Additive Effect of 1-Propanol and 2-Propanol on Molecular Organization of H_2O in the Water-Rich Region: Excess Chemical Potential, Partial Molar Enthalpy and Volume of 1-Propanol in 1-Propanol–2-Propanol–H_2O at 25 °C

Jianhua Hu, Wesley Min-Da Chiang,[†] Peter Westh,[††] Daniel Heng Chi Chen,[†] Charles Allen Haynes, and Yoshikata Koga[*,†††,#]

Biotechnology Laboratory, and †Department of Chemistry, The University of British Columbia,
Vancouver, B. C. Canada

††Department of Chemistry, Roskilde University, DK-4000 Roskilde, Denmark.

†††Materials and Structures Laboratory, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8503

(Received February 15, 2000)

Excess chemical potential, $\mu_{1P}{}^{E}$, partial molar enthalpy, $H_{1P}{}^{E}$ and volume of 1-propanol, $V_{1P}{}^{E}$, were determined as a function of mole fraction of 1-propanol, x_{1P}, in mixed solvents of aqueous 2-propanol with various initial mole fraction of 2-propanol, $x_{2P}{}^{0}$. The 1-propanol–1-propanol interaction functions, $H_{1P-1P}{}^{E} \equiv N(\partial H_{1P}{}^{E}/\partial n_{1P})$, and $V_{1P-1P}{}^{E} \equiv N(\partial V_{1P}{}^{E}/\partial n_{1P})$, were evaluated by graphical differentiation. The x_{1P}-dependence of all these quantities indicates that 1-propanol and 2-propanol modify the molecular organization of H_2O in the same and additive manner in the water-rich region. The additive effect of 1-propanol and that of 2-propanol are in the ratio of (0.07/0.08).

We have been studying binary aqueous solutions by measuring excess partial molar quantities of the i-th component, $F_i{}^E$, where F is either H, S, or V. $F_i{}^E$ is written as,

$$F_i{}^E \equiv (\partial F^E/\partial n_i)_{nj,p,T} = F^E/N + (1-x_i)\{\partial(F^E/N)/\partial x_i\}_{nj,p,T} \quad (1)$$

where $j \neq i$ and x_i is the mole fraction of the i-th component. This quantity, $F_i{}^E$, is the actual contribution of the i-th component towards F of the entire system. Or it shows the actual situation of the i-th component in terms of F. Since we determined $F_i{}^E$ directly, with a high precision, and in small increments in x_i, we were able to take the following derivative with a reasonable accuracy, several per cent.

$$F_{i-i}{}^E \equiv N\,(\partial F_i{}^E/\partial n_i)_{nj,p,T} = (1-x_i)(\partial F_i{}^E/\partial x_i)_{nj,p,T} \quad (2)$$

$F_{i-i}{}^E$ in Eq. 2 signifies the effect of an infinitesimal amount of the incoming i-th component on the actual situation of the existing i-th component in terms of F. Thus, $F_{i-i}{}^E$ provides a *model-free, experimentally accessible* measure for the i–i interaction in terms of F.[1,2] Hence, we call $F_{i-i}{}^E$ the interaction function.

By the aides of these quantities from Eqs. 1 and 2, we learned the effect of alcohols on the molecular organization of solvent H_2O.[1–6] Briefly, (1) the "iceberg" formation in the immediate vicinity of solute [7–9] is confirmed; (2) the "iceberg" portion is rigid enough not to make contribution to volume or entropy fluctuations; (3) the hydrogen bond probability of bulk H_2O away from "iceberg" is reduced and hence the degree of fluctuation decreases progressively as solute composition increases; (4) "iceberg"-clad solutes interact with each other via fluctuating bulk H_2O; (5) the interaction is repulsive (unfavourable) in terms of enthalpy but attractive (favourable) entropy-wise; (6) the entropic attraction surpasses the enthalpic repulsion and hence the net interaction is attractive in terms of chemical potential; (7) up to a certain threshold value of solute composition, the hydrogen bond probability of bulk H_2O is still high enough for hydrogen bond percolation, i.e., the hydrogen bond network is connected throughout the entire bulk of H_2O; (8) the threshold value depends on the size of hydrophobic moiety, and the larger the size, the smaller the threshold value; (9) above this threshold value, bulk H_2O loses its percolation nature and the solution consists of two kinds of clusters rich in solute and H_2O respectively. We call this mode of mixing below the threshold Mixing Scheme I, and that above the threshold Mixing Scheme II. The transition from Mixing Scheme I to II is associated with anomalies in the interaction functions, Eq. 2. It occurs in a narrow composition range, nominally called point X, M, and Y on the mole fraction scale (See Figs. 5–7, for example). We interpret point X to be the point at which the strongest hydrogen bonds reach the percolation threshold, at point Y the weakest ones lose bond percolation and M is the representative mid point.[1–6]

Permanent address: Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, B. C. Canada V6T 1Z1

The methodology described above is particularly powerful in multi-component systems in that it is only the target component, i, the amount of which is perturbed, and the response of the entire system is determined. In this manner, we learn the thermodynamic effect of the target component without resorting to any model system. We have applied the methodology in studying three component systems: 2-butoxyethanol–dimethylsulfoxide–H_2O,[10] *tert*-butanol–dimethylsulfoxide–H_2O,[11] and lysozyme–alcohols–H_2O.[12] We have had some success in elucidating the effects of solutes on the molecular organization of H_2O.[10–13] Recently, we studied 1-propanol–urea–H_2O[14] and 1-propanol–NaCl–H_2O.[15] By determining the partial molar quantities, Eq. 1, and the interaction functions, Eq. 2, of 1-propanol in the "mixed" solvent of aqueous urea[14] and aqueous NaCl,[15] we learned the detailed manners by which urea and NaCl modify the molecular arrangement of H_2O. Namely, urea molecules[14] lock onto the hydrogen bond network of H_2O, keep the hydrogen bond percolation intact, but reduce the degree of fluctuation in hydrogen bond strength that is inherent in liquid H_2O.[16,17] An NaCl molecule, on the other hand, "binds" to 7 to 8 molecules of H_2O, and leaves the remainder of H_2O unaffected at all.[15] In these works, the behaviour of thermodynamic quantities, Eqs. 1 and 2, of 1-propanol only was used to study the effect of another component of H_2O. This was necessitated by the fact that determination of the excess partial molar enthalpy ($F = H$ in Eq. 1) of solid samples is much more problematic than for liquid counterparts.

In this paper, we test the soundness of this methodology by studying 1-propanol–2-propanol–H_2O system. Since 1-propanol (abbreviated as 1P) and 2-propanol (2P) are typical of alcohols, their effects individually on H_2O are well-known, as described above. Point M for 1P is at $x_{1P} = 0.07$ and that for 2P at $x_{2P} = 0.08$.[3] Otherwise, the effects of both propanols on H_2O are the same. Hence, when both propanols are added to H_2O, they are likely to modify H_2O in the same and strictly additive manner. We thus measure H_{1P}^E, S_{1P}^E, and V_{1P}^E in mixed solvents of aqueous 2-propanol with various initial mole fractions, x_{2P}^0, and see if we could recover the effect of 2P on H_2O that we learned earlier.[3]

In thermodynamic studies of aqueous solutions of biological importance, there is a need to investigate interactions of small amphiphilic solutes under complex—and hence more realistic in a biophysical sense—conditions. Previous thermodynamic works with alcohol and other organics in aqueous solutions have indeed contributed significantly to our current understanding of the "hydrophobic effect" and other biomolecular interactions. However, the vast majority of these works were conducted with binary, highly dilute solutions i.e. under conditions far from those of the crowded environment of the cell. The potential of our thermodynamic methodology to single out effects in complex systems may provide one access to investigations of more realistic systems and thus a more detailed knowledge of water–biomolecule relationships. In this work we show this potential through work with a ternary system of well characterized components over a broad range of compositions.

Experimental

1-Propanol (99.5+%, HPLC grade) and 2-propanol (99.5%, HPLC grade) from Sigma-Aldrich were used as supplied for vapour pressure and enthalpy measurements. In addition, 1-propanol (Merck, Darmstadt, > 99.8%) was used for density determination. H_2O was triply distilled, the second and third times in a glass still.

Excess partial molar enthalpies were determined by an LKB Bromma 8700 titration calorimeter using a burette method.[18] Vapour pressures were measured by a static method.[19,20] In addition, a small portion of the equilibrium gas phase was sent directly into a gaschromatograph for analysis of the ratios p_{1P}/p_W and p_{2P}/p_W, where p_{1P}, p_{2P} and p_W are the partial pressures of 1P, 2P and H_2O respectively. An automatic densimeter[21] was used to determine the density of ternary solutions by titrating 1P into 2P–H_2O of various initial mole fractions of 2P.

Results

Figure 1 shows the excess chemical potential, μ_{2P}^E, partial molar enthalpy,[3] H_{2P}^E, and entropy times temperature, TS_{2P}^E, of 2P in binary aqueous 2P. These data are given in Table 1. In the figure, μ_{1P}^E,[14] H_{1P}^E,[3] and TS_{1P}^E[14] are also plotted. These data and their mole fraction dependence were instrumental in learning the details of mixing schemes in the respective binary aqueous solution described in the Introduction. As is evident in the figure, there is a strong enthalpy–entropy compensation generally prevalent in aqueous solutions.[22] A subtle variation in μ_{1P}^E is a result of large, compensating variations in H_{1P}^E and S_{1P}^E, both having almost the same x_{1P}-dependences. The same is true for 2P–H_2O.

Table 2 lists the partial pressure data of ternary 1P–2P–H_2O calculated from the total pressure and gas chromatographic results. The uncertainty for p_{2P} is larger, about 15%, while that for p_{1P} is a few per cent. The reason for a higher uncertainty

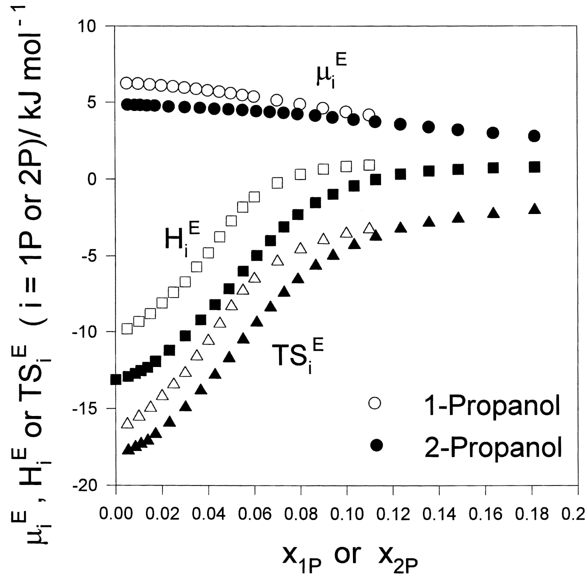

Fig. 1. Excess chemical potential, μ_i^E (circle), excess partial molar enthalpy, H_i^E (square), and excess partial molar entropy times temperature, TS_i^E (triangle) of 1-propanol (hollow symbols) and 2-propanol (filled symbols) at 25 °C in binary aqueous solutions. Hollow symbols, i = 1P; filled symbolsd, i = 2P.

Table 1. Excess Chemical Protential, μ_{2P}^E, Partial Molar Enthalpy, H_{2P}^E, and Entropy, S_{2P}^E of 2-Propanol in Binary Aqueous 2-Propanol at 25 °C (All in Units of kJ mol^{-1})

x_{2P}	μ_{2P}^E	H_{2P}^E	TS_{2P}^E
	±0.01	±0.07	±0.08
0		−13.10	
0.002591	4.95	−13.05	−18.00
0.005395	4.83	−12.90	−17.73
0.008440	4.81	−12.70	−17.51
0.01091	4.81	−12.50	−17.31
0.01378	4.79	−12.30	−17.09
0.01715	4.77	−11.90	−16.67
0.02316	4.72	−11.20	−15.92
0.03008	4.68	−10.25	−14.93
0.03670	4.63	−9.20	−13.83
0.04290	4.59	−8.20	−12.79
0.04899	4.55	−7.15	−11.69
0.05507	4.50	−6.00	−10.50
0.06101	4.43	−4.95	−9.38
0.06694	4.39	−4.00	−8.39
0.07285	4.32	−3.10	−7.42
0.07890	4.24	−2.30	−6.54
0.08658	4.14	−1.50	−5.64
0.09419	4.02	−0.95	−4.97
0.10337	3.88	−0.40	−4.28
0.11270	3.74	0.00	−3.74
0.12354	3.57	0.35	−3.22
0.13586	3.39	0.55	−2.84
0.14854	3.22	0.65	−2.57
0.16365	3.02	0.70	−2.27
0.18147	2.81	0.80	−2.01

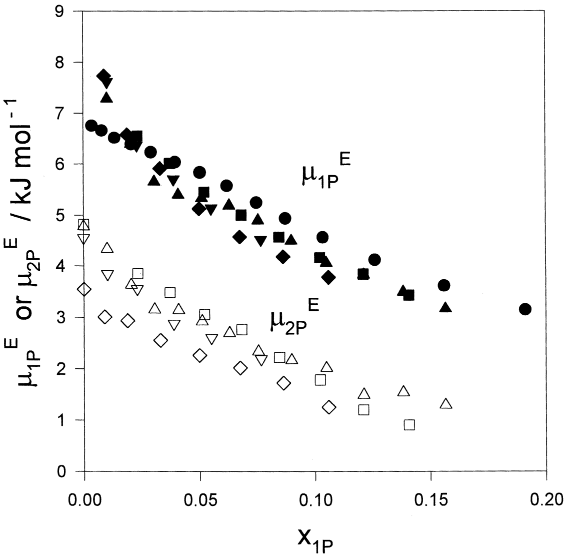

Fig. 2. Excess chemical potential of 1-propanol, μ_{1P}^E (filled symbols), and that of 2-propanol, μ_{2P}^E (hollow symbols), in 1-propanol–2-propanol–H$_2$O at 25 °C. Circle, x_{2P}^0 = 0; square, x_{2P}^0 = 0.01401; triangle up, x_{2P}^0 = 0.02813; triangle down, x_{2P}^0 = 0.04892; diamond, x_{2P}^0 = 0.1252.

Table 2. Total and Partial Pressure in 1-Propanol–2-Propanol–H$_2$O at 25 °C (All in Units of Torr [a)])

x_{1P}	p	p_{1P}	p_{2P}
	±0.008	±5%	±15%
	x_{2P}^0 = 0.01401		
0	27.932	0	4.2
0.02323	32.069	6.23	2.8
0.03705	33.911	8.00	2.4
0.05204	35.128	8.96	1.9
0.06813	35.694	9.80	1.7
0.08450	35.884	10.2	1.3
0.1022	35.969	10.5	1.1
0.1210	35.974	10.9	0.8
0.1408	35.970	10.8	0.7
	x_{2P}^0 = 0.02813		
0	31.457	0	8.3
0.01013	33.304	3.65	6.8
0.02042	34.715	5.13	5.1
0.03047	35.751	5.70	4.1
0.04077	36.413	6.88	4.1
0.05101	36.685	8.37	3.7
0.06288	36.803	9.74	3.3
0.07538	36.862	10.4	2.8
0.08983	36.802	10.5	2.6
0.1050	36.743	10.3	2.4
0.1212	36.666	10.9	1.9
0.1383	36.589	10.8	1.9
0.1566	36.534	10.7	1.7
	x_{2P}^0 = 0.04892		
0	36.109	0	13.2
0.01019	37.309	4.20	9.8
0.02298	38.186	5.73	8.6
0.03880	38.500	7.40	6.4
0.05509	38.597	8.36	5.7
0.07663	38.270	9.08	4.7
	x_{2P}^0 = 0.1252		
0	44.656	0	21.7
0.008940	44.132	3.86	17.8
0.01881	43.516	5.10	17.2
0.03299	42.774	6.84	14.5
0.04988	42.085	7.54	12.7
0.06751	41.526	8.17	11.3
0.08625	40.992	8.91	9.8
0.1059	40.525	7.93	7.9

a) 1 Torr ≈ 133.322 Pa.

for 2P is that 2P appears as the middle peak in the chromatogram, and the separation among H$_2$O, 2P and 1P is not perfect. The excess chemical potential of i (= 1P or 2P) is calculated as

$$\mu_i^E = RT\ln\{p_i/(x_i\, p_i^0)\}, \tag{3}$$

where p_i^0 is the vapour pressure of pure i. The results are shown in Fig. 2 as a function of x_{1P}, with various initial mole fraction of 2P, x_{2P}^0.

Table 3 contains the excess partial molar enthalpy of 1P, H_{1P}^E, as 1P is successively titrated into 2P–H$_2$O with a given initial mole fraction, x_{2P}^0. The uncertainty is estimated as ±0.07 kJ mol^{-1}. They are plotted in Fig. 3. Also plotted in Fig. 3 are μ_{1P}^E data shown in Fig. 2. As is evident from Fig. 3, enthalpy–entropy compensation is operative also in ternary

Table 3. The Excess Partial Molar Enthalpies of 1-Propanol, H_{1P}^E, in Aqueous Solutions of Various Initial Mole Fraction of 2-Propanol, X_{2P}^0, at 25 °C (H_{1P}^E is in Units of kJ mol^{-1}, Uncertainty is ±0.07 kJ mol^{-1})

$X_{2P}^0 = 0.0$		$X_{2P}^0 = 0.01389$		$X_{2P}^0 = 0.02832$		$X_{2P}^0 = 0.05002$		$X_{2P}^0 = 0.1260$	
X_{1P}	H_{1P}^E	X_{1P}	H_{1P}^E	X_{1P}	H_{1P}^E	X_{1P}	H_{1P}^E	X_{1P}	H_{1P}^E
0.00161	−10.09	0.001120	−9.06			0.001374	−2.95	0.004221	2.73
0.00483	−10.19	0.003355	−8.78	0.003563	−6.76	0.004115	−2.70	0.007017	2.81
0.00802	−9.61	0.005581	−8.43	0.005926	−6.36	0.009552	−1.64	0.009797	2.89
0.0112	−9.23	0.01000	−8.26	0.008277	−5.94	0.01225	−1.22	0.01256	2.78
0.0144	−8.87	0.01220	−7.42	0.01295	−5.07	0.01493	−0.78	0.01531	2.72
0.0157	−8.35	0.01438	−7.23	0.01527	−4.59	0.01760	−0.34	0.01804	2.67
0.0175	−8.35	0.01656	−6.87	0.01987	−3.71	0.02289	−0.27	0.02076	2.64
0.0206	−7.71	0.01873	−6.46	0.02216	−3.29	0.02551	0.77	0.02347	2.53
0.0276	−7.04	0.02088	−5.91	0.02443	−2.71	0.02812	0.99	0.02615	2.54
0.0311	−6.35	0.02517	−5.33	0.02670	−2.38	0.03330	1.27	0.02883	2.37
0.0347	−5.88	0.02730	−4.92	0.02895	−1.93	0.03587	1.26	0.03149	2.30
0.0382	−5.12	0.02942	−4.48	0.03119	−1.55	0.03842	1.38	0.03413	2.10
0.0417	−4.55	0.03153	−4.11	0.03343	−1.21	0.04097	1.43	0.03676	2.12
0.0451	−3.79	0.03363	−3.65	0.03565	−0.83	0.04601	1.40	0.03938	2.00
0.0486	−3.17	0.03572	−3.24	0.04007	−0.11	0.04851	1.55	0.04198	2.03
0.0520	−2.42	0.03781	−2.84	0.04226	0.29	0.05099	1.49	0.04457	1.94
0.0554	−1.93	0.03988	−2.31	0.04440	0.36	0.05594	1.26	0.04714	1.90
0.0587	−1.33	0.04195	−2.05	0.04661	0.47	0.05839	1.17	0.05225	1.78
0.0618	−0.98	0.04400	−1.68	0.04876	0.55			0.05730	1.91
0.0651	−0.61	0.04605	−1.33	0.05093	0.75				
0.0683	−0.33	0.05012	−0.77	0.05307	0.84				
0.0716	−0.28	0.05214	−0.50	0.05521	0.92				
0.0748	0.15	0.05616	−0.08						
0.0812	0.37	0.05815	0.13						
0.0844	0.48	0.06014	0.22						
0.0884	0.53	0.06212	0.34						
0.0923	0.72	0.06409	0.45						
0.0963	0.73	0.06605	0.56						
0.1000	0.79	0.06801	0.63						
0.1040	0.75	0.06995	0.66						
		0.07189	0.79						
		0.07382	0.78						
		0.07545	0.85						
		0.07957	0.92						
		0.08146	1.00						
		0.08335	0.92						
		0.08524	0.96						

1P–2P–H_2O. Hence, for a given x_{2P}^0 the values of TS_{1P}^E would be more negative than H_{1P}^E with almost the same x_{1P}-dependence as H_{1P}^E. For $x_{2P}^0 < 0.05$, a positive slope of TS_{1P}^E is slightly steeper than that of H_{1P}^E, since μ_{1P}^E has a small negative slope. All of these findings are the same in each respective binary system in Fig. 1.

Table 4 lists the density data as 1P was successively added to 2P–H_2O with various initial mole fractions of 2P, x_{2P}^0. The excess partial molar volumes of 1P were calculated by Eq. 1. In determining $\{\partial(V^E/N)/\partial x_{1P}\}$, the values of $\{\delta(V^E/N)/\delta x_{1P}\}$ for every other increment were plotted and read off a smooth curve drawn through all the data points.[23,24] The resulting V_{1P}^E data are shown in Fig. 4.

Discussion

The filled diamond symbol in Fig. 3 shows H_{1P}^E data for a mixed solvent 2P–H_2O at $x_{2P}^0 = 0.1260$, which is already in Mixing Scheme II in 2P–H_2O.[3] For the remaining four series with $x_{2P}^0 \le 0.05$, H_{1P}^E data follow a similar x_{1P}-dependence except for a parallel shift towards the left as x_{2P}^0 increases. This hints that 2P has already modified H_2O in a way pertinent to Mixing Scheme I, and that 1P affects in the same continuing manner what is left by 2P in the hydrogen bond network of H_2O. Thus, 1P works on H_2O for the rest of the way to drive the system eventually to Mixing Scheme II. To see this in another way, the enthalpic 1P–1P interaction, $H_{1P\text{–}1P}^E$, Eq. 2 was evaluated. Smooth curves were drawn through H_{1P}^E data points in Fig. 3 by means of a flexible ruler. The values of H_{1P}^E were read off the smooth curves drawn at the interval of $\delta x_{1P} = 0.002$. The quotient $\delta H_{1P}^E/\delta x_{1P}$ was calculated with $\delta x_{1P} = 0.004$. The resulting values of $H_{1P\text{–}1P}^E$ are plotted in Fig. 5. The uncertainty is estimated as ±15 kJ mol^{-1}. Within this uncertainty, $H_{1P\text{–}1P}^E$ seems to follow the same route up to point X, the onset of transition of Mixing Scheme, and to Y, the end point of transition, except for a parallel shift to the left. The entropy analog, $TS_{1P\text{–}1P}^E$, is also expected to follow the exactly

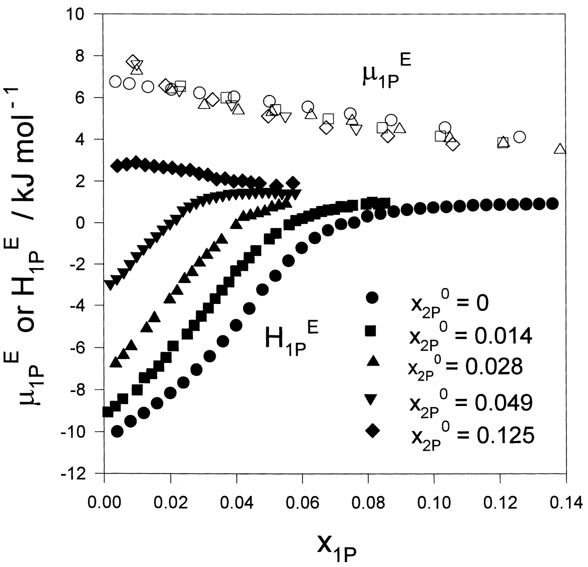

Fig. 3. Excess partial molar enthalpy of 1-propanol, H_{1P}^E (filled symbols), and excess chemical potential of 1-propanol, μ_{1P}^E (hollow symbols) in 1-propanol–2-propanol–H$_2$O at 25 °C. For H_{1P}^E: circle, $x_{2P}^0 = 0$; square, $x_{2P}^0 = 0.01389$; triangle up, $x_{2P}^0 = 0.02832$; triangle down, $x_{2P}^0 = 0.05002$; diamond, $x_{2P}^0 = 0.1260$. For μ_{1P}^E same as in Fig. 2.

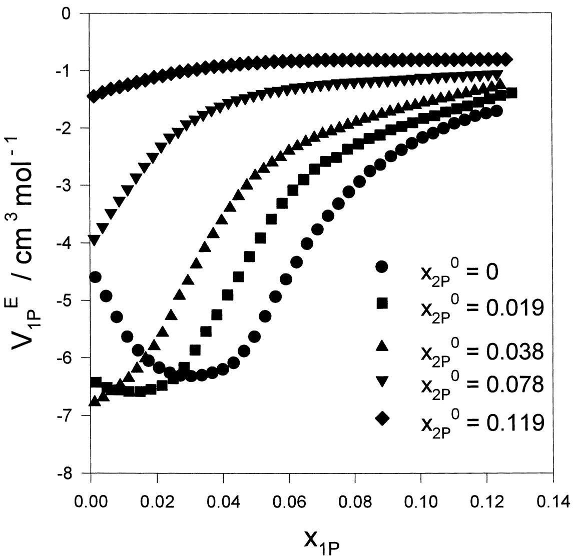

Fig. 4. Excess partial molar volume of 1-propanol, V_{1P}^E, in 1-propanol–2-propanol–H$_2$O at 25 °C. Circle, $x_{2P}^0 = 0$; square, $x_{2P}^0 = 0.01961$; triangle up, $x_{2P}^0 = 0.03803$; triangle down, $x_{2P}^0 = 0.07777$; diamond, $x_{2P}^0 = 0.1189$.

the same x_{1P}-dependence, due to a strong entropy–enthalpy compensation apparent in Fig. 3. The V_{1P}^E data, Fig. 4, show the same behaviour for three series with $x_{2P}^0 \leq 0.038$, well within Mixing Scheme I of 2P–H$_2$O. The volumetric interaction function, $V_{1P\text{-}1P}^E$, Eq. 2, was similarly calculated and is plotted in Fig. 6. The x_{1P}-dependence of $V_{1P\text{-}1P}^E$ for the three series are parallel at least to point X. We suggest, therefore, that 1P and 2P modify the molecular organization of H$_2$O in the same way pertinent to Mixing Scheme I and strictly in an additive manner.

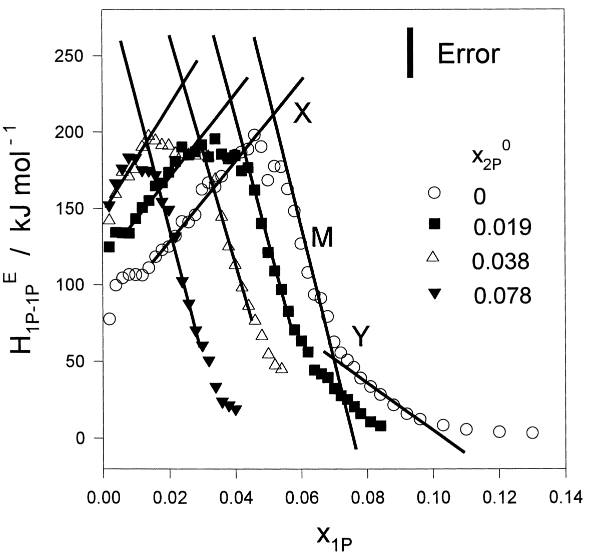

Fig. 5. Enthalpic 1-propanol–1-propanol interaction, $H_{1P\text{-}1P}^E$, in 1-propanol–2-propanol–H$_2$O at 25 °C. Circle, $x_{2P}^0 = 0$; square, $x_{2P}^0 = 0.01389$; triangle up, $x_{2P}^0 = 0.02832$; triangle down, $x_{2P}^0 = 0.05002$.

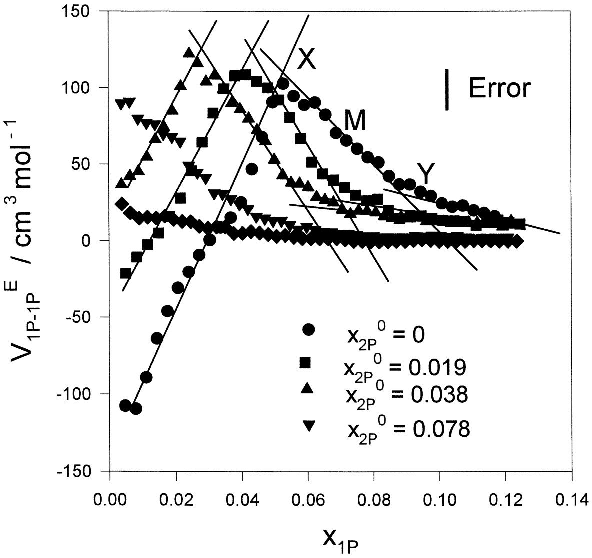

Fig. 6. Volumetric 1-propanol–1-propanol interaction, $V_{1P\text{-}1P}^E$, in 1-propanol–2-propanol–H$_2$O at 25 °C. Circle, $x_{2P}^0 = 0$; square, $x_{2P}^0 = 0.01961$; triangle up, $x_{2P}^0 = 0.03802$; triangle down, $x_{2P}^0 = 0.07777$.

In Fig. 7, the loci of X–M–Y evaluated from Fig. 5 ($H_{1P\text{-}1P}^E$) and Fig. 6 ($V_{1P\text{-}1P}^E$) are plotted in the x_{1P}–x_{2P} field. The boundary between Mixing Scheme I and II can be regarded as a straight line connecting the respective mid-points $x_{2P} = 0.08$ and $x_{1P} = 0.07$ for the respective binary system. This suggests again that 1P and 2P work in the additive manner to drive the system to Mixing Scheme II. Furthermore, 2P requires more by the factor of (0.08/0.07) to do the same thing on H$_2$O. Namely, the effect of the initial mole fraction of 2P, x_{2P}^0, is

Table 4. Density of 1-Propanol–2-Propanol–H_2O at 25 °C (Units of g cm^{-3}, Uncertainty is $\pm 1.5\times 10^{-5}$ g cm^{-3})

x_{1P}	d	x_{1P}	d	x_{1P}	d	x_{1P}	d	x_{1P}	d	x_{1P}	d
		$x_{2P}{}^0 = 0.01961$						$x_{2P}{}^0 = 0.07777$			
0	0.98632	0.00332	0.98500	0.00664	0.98371	0	0.96332	0.00254	0.96235	0.00508	0.96136
0.00995	0.98246	0.01328	0.98122	0.01695	0.98001	0.00763	0.96036	0.01018	0.95934	0.01272	0.95830
0.01992	0.97882	0.02325	0.97762	0.02656	0.97643	0.01526	0.95726	0.01781	0.95622	0.02035	0.95517
0.02989	0.97522	0.03320	0.97400	0.03653	0.97273	0.02290	0.95412	0.02545	0.95307	0.02799	0.95201
0.03985	0.97144	0.04318	0.97012	0.04650	0.96875	0.03053	0.95095	0.03308	0.94989	0.03563	0.94883
0.04982	0.96735	0.05313	0.96594	0.05646	0.96448	0.03817	0.94779	0.04072	0.94674	0.04327	0.94570
0.05978	0.96301	0.06311	0.96150	0.06642	0.96001	0.04581	0.94465	0.04836	0.94362	0.05090	0.94262
0.06975	0.95851	0.07307	0.95703	0.07640	0.95555	0.05345	0.94159	0.05599	0.94058	0.05854	0.93957
0.07971	0.95407	0.08303	0.95261	0.08635	0.95114	0.06108	0.93859	0.06363	0.93760	0.06617	0.93663
0.08968	0.94968	0.09300	0.94827	0.09633	0.94687	0.06872	0.93568	0.07127	0.93472	0.07382	0.93380
0.09964	0.94548	0.10298	0.94412	0.10630	0.94276	0.07636	0.93285	0.07890	0.93192	0.08145	0.93100
0.10961	0.94141	0.11294	0.94006	0.11627	0.93872	0.08399	0.93007	0.08654	0.92916	0.08909	0.92824
0.11958	0.93726	0.12290	0.93594	0.12623	0.93464	0.09164	0.92736	0.09418	0.92645	0.09673	0.92558
0.12955	0.93335					0.09927	0.92461	0.10181	0.92371	0.10436	0.92284
						0.10691	0.92197	0.10946	0.92113	0.11200	0.92028
		$x_{2P}{}^0 = 0.03803$				0.11455	0.91945	0.11710	0.91864	0.11965	0.91782
0	0.97854	0.00256	0.97767	0.00513	0.97681	0.12219	0.91701	0.12474	0.91622		
0.00769	0.97594	0.01026	0.97507	0.01282	0.97419						
0.01539	0.97332	0.01796	0.97241	0.02052	0.97148			$x_{2P}{}^0 = 0.1189$			
0.02309	0.97056	0.02566	0.96959	0.02822	0.96861	0	0.94551	0.00259	0.94449	0.00520	0.94346
0.03078	0.96760	0.03335	0.96658	0.03592	0.96553	0.00780	0.94245	0.01040	0.94144	0.01300	0.94044
0.03848	0.96447	0.04105	0.96339	0.04362	0.96230	0.01560	0.93947	0.01820	0.93850	0.02080	0.93751
0.04619	0.96120	0.04876	0.96009	0.05132	0.95897	0.02339	0.93655	0.02600	0.93559	0.02860	0.93462
0.05389	0.95786	0.05646	0.95672	0.05902	0.95560	0.03120	0.93368	0.03380	0.93273	0.03640	0.93179
0.06159	0.95449	0.06415	0.95336	0.06672	0.95221	0.03900	0.93087	0.04161	0.92994	0.04421	0.92901
0.06929	0.95112	0.07185	0.95001	0.07442	0.94892	0.04680	0.92809	0.04941	0.92716	0.05201	0.92626
0.07699	0.94785	0.07955	0.94678	0.08212	0.94572	0.05461	0.92538	0.05721	0.92451	0.05981	0.92365
0.08469	0.94466	0.08725	0.94360	0.08982	0.94255	0.06241	0.92280	0.06502	0.92194	0.06761	0.92111
0.09239	0.94151	0.09495	0.94037	0.09752	0.93934	0.07021	0.92027	0.07281	0.91944	0.07542	0.91861
0.10009	0.93832	0.10266	0.93730	0.10522	0.93631	0.07802	0.91780	0.08062	0.91701	0.08322	0.91623
0.10779	0.93532	0.11036	0.93432	0.11293	0.93335	0.08582	0.91545	0.08842	0.91467	0.09103	0.91389
0.11549	0.93239	0.11806	0.93142	0.12063	0.93047	0.09363	0.91312	0.09623	0.91227	0.09883	0.91151
0.12320	0.92951	0.12576	0.92858			0.10143	0.91075	0.10403	0.91001	0.10663	0.90928
						0.10924	0.90855	0.11184	0.90781	0.11444	0.90706
						0.11704	0.90635	0.11965	0.90563	0.12224	0.90494
						0.12485	0.90425	0.12745	0.90355		

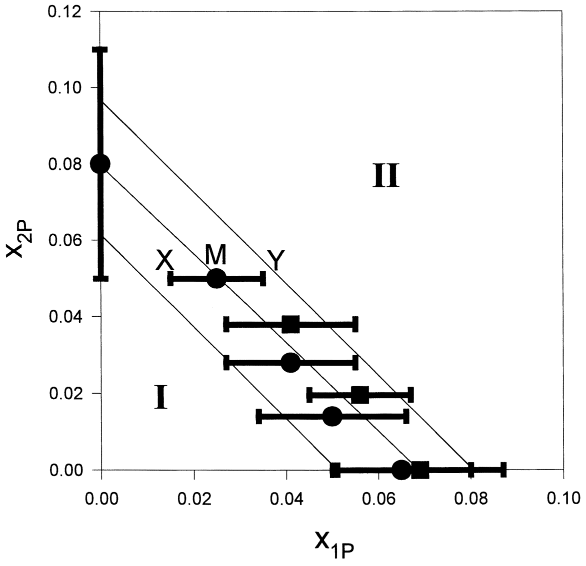

Fig. 7. Loci of Mixing Scheme boundary between I and II in 1-propanol–2-propanol–H_2O at 25 °C. Circle from $H_{1P\text{–}1P}{}^{E}$; square from $V_{1P\text{–}1P}{}^{E}$. *X* is the onset of transition, *Y* the end point, and *M* is the representative mid point. See text for detail.

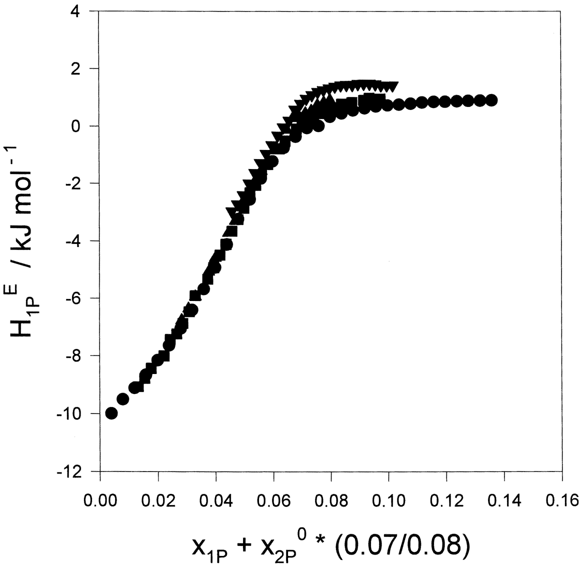

Fig. 8. Excess partial molar enthalpy of 1-propanol, $H_{1P}{}^{E}$, against x_{1P}+(0.07/0.08) $x_{2P}{}^{0}$, in 1-propanol–2-propanol–H_2O at 25 °C. Symbols are the same as in Fig. 3. See text for detail.

equivalent to that of 1P at x_{1P} = (0.07/0.08) $x_{2P}{}^{0}$. Figures 8 and 9 show the plots of $H_{1P}{}^{E}$ and $V_{1P}{}^{E}$ against $\{x_{1P} + (0.07/0.08)x_{2P}{}^{0}\}$. Thus, we add to the above conclusion that the additive effect of 1P and 2P on H_2O within Mixing Scheme I is in the ratio of (0.07/0.08).

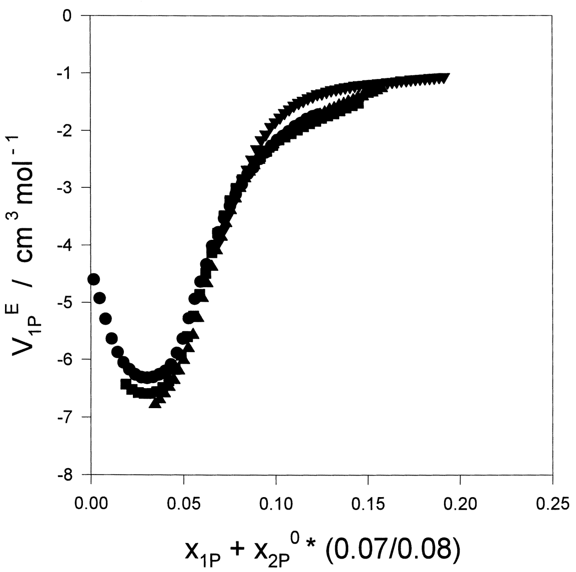

Fig. 9. Excess partial molar volume of 1-propanol, $V_{1P}{}^{E}$, against x_{1P}+(0.07/0.08) $x_{2P}{}^{0}$, in 1-propanol–2-propanol–H_2O at 25 °C. Symbols are the same as in Fig. 4. See text for detail.

In this work we studied the thermodynamic behaviour of 1P only in terms of Eqs. 1 and 2 with the presence of a third component, 2P. With the previous knowledge of what 1P does to H_2O,[1–6] we recovered the effect of 2P on H_2O, which we knew from previous studies on binary 2P–H_2O.[1–6] This means that this method of using the thermodynamic behaviour of 1P as a probe to learn the effect of a third component on H_2O is sound. Thus, the conclusions deduced earlier on the effects of urea[14] and NaCl[15] on H_2O have now an additional, though indirect, support.

We might add in closing that it is the integrity of H_2O that dictates the nature of aqueous solutions in the water-rich region, where Mixing Scheme I is operative. In studying aqueous solutions of biological importance, it would be fruitful to pay more attention to the state of H_2O. For example, the transition from Mixing Scheme I to II has a profound effect on the structure and hence the function of Lysozyme.[12,13] Namely, while a mixed aqueous solvent is in Mixing Scheme I, in which the bulk H_2O portion of the mixture retains its integrity of liquid H_2O, Lysozyme curls up into the native state. When the mixed aqueous alcohol loses its H_2O-like property in Mixing Scheme II, it does not need to take a globular form any longer, and becomes denatured.[12,13]

We thank Eric C. H. To and Jason S.Y. Sze for help in preliminary experiments. This work was supported by NSERC of Canada and Lundbeck Foundation of Denmark. The guest professorship for one of us (YK) was financed by the Ministry of Education, Science, Sports and Culture.

References

1 Y. Koga, *J. Phys. Chem.*, **100**, 5172 (1996).

2 Y. Koga, *J. Crystallogr. Soc. Jpn.*, **37**, 172 (1995).

3 S. H. Tanaka, H. I. Yoshihara, A. W.-C. Ho, F. W. Lau, P. Westh, and Y. Koga, *Can. J. Chem.*, **47**, 4613 (1996).

4 Y. Koga, and P. Westh, *Bull. Chem. Soc. Jpn.*, **69**, 1505 (1996).

5 K. Tamura, A. Osaki, and Y. Koga, *Phys. Chem. Chem. Phys.*, **1**, 121 (1999).

6 Y. Koga, *Can. J. Chem.*, **77**, 2039 (1999).

7 F. Franks, and D. J. G. Ives, *Qurat. Rev.*, **20**, 1 (1966).

8 "Water-a comprehensive treatise," ed by F. Franks, Plenum Press, New York (1973–1995), Vols. 2 and 4.

9 F. Franks, J. E. Desnoyers, In "*Water Science Review I*," ed by F. Franks, (1985) p. 175.

10 P. Westh and Y. Koga, *J. Phys. Chem.*, **100**, 433 (1996).

11 Ch. Trandum, P. Westh, C. A. Haynes and Y. Koga, *J. Phys. Chem.*, **102**, 5182 (1998).

12 Y. Koga, P. Westh, Ch. Trandum, and C. A. Haynes, *Fluid Phase Equilib.*, **136**, 207 (1997).

13 P. Westh, and Y. Koga, *J. Phys. Chem. B*, **101**, 5755 (1997).

14 E.C.H. To, J. Hu, C.A. Haynes, and Y. Koga, *J. Phys. Chem. B*, **102**, 10958 (1998).

15 H. Matsuo, E. C. H. To, D. C. Y. Wong, S. Sawamura, Y. Taniguchi, and Y. Koga, *J. Phys. Chem. B*, **103**, 2981 (1999).

16 Y. Koga, P. Westh, S. Sawamura, and Y. Taniguchi, *J. Chem. Phys.*, **105**, 2028 (1996).

17 Y. Koga, K. Tamura, *Netsusokutei, (Calorimetry and Thermal Analysis)*, **27**, 195 (2000).

18 Y. Koga, *Can. J. Chem.*, **66**, 1187 (1988).

19 Y. Koga, *J. Phys. Chem.*, **95**, 4120 (1991).

20 Y. Koga, W. W. Y. Siu, and T. Y. H. Wong, *J. Phys. Chem.*, **94**, 7700 (1990).

21 C. Dethlefsen, P. G. Sorensen, and Aa. Hvidt, *J. Solution Chem.*, **13**, 191 (1984).

22 R. Rumry and S. Rajender, *Biopolymers*, **9**, 1125 (1970).

23 Y. Koga, J. Kristiansen, and Aa. Hvidt, *J. Chem. Thermodyn.*, **25**, 51 (1993).

24 Y. Koga, *J. Phys. Chem.*, **96**, 10466 (1992).