and thermodynamics of such systems.

#### ■ APPENDIX

Within the mean-field approximation, the isothermal–isobaric partition function  $\Delta$  of a fluid consisting of  $N$  identical

molecules is expressed as

$$\Delta = \frac{1}{N!}(\Delta_{part})^N \quad (\text{A.1})$$

where  $\Delta_{part}$  stands for the partition function of a particle. We now assume that  $\Delta_{part}$  can be split as

$$\Delta_{part} = (\Delta_{part})_{A_i} + (\Delta_{part})_A \quad (\text{A.2})$$

where  $(\Delta_{part})_{A_i}$  and  $(\Delta_{part})_A$  represent sums over states in which an individual particle belongs to an associated species or exists as a monomer, respectively. One may think of an hypothetical fluid, A, in which associational degrees of freedom are frozen, and likewise for a hypothetical fully associated fluid,  $A_i$ , with frozen monomeric degrees of freedom. Following eq A.1, we have

$$\Delta_A = \frac{1}{N!}(\Delta_{part})_A^N \quad (\text{A.3})$$

$$\Delta_{A_i} = \frac{1}{N!}(\Delta_{part})_{A_i}^N \quad (\text{A.4})$$

where

$$(\Delta_{part})_{A_i} = \exp\left(\frac{S_{A_i}}{R} - \frac{H_{A_i}}{RT} + \ln N - 1\right) \quad (\text{A.5})$$

$$(\Delta_{part})_A = \exp\left(\frac{S^A}{R} - \frac{H^A}{RT} + \ln N - 1\right) \quad (\text{A.6})$$

In eqs A.5 and A.6  $H^{A_i}$ ,  $H^A$ ,  $S^{A_i}$ , and  $S^A$  represent the molar enthalpies and molar entropies of the hypothetical fluids. Now, substitution into eq A.2 yields

$$\Delta_{part} = \exp\left(-\frac{G^A}{RT}\right) \left[1 + \exp\left(\frac{\Delta G}{RT}\right)\right] \quad (\text{A.7})$$

where we have used the thermodynamic identity  $G = H - TS$ . The quantity  $\Delta G \equiv G^A - G^{A_i} = \Delta H - T\Delta S$  may be seen as the Gibbs energy of dissociation for a mole of particles, with  $\Delta H = H^A - H^{A_i}$  and  $\Delta S = S^A - S^{A_i}$  standing for the molar enthalpy and the molar entropy of dissociation, respectively. On employing  $G = -RT \ln \Delta$ , one readily finds

$$G(T, p) = G^A(T, p) - RT \ln \left[1 + \exp\left(\frac{\Delta H(T, p)}{RT} - \frac{\Delta S(T, p)}{R}\right)\right] \quad (\text{A.8})$$

where the explicit dependence of the macroscopic quantities  $\Delta H$  and  $\Delta S$  on  $T$  and  $p$  has been noted. To leading order,  $\Delta H$  and  $\Delta S$  are given by

$$\Delta H(T, p) = \Delta H_0 + \Delta C_p(T - T_0) + \left(\frac{\partial \Delta H}{\partial p}\right)_T (p - p_0) \quad (\text{A.9})$$

$$\Delta S(T, p) = \Delta S_0 + \Delta C_p \ln\left(\frac{T}{T_0}\right) + \left(\frac{\partial \Delta S}{\partial p}\right)_T (p - p_0) \quad (\text{A.10})$$

where a reference state, denoted by subscript “0”, has been introduced, while  $\Delta C_p \equiv T(\partial \Delta S / \partial T)_p = (\partial \Delta H / \partial T)_p$ . Furthermore, one can define the volume of dissociation as  $\Delta V \equiv (\partial \Delta G / \partial p)_T$ , and express it as

$$\Delta V(T, p) = \Delta V_0 + \left(\frac{\partial \Delta V}{\partial T}\right)_T (T - T_0) + \left(\frac{\partial \Delta V}{\partial p}\right)_T (p - p_0) \quad (\text{A.11})$$

Given these rather general expressions, we now anticipate our assumption that  $\Delta H$ ,  $\Delta S$ , and  $\Delta V$  are constant. As shown previously,<sup>11,13</sup> this assumption is a reasonable approximation within moderately small temperature and pressure ranges. Thus, the response functions are derived from eq A.8 via standard formulas, namely,  $C_p \equiv -T(\partial^2 G / \partial T^2)_p$ ,  $V_p \equiv (\partial V / \partial T)_p = \partial^2 G / \partial p \partial T$ , and  $V_T \equiv -(\partial V / \partial p)_T = -(\partial^2 G / \partial p^2)_T$  to get

$$C_p = C_p^A + R \left(\frac{\Delta H}{RT}\right)^2 \frac{\exp(\Delta H/RT + \Delta S/R)}{[\exp(\Delta H/RT) + \exp(\Delta S/R)]^2} \quad (\text{A.12})$$

$$V_p = V_p^A + \frac{\Delta H \Delta V}{RT^2} \frac{\exp(\Delta H/RT + \Delta S/R)}{[\exp(\Delta H/RT) + \exp(\Delta S/R)]^2} \quad (\text{A.13})$$

$$V_T = V_T^A + \frac{\Delta V^2}{RT} \frac{\exp(\Delta H/RT + \Delta S/R)}{[\exp(\Delta H/RT) + \exp(\Delta S/R)]^2} \quad (\text{A.14})$$

The second term on the right-hand side of each of the eqs A.12–A.14, which is the association contribution to each of those response functions, is the same for all of them except for the prefactors  $\Delta H^2$ ,  $\Delta H \Delta V$ , and  $\Delta V^2$ . In accord with explanatory comments in the Introduction, eqs A.12–A.14 explicitly include parameters characterizing energetic, entropic, and volumetric effects of H-bonding (i.e.,  $\Delta H$ ,  $\Delta S$ , and  $\Delta V$ ), and consistently reflect the content of eqs 1–3.

By adopting—as is frequently done—the ideal gas as a reference state, one has  $C_p = C_p^{\text{ig}} + C_p^{\text{res}}$ , where  $C_p^{\text{res}}$  (the residual heat capacity) is that part of  $C_p$  arising from intermolecular interactions. Beyond that, the  $C_p^{\text{res}}$  of an associated liquid may be split into an associational part and a “nonspecific” one arising from dispersive interactions etc., i.e.,  $C_p^{\text{res}} = C_p^{\text{ns}} + C_p^{\text{assoc}}$ . Since  $C_p^A = C_p^{\text{ig}} + C_p^{\text{ns}}$ , eq A.12 turns into

$$C_p^{\text{res}} = C_p^{\text{ns}} + R \left(\frac{\Delta H}{RT}\right)^2 \frac{\exp(\Delta H/RT + \Delta S/R)}{[\exp(\Delta H/RT) + \exp(\Delta S/R)]^2} \quad (\text{A.15})$$

The extension of the model to a binary mixture composed by an associated liquid and one whose molecules are unable to self-associate, inert, or noninert (see Introduction) leads to the following expression for excess magnitudes:

$$Y^E = Y^{\text{ns}, E} + Y^{\text{assoc}, E} = Y^{\text{ns}, E} + Y^{\text{assoc}, M} - xY^{\text{assoc}, P} \quad (\text{A.16})$$

where  $Y$  can be  $C_p$ ,  $V_p$ , or  $V_T$  and  $x$  is the mole fraction of self-associated liquid, whereas  $Y^{\text{assoc}, M}$  and  $Y^{\text{assoc}, P}$  refer to the associational contribution for 1 mol of mixture and 1 mol of pure fluid, respectively, and  $Y^{\text{ns}, E} = Y^{A, E}$ . In a mixture, only a fraction of the total number of molecules (the mole fraction  $x$ ) is responsible for association effects, so  $Y^{\text{assoc}, M} = xY^{\text{assoc}, M^*}$ , where  $Y^{\text{assoc}, M^*}$  denotes the associational contribution for a mixture (with mole

fraction  $x$ ) containing 1 mol of molecules capable of self-association. Therefore

$$Y^E = Y^{ns,E} + Y^{assoc,E} = Y^{ns,E} + x[Y^{assoc,M^*} - Y^{assoc,P}] \quad (\text{A.17})$$

and

$$C_p^E = C_p^{ns,E} + xR \left\{ \left( \frac{\Delta H^M}{RT} \right)^2 \frac{\exp(\Delta H^M/RT + \Delta S^M/R)}{[\exp(\Delta H^M/RT) + \exp(\Delta S^M/RT)]^2} - \left( \frac{\Delta H^P}{RT} \right)^2 \frac{\exp(\Delta H^P/RT + \Delta S^P/R)}{[\exp(\Delta H^P/RT) + \exp(\Delta S^P/RT)]^2} \right\} \quad (\text{A.18})$$

$$V_p^E = V_p^{ns,E} + xR \left\{ \frac{\Delta H^M \Delta V^M}{(RT)^2} \frac{\exp(\Delta H^M/RT + \Delta S^M/R)}{[\exp(\Delta H^M/RT) + \exp(\Delta S^M/RT)]^2} - \frac{\Delta H^P \Delta V^P}{(RT)^2} \frac{\exp(\Delta H^P/RT + \Delta S^P/R)}{[\exp(\Delta H^P/RT) + \exp(\Delta S^P/RT)]^2} \right\} \quad (\text{A.19})$$

$$V_T^E = V_T^{ns,E} + xRT \left\{ \left( \frac{\Delta V^M}{RT} \right)^2 \frac{\exp(\Delta H^M/RT + \Delta S^M/R)}{[\exp(\Delta H^M/RT) + \exp(\Delta S^M/RT)]^2} - \left( \frac{\Delta V^P}{RT} \right)^2 \frac{\exp(\Delta H^P/RT + \Delta S^P/R)}{[\exp(\Delta H^P/RT) + \exp(\Delta S^P/RT)]^2} \right\} \quad (\text{A.20})$$

Finally, for the case of a mixture of two associated liquids, the associational part in eq A.16 must be replaced by

$$Y^{assoc,E} = Y^{assoc,M} - xY^{assoc,P_1} - xY^{assoc,P_2} \quad (\text{A.21})$$

where subscripts “1” and “2” refer to the two pure associated liquids. Hence,  $Y^{assoc,E}$  results from three association peaks.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Microsoft Excel files contain the experimental data for  $C_p^E(T)$  and  $V_p^E(T)$  for each system. Although not discussed in this work, data for the excess volume  $V^E(T)$  are also deposited for completeness. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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