

# Excess Partial Molar Enthalpy of 1-Propanol in 1-Propanol–NaCl–H<sub>2</sub>O at 25 °C: The Effect of NaCl on Molecular Organization of H<sub>2</sub>O<sup>†</sup>

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Excess partial molar enthalpies of 1-propanol,  $H_{1P}^E$ , in 1-propanol–NaCl–H<sub>2</sub>O were measured directly, accurately, and in small increments in mole fraction of 1-propanol,  $x_{1P}$ , at 25 °C in the range  $x_{NaCl} < 0.04$ .  $x_{NaCl}$  is the mole fraction of NaCl. The enthalpic interaction function,  $H_{1P-1P}^E$ , between 1-propanol molecules was then evaluated.  $H_{1P-1P}^E$  is a convenient, model-free measure for the intermolecular interaction in terms of enthalpy. The behavior of these thermodynamic quantities was compared with that of the binary 1-propanol–H<sub>2</sub>O. Based on the knowledge accumulated in our laboratory on the binary aqueous 1-propanol, the effect of NaCl on H<sub>2</sub>O became apparent. Our tentative conclusions are that (1) a NaCl molecule “binds” to seven or eight molecules of H<sub>2</sub>O on dissolving into H<sub>2</sub>O, and (2) the remainder of bulk H<sub>2</sub>O away from solute NaCl is not affected and stays almost the same as pure H<sub>2</sub>O.

## 1. Introduction

Studies on aqueous electrolytes have made remarkable progress since a pivotal paper by K. S. Pitzer.<sup>1</sup> For aqueous NaCl, the experimental data are comprehensively compiled on the basis of Pitzer-type equations.<sup>2,3</sup> While these equations have helped advance the understanding of aqueous NaCl tremendously, in this paper we study the effect of NaCl on H<sub>2</sub>O from a different approach.

We have been learning about aqueous solutions of nonelectrolytes by the aides of the second and third derivatives of Gibbs energy,  $G$ .<sup>4–7</sup> As a result, a general view emerged as the effect of a hydrophobic solute on H<sub>2</sub>O. Briefly, (1) the “iceberg formation” in the immediate vicinity of solute<sup>8–10</sup> is confirmed;<sup>4,5</sup> (2) the iceberg portion is rigid enough not to make a contribution to volume and entropy fluctuations;<sup>6,7,11</sup> (3) the iceberg formation causes reduction in hydrogen bond probability of bulk H<sub>2</sub>O away from solutes and hence the degree of fluctuation decreases progressively as solute increases;<sup>4–7,12,13</sup> (4) iceberg clad solutes interact with each other via fluctuating bulk H<sub>2</sub>O;<sup>4,5,7,11</sup> (5) the interaction is repulsive in terms of enthalpy but attractive entropically;<sup>4,5</sup> (6) the entropic attraction is stronger than the enthalpic repulsion, and hence the net interaction is attractive in terms of chemical potential;<sup>4,5</sup> (7) up to a certain threshold value of solute composition, the hydrogen bond probability of bulk H<sub>2</sub>O is still high enough for hydrogen bond percolation, i.e., the hydrogen bond network is connected throughout the entire bulk of H<sub>2</sub>O;<sup>4,5</sup> (8) the threshold value depends on the size of hydrophobic moiety, the larger its size the smaller the threshold value;<sup>14</sup> (9) above this threshold, bulk H<sub>2</sub>O loses its percolation nature and the solution consists of two kinds of clusters rich in solute and H<sub>2</sub>O, respectively. Below

the threshold, the solution is preparing for formation of an addition compound of  $A(H_2O)_m$  type on freezing.<sup>4,5</sup> We call this mode of mixing “mixing scheme I”. Above the threshold, mixing scheme II is operative, in which the solution is preparing for liquid–liquid phase separation. The transition from mixing scheme I to II is associated with anomalies in the third derivatives of  $G$ .

The same methodology was recently applied in studying ternary systems.<sup>15–18</sup> It was generally found that two solutes work together in modifying the molecular organization of H<sub>2</sub>O in an additive, cooperative manner in mixing scheme I. This finding led us to a plan in which a typical hydrophobic solute, 1-propanol, for example, is chosen and its thermodynamic behavior is studied in aqueous solution with the presence of a third component, to learn the effect of the latter on H<sub>2</sub>O. This is particularly convenient for solid samples, for determination of their partial molar enthalpies is much more problematic than for liquid counterparts. Such a study on 1-propanol–urea–H<sub>2</sub>O met some success in understanding the unique effect of urea on H<sub>2</sub>O.<sup>19</sup> It was suggested that urea molecules lock into the hydrogen bond network of H<sub>2</sub>O, keep the hydrogen bond connectivity intact, but reduce the degree of fluctuation that is characteristic of liquid H<sub>2</sub>O.

The present study is a natural extension for NaCl. However, an additional complication due to ionic dissociation of NaCl is not addressed in this work. We measured the excess partial molar enthalpy of 1-propanol,  $H_{1P}^E$ , with various amounts of NaCl as the third component. We attempt at learning the effect of NaCl on H<sub>2</sub>O by observing the behavior of these thermodynamic quantities.

## 2. Experimental Section

ACS reagent grade NaCl (99+%) was obtained from Aldrich. It was heated in an oven at  $150 \pm 5$  °C for several days and stored in a desiccator. 1-Propanol (99.5+%, HPLC grade) from

<sup>†</sup> This paper is dedicated to the late Professor K. S. Pitzer.

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**TABLE 1: Excess Partial Molar Enthalpies of 1-Propanol,  $H_{1P}^E$ , at 25.00 °C for Given  $x_{NaCl}^0$  <sup>a</sup>**

$x_{1P}$	$H_{1P}^E$ (kJ mol <sup>-1</sup> )	$x_{1P}$	$H_{1P}^E$ (kJ mol <sup>-1</sup> )	$x_{1P}$	$H_{1P}^E$ (kJ mol <sup>-1</sup> )
$x_{NaCl}^0 = 0.0007309$					
0.00165	-9.99	0.00493	-9.73	0.00820	-9.47
0.01144	-9.24	0.01467	-8.73	0.01787	-8.48
0.02105	-7.65	0.02421	-7.42	0.02735	-6.93
0.01750	-8.45	0.02090	-8.04	0.02428	-7.49
0.02763	-7.01	0.03096	-6.36	0.03426	-5.86
0.03755	-5.23	0.04081	-4.73	0.04405	-4.06
0.04726	-3.35	0.05046	-2.63	0.05388	-2.13
0.05753	-1.53	0.06115	-1.24		
$x_{NaCl}^0 = 0.01092$					
0.00153	-9.06	0.00459	-8.89	0.00762	-8.53
0.01064	-8.27	0.01364	-7.95	0.01663	-7.67
0.01959	-7.13	0.02267	-6.68	0.02588	-6.08
0.02906	-5.61	0.03223	-4.90	0.03537	-4.34
0.03849	-3.67	0.04159	-3.16	0.04483	-2.47
0.04821	-1.82	0.05156	-1.29	0.05488	-0.87
0.05819	-0.62	0.06147	-0.18	0.06473	0.02
$x_{NaCl}^0 = 0.01962$					
0.00165	-8.41	0.00494	-8.26	0.00820	-7.82
0.01145	-7.56	0.01467	-7.23	0.01788	-6.73
0.02106	-6.32	0.02422	-5.81	0.02736	-5.27
0.03048	-4.71	0.03358	-4.10	0.03666	-3.44
0.03973	-2.80	0.04305	-2.13	0.05020	-0.96
0.05373	-0.52	0.05723	-0.24	0.06071	-0.01
0.06417	0.20	0.06760	0.27	0.07100	0.37
0.07438	0.43	0.07774	0.45	0.08513	0.54
0.09266	0.59	0.10007	0.63		
$x_{NaCl}^0 = 0.03507$					
0.00486	-6.98	0.00807	-6.79	0.01269	-6.47
0.01444	-6.07	0.01760	-5.68	0.02073	-5.18
0.02694	-4.06	0.03001	-3.43	0.03307	-2.74
0.03610	-2.10	0.03912	-1.50	0.04510	-0.58
0.04832	-0.31	0.05177	-0.12	0.05521	0.44
$x_{NaCl}^0 = 0.04983^b$					
0.00489	-5.97	0.00812	-5.65	0.01133	-5.28
0.01769	-4.52	0.02084	-3.92	0.02397	-3.15
0.02707	-1.59	0.03016	-0.74		

<sup>a</sup> The uncertainty in  $H_{1P}^E$  is  $\pm 0.07$  kJ mol<sup>-1</sup>. <sup>b</sup> The last set of data were not plotted in Figure 1.

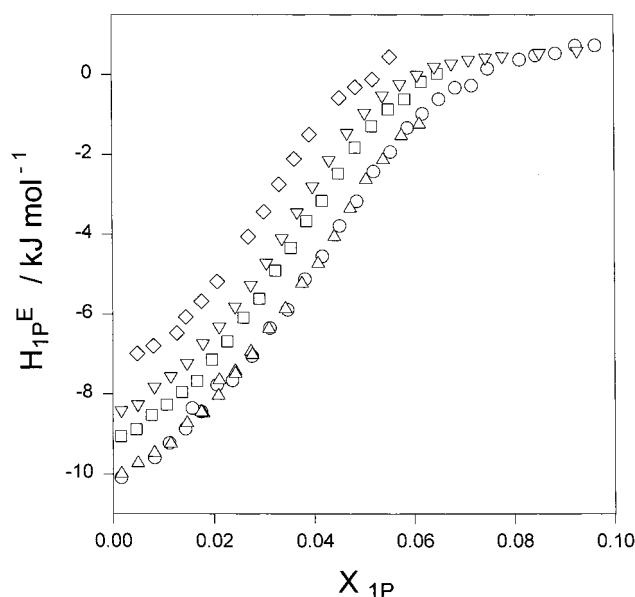
Aldrich-Sigma was opened in a dry nitrogen atmosphere and subsequently stored over molecular sieve 3A. H<sub>2</sub>O is triply distilled; last two times in a Pyrex glass still immediately before use.

Excess partial molar enthalpies were determined by an LKB Bromma 8700 titration calorimeter using a buret method.<sup>20</sup>

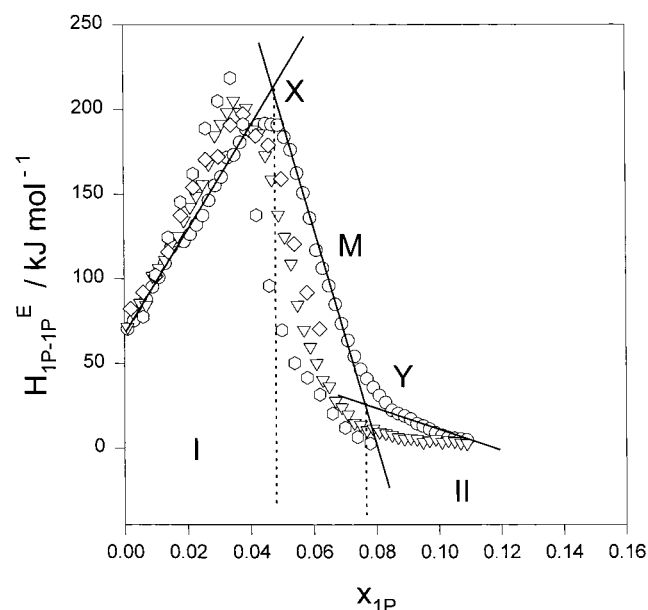
### 3. Results and Discussion

The excess partial molar enthalpies of 1-propanol,  $H_{1P}^E$ , at a given initial mole fraction of NaCl,  $x_{NaCl}^0$ , are listed in Table 1 and plotted in Figure 1. The uncertainty is  $\pm 0.07$  kJ mol<sup>-1</sup>. For a higher composition of NaCl,  $x_{NaCl} > 0.04$ , there was a difficulty in determining  $H_{1P}^E$  due to slowing down in thermal equilibration, particularly near the phase separation. We note in Figure 1 that, on addition of NaCl,  $H_{1P}^E$  generally shifts upward but the slopes of  $H_{1P}^E$  vs  $x_{1P}$  appear to remain almost constant, if not increasing slightly. To see this more clearly, we evaluate enthalpic interaction functions. Smooth curves are drawn through all the data points of  $H_{1P}^E$ , the values of  $H_{1P}^E$  were read off at the interval  $\delta x_{1P} = 0.002$ , and the enthalpic interaction function between 1-propanols<sup>4,5</sup> was calculated as,

$$H_{1P-1P}^E = N(\partial H_{1P}^E / \partial n_{1P})_{n_{W,mNaCl}} \approx (1 - x_{1P})(\delta H_{1P}^E / \delta x_{1P}) \quad (1)$$

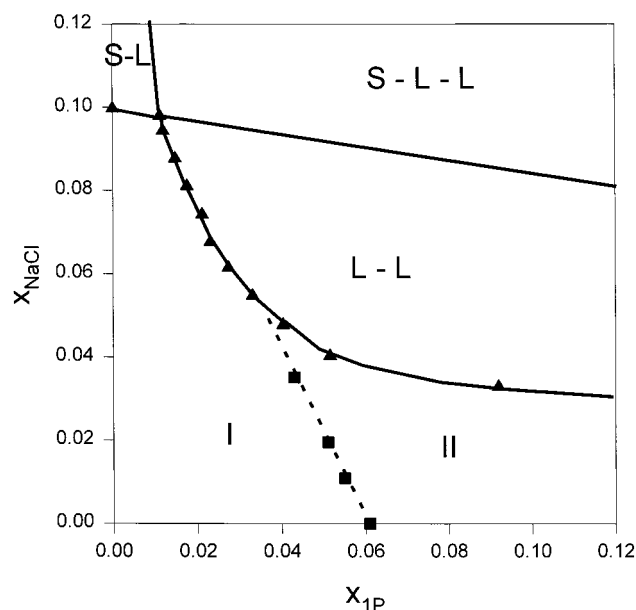


**Figure 1.** Excess partial molar enthalpy of 1-propanol,  $H_{1P}^E$ , at 25.00 °C for given  $x_{NaCl}^0$ : (○),  $x_{NaCl}^0 = 0.0$ , from ref 14; (△),  $x_{NaCl}^0 = 0.0007309$ ; (□),  $x_{NaCl}^0 = 0.01092$ ; (▽),  $x_{NaCl}^0 = 0.01962$ ; (◇),  $x_{NaCl}^0 = 0.03503$ .



**Figure 2.** Enthalpic interaction,  $H_{1P-1P}^E$ , vs  $x_{1P}$  at 25.00 °C for given values of  $x_{NaCl}^0$ : (○),  $x_{NaCl}^0 = 0$ , from ref 14; (◇),  $x_{NaCl}^0 = 0.01092$ ; (▽),  $x_{NaCl}^0 = 0.01962$ ; (○),  $x_{NaCl}^0 = 0.03503$ .

where  $\delta H_{1P}^E$  is the difference in the values of  $H_{1P}^E$  at the interval  $\delta x_{1P} = 0.004$ . Through this process, the uncertainty increases and is estimated as  $\pm 10$  kJ mol<sup>-1</sup>. They are plotted in Figure 2. The enthalpic interaction function, eq 1, is a convenient way to evaluate intermolecular interaction in terms of enthalpy.<sup>4,5</sup> Namely, if  $H_{1P-1P}^E$  is negative, it implies that an infinitesimal increase in  $n_{1P}$  results in more favorable enthalpic situation of the existing 1-propanol. Hence, we say the interaction between 1-propanol molecules is attractive in terms of enthalpy. If positive, then repulsive. The same argument is applicable for chemical potential and entropy, except that the sign is reversed for entropy. As argued earlier,<sup>4,5</sup> an anomalous behavior of  $H_{1P-1P}^E$  shown in Figure 2 is indicative of the transition of mixing scheme from I to II. Point X is the onset of the transition and point Y is the end point. The midpoint M is the nominal



**Figure 3.** Phase and mixing scheme diagram of 1-propanol–NaCl–H<sub>2</sub>O at 25 °C: (—) phase boundary; (---) mixing scheme boundary; (▲) from ref 26; (■) this work.

transition point. Supporting evidence for this argument will not be repeated here. They are reviewed earlier<sup>4,5</sup> and complemented recently.<sup>14</sup>

Figure 2 shows that the mixing scheme boundary (X, M, Y) moves progressively toward smaller values of  $x_{1P}$  on increasing  $x_{NaCl}$ . As shown in Figure 3, the locus of point M is linear in the  $x_{NaCl}$  vs  $x_{1P}$  field. Figure 2 also shows that the values of  $H_{1P-1P}^E$  remain almost the same at  $x_{1P} = 0$  and at point X within the estimated uncertainty; if any increase at all, it is very close to the limit of uncertainty. The linear increase in  $H_{1P-1P}^E$  follows the same route from  $x_{1P} = 0$  to point X, regardless of the amount of NaCl added. The main effect of NaCl is to push point X and hence the mixing scheme boundary to the left on Figure 2. These findings are in direct contrast to the case of urea, in which point M stayed at the same value of  $x_{1P}$  and  $H_{1P-1P}^E$  decreased progressively on addition of urea.<sup>19</sup> We suggest for the present case that the hydrogen bond network of bulk H<sub>2</sub>O away from NaCl ions is not affected and it accommodates 1-propanol in the same way as in pure H<sub>2</sub>O. The predominant effect of NaCl is to limit the availability of H<sub>2</sub>O for incoming 1-propanol to drive the system to mixing scheme II. NaCl is a well-known example of a structure breaker when introduced in H<sub>2</sub>O.<sup>21</sup> In the immediate vicinity of Na<sup>+</sup> and Cl<sup>−</sup>, therefore, the hydrogen bond network of H<sub>2</sub>O may be broken to give way to direct bonds to ions. However, we suggest that the bulk H<sub>2</sub>O away from NaCl remains almost like pure H<sub>2</sub>O. This is not quite conclusive in the absence of other third derivative data including the entropy analogue of eq 1. Nevertheless, if we assume this is true, the numerical information given in Figure 2 will provide a way to estimate how many H<sub>2</sub>O molecules are bound to NaCl. For the increase in  $x_{NaCl}^0$  from 0 to 0.035, point M moved from  $x_{1P} = 0.062$  to 0.044. It follows<sup>22</sup> then that seven or eight molecules of H<sub>2</sub>O are bound to a molecule of NaCl and are made unavailable for 1-propanol to change the mixing scheme from I to II. This number, 7 or 8, is interesting in the light of recent studies of gas-phase clusters of X<sup>−</sup>(H<sub>2</sub>O)<sub>m</sub> type (X<sup>−</sup> = Cl<sup>−</sup>, Br<sup>−</sup>, and I<sup>−</sup>) by predissociation vibrational spectroscopy.<sup>23,24</sup> When  $m = 4$  or 5, the spectra became almost the same as that of liquid H<sub>2</sub>O. To our knowledge, there is no similar study on Na<sup>+</sup>(H<sub>2</sub>O)<sub>m</sub>, however.

Figure 3 also shows the phase boundary.<sup>25,26</sup> Our spot checks by turbidity titration were found satisfactory within  $\pm 0.001$  in  $x_{1P}$ . Thus, the single phase domain is now divided into two regions I and II, where the mixing scheme is qualitatively different. Below  $x_{NaCl} < 0.04$ , Figure 3 is consistent with our earlier understanding that the solution in mixing scheme II consists of two kinds of clusters rich in 1-propanol and H<sub>2</sub>O, respectively. Namely, the solution in region II is preparing for phase separation at a higher value of  $x_{NaCl}$ . However, the mixing scheme boundary, the broken line in Figure 3, seems to merge into the phase boundary at about  $x_{NaCl} \approx 0.06$ . No mixing scheme II is present for  $x_{NaCl} > 0.06$ ? Does the mixing scheme boundary bend toward smaller values of  $x_{1P}$  as  $x_{NaCl}$  increases?

Clearly, further studies are required to cover the region  $x_{NaCl} > 0.04$ , to resolve unsettled questions, and to deepen insight into the molecular nature of aqueous alkali halides. First of all, the degree of ionic dissociation of NaCl in aqueous 1-propanol must be determined and mapped in Figure 3. Furthermore, other second derivative data, partial molar entropy, partial molar volume, heat capacity, thermal expansivity, and compressibility are necessary. Such investigation is underway.

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- (22) At point M for  $x_{NaCl}^0 = 0$ ,  $x_{1P} = 0.062$ . This translates to the ratio of 15 H<sub>2</sub>O/1 1-propanol. For  $x_{NaCl}^0 = 0.035$ , point M occurs at  $x_{1P} = 0.044$ . This corresponds to the molecular ratio, 21 H<sub>2</sub>O/1 1-propanol/0.8 NaCl. Assuming that the same ratio of H<sub>2</sub>O vs 1-propanol is required to drive the system to mixing scheme II, the difference, (21 − 15 =), 6 H<sub>2</sub>O molecules are not available for 1-propanol due to the presence of 0.8 NaCl molecules. Hence 6/0.8 = 7.5 molecules of H<sub>2</sub>O are bound to a NaCl molecule and made unavailable to interact with 1-propanol.
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