Interactions in 1-Propanol−Urea−H₂O: Chemical Potentials, Partial Molar Enthalpies, and Entropies at 25 °C

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The excess partial molar enthalpies of 1-propanol were determined in aqueous urea solutions. The total vapor pressures of 1-propanol−urea−H₂O were also measured. The numerical analysis applied in a previous paper (*J. Phys. Chem. B* **1998**, *102,* 5182) was used to calculate partial pressures and, hence, the excess chemical potentials of each component. Thus, the excess partial molar entropies of 1-propanol were obtained. From these partial molar quantities, the interaction functions between a pair of solute molecules were calculated following the method developed by us (*J. Phys. Chem. B* **1996**, *100,* 5172). All these data seem to indicate that urea molecules lock into the hydrogen bond network of H₂O, keep the connectivity of hydrogen bond intact, but reduce the degree of fluctuation that is characteristic of liquid water. 1-Propanol molecules modify the hydrogen bond network in the same manner with or without urea, and hence the same amount of 1-propanol is required to break down the connectivity, i.e., the loss of hydrogen bond percolation. However, the H₂O-mediated interaction between 1-propanol solutes is weakened since the hydrogen bond fluctuation responsible for such an interaction is reduced by the presence of urea.

1. Introduction

At the risk of oversimplification, the word "interaction" could carry two meanings in biothermodynamic literature. The first is a direct kind in which a solute binds directly on sites of another biopolymer.[1,2] A binding (interaction) equilibrium is assumed to establish and the standard Gibbs energy difference related to the binding equilibrium constant is the starting point of subsequent thermodynamic analysis. The second is an indirect, water-mediated interaction,[3−7] obtained as an enthalpic virial expansion coefficient. The McMillan−Mayer theory of solution provides the basis for the meaning of the virial coefficients.

Thus, it is quite possible that a set of enthalpy data could provide two different pictures, a direct and an indirect interaction, depending on the method used for data analysis.

We have been measuring the excess partial molar enthalpies, H_i^E, of the ith component (and entropies for some cases) in aqueous solutions of nonelectrolytes.[8−16] They were determined accurately and in small increments in composition. Therefore, it was possible to differentiate once more with respect to a given, the jth, component

$$H_{ij}^E \equiv N(\partial H_i^E/\partial n_j)_{nk\neq nj} \tag{1}$$

within a reasonable uncertainty, an order of percent. This quantity, H_{ij}^E, was argued to be a measure of the $i−j$ interaction in terms of enthalpy in the Gibbs ensemble or (p, T, n_i) variable system without resorting to any model.[8,9] If $H_{ij}^E < 0$, the $i−j$

interaction is enthalpically favorable and vice versa. The same argument is applicable[8,9] to the entropy analogue, S_{ij}^E, except that the sign is reversed.

To reiterate, the excess partial molar enthalpy of i, H_i^E, is defined as

$$H_i^E = (\partial H^E/\partial n_i)_{nk\neq ni} \tag{2}$$

Hence, H_i^E is the enthalpic contribution of the ith component to the entire system. Or, it shows the enthalpic situation of the ith component in the mixture. Then, H_{ij}^E, calculated by eq 1, shows the effect of the jth component on the enthalpic situation of i, and thus H_{ij}^E is a measure of the enthalpic $i−j$ intercation. This quantity provides a convenient and model-free measure on the intermolecular interaction in the Gibbs ensemble, the (p, T, n_i) variable system—the most important information needed by experimentalists. Using this, we have advanced the understandings of the nature of aqueous solutions of nonelectrolytes.[8,9] For example, we learned that both kinds of interaction, a direct and an indirect (water-mediated) interactions, are prevalent only in a specific composition range. Namely, in the most water-rich region, two solutes modify the hydrogen bond network of H₂O, and the interactions between i and j components occur via a modified hydrogen bond network. As the concentration of solute increases, the connectivity of the hydrogen bond network is reduced gradually and at a narrow composition range the connectivity of the hydrogen bond network in the bulk H₂O is lost completely. The system undergoes what we call the "transition of mixing scheme", and the mixture then consists of clusters rich in each component. Within each cluster then direct $i−j$ interactions are operative.

Such deeper insights gained by using our methodology into the nature of aqueous solutions will no doubt benefit under-

TABLE 1: 1-Propanol−Urea−H$_2$O Vapor Pressure at 25.00 °C

x_{1P}	x_U	p	x_{1P}	x_U	p	x_{1P}	x_U	p
				Series 1				
0	0	23.756	0.0396	0	31.608	0.1036	0	34.986
0.0037	0	24.741	0.0503	0	32.928	0.1261	0	35.151
0.0079	0	25.795	0.0619	0	33.891	0.1561	0	35.274
0.0135	0	27.023	0.0748	0	34.459	0.1911	0	35.364
0.0206	0	28.484	0.0872	0	34.754	0.2241	0	35.427
0.0291	0	30.029						
				Series 2				
0	0.0306	23.071	0.0238	0.0301	28.278	0.0786	0.0286	33.733
0.0023	0.0306	23.689	0.0321	0.0299	29.719	0.0886	0.0283	33.951
0.0050	0.0305	24.338	0.0414	0.0296	31.071	0.1011	0.0279	34.136
0.0082	0.0305	25.100	0.0515	0.0293	32.230	0.1166	0.0275	34.281
0.0121	0.0304	25.956	0.0603	0.0291	32.935	0.1362	0.0270	34.391
0.0172	0.0303	27.013	0.0693	0.0288	33.420	0.1566	0.0265	34.463
				Series 3				
0	0.0441	22.784	0.0250	0.0434	28.214	0.0787	0.0409	33.478
0.0027	0.0440	23.557	0.0297	0.0433	29.046	0.0914	0.0404	33.748
0.0055	0.0440	24.196	0.0352	0.0431	29.899	0.1048	0.0399	33.924
0.0088	0.0439	24.931	0.0411	0.0428	30.731	0.1210	0.0393	34.062
0.0123	0.0438	25.720	0.0477	0.0426	31.519	0.1397	0.0387	34.157
0.0162	0.0437	26.545	0.0552	0.0424	32.246	0.1669	0.0378	34.251
0.0204	0.0436	27.376	0.0669	0.0414	33.020	0.2071	0.0368	34.314
				Series 4				
0	0.0746	22.138	0.0199	0.0733	26.810	0.0642	0.0702	32.880
0.0037	0.0743	23.163	0.0276	0.0728	28.209	0.0818	0.0690	33.350
0.0082	0.0741	24.281	0.0381	0.0721	29.851	0.1025	0.0675	33.641
0.0131	0.0738	25.390	0.0499	0.0713	31.286	0.1268	0.0658	33.783
				Series 5				
0	0.1007	21.571	0.0256	0.0988	26.946	0.0770	0.0941	32.161
0.0027	0.1005	22.281	0.0325	0.0982	28.086	0.0885	0.0930	32.522
0.0060	0.1003	23.085	0.0428	0.0972	29.548	0.0983	0.0922	32.686
0.0099	0.1000	23.969	0.0542	0.0962	30.781	0.1154	0.0906	33.131
0.0149	0.0996	24.880	0.0653	0.0952	31.619	0.1439	0.0881	33.408
0.0199	0.0992	25.883						
				Series 6				
0	0.1921	19.745	0.0307	0.1880	26.173	0.0808	0.1798	30.915
0.0038	0.1917	20.869	0.0411	0.1864	27.683	0.0953	0.1774	31.339
0.0091	0.1911	22.045	0.0529	0.1844	29.031	0.1128	0.1746	31.620
0.0152	0.1903	23.346	0.0657	0.1823	30.107	0.1391	0.1707	31.832
0.0220	0.1893	24.663						

standings on the role of mixed aqueous solvents used in a wide variety of reactions including biological processes. Indeed, we showed that the transition of mixing scheme in aqueous alcohol is crucial on the stability and the structure of lysozyme.[11]

In this paper, we apply the same methodology to 1-propanol−urea−H$_2$O and discuss interactions between 1-propanol−1-propanol and 1-propanol−urea in terms of enthalpy and entropy. Namely, an attempt is made at elucidating the effect of urea on H$_2$O using the thermodynamic behavior of 1-propanol as a probe.

2. Experimental Section

1-Propanol (Aldrich, 99.5+%, HPLC) and urea (Aldrich, 99%, ACS) were used as supplied. H$_2$O was triply distilled; last twice in a glass still immediately before use. Excess partial molar enthalpies were determined by an LKB Bromma 8700 titration calorimeter using a buret method.[14] Vapor pressures were measured by a static method described elsewhere.[13,15] The total pressure data were analyzed numerically in the same way as described in the previous paper[13] (called paper I hereinafter).

3. Results

The measured total pressure data corrected for 25.00 °C are listed in Table 1. Various corrections are detailed in paper I.[13] From these data the partial pressures were calculated in the same manner as in paper I.[13] For the present case, however, the partial pressure of urea is negligibly small in comparison with those of 1-propanol and of H$_2$O. Hence the basic Gibbs−Duhem relation employed is

$$x_U \delta \ln a_U + x_{1P} \delta \ln p_{1P} + x_W \delta \ln p_W = 0 \tag{3}$$

$$p = p_{1P} + p_W$$

a_U ($= x_U \gamma_U$) is the activity of urea in solution. Otherwise, the method of data analysis is identical with that used in paper I.[13] For convenience, the reference states were taken at each component's pure state. Hence, for urea

$$\mu_U = \mu_U{}^0 + RT \ln a_U = \mu_U{}^0 + RT \ln x_U + RT \ln \gamma_U \tag{4}$$

$\mu_U{}^0$ is the chemical potential of pure solid urea. Hence, at saturation,

$$\mu_U = \mu_U{}^0$$

Therefore,

$$a_U{}^{sat} = x_U{}^{sat} \gamma_U{}^{sat} = 1$$

Superscript "sat" signifies saturation. The results are shown in

TABLE 2: Partial Pressures, P_i/Torr (i = 1P, W, U)

X_U		x_{1P} 0.0	0.005	0.01	0.015	0.02	0.025	0.03	0.035	0.04	0.045	0.05	0.055	0.06	0.07	0.08	0.09	0.10	0.11	0.12
0.0	p_t	23.76	24.93	26.09	27.16	28.19	29.14	30.02	30.83	31.55	32.19	32.74	33.21	33.60	34.16	34.46	34.60	34.68	34.85	34.79
	p_W	23.76	23.64	23.52	23.41	23.30	23.21	23.11	23.02	22.94	22.87	22.79	22.73	22.68	22.58	22.51	22.47	22.47	22.47	22.47
	α_U	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	p_{1P}	0.0	1.292	2.565	3.751	4.879	5.935	6.913	7.806	8.611	9.325	9.948	10.48	10.93	11.57	11.95	12.13	12.12	12.38	12.38
0.01	p_t	23.52	24.73	25.94	27.05	28.06	28.99	29.83	30.58	31.26	31.85	32.38	32.84	33.23	33.83	34.23	34.46	34.57	34.60	34.61
	p_W	23.52	23.43	23.26	23.15	23.04	22.94	22.86	22.76	22.68	22.61	22.54	22.47	22.41	22.31	22.24	22.19	22.15	22.14	22.15
	α_U	0.055	0.055	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.068	0.068	0.068
	p_{1P}	0.0	1.299	2.670	3.892	5.014	6.040	6.973	7.819	8.577	9.253	9.849	10.37	10.82	11.52	11.99	12.27	12.42	12.46	12.46
0.03	p_t	23.10	24.32	25.52	26.63	27.64	28.56	29.40	30.16	30.83	31.43	31.96	32.42	32.81	33.42	33.83	34.07	34.19	34.23	34.25
	p_W	23.10	23.01	22.86	22.75	22.64	22.54	22.45	22.36	22.27	22.20	22.12	22.06	22.00	21.89	21.81	21.74	21.73	21.69	21.65
	α_U	0.147	0.147	0.152	0.152	0.152	0.152	0.152	0.152	0.152	0.152	0.152	0.153	0.153	0.154	0.155	0.158	0.156	0.161	0.165
	p_{1P}	0.0	1.312	2.662	3.879	4.997	6.022	6.954	7.799	8.559	9.236	9.836	10.36	10.82	11.53	12.02	12.33	12.47	12.55	12.60
0.05	p_t	22.67	23.92	25.11	26.21	27.22	28.14	28.98	29.73	30.41	31.01	31.54	32.00	32.40	33.02	33.43	33.69	33.82	33.87	33.89
	p_W	22.67	22.59	22.44	22.33	22.23	22.13	22.03	21.94	21.86	21.78	21.70	21.63	21.57	21.46	21.37	21.32	21.24	21.22	21.22
	α_U	0.231	0.231	0.236	0.236	0.236	0.236	0.236	0.236	0.236	0.236	0.237	0.237	0.238	0.239	0.241	0.241	0.249	0.249	0.248
	p_{1P}	0.0	1.326	2.665	3.876	4.991	6.012	6.943	7.788	8.549	9.231	9.835	10.36	10.83	11.55	12.06	12.36	12.57	12.65	12.67
0.07	p_t	22.25	23.51	24.70	25.79	26.80	27.71	28.55	29.30	29.979	30.58	31.11	31.58	31.98	32.61	33.03	33.30	33.44	33.50	33.54
	p_W	22.25	22.17	22.02	21.91	21.81	21.71	22.61	21.52	21.43	21.36	21.28	21.21	21.15	21.03	20.94	20.84	20.83	20.77	20.68
	α_U	0.312	0.312	0.316	0.316	0.316	0.316	0.316	0.316	0.316	0.316	0.317	0.317	0.318	0.320	0.322	0.329	0.325	0.332	0.344
	p_{1P}	0.0	1.340	2.671	3.877	4.988	6.007	6.937	7.783	8.545	9.226	9.832	10.37	10.83	11.58	12.10	12.46	12.61	12.74	12.86
0.09	p_t	21.83	23.10	24.28	25.37	26.37	27.29	28.12	28.87	29.55	30.16	30.69	31.16	31.56	32.20	32.64	32.91	33.07	33.14	
	p_W	21.83	21.75	21.60	21.49	21.39	21.29	21.19	21.10	21.02	20.93	20.85	20.78	20.71	20.59	20.49	20.45	20.33	20.29	
	α_U	0.389	0.389	0.392	0.393	0.393	0.393	0.393	0.393	0.393	0.394	0.395	0.396	0.397	0.399	0.402	0.400	0.412	0.415	
	p_{1P}	0.0	1.353	2.679	3.880	4.987	6.002	6.931	7.774	8.537	9.223	9.835	10.37	10.84	11.60	12.14	12.46	12.74	12.85	
0.11	p_t	21.41	22.70	23.87	24.95	25.95	26.86	27.69	28.45	29.12	29.73	30.26	30.73	31.14	31.79	32.24	32.53	32.69		
	p_W	21.41	21.33	21.18	21.07	20.97	20.87	20.77	20.67	20.59	20.50	20.43	20.36	20.29	20.17	20.06	19.92	19.90		
	α_U	0.464	0.464	0.468	0.468	0.468	0.468	0.468	0.469	0.470	0.470	0.470	0.471	0.472	0.474	0.477	0.490	0.487		
	p_{1P}	0.0	1.367	2.687	3.882	4.984	5.998	6.926	7.773	8.538	9.224	9.836	10.38	10.85	11.62	12.17	12.61	12.79		
0.13	p_t	20.99	22.29	23.46	24.54	25.53	26.44	27.27	28.02	28.70	29.30	29.84	30.31	30.72	31.38	31.84	32.14			
	p_W	20.99	20.91	20.76	20.65	20.54	20.44	20.34	20.26	20.17	20.09	20.01	19.93	19.86	19.73	19.61	19.61			
	α_U	0.537	0.537	0.541	0.542	0.542	0.542	0.542	0.542	0.542	0.542	0.543	0.544	0.545	0.548	0.553	0.544			
	p_{1P}	0.0	1.381	2.696	3.885	4.986	5.997	6.923	7.765	8.527	9.216	9.833	10.38	10.86	11.65	12.22	12.52			
0.15	p_t	20.56	21.88	23.04	24.12	25.11	26.01	26.84	27.59	28.27	28.88	29.42	29.89	30.31	30.97	31.44	31.751			
	p_W	20.56	20.49	20.34	20.23	20.12	20.02	19.93	19.84	19.74	19.66	19.57	19.50	19.42	19.29	19.18	18.91			
	α_U	0.608	0.608	0.613	0.613	0.613	0.613	0.613	0.613	0.614	0.615	0.616	0.618	0.619	0.622	0.626	0.655			
	p_{1P}	0.0	1.394	2.705	3.890	4.982	5.989	6.911	7.757	8.527	9.221	9.842	10.40	10.88	11.68	12.26	12.84			
0.17	p_t	20.14	21.48	22.63	23.70	24.68	25.59	26.41	27.16	27.84	28.45	28.99	29.47	29.89	30.56					
	p_W	20.14	20.07	19.92	19.81	19.70	19.60	19.49	19.39	19.31	19.22	19.14	19.06	18.99	18.85					
	α_U	0.678	0.678	0.683	0.683	0.683	0.684	0.685	0.686	0.687	0.687	0.688	0.690	0.691	0.694					
	p_{1P}	0.0	1.408	2.713	3.890	4.982	5.991	6.920	7.767	8.534	9.229	9.853	10.41	10.90	11.71					
0.19	p_t	19.72	21.07	22.22	23.28	24.26	25.16	25.99	26.74	27.42	28.02	28.57	29.05	29.47						
	p_W	19.72	19.65	19.49	19.37	19.26	19.16	19.06	18.97	18.88	18.79	18.71	18.63	18.56						
	α_U	0.747	0.747	0.753	0.754	0.755	0.756	0.756	0.756	0.757	0.757	0.758	0.759	0.761						
	p_{1P}	0.0	1.422	2.725	3.905	4.996	6.003	6.923	7.765	8.535	9.230	9.856	10.42	10.91						

Table 2. The excess chemical potentials were calculated from the data in Table 2 as

$$\mu_i^E = RT \ln \{p_i/(p_i^0 x_i)\} \tag{5}$$

for i = 1-propanol and H_2O, and

$$\mu_U^E = RT \ln \gamma_U \tag{6}$$

The consistency check as detailed in paper I[13] was found satisfactory within ±0.05 kJ mol^{-1} for the range $x_U \geq 0.04$ and $x_{1P} \geq 0.0125$ and better than ±0.01 kJ mol^{-1} in the range $x_U \geq 0.06$ and $x_{1P} \geq 0.0175$. Hence the uncertainties in the excess chemical potentials are at the worst similar to the above values in each of the appropriate ranges.

For binary 1-propanol–H_2O (i.e., $x_U = 0$), the vapor pressure data were analyzed by the Boissonnass method.[15] For aqueous urea solutions ($x_{1P} = 0$), the partial pressure of urea is taken as zero; hence, $p_W = p$. The excess chemical potentials of H_2O, μ_W^E, were calculated by eq 5. The excess chemical potentials of urea, μ_U^E, were then calculated stepwise from the saturation point using the Gibbs–Duhem relation

$$x_U \delta\mu_U^E + x_W \delta\mu_W^E = 0 \tag{7}$$

with μ_U^E (at saturation) $= -RT \ln(x_U^{sat})$. Figures 1 and 2 show the plots of μ_{1P}^E and μ_U^E, respectively, together with literature values. The excess partial molar enthalpies of 1-propanol, H_{1P}^E, in various solvent mixtures of urea–H_2O are listed in Table 3 and plotted in Figure 3. The uncertainty in H_{1P}^E is ±0.05 kJ mol^{-1}. From the graphically interpolated values of H_{1P}^E and the values of μ_{1P}^E, the excess partial molar entropies of 1-propanol, S_{1P}^E, were calculated. The values of TS_{1P}^E are listed in Table 4 and plotted in Figure 4. The uncertainty in TS_{1P}^E is ±0.1 kJ mol^{-1}.

4. Discussions

Various approaches are possible in understanding the nature of the 1-propanol–urea–H_2O system using the results shown above. A commonly adopted method is to devise a model and to calculate thermodynamic quantities accordingly. The thermodynamic functions thus calculated are then compared with
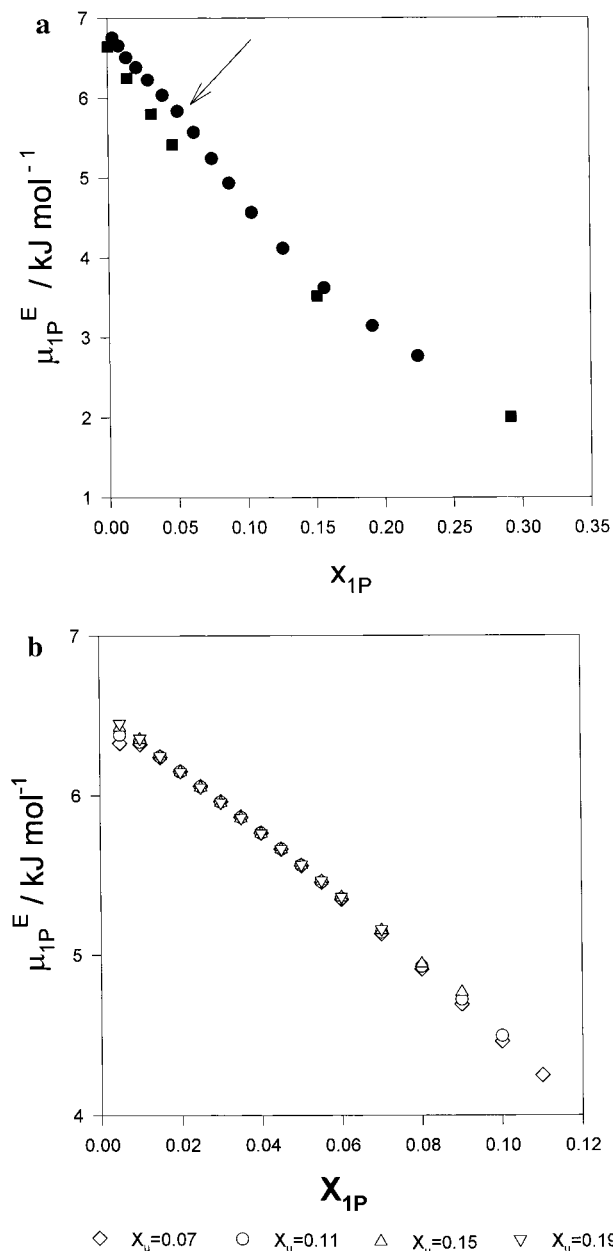
1-Propanol in Aqueous Urea

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Figure 1. Excess chemical potential of 1-propanol, μ_{1P}^E, against mole fraction of 1-propanol, x_{1P} at 25.00 °C: (a) for binary aqueous 1-propanol, i.e., $x_U = 0$, (●) this work, (■) ref17; (b) for ternary 1-propanol−urea−H$_2$O, (◇) $x_U = 0.07$, (○) $x_U = 0.11$, (△) $x_U = 0.15$, (▽) $x_U = 0.19$.

Figure 2. Excess chemical potential of urea, μ_U^E, against mole fraction of urea, x_U at 25.00 °C. (a) For binary aqueous urea, i.e., $x_{1P} = 0$, (▽) this work, (○) calculated in the same way as this work using the raw data of ref 18, (□) ref 18, (△) ref 19, (○̇) ref 20, (◇) ref 17; (b) for ternary 1-propanol−urea−H$_2$O, (○) $x_{1P} = 0.02$, (○) $x_{1P} = 0.03$, (□) $x_{1P} = 0.04$, (▽) $x_{1P} = 0.05$, (○) $x_{1P} = 0.07$, (△) $x_{1P} = 0.09$, (◇) $x_{1P} = 0.11$.

the experimental results. In contrast, we do not build any model. Rather, we try to learn what the data speak themselves. Despite general reluctance (since differentiation increases uncertainty by some 10-folds), we differentiate the partial molar quantities graphically and obtain the interaction functions (eq 1 and equivalent ones). For this, the partial molar quantities must be determined accurately and in small increments. As shown below, we could obtain H_{ij}^E within several percent.

μ_{1P}^E (Figure 1a) for binary 1-propanol−H$_2$O shows a subtle change in curvature at about $x_{1P} = 0.07$, where the mixing scheme, a detailed manner in which 1-propanol mixes with H$_2$O, was suggested to change in this binary solution.[16] The literature data points determined by analyzing gas-phase composition by gas chromatography[17] are not closely spaced enough to see this. This transition of mixing scheme was much conspicuous in the behavior of H_{1P}^E.[16]
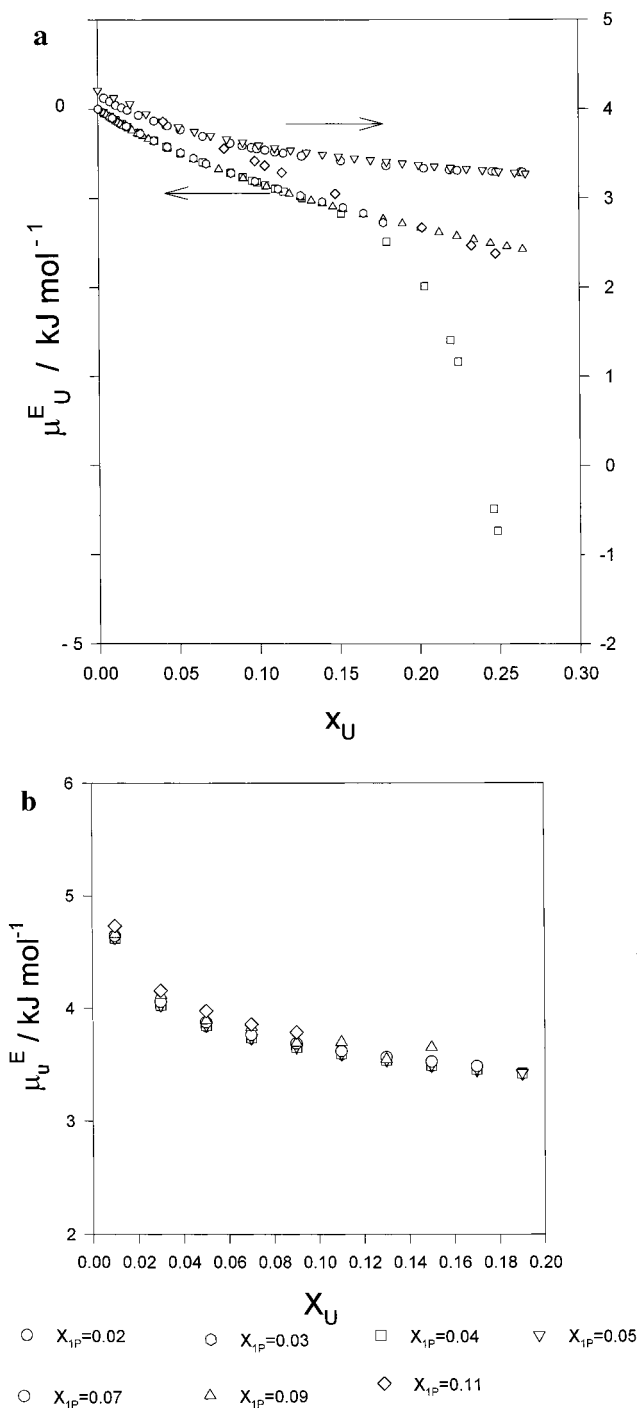
Figure 2a shows a discrepancy between μ_U^E values of this work and literature values, even after an appropriate vertical shift to correct for the difference in the choice of reference state. It turned out that literature data cited in Figure 2a are all subjected to some systematic error due to curve-fitting. Namely, the measured data, (the ratio of gas chromatographic signals[17] or the osmotic coefficients[18−20]) were curve-fitted to an analytic function, which was used to arithmetically calculate μ_U^E or γ_U^E. To demonstrate this, the isopiestic data between urea−H$_2$O and

TABLE 3: Excess Partial Molar Enthalpies of 1-Propanol, H_{1P}^E, in Aqueous Solutions of Various Initial Mole Fraction of Urea, x_U^0, at 25 °C[a]

$x_U^0 = 0.0$		$x_U^0 = 0.0$		$x_U^0 = 0.03040$		$x_U^0 = 0.03040$		$x_U^0 = 0.04985$		$x_U^0 = 0.04985$	
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	x_{1P}	H_{1P}^E
0.00161	−10.09	0.0618	−0.98	0.00167	−8.60	0.0712	−0.45	0.0172	−7.92	0.0660	−0.99
0.00483	−10.19	0.0651	−0.61	0.00499	−8.35	0.0746	−0.20	0.0514	−7.51	0.0696	−0.64
0.00802	−9.61	0.0683	−0.33	0.00829	−7.99	0.0779	−0.02	0.0854	−7.34	0.0731	−0.41
0.0112	−9.23	0.0716	−0.28	0.0116	−7.50	0.0812	0.09	0.0119	−6.95	0.0766	−0.18
0.0144	−8.87	0.0748	0.15	0.0148	−7.46	0.0878	0.33	0.0153	−6.66	0.0800	−0.06
0.0157	−8.35	0.0812	0.37	0.0181	−7.05	0.0910	0.37	0.0186	−6.37	0.0835	0.06
0.0175	−8.35	0.0844	0.48	0.0213	−6.71	0.0945	0.44	0.0219	−6.16	0.0869	0.22
0.0206	−7.71	0.0884	0.53	0.0245	−6.33	0.0982	0.44	0.0252	−5.96	0.0903	0.23
0.0276	−7.04	0.0923	0.72	0.0276	−5.92	0.102	0.53	0.0285	−5.39	0.0969	0.31
0.0311	−6.35	0.0963	0.73	0.0339	−5.21	0.106	0.55	0.0317	−5.01	0.101	0.51
0.0347	−5.88	0.100	0.79	0.0370	−4.73	0.113	0.67	0.0349	−4.49	0.104	0.41
0.0382	−5.12	0.104	0.75	0.0401	−4.15	0.117	0.61	0.0381	−4.07	0.108	0.50
0.0417	−4.55			0.0435	−3.71	0.120	0.65	0.0413	−3.71	0.112	0.51
0.0451	−3.79			0.0470	−3.20	0.124	0.66	0.0445	−3.20	0.116	0.49
0.0486	−3.17			0.0506	−2.61	0.127	0.68	0.0479	−2.98	0.120	0.57
0.0520	−2.42			0.0575	−1.78	0.131	0.68	0.0513	−2.34	0.127	0.57
0.0554	−1.93			0.0610	−1.64	0.134	0.67	0.0552	−1.95	0.131	0.55
0.0587	−1.33			0.0678	−0.72			0.0588	−1.74	0.134	0.57

$x_U^0 = 0.1020$		$x_U^0 = 0.1020$		$x_U^0 = 0.1501$		$x_U^0 = 0.1501$		$x_U^0 = 0.2035$		$x_U^0 = 0.2035$	
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	x_{1P}	H_{1P}^E
0.00189	−6.14	0.0673	−0.95	0.00195	−5.03	0.0703	−0.95	0.00209	−4.15	0.0749	−0.51
0.00565	−5.94	0.0712	−0.64	0.00583	−4.70	0.0780	−0.40	0.00625	−3.96	0.0791	−0.48
0.00938	−5.80	0.0749	−0.46	0.00968	−4.67	0.0818	−0.30	0.0104	−3.70	0.0832	−0.30
0.0131	−5.45	0.0787	−0.34	0.0135	−4.49	0.0894	−0.04	0.0145	−3.56	0.0873	−0.22
0.0168	−5.26	0.0824	−0.14	0.0173	−4.35	0.0931	−0.07	0.0185	−3.34	0.0914	−0.09
0.0204	−4.98	0.0861	−0.04	0.0248	−3.84	0.0968	0.07	0.0266	−3.05	0.0955	−0.03
0.0276	−4.37	0.0897	0.01	0.0285	−3.52	0.100	0.17	0.0305	−2.71	0.104	0.09
0.0312	−4.05	0.0970	0.11	0.0322	−3.39	0.104	0.11	0.0344	−2.60	0.107	0.14
0.0347	−3.60	0.101	0.17	0.0358	−2.99	0.108	0.20	0.0383	−2.28	0.111	0.15
0.0383	−3.24	0.104	0.25	0.0394	−2.63	0.121	0.27	0.0422	−2.19	0.115	0.16
0.0418	−2.95	0.108	0.27	0.0430	−2.36	0.125	0.30	0.0460	−1.95	0.119	0.25
0.0452	−2.69	0.112	0.33	0.0466	−2.32	0.129	0.34	0.0536	−1.57	0.123	0.25
0.0487	−2.30	0.116	0.29	0.0545	−1.58			0.0577	−1.43	0.127	0.25
0.0521	−2.00	0.120	0.29	0.0585	−1.46			0.0620	−1.08	0.130	0.27
0.0557	−1.68	0.132	0.40	0.0625	−1.26			0.0664	−0.76		
0.0635	−1.15			0.0664	−1.07			0.0706	−0.72		

[a] H_{1P}^E is in units of kJ mol^{-1}.
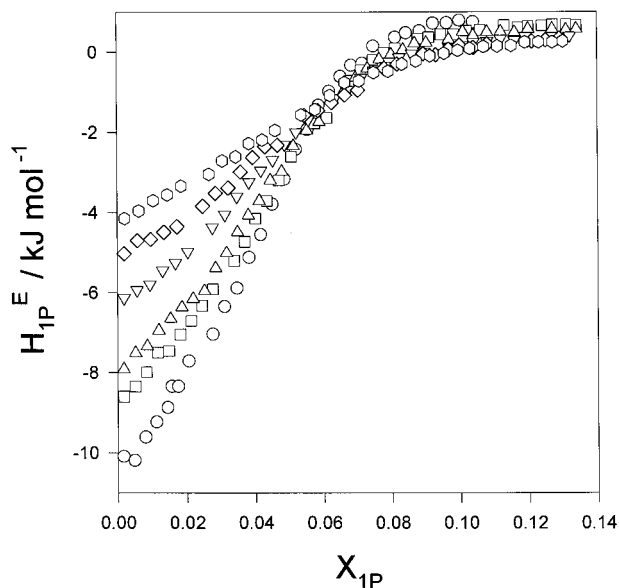
Figure 3. Excess partial molar enthalpy of 1-propanol, H_{1P}^E, against mole fraction of 1-propanol, x_{1P}, (○) $x_U^0 = 0.0$, (□) $x_U^0 = 0.03040$, (△) $x_U^0 = 0.04985$, (▽) $x_U^0 = 0.1020$, (◇) $x_U^0 = 0.1501$, (⬡) $x_U^0 = 0.2035$.

TABLE 4: Values of TS_{1P}^E/kJ mol^{-1}

	x_U			
x_{1P}	0	0.05	0.10	0.15
0.02	−14.20	−12.36	−11.09	−10.32
0.025	−13.43	−11.74	−10.59	−9.86
0.03	−12.67	−11.07	−10.06	−9.37
0.035	−11.58	−10.42	−9.46	−8.86
0.04	−10.59	−9.55	−8.84	−8.35
0.045	−9.45	−8.77	−8.25	−7.87
0.05	−8.31	−8.03	−7.69	−7.44
0.055	−7.28	−7.38	−7.18	−7.05
0.06	−6.50	−6.77	−6.72	−6.67
0.07	−5.35	−5.76	−5.86	−5.99
0.08	−4.55	−4.96	−5.18	−5.37
0.09	−3.96	−4.40	−4.67	−4.88
0.1	−3.54	−4.01	−4.26	
0.11	−3.25	−3.71		

H_2O,[21] from which μ_W^E and hence μ_U^E were calculated in the same way as above. These results are plotted in Figure 2a. The original authors of ref 18 used a fifth-order polynomial within the range $x_U < 0.1$. Forcing the same polynomial beyond the stated limit, i.e., $x_U > 0.1$, brings about a wide deviation as shown in Figure 2a. Despite this, the values of μ_U^E calculated directly from the raw isopiestic data produced a reasonable match to our values from vapor pressure measurement. We conclude, therefore, that the discrepancy came from an artifact associated with curve-fittings used in the literature cited and
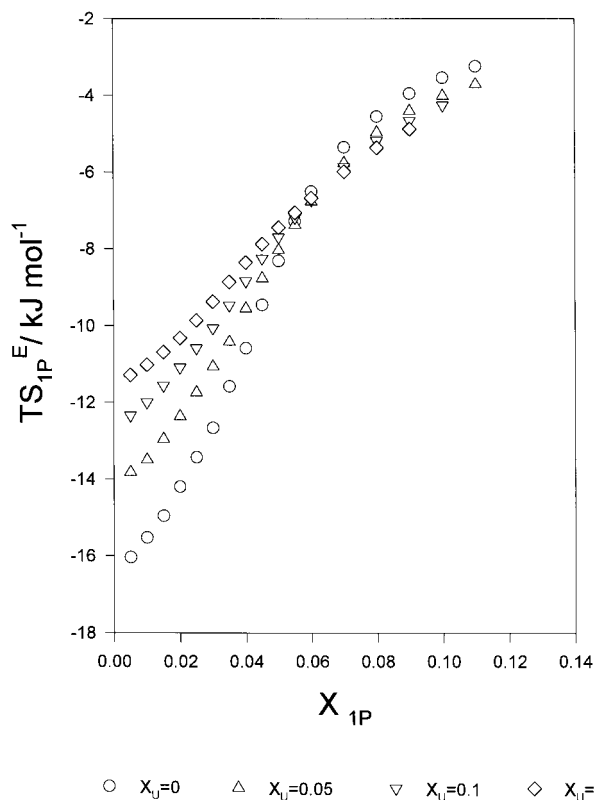
NaCl−H_2O[18] were converted to the equilibrium H_2O vapor pressures using the compiled thermodynamic data for NaCl−

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Figure 4. Excess partial molar entropy of 1-propanol, TS_{1P}^E, against mole fraction of 1-propanol, x_{1P} at 25.00 °C: (○) $x_U = 0.0$, (△) $x_U = 0.05$, (▽) $x_U = 0.1$, (◇) $x_U = 0.15$.

that our values of μ_U^E or those recalculated directly using the H_2O vapor pressure data from isopiestic measurements are likely to be closer to reality. Thus, Figure 1a indicates that for binary aqueous 1-propanol, μ_{1P}^E decreases on increasing x_{1P}. This indicates the interaction in terms of chemical potential, μ_{ii}^E (i = 1-propanol), is negative, a net attraction in chemical potential—the "hydrophobic attraction".

Figures 1b and 2b suggest the effect of a third component on the excess chemical potentials is small, which has been noted before for this ternary aqueous solution.[17] However, in terms of the excess partial molar enthalpy and entropy of 1-propanol (Figures 3 and 4) the effects of urea are quite apparent. This is a manifestation of enthalpy−entropy compensation prevalent particularly in aqueous solutions.[22]

In binary 1-propanol−H_2O, the excess partial molar enthalpy[16] (Figure 3), entropy (Figure 4), and the partial molar volume data calculated using the density data[23] indicate that 1-propanol behaves as a typical hydrophobic solute as 2-butoxyethanol, the detailed mixing schemes of which have been extensively studied and reviewed earlier.[8,9] Thus, in the most water-rich region, 1-propanol enhances the hydrogen bond network of H_2O in its immediate vicinity, i.e., the "iceberg formation". This was supported by a large enthalpy gain (−11 kJ mol⁻¹, Figure 3 for $x_U = 0$) and a larger entropy loss (−16 kJ mol⁻¹ as TS_{1P}^E, Figure 4 for $x_U = 0$) at infinite dilution, $x_{1P} = 0$. As the mole fraction of 1-propanol, x_{1P}, increases, both H_{1P}^E and TS_{1P}^E become progressively less negative. Thus, 1-propanols are interacting with each other, even at this low concentration. Hence the interaction must be operative via the hydrogen bond network of H_2O that is highly fluctuating.[24] The interaction functions, H_{ii}^E and TS_{ii}^E (i = 1-propanol) are both positive, indicating that the interaction is repulsive in enthalpy but attractive entropy wise (Figure 5). The latter entropy
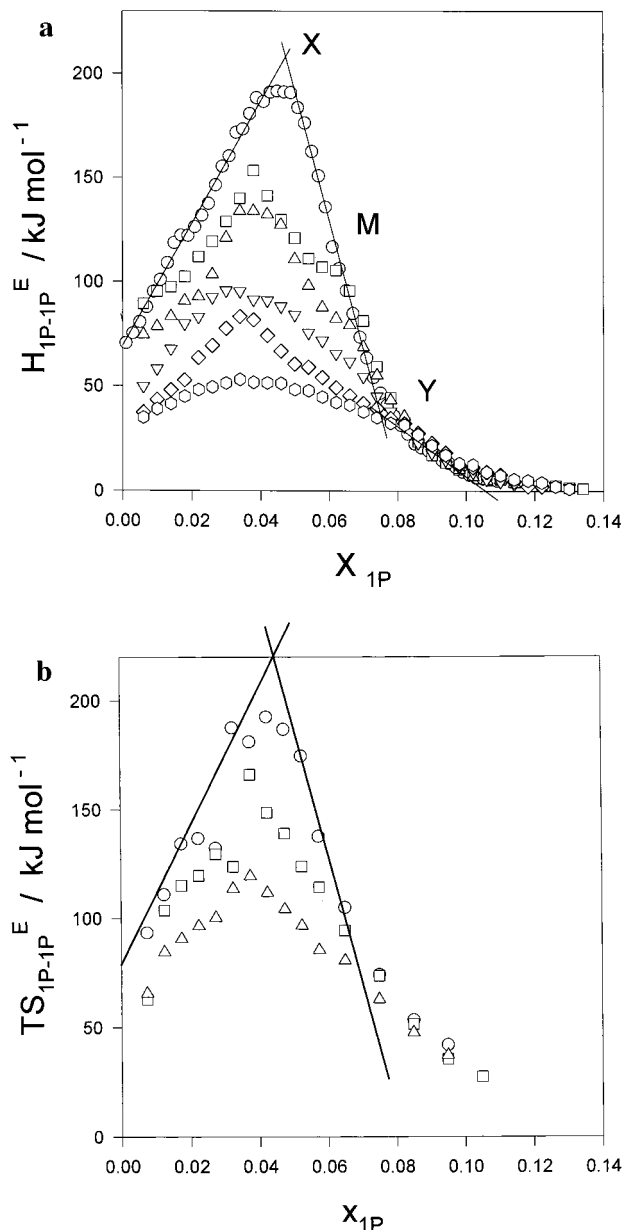

Figure 5. Interaction between 1-propanol and 1-propanol: (a) the enthalpic interaction function, H_{1P-1P}^E, against mole fraction of 1-propanol, x_{1P}, (○) $x_U^0 = 0.0$, (□) $x_U^0 = 0.03040$, (△) $x_U^0 = 0.04985$, (▽) $x_U^0 = 0.1020$, (◇) $x_U^0 = 0.1501$, (⬠) $x_U^0 = 0.2035$; (b) the entropic interaction function, TS_{1P-1P}^E against x_{1P}, (○) $x_U = 0.015$, (□) $x_U = 0.040$, (△) $x_U = 0.125$.

attraction, however, is stronger than the enthalpy repulsion, resulting in the net attraction in terms of excess chemical potential, as mentioned above.

The excess partial molar volume of the solute, V_i^E, shows an initial decrease on increasing its composition, at the same time the excess partial molar volume of H_2O, V_W^E, increases slightly.[25] While the latter increase is consistent with the "iceberg formation", the degree of increase is about $1/100$ of what would be expected if the entire bulk of H_2O eventually becomes all icelike.[25] Furthermore, the initial decrease in V_i^E is understood as being due to a decrease in bulkiness, or a decrease in the hydrogen bond probability, of the portion of H_2O away from the existing solutes, where a new coming solute settles in.[8,9,25] From this, and other evidence reviewed earlier,[8,9] we concluded that while the hydrogen bond probability of H_2O is enhanced in the immediate vicinity of solute, in the bulk H_2O away from

the solute the hydrogen bond probability decreases progressively. We call this mode of mixing "Mixing scheme I".

The interaction function, H_{ii}^E (a third derivative of G) increases sharply in mixing scheme I to point X, and thereupon it drops dramatically in a narrow composition range to point Y, with the nominal midpoint M (Figure 5). This must be an indication of a qualitative change in mixing scheme, or the transition of mixing scheme. Beyond point Y onward, H_{ii}^E remains small. This region coincides with the region of phase separation, typically for aqueous 2-butoxyethanol.[8,9] X-ray[26−29] and light[30,31] scattering works indicate that the solution in this region consists of clusters of some 10 Å in diameter, reminiscent to the supercritical region. Hence, we concluded that the solution in this region, beyond point Y, consists of two kinds of clusters, rich in each component, preparing for phase separation at a right temperature. Hence, the hydrogen bond connectivity originally present in liquid H_2O is now completely lost. We call this "Mixing scheme II".

At the boundary region between mixing schemes I and II, other third derivatives of G show similar anomalous behaviors as H_{ii}^E and S_{ii}^E.[8,9] As temperature increases, the locus of boundary moves toward the zero mole fraction of solute and seems to extrapolate to about 80−85 °C. An estimate[32] indicates that for pure liquid H_2O the hydrogen bond probability decreases to about 0.39 at about 80 °C, which is the bond percolation threshold of ice Ih structure.[24,32] Namely, the hydrogen bond network in H_2O is no longer connected throughout of the entire bulk of H_2O above 80 °C. These two pieces of information seem to indicate to us that in mixing scheme I the hydrogen bond connectivity is still retained though the hydrogen bond probability decreases in bulk H_2O away from solute. Hence, the transition from mixing scheme I to II can be rephrased as the loss of percolation nature originally present in liquid H_2O.

The liquid−solid phase diagram for aqueous 2-butoxyethanol[33] indicates that the boundary between mixing schemes I and II ends on lowering temperature at the incongruent melting point of an addition compound (clathrate). Thus, in mixing scheme I, the solution is preparing for forming the addition compound on freezing. When the solution is cooled in mixing scheme I, pure ice separates out at a temperature below 0 °C, leaving the solution more concentrated toward the addition compound. A portion of bulk H_2O away from solutes freezes out as ice at a progressively lower temperature−freezing point depression. This could be understood at the molecular level that the hydrogen bond probability is progressively lower than that for pure H_2O, and hence a progressively lower temperature is required to freeze out such a portion as ice Ih.

We now turn to the present ternary 1-propanol−urea−H_2O. As urea content increases, the absolute values of H_{1P}^E and TS_{1P}^E are reduced in an almost equal manner (Figures 3 and 4). Hence, the resulting chemical potential of 1-propanol remains almost unchanged upon addition of urea. The interaction functions between 1-propanol−1-propanol are shown in Figure 5. While the entropic interaction, TS_{1P-1P}^E, has some scatter (Figure 5b), the enthalpic interaction function, H_{1P-1P}^E (Figure 5a), shows the same kind of anomalous behavior as for the binary 1-propanol−H_2O.[16] Namely, in mixing scheme I, H_{1P-1P}^E increases sharply and at point X the transition to mixing scheme II begins to occur and completes at point Y. Beyond point Y, the solution is in mixing scheme II. The midpoint between X and Y is the nominal boundary value, M. While the absolute value of H_{1P-1P}^E decreases on increasing urea content, suggesting that urea weakens the water-mediated 1-propanol−1-propanol interactions, the loci of M seem to remain unchanged.
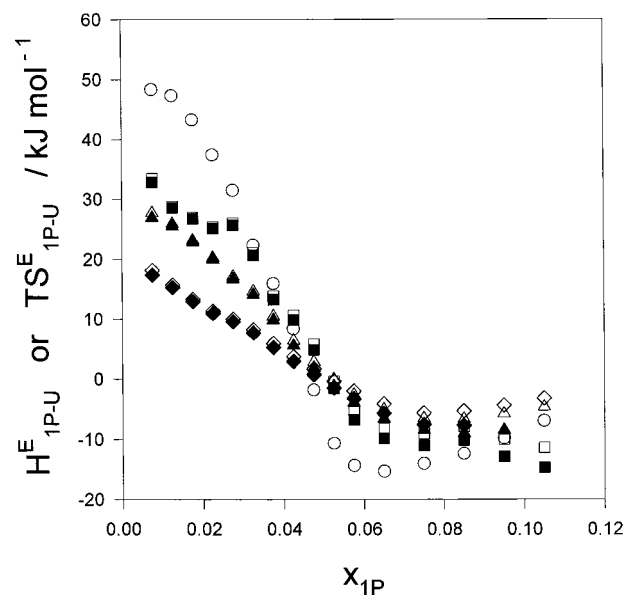

Figure 6. Interaction between 1-propanol and urea. The enthalpic interaction functions, H_{1P-U}^E, are shown by open symbols, and the entropic interaction functions, TS_{1P-U}^E, are shown by filled symbols. (○) $x_U = 0.015$, (□) $x_U = 0.040$, (△) $x_U = 0.075$, (◇) $x_U = 0.125$.
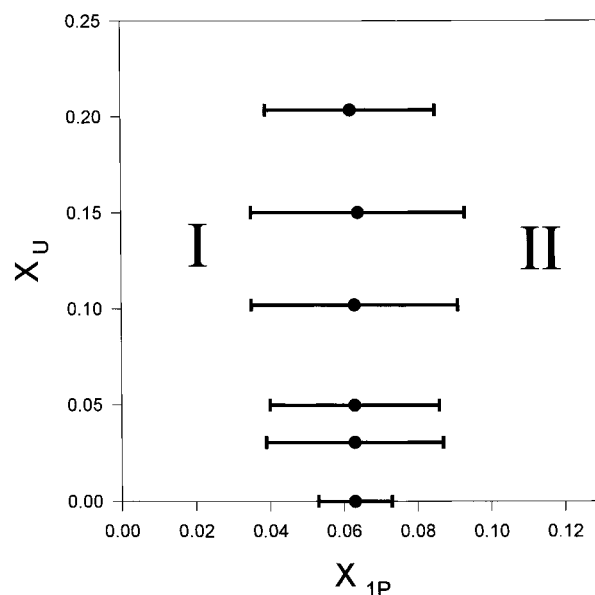

Figure 7. Loci of transition of mixing scheme from I to II.

The 1-propanol−urea interactions (Figure 6) also decrease on addition of urea. In addition, the curvature changes suddenly at about the boundary between I and II, $x_{1P} = 0.07$, and this loci do not change on increasing urea content. All of these findings seem to suggest that urea molecules lock into the hydrogen bond network of H_2O by replacing H_2O molecules, for urea possesses proton donors and acceptors within a molecule. However, N−C≡O, acting like O in the hydrogen bond network, reduces the degree of fluctuation which would have otherwise existed in H_2O alone. If the H_2O-mediated interaction between 1-propanol molecules requires the highly fluctuating hydrogen bond network, then it is feasible that H_{1P-1P}^E would be reduced as urea locks into the hydrogen bond network of H_2O and reduces the degree of fluctuation. As for the transition from mixing scheme I to II, the loci of x_{1P} remain the same independent of the urea content, since the transition occurs when the hydrogen bond connectivity (percolation)[24,32] breaks down (Figure 7). Namely, urea seems to keep the connectivity of the hydrogen

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bond intact but reduces a wide fluctuation in the strength of hydrogen bond that is characteristic to pure H_2O and that is responsible for the H_2O-mediated solute−solute interactions in the water-rich region.

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