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MIXING SCHEMES IN TERNARY AQUEOUS SOLUTIONS
Thermodynamic approach

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Abstract

The enthalpic interaction functions introduced by us earlier were evaluated in some ternary aqueous solutions. They are determined purely experimentally without resorting to any model system. From them, the pair interaction coefficients based on the virial expansion were evaluated, which will serve for a future theoretical development based on the McMillan-Mayer theory of solution. Secondly, our new methodology of using the mole fraction dependence of the enthalpic interaction function as a probe to elucidate the effect of a third component on the molecular organization is introduced. The conclusions for selected third components in ternary aqueous 1-propanol are reviewed.

Keywords: enthalpic interaction functions, pair interaction coefficients, the effect of selected solutes on the molecular organization of H_2O, ternary aqueous solutions

Introduction

Second derivatives of G

Table 1 [1, 2] lists the thermodynamic quantities in the Gibbs ensemble, the (p, T, n_i) variable system, where n_i is the amount of the *i*-th component. They are all some derivative of G with respect to independent variables or a combination thereof, and are classified by the order of derivative. The higher the order of derivative the deeper the information it contains. At this point in time, we can determine most of the second derivative quantities. In particular, we have been determining directly, accurately and in small increments the excess partial molar enthalpies of the *i*-th component, H_i^E. It is measured as the enthalpic response of the system when n_i is perturbed. Namely,

$$H_i^E = \left(\frac{\partial H^E}{\partial n_i}\right)_{p,T,nj\neq i} \quad (1)$$

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Hence H_i^E shows the actual contribution of the *i*-th component towards the total excess enthalpy, or the actual enthalpic situation of the *i*-th component in the system. Analogous quantities for the excess volume, V_i^E, and entropy, S_i^E, can also be determined. The details are summarized earlier [1, 2]. Other second derivatives, the response functions are related to fluctuations of the system. In particular, the expansivity, α_p, is related to the entropy-volume cross fluctuation, which is an important quantity in monitoring aqueous solutions in that H_2O has a unique feature of containing a negative contribution due to formation of ice-like patches by hydrogen bonding. We have introduced the fluctuation density, ${}^{SV}\delta$, which shows primarily the amplitude of fluctuation, and the normalized fluctuation, ${}^{SV}\Delta$, which signifies the am-

Table 1 Thermodynamic quantities in (p, T, n_i) variable system

0th	G		
1st	H	$H=G-T(\partial G/\partial T)$	$H^E=G^E-T(\partial G^E/\partial T)$
(4)*	S	$S=-(\partial G/\partial T)$	$S^E=-(\partial G^E/\partial T)$
	V	$V=(\partial G/\partial p)$	$V^E=(\partial G^E/\partial p)$
	μ_i	$\mu_i=(\partial G/\partial n_i)$	$\mu_i^E=(\partial G^E/\partial n_i)$
2nd	H_i	$H_i=(\partial H/\partial n_i)$	$H_i^E=(\partial H^E/\partial n_i)$
(7)*	S_i	$S_i=(\partial S/\partial n_i)$	$S_i^E=(\partial S^E/\partial n_i)$
	V_i	$V_i=(\partial V/\partial n_i)$	$V_i^E=(\partial V^E/\partial n_i)$
	C_p	$C_p=(\partial H/\partial T)=T(\partial S/\partial T)$	${}^S\delta\equiv C_p/V,\ {}^S\Delta={}^S\delta R/V$
	κ_T	$\kappa_T=-(\partial V/\partial p)/V$	${}^V\delta\equiv T\kappa_T,\ {}^V\Delta={}^V\delta R/V$
	α_p	$\alpha_p=(\partial V/\partial T)/V$	${}^{SV}\delta\equiv T\alpha_p,\ {}^{SV}\Delta={}^{SV}\delta R/V$
	μ_{i-j}	$\mu_{i-j}\equiv N(\partial\mu_i/\partial n_j)$	$\mu_{i-j}^E\equiv N(\partial\mu_i^E/\partial n_j)$
3rd	H_{i-j}	$H_{i-j}\equiv N(\partial H_i/\partial n_j)$	$H_{i-j}^E\equiv N(\partial H_i^E/\partial n_j)$
(11)*	S_{i-j}	$S_{i-j}\equiv N(\partial S_i/\partial n_j)$	$S_{i-j}^E\equiv N(\partial S_i^E/\partial n_j)$
	V_{i-j}	$V_{i-j}\equiv N(\partial V_i/\partial n_j)$	$V_{i-j}^E\equiv N(\partial V_i^E/\partial n_j)$
	${}^S\delta_i,\ {}^S\Delta_i$	${}^S\delta_i\equiv N(\partial{}^S\delta/\partial n_i),\ {}^S\Delta_i\equiv N(\partial{}^S\Delta/\partial n_i)$	
	${}^V\delta_i,\ {}^V\Delta_i$	${}^V\delta_i\equiv N(\partial{}^V\delta/\partial n_i),\ {}^V\Delta_i\equiv N(\partial{}^V\Delta/\partial n_i)$	
	${}^{SV}\delta_i,\ {}^{SV}\Delta_i$	${}^{SV}\delta_i\equiv N(\partial{}^{SV}\delta/\partial n_i),\ {}^{SV}\Delta_i\equiv N(\partial{}^{SV}\Delta/\partial n_i)$	
		$(\partial C_p/\partial T)$	
		$(\partial C_p/\partial p)=(\partial\alpha_p/\partial T)$	
		$(\partial\alpha_p/\partial p)=-(\partial\kappa_T/\partial T)$	
		$(\partial\kappa_T/\partial p)$	
		$(\partial\mu_{i-j}/\partial n_k)$	
4th			
(16)*			

* The total number of derivates belonging to each category

plitude and the wavelength though qualitatively [3, 4]. Thus, $^{SV}\Delta$, for example is written as,

$$^{SV}\Delta \equiv R\langle(\Delta S/V)(\Delta V/V)\rangle = RT\alpha_p/V, \tag{2}$$

where R is the gas constant [3, 4]. Equivalent expressions for the entropy-, and the volume-fluctuation were also given and their physical meanings discussed at some length earlier [3, 4].

Interactions and partial molar fluctuations

Third derivatives of G

Since we have precise H_i^E and $^{SV}\Delta$ data in small increments in the composition, we were able to take the derivative graphically, without resorting to any fitting function, and obtain the following quantities [1–4]

$$H_{ij}^E \equiv N(\partial H_i^E/\partial n_j), \tag{3}$$

$$^{SV}\Delta_i \equiv N(\partial\, ^{SV}\Delta/\partial n_i). \tag{4}$$

In the above and subsequent partial derivatives, it is implicit that the variables other than that of differentiation are kept constant. Analogous quantities using other second derivatives were also evaluated. H_{ij}^E, Eq. (3), signifies the effect of the j-th component on the enthalpic situation of the i-th component, or the i–j interaction in terms of enthalpy. $^{SV}\Delta_i$, Eq. (4), on the other hand, shows the effect of the i-th component on the entropy-volume cross fluctuation of the entire system, or the effect of the i-th component on the water-likeness in the solution. In Fig. 1, we show the mole fraction dependence of H_{1P-1P}^E [5] and $^{SV}\Delta_{1P}$ [3] for the binary 1-propanol–H_2O. x_{1P} is the mole fraction of 1-propanol (abbreviated as 1P). The exact proportionality of the x_{1P}-dependence between the two quantities (when the y-axis is scaled) has led us to conclude that the enthalpic interaction and the partial molar S–V fluctuation share the same cause, and that the 1P–1P interaction is occurring via the bulk H_2O, which is characterized by $^{SV}\Delta_{1P}$.

Mixing schemes in binary aqueous alcohols

Using these second and third derivative quantities we have studied aqueous alcohols [1–5]. We shall not repeat the full detail of the discussion here. Instead, we briefly state our findings:

1) A solute mono-ol forms the so-called iceberg in its immediate vicinity with concomitant reduction in the hydrogen bond probability of H_2O away from the solute, which decreases progressively as the composition of solute increases.

2) The iceberg-clad solutes interact with each other via fluctuating bulk H_2O, i.e. water-mediated interaction. The iceberg portions do not participate in fluctuation.

3) Up to a certain threshold value of solute composition, the hydrogen bond probability remains still high enough for hydrogen bond percolation, i.e. the hydrogen bond network is connected throughout the entire bulk of H_2O. Thus, the characteristics of liquid H_2O is still retained. We call this mode of mixing, up to the threshold, Mixing Scheme I. The solution in Mixing Scheme I is preparing for the possible formation of an addition compound on freezing. The iceberg-clad solutes are likely to make constituent units of the addition compound.

4) Above this threshold the bulk H_2O loses the bond percolation nature, and the solution consists of two kinds of clusters, each rich in solute and H_2O respectively. This is called Mixing Scheme II. The solution in Mixing Scheme II is preparing for a possible liquid-liquid phase separation at a higher temperature.

5) The boundary between Mixing Scheme I to II is associated with anomalies in the third derivative quantities of G, as shown in Fig. 1. It occurs in a narrow composition range, from point X to Y, with a nominal mid point M (Fig. 1).

6) The threshold value depends on the size of hydrophobic moiety. The larger its size, the smaller the threshold value.

We emphasize that all of these and other findings on aqueous mono-ols are the interpretations of our data, the experimentally obtained second and third derivatives of G, without resorting to any model system.

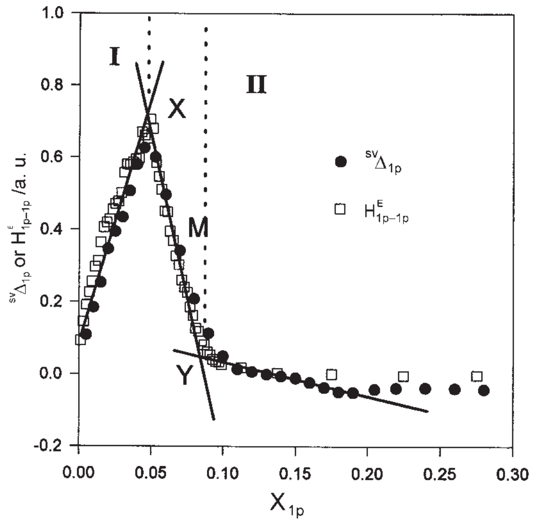

Fig. 1 Enthalpic interaction, H^E_{1P-1P}, and partial molar entropy-volume cross fluctuation, $^{SV}\Delta_{1P}$, in binary 1-propanol–H_2O at 25°C. Data from [3] and [5]

Interactions in ternary aqueous solutions

We have so far studied the following ternary aqueous solutions: 1-propanol (abbreviated as 1P)–2-propanol (2P)–H_2O(W) [6], 1P–(1,2- and 1,3-)propanediol (12P and 13P)–W [7], 1P–glycerol (Gly)–W [8], 1P–tetramethyl urea (TMU)–W [9], 1P–acetone (AC)–W [9], 1P–*d*-fructose (FR)–W [10], 1P–urea–W [11], 1P–NaCl–W [12], and *tert*-butanol (TBA)–dimethyl solfoxide (DMSO)–W [13]. For all these ternary systems, we evaluate the *i*–*j* enthalpic interaction at the infinite dilution, $H^{E}_{ij}(\infty)$, Eq. (3), and list them in Table 2. Also listed in the table is $H^{E}_{ii}(\infty)$ and $H^{E}_{jj}(\infty)$ in the respective binary systems, *i*–W and *j*–W.

Table 2 Enthalpic interactions at infinite dilution, $H^{E}_{ij}(\infty)$, Eq. (3), and $h_{ij}(\infty)$, Eqs (7) and (8). For abbreviation of solute, see text

Solutes, *i*, *j*	$H^{E}_{ij}(\infty)$/kJ mol^{-1}	$h_{ij}(\infty)$/J mol^{-2}	Reference
	Ternary systems		
1P, 2P	57	513	[6]
1P, 12P	82	739	[7]
1P, 13P	68	612	[7]
1P. Gly	78	703	[8]
1P, TMU	168	1513	[9]
1P, AC	110	991	[9]
1P, FR	99	891	[10]
1P, urea	44	396	[11]
1P, NaCl	72	649	[12]
TBA, DMSO	116	1045	[13]
Solute, *i*	$H^{E}_{ii}(\infty)$/kJ mol^{-1}	$h_{ii}(\infty)$/J mol^{-2}	Reference
	Binary systems		
1P	80	721	[5]
2P	60	540	[5]
12P	58	522	[14]
13P	83	748	[14]
Gly	43	387	[15]
TMU	225	2027	[16]
AC	120	1081	[16]
urea	–38	–342	[17]
TBA	100	905	[25]
DMSO	50	450	[18]

In the limited water-rich region, it is customary to expand H^E for a ternary system consisting with *i*, *j*, and W (H_2O, solvent) in a virial series as [19–23],

$$H^{\mathrm{E}}=h_{\mathrm{ii}}m_{\mathrm{i}}^{2}+h_{\mathrm{jj}}m_{\mathrm{j}}^{2}+2h_{\mathrm{ij}}m_{\mathrm{i}}m_{\mathrm{j}}+h_{\mathrm{iii}}m_{\mathrm{i}}^{3}+h_{\mathrm{jjj}}m_{\mathrm{j}}^{3}+h_{\mathrm{ijj}}m_{\mathrm{i}}m_{\mathrm{j}}^{3}+... \tag{5}$$

where m_i is the molarity of the *i*-th component and h_{ij} and h_{ijj} etc. stand for the *i–j* pair and the *i–j–j* triplet interactions in terms of enthalpy. Their significance rests on the McMillan–Mayer theory of solution [24]. These coefficients are usually determined experimentally in the Gibbs (p, T, n_i, n_j, n_W) variable system, while the McMillan–Mayer theory was constructed in the (V, T, μ_W, m_i, m_j) system and the rigorous connection between the two variable systems is not immediately obvious [10]. Indeed, the above equation, Eq. (5), is often used as a convenient and unitary representation of experimental data [20]. If Eq. (5) is correct in a certain limited composition range, it follows that H_i^E can be written as,

$$H_{\mathrm{i}}^{\mathrm{E}}=\frac{\partial H^{\mathrm{E}}}{\partial m_{\mathrm{i}}}=2h_{\mathrm{ii}}m_{\mathrm{i}}+2h_{\mathrm{ij}}m_{\mathrm{j}}+3h_{\mathrm{iii}}m_{\mathrm{i}}^{2}+3h_{\mathrm{ijj}}m_{\mathrm{j}}^{2}+6h_{\mathrm{iij}}m_{\mathrm{i}}m_{\mathrm{j}}+... \tag{6}$$

and an equivalent expression for H_j^E by interchanging $i \leftrightarrow j$. Then the enthalpic interaction function introduced above, Eq. (3), can be written as,

$$H_{\mathrm{ii}}^{\mathrm{E}}\equiv N\frac{\partial H_{\mathrm{i}}^{\mathrm{E}}}{\partial n_{\mathrm{i}}}=(55.51+m_{\mathrm{i}}+m_{\mathrm{j}})(2h_{\mathrm{ii}}+6h_{\mathrm{iii}}m_{\mathrm{i}}+6h_{\mathrm{iij}}m_{\mathrm{j}}+...) \tag{7}$$

and

$$H_{\mathrm{ij}}^{\mathrm{E}}\equiv N\frac{\partial H_{\mathrm{i}}^{\mathrm{E}}}{\partial n_{\mathrm{j}}}=(55.51+m_{\mathrm{i}}+m_{\mathrm{j}})(2h_{\mathrm{ij}}+6h_{\mathrm{ijj}}m_{\mathrm{j}}+6h_{\mathrm{iij}}m_{\mathrm{i}}+...) \tag{8}$$

However, for aqueous solutions of alcohols including *tert*-butanol (TBA), Eq. (6) can be curve-fitted to the excess partial molar enthalpy data only in the water-rich region [25]. In the other composition regions, a qualitatively different thermodynamic behaviour is operative [1, 2, 5, 25] and the excess partial molar enthalpy data cannot be accounted for by a single analytic function like Eq. (6) in the entire composition range. Davis *et al*. [26] devised a four-segment model and fitted a different simple analytic function for each segment. There are, however, some problems associated with imperfect smoothness at the segment boundaries, which is fatal when the third derivative quantity is required.

The values of $H_{ij}^E(\infty)$ at infinite dilution in Table 2 can be converted to h_{ii} or h_{ij} via Eqs (7) and (8). The latter data are also shown in Table 2. These data may serve for a future theoretical development based on the McMillan–Mayer theory of solution. In principle, the triplet interaction terms, h_{iji} etc., can be evaluated using our data. The range of the third component composition, however, was rather limited, and thus we have not much confidence in the triplet terms at this point in time. Most of our studies of ternary systems of 1P–*j*–H_2O type were motivated to elucidate the effect of the third component *j* on the molecular organization of H_2O by determining the x_{1P}-dependence of H_{1P-1P}^E, which changes depending on the nature of j. Such changes induced by the presence of j were used to elucidate the effect of j on H_2O, as shown below.

The effect of the third component on the molecular organization of H_2O

From our previous studies on binary aqueous alcohols [1–5], we learned the detail of the mixing schemes as mentioned above. In the water-rich region, in particular, the mole fraction dependence of H^E_{ii} in the binary aqueous solution of i , Fig. 1 for example, shows the process how i affects the nature of liquid H_2O. As mentioned above, the enthalpic 1P-1P interaction, H^E_{1P-1P}, and the partial molar S–V cross fluctuation, ${}^{SV}\Delta_{1P}$, follow the same dependence. Our strategy is then to monitor the change in the mole fraction dependence of H^E_{ii} on addition of the j-th component. Namely, the x_{1P}-dependence of H^E_{1P-1P} was used as a probe to elucidate the effect of j on the molecular organization of H_2O. Such an induced change reflects the effect of j on the molecular organization of H_2O. Figures 2 to 7 show the H^E_{1P-1P} data for selected ternary systems.

1-Propanol (1P)–NaCl–H_2O (Fig. 2)

The uncertainty in this figure is estimated as ±5 kJ mol^{-1}. On addition of NaCl, H^E_{1P-1P} starts at the same value at x_{1P}=0, and ends at point X at progressively smaller values of x_{1P} with the same value of H^E_{1P-1P} within the uncertainty. This suggests that in the presence of NaCl the amount of H_2O that interacts with 1P is reduced progressively proportional to the amount of NaCl present. This proportionally factor indicates that 7 to 8 molecules of H_2O are bound to one NaCl. From the fact that the values of H^E_{1P-1P} are

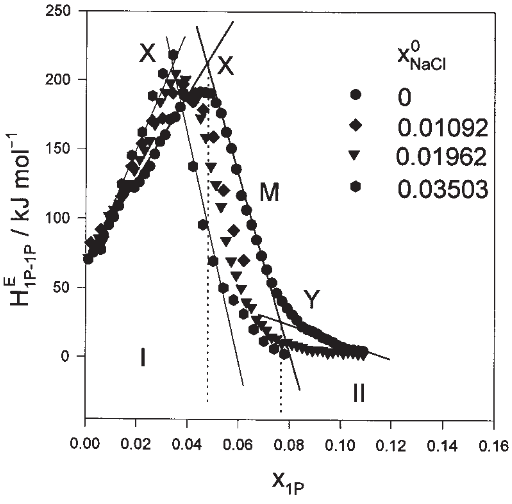

Fig. 2 Enthalpic interaction, H^E_{1P-1P}, in 1-propanol–NaCl–H_2O at 25°C. Data from [12]

the same at both ends, x_{1P}=0 and point X, and the fact that the trace from point X to Y are parallel, we concluded that the remaining bulk H_2O is unaffected by the presence of NaCl [12]. A recent simulation study on the effect of the Na^+ ion on H_2O supports this conclusion [27]. White *et al.* [27] concluded that the first hydration shell of Na^+ contains 5.2 molecules of H_2O and there was no effect of Na^+ on the orientation of H_2O molecules beyond the first hydration shell.

1P–urea–H_2O (Fig. 3)

In contrast to the case of NaCl above, on addition of urea the value of H^E_{1P-1P} is reduced without changing the locus of point X and Y much. We concluded therefore that the presence of urea does not change the hydrogen bond connectivity much, but reduces the degree of fluctuation. The most likely scenario is that urea participates in forming the hydrogen bond network with H_2O and by so doing rigidifies the network [11]. Another recent simulation study concluded that urea leads to stiffening of the short-time dynamics of both urea and H_2O [28].

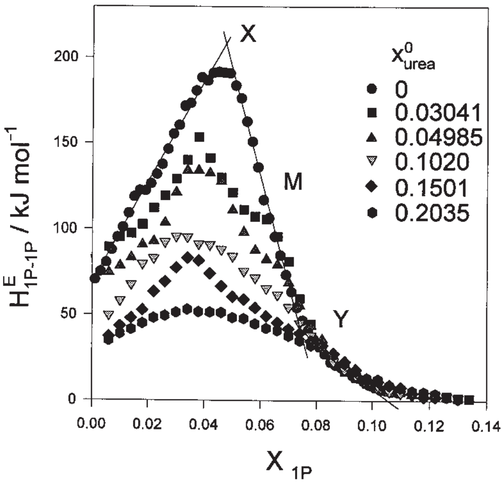

Fig. 3 Enthalpic interaction, H^E_{1P-1P}, in 1-propanol–urea–H_2O at 25°C. Data from [11]

1P–2-propanol (2P)–H_2O (Fig. 4)

From previous studies on binary aqueous solutions, [1–3, 5], we know that the effect of 2P on H_2O is the same as that of 1P. Thus, within Mixing Scheme I, the presence of 2P is equivalent of the presence 1P. Namely, 1P continues to modify the remaining bulk H_2O for the rest of the way in driving the system to Mixing Scheme II. Thus, the x_{1P}-dependence of H^E_{1P-1P} should be shifted parallel to the left (towards a progressively smaller value of x_{1P}). This is exactly what is seen in Fig. 4 [6]. Thus a similarly hydrophobic third component (in comparison with 1P) causes the x_{1P}-dependence of H^E_{1P-1P} to shift to the left.

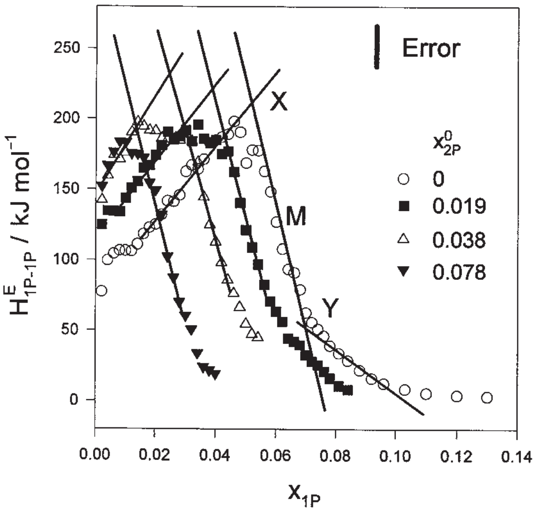

Fig. 4 Enthalpic interaction, $H^{\mathrm{E}}_{\mathrm{1P-1P}}$, in 1-propanol–2-propanol–H_2O at 25°C. Data from [6]

1P–glycerol(Gly)–H_2O (Fig. 5)

The effect of Gly is primarily to reduce the values of $H^{\mathrm{E}}_{\mathrm{1P-1P}}$ reflecting that the degree of fluctuation in the bulk H_2O is reduced, Fig. 5. Thus, the effect of a hydrophilic moiety, –OH group, is primarily to reduce the degree of fluctuation in H_2O. There is a small but definite trend of shift of point X to the left, suggesting some small hydrophobicity of Gly.

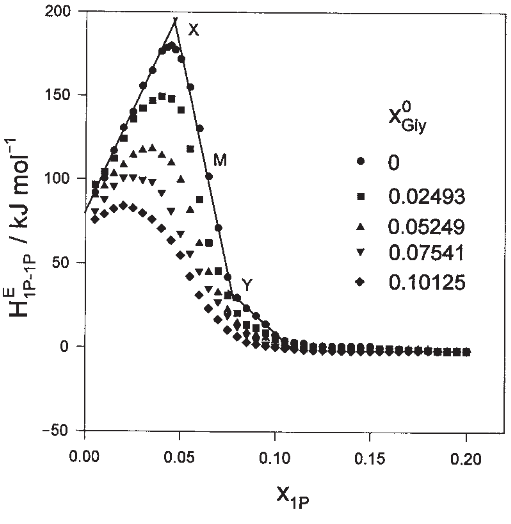

Fig. 5 Enthalpic interaction, $H^{\mathrm{E}}_{\mathrm{1P-1P}}$, in 1-propanol–glycerol–H_2O at 25°C. Data from [8]

1P–1,2-propanidiol(12P)–H_2O (Fig. 6); 1P–1,3propanediol(13P)–H_2O (Fig. 7)

The cases of 12P and 13P, Figs 6 and 7, show both effects of hydrophobicity and hydrophilicity and each effect is somewhere in between that of 2P with one –OH and that of Gly with three –OH groups. The subtle difference between 12P and 13P, with or without a $-CH_3$ group may be judged by plotting the locus of point X, say, as the function of the initial composition, x_j^0, where *j*=12P or 13P, but it is not immediately conclusive [7]. However, it is clear that a hydrophilic –OH group serves to reduce the degree of fluctuation inherent in liquid H_2O.

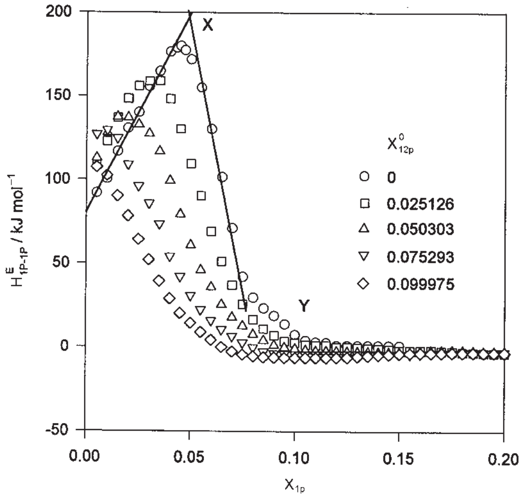

Fig. 6 Enthalpic interaction, H^{E}_{1P-1P}, in 1-propanol–1,2-propanediol–H_2O at 25°C. Data from [7]

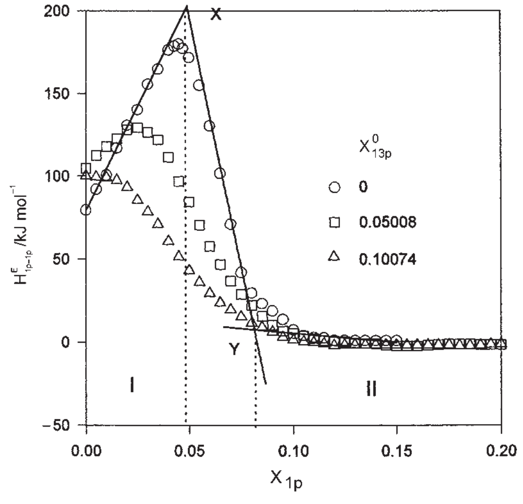

Fig. 7 Enthalpic interaction, H^{E}_{1P-1P}, in 1-propanol–1,3-propanediol–H_2O at 25°C. Data from [7]

In closing, we demonstrated the power of this method of using the x_{1P}-dependence of H^{E}_{1P-1P} as a probe to elucidate the effect of a third component on the molecular organization of H_2O. Such information is crucial in understanding molecular processes occurring in aqueous media, including aqueous solutions of biological importance. We plan to expand this methodology to other third components, ions, amino acids, saccharides, etc.

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