# Preferential Solvation of a Dipolar Solute in Mixed Binary Solvent. A Study by UV–Visible Spectroscopy

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The preferential solvation in mixed binary solvent, e.g., ethanol + acetonitrile, ethanol + propionitrile, and ethanol + butyronitrile, has been studied by monitoring the solvatochromic charge-transfer band of N-alkylpyridinium iodide. It appears that alcohols are preferred over the nitriles. A model for describing the preferential solvation of a dipolar solute in binary solvent mixture has been developed and discussed in relation to other existing approaches. The role of (a) solvent-solvent interaction and (b) difference in size of the component solvent molecules in determining the preferential solvation has also been discussed.

#### Introduction

The phenomenon of solvation is of paramount importance in solution chemistry. This involves the modification of physicochemical properties of a solute due to its interaction with the solvent molecules in the immediate environment or the cybotactic region. The molecular approach to the problem is fraught with the inherent difficulty that only a little is known about the nature of the cybotactic region. The use of binary solvent mixtures adds further dimension to the problem. Here, due to the difference in the specificities of interaction of solute with the component solvents, the composition of the solvents in the immediate vicinity of the solute may be different from that in the bulk. This phenomenon, commonly known as preferential solvation (PS), has been found to be important for explaining spectroscopic, equilibrium, and kinetic data in mixed binary solvents.<sup>1-5</sup> Recently, we have observed that N-alkylpyridinium iodides (NAPI) provide a suitable indicator for the study of PS in mixed binary solvent using UV-visible spectroscopy.<sup>6</sup> The position of the longest wavelength band of NPAI which arises due to a charge-transfer (CT) process within the contact ion pair species has been shown to vary nonlinearly with the solvent composition. The extent of PS,  $\delta_{is}$ , as measured by the equation  $\delta_{is} = x_i^L - x_i$ , where  $x_i^L$  and  $x_i$  denote the local and the bulk mole fraction, respectively, can be obtained from experimental data.

Several theoretical approaches to the problem of PS are found in the literature. Among these are the stepwise solvent exchange (SSE) model of Covington et al.,<sup>7</sup> quasi-lattice quasi-chemical (QLQC) theory of Marcus,<sup>8</sup> Kirkwood-Buff (KB) formalism,<sup>9,10</sup> the thermodynamic model of Frankel et al.,<sup>11</sup> the competitive preferential solvation (COPS) theory of Nagy,<sup>12</sup> and the statistical mechanical coordinated cluster theory (CCT) of Blander et al.<sup>13</sup> The interrelation between the SSE model and CCT has recently been discussed by Covington et al.<sup>14</sup> and a comparison of the KB

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and QLQC approaches has been made by Marcus.<sup>15</sup> In this paper we shall address the problem of PS. A suitable model has been developed to describe PS as a function of solvent composition and temperature. The interrelation of this model with other existing models will be discussed. Finally, some results on PS of NAPI in ethanol + nitrile binary systems as studied by UV-vis spectroscopy will be discussed. In this work we have studied the PS of N-ethyl-4-cyanopyridinium iodide (4CN-NEPI) in mixed binary solvents containing ethanol. Acetonitrile, propionitrile, and butyronitrile have been used as cosolvents.

#### **Experimental Section**

Materials. 4CN-NEPI was prepared by quaternizing 4cyanopyridine (Koch Light) with ethyl iodide in acetone medium in the dark. The product was purified by repeated crystallization from pure ethanol.<sup>21</sup> Solvents were purified by standard procedures.<sup>22</sup> Commercial "dry ethanol" was refluxed for several hours with calcium oxide and then distilled. All the nitriles were of GR quality (Merck) and were treated with fused calcium chloride to remove water. Traces of moisture and other oxidizable impurities in the solvents were eliminated by distillation with calcium hydride immediately prior to the experiment.

Spectroscopic measurements were taken in a Shimadzu UV 160-A recording spectrophotometer provided with a peak detection algorithm. The concentration of the solute varied from  $10^{-3}$  to  $10^{-4}$  mol dm<sup>-3</sup> depending on the solvent composition.

#### The Model

The present model is very similar to the simple binding site model developed by Katriel and Ratner<sup>16</sup> to describe the behavior and optical response of binuclear mixed valence metal complexes in mixed binary solvents. In a dilute solution where solute-solute interactions are negligible we may consider a solute to be surrounded by the solvent only. Let us consider a volume V of solution containing one molecule of the solute (S). The solvent molecules around the solute may be thought of as distributed between two distinctly different regions. The one in the immediate vicinity of the solute with a volume  $V_c$ , housing a definite number (say z) of solvents. The rest of the volume may be defined as the "bulk" solvent. In mixed binary solvent let us suppose that  $N_i$  and  $N_i^0$ are the number of molecules of the *i*th component solvent in the local vicinity and in the bulk, respectively. Thus we have

$$N_1 + N_2 = z \tag{1}$$

$$N_1 + N_1^0 = N_1^{\mathrm{T}} \tag{2}$$

$$N_2 + N_2^0 = N_2^{\rm T} \tag{3}$$

where  $N_i^{T}$  is the total number of molecules of the *i*th solvent

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component in the volume V and eqs 2 and 3 represent particle conservation. Let us now define the interaction parameters. The interaction of the solute with the solvent molecule of the *i*th solvent component is denoted by  $\epsilon_{si}$ . The solvent-solvent interactions in the region  $V_c$  and in the bulk are represented by the parameters  $\epsilon_{ij}$  and  $\epsilon_{ij}^0$ , respectively. In general  $\epsilon$ 's are negative quantities describing the relative attractive interactions.

The free energy functional for the system under study may be written as

$$G = [N_1\epsilon_{s1} + N_2\epsilon_{s2}] + [N_1^2\epsilon_{11}/2 + N_2^2\epsilon_{22}/2 + N_1N_2\epsilon_{12}] + [(N_1^0)^2\epsilon_{11}^0/2 + (N_2^0)^2\epsilon_{22}^0/2 + N_1^0N_2^0\epsilon_{12}^0] - kT[z \ln z - N_1 \ln N_1 - N_2 \ln N_2 + (N_1^0 + N_2^0) \ln (N_1^0 + N_2^0) - N_1^0 \ln N_1^0 - N_2^0 \ln N_2^0] - N_1^0 \ln N_1^0 - N_2^0 \ln N_2^0]$$
(4)

The first set of terms indicate the interaction energy terms due to solute-solvent interaction. The second and third set of terms indicate the solvent-solvent interaction in the solvation shell and the bulk, respectively. The last term is the entropy term. The condition of equilibrium will be determined by the minimum value of G. The four variables (viz.,  $N_1$ ,  $N_2$ ,  $N_1^0$ , and  $N_2^0$ ) in eq 4 are related by eq 1-3. Hence the system has only one independent variable. Thus we may write the minimum condition of G as

$$\partial G/\partial N_1 = 0$$

and we have

$$kT \ln \left[ (N_1 N_2^0) / (N_1^0 N_2) \right] = \epsilon_{s2} - \epsilon_{s1} + (N_1 - N_2)\epsilon_{12} - (N_1^0 - N_2^0)\epsilon_{12}^0 - N_1\epsilon_{11} + N_1^0\epsilon_{11}^0 + N_2\epsilon_{22} - N_2^0\epsilon_{22}^0$$
(5)

The quantity  $(N_1N_2^0)/(N_1^0N_2)$  may be looked upon as equal to  $(x_1^Lx_2)/(x_1x_2^L)$  and denoting it by  $K_{pS}$ , we have

$$kT \ln K_{\rm PS} = \epsilon_{\rm s2} - \epsilon_{\rm s1} + (N_1 - N_2)\epsilon_{12} - (N_1^0 - N_2^0)\epsilon_{12}^0 - N_1\epsilon_{11} + N_1^0\epsilon_{11}^0 + N_2\epsilon_{22} - N_2^0\epsilon_{22}^0$$
(6)

The quantity  $K_{PS}$  defined as above is known to be a good measure of PS,<sup>9,11</sup>  $K_{PS} = 1$  representing the case of no PS. It is apparent from eq 6 that  $K_{PS}$  is determined by solute-solvent as well as solvent-solvent interactions. It also appears from (6) that as  $T \rightarrow \infty$ , the argument of the logarithm would approach a value of unity. Thus the extent of PS would be less as temperature is increased and there would be no PS at very high temperature. This aspect of PS is yet to be studied by experiment.

Relationship of  $K_{PS}$  with Other Parameters Representing PS. The parameter  $\delta_{1s}$  used to describe PS in Marcus and Ben-Naim theory is related to  $K_{PS}$  by eq 7 for all values of  $x_1$ . Thus the value

$$\delta_{1s} = x_1^{L} - x_1$$
  
=  $x_1(1 - x_1)(K_{PS} - 1) / [1 + x_1(K_{PS} - 1)]$  (7)

of  $\delta_{1s}$  would be determined by solute-solvent as well as solventsolvent interaction. This is also evident from QLQC theory of Marcus where the nonideality of solvent interaction appears through  $\Delta G_{12}^{E}$  ( $x_1 = 0.5$ ). According to the present model we note that solvent-solvent term in eq 6 vanishes if  $\epsilon_{11} = \epsilon_{22} = \epsilon_{12}$ and  $\epsilon_{ij} = \epsilon_{ij}^{0}$ , which is the condition of solvent ideality. If we put  $K_{PS} = K_{P1}/K_{P2}$ , we have

$$\delta_{1s} = x_1(1-x_1)(K_{P1}-K_{P2})/(K_{P1}x_1+K_{P2}x_2)$$
(8)

We may compare eq 8 with the expression of  $\delta_{1s}$  obtained from KB approach,<sup>9</sup> viz.

$$\delta_{1s} = x_1(1 - x_1)(G_{1s} - G_{2s})/(x_1G_{1s} + x_2G_{2s} + V_c)$$
  
=  $x_1(1 - x_1)(G_{1s} - G_{2s})/[x_1(G_{1s} + V_c) + x_2(G_{2s} + V_c)]$  (9)

where  $G_{ls}$  and  $V_c$  are the Kirkwood-Buff parameters and the volume of solvation shell, respectively. Thus,  $K_{Pi}$ 's are related to KB parameters as

$$K_{\rm Pi} = (G_{\rm is} + V_{\rm c}) \times {\rm constant} = (G_{\rm is}/V_{\rm c} + 1) \times {\rm constant}$$
 (10)

The second step of the above equation has been written to make the constant dimensionless. Thus  $K_{Pi}$ 's are closely related to  $G_{is}$ . Noting the fact that  $x_1G_{1s} + x_2G_{2s} + V_c \approx V_c$ , the constant in eq

comes out as 
$$(K_{P1}x_1 + K_{P2}x_2)$$
. Thus

$$K_{\rm P1}/(K_{\rm P1}x_1 + K_{\rm P2}x_2) = (G_{\rm 1s}/V_{\rm c} + 1)$$
(11)

The left-hand side of eq 11 is the ratio  $x_1^L/x_1$  as can be seen from the definition of  $K_{PS}$ . Thus

$$x_i^{\rm L} = K_{\rm Pi} x_i / \sum K_{\rm Pi} x_i$$

From the above expression it is apparent that  $K_{Pi}$ 's have the same meaning as the affinity constants in the COPS theory.<sup>12,17</sup> In the SSE model of Covington, PS is explained in terms of a chemical model. It is assumed that the following stepwise equilibria exist.

$$SA_{i-1}B_{j+1} + A \xrightarrow{K_i} SA_iB_j + B; \quad i = 1, ..., z; i + j = z$$
$$K_i = (x_{i,j}/x_{i-1,j+1})/(x_1/x_2)$$

where A and B represent solvent components 1 and 2, respectively, and  $x_{i,j}$  is mole fraction of the species  $SA_iB_j$ . The constant  $K_i$ depends on the state of solvation of S, i.e., on the value of *i*. The preferential solvation is determined by the parameter  $\Delta G_{PS}$  defined as

$$\Delta G_{\rm PS} = -\sum_{i=1}^{z} RT \ln K_i = -RT \ln K$$

where  $K = \prod_{i=1}^{z} K_i$  is the equilibrium constant for the overall process

$$SB_z + zA \rightleftharpoons SA_z + zB$$

The value of  $K_{\rm PS}$  may be calculated<sup>6</sup> by using the above model as follows. Let  $\langle N_1 \rangle$  and  $\langle N_2 \rangle$  be the average number of A and B in the solvation shell. Then

$$K_{\rm PS} = \frac{\langle N_1 \rangle}{\langle N_2 \rangle} / \left( \frac{x_1}{x_2} \right) = \frac{\sum_{i=1}^{z} i(\prod_{\gamma=1}^{i} K_{\gamma}) Y^{i-1}}{z + \sum_{i=1}^{z} (z-i)(\prod_{\gamma=1}^{i} K_{\gamma}) Y^{i}} \quad (12)$$

where  $Y = (x_1/x_2)$ .

10

If we assume that the change in the free energy accompanying the substitution of one molecule of B by one molecule of A is equal for all the equilibria, it can be shown that<sup>18</sup>

$$K_i = K^{1/2}[(z - i + 1)/i]$$
(13)

In this case  $K_{PS}$  comes out to be

$$K_{\rm PS} = K^{1/z} = (K_1 K_2 ... K_z)^{1/z}$$

But the relation 13 assumes ideal mixing of solvent components in the solvation shell. But if solvent nonideality is taken into account as is done in CCT, we have the following relation<sup>14</sup> instead of (13)

$$K_i = K^{1/z}[(z - l + 1)/i] \exp(-\Delta g_i^{\rm E}/RT)$$

Here the exponential term takes care of solvent nonideality. Using the above expression we may write eq 12 as

$$K_{\rm PS} = K^{1/z} f(Y)$$

where f(Y) is a function dependent on solvent composition, given by

$$f(Y) = \left[\sum_{i=1}^{z} (z-1) c_{i-1} (K^{1/z} Y)^{i-1} \exp(-\Delta g_i^{\mathrm{E}} / RT)\right] / \left[1 + \sum_{i=1}^{z} (z-1) c_{i-1} \left(\frac{z-i}{i}\right) (K^{1/z} Y)^i \exp(-\Delta g_i^{\mathrm{E}} / RT)\right]$$
(14)

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Figure 1. A plot of  $E_{12}$  vs  $x_1$  at 298 K: (O) ethanol + acetonitrile; ( $\odot$ ) ethanol + propionitrile; and  $(\Delta)$  ethanol + butyronitrile.

At this point it is interesting to note that the phenomenon of solvation has a close analogy with adsorption and PS resembles preferential adsorption as pointed out by Langford and others.<sup>11</sup> The parameter  $K_{PS}$  may then be looked upon as the equilibrium constant for the solvent exchange equilibrium

It may be seen that in the case when solvent-solvent interactions are negligible, the value of  $K_{PS}$  would be a constant independent of the solvent composition and is simply the geometric mean of the  $K_i$ 's. Such a situation is similar to the Langmuirian adsorption of solvents 1 and 2 on to the solute sites. But the presence of solvent-solvent interaction may lead to a composition dependence of  $K_{PS}$ . This conclusion also obtainable from eq 6. Only in the limit of  $Y \rightarrow 0$  one has

$$K_{\rm PS} = K^{1/z} \exp(-\Delta g_1^{\rm E}/RT) = K_1/z$$

i.e.  $K_{PS}$  is then equal to  $K^{1/z}$  corrected for activity effects of solvents. The above result is also tantamount to saying that, in the limiting case of  $x_1 \rightarrow 0$ , the only determining equilibrium is<sup>6,8</sup>

$$SB_{z} + A \xrightarrow{K_{1}} SB_{z-1}A + B$$

### **Results and Discussion**

The CT band continuously changes to higher wavelength as nitriles are added to ethanol. The bandwidth and shape, however, practically remain unaffected. The CT absorption in solution appears as a broad structureless band, rendering the position of the band maximum,  $E_{12}$ , somewhat inaccurate (within 0.3 kcal mol<sup>-1</sup>). However, the overall band shift is greater than this inaccuracy. Figure 1 shows the  $E_{12}$  values for 4CN-NEPI in mixed solvents as a function of  $x_1$ , the bulk mole fraction of ethanol. It appears that  $E_{12}$  deviates from linearity. A hypothetical line (ideal line) assuming linearity over the entire mole fraction range is shown as the dotted line in the Figure 1.

The spectroscopic transition energy leading to the CT band in NAPI involves the solvated contact ion pair (Py+,I<sup>-</sup>) as the ground state and a neutral species (Py,I) surrounded by the same solvent environment (as in the ground state) as the Franck-Condon (FC) excited state. Here the ground state is appreciably stabilized by the polar solvent molecules but solute-solvent interactions in the FC excited state are practically negligible since the dipole moment in this state is smaller than that of the ground state. It has been shown in a previous communication<sup>6</sup> that if we neglect solventsolvent interaction during the spectroscopic transition, the observed  $E_{12}$  in a mixed binary solvent may be written as

$$E_{12} = x_1^{\rm L} E_1 + x_2^{\rm L} E_2 \tag{16}$$

where  $E_1$  is the transition energy in pure *i*th solvent. The fact that the observed  $E_{12}$  values vary nonlinearly with  $x_1$  indicates that the local mole fraction  $x_i^{L}$  differs from the bulk value. It may be noted that the quantity  $(E_{12} - x_1E_1 - x_2E_2)/(E_1 - E_2)$ 

TABLE I: Parameters Representing PS in Ethanol + Nitrile Binary Solvent Mixtures at 298 K

cosolvents	x1 <sup>a</sup>	$E_{12}^{b}$	δ1.	K <sub>PS</sub>	K' <sub>PS</sub>
acetonitrile	0.000	67.70	0.000	<u>с</u>	c
	0.020	68.32	0.049	3.64	3.71
	0.035	69.06	0.124	5.20	5.32
	0.050	69.40	0.150	4.75	4.84
	0.090	70.70	0.268	5.63	5.89
	0.180	71.83	0.315	4.46	4.73
	0.280	73.50	0.417	5.91	6.57
	0.370	73. <del>9</del> 0	0.375	4.99	5.54
	0.470	74.07	0.296	3.69	4.07
	0.570	74.36	0.231	3.04	3.33
	0.670	74.55	0.154	2.31	2.48
	0.780	75.24	0.128	2.78	3.09
	0.890	75.14	0.006	1.06	1.07
propionitrile	0.000	63.40	0.000	С	С
	0.024	64.10	0.032	2.39	2.39
	0.060	66.33	0.173	4.75	4.58
	0.119	68.23	0.264	4.60	4.31
	0.177	69.22	0.285	3.99	3.70
	0.233	69.66	0.264	3.25	3.01
	0.342	71.12	0.271	3.04	2.77
	0.448	72.02	0.236	2.67	2.41
	0.549	72.93	0.207	2.55	2.28
	0.040	/3.38	0.146	2.09	1.89
	0.739	74.03	0.105	1.91	1.74
	0.030	75.22	0.029	1.24	1.21
buturonitrilo	0.910	13.32 41.99	0.030	1.01	1.48
outyromtrite	0.000	62.52	0.000	C A A 2	C 1 20
	0.029	65.55	0.000	4.43	4.30
	0.072	67 27	0.109	4.50	4.22
	0.142	68 50	0.240	3.75	2.22
	0.207	69 33	0.202	3.00	2.57
	0.389	70.59	0.230	2 53	2.02
	0.497	71 48	0.183	215	1.85
	0.597	72.71	0.170	2.22	1.86
	0.690	73.16	0.109	1.78	1.55
	0.776	73.69	0.060	1.48	1.33
	0.856	74.38	0.029	1.30	1.20
	0.930	75.08	0.005	1.08	1.06
	1.000	76.00	0.000	с	с
				-	-

<sup>a</sup> Mole fraction of ethanol. <sup>b</sup> Transition energy in kcal mol<sup>-1</sup>.

represents the extent of PS of the solute by the component 1, i.e.,  $\delta_{1s}$ . Now  $(x_1E_1 + x_2E_2)$  represents the value in the ideal line and from Figure 1 we can find that  $\delta_{1s}$  is always positive. Thus the solute is preferentially solvated by ethanol over the nitriles. The values of  $\delta_{1s}$  for different solvent mixtures have been listed in Table I. As may be seen,  $\delta_{1s}$  tends to zero at the two extreme ends and passes through a maximum, and the corresponding  $x_1$  value is always less than 0.5, i.e., PS is asymmetric. In order to explain the preference of the solute toward ethanol over nitriles we observe that PS may be either due to dielectric enrichment<sup>19</sup> where solvent with a higher dielectric constant is preferred near a polar solute or due to specific short-range interactions or both. Our earlier results indicate that the H-bond-donating ability of the solvents play a major role in the PS of NAPI.<sup>6,20</sup> Thus, ethanol with a greater H-bond-forming ability is preferred over the nitriles.

 $K_{\rm PS}$  values for the systems may be calculated from the  $\delta_{\rm 1s}$  values by using the relation

$$(K_{\rm PS} - 1) = \delta_{\rm 1s} / x_{\rm 1} (1 - x_{\rm 1} - \delta_{\rm 1s})$$

The value of  $K_{PS}$  have been listed in Table I. It may be seen from Figure 2 that  $K_{PS}$  values are not constant. Thus solvent-solvent interaction plays a role in PS.

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Figure 2. Representative plots of log  $K_{PS}$  vs  $x_1$  at 298 K.

To have some idea about the role played by solvent nonideality we may take  $\epsilon_{ij} = \epsilon_{ij}^0$  as an approximation and simplify the right-hand side of eq 6. The result is

$$kT \ln K_{PS} = \epsilon_{s2} - \epsilon_{s1} + 2z\Delta\epsilon_{12}(x_1^{L} - x_1) + z\left(2 - \frac{N_1^{T} + N_2^{T}}{z}\right)\Delta\epsilon_{12}x_1 + \text{constant}$$
$$= \epsilon_{s2} - \epsilon_{s1} + 2z\left[(x_1^{L} - x_1) + \left(1 - \frac{N_1^{T} + N_2^{T}}{2z}\right)x_1\right]\Delta\epsilon_{12} + constant (17)$$

where  $\Delta \epsilon_{12} = 2\epsilon_{12} - \epsilon_{11} - \epsilon_{22}$ .

Thus the solvent-solvent interaction term is determined by the parameter  $\Delta \epsilon_{12}$ . For the PS of NAPI the first term within the square bracket in eq 17 is positive (as found in the present case) but the second term is negative and largely compensates the positive term  $(N_1^T + N_2^T \gg 2z)$ . The nature of the variation of log  $K_{PS}$  with  $x_1$  (Figure 2) suggests that  $\Delta \epsilon_{12}$  is positive for mixed solvents containing ethanol + nitrile in the range  $0.1 < x_1 < 0.9$ which means that the two solvent components repel each other.

Effect of Difference in the Molar Volume ( $\overline{V}$ ) of the Solvents. The above discussion assumes that the molar volumes of the two component solvents are the same. But if  $\bar{V}_1 \neq \bar{V}_2$  eq 1 no longer holds and is replaced by

$$N_1 \bar{V}_1 + N_2 \bar{V}_2 = \text{constant}$$

Further the entropy term in (4) would be replaced by the volume

fractions instead of mole fractions. In that event we get eq 5a in place of eq 5.

$$kT \ln \left[ \frac{N_1}{N_1^0} \left( \frac{N_2^0}{N_2} \right)^{\gamma} \right] = (\gamma \epsilon_{s2} - \epsilon_{s1}) - (N_1 \epsilon_{11} - \gamma N_2 \epsilon_{22} + N_2 \epsilon_{12} - \gamma N_1 \epsilon_{12} - N_1^0 \epsilon_{11}^0 + \gamma N_2^0 \epsilon_{22}^0 - N_2^0 \epsilon_{12}^0 + \gamma N_1^0 \epsilon_{12}^0)$$
(5a)

where  $\gamma = \bar{V}_1 / \bar{V}_2$ . Thus  $(x_1^{L} / x_1) / (x_2^{L} / x_2)^{\gamma} = K'_{PS}$  is then descriptor of PS. Now  $K'_{PS}$  is related to the equilibrium constant for the following solvent-exchange equilibrium.

 $\bar{V}_1$ -solvent 2 (S) +  $\bar{V}_2$ -solvent 1  $\rightleftharpoons$  $\bar{V}_2$ -solvent 1 (S) +  $\bar{V}_1$ -solvent 2

 $K'_{PS}$  values have also been listed in Table I. It appears that  $K'_{PS}$ also depends on the solvent composition, indicating that solvent-solvent interactions are important. It also appears that the second set of term in the right-hand side of eq 5a representing solvent-solvent interaction does not vanish if we assume the condition of solvent ideality. The contribution due to solventsolvent interaction toward ln  $K'_{PS}$  then becomes  $-(1 - \gamma)[N_1 - \gamma]$  $N_1^0 + N_2 - N_2^0 \epsilon$ , i.e., dependent on  $(\overline{V}_1 - \overline{V}_2)$ . This means that even if solute-solvent interactions were absent and solvent mixture behaved ideally there would be a PS due to the difference in the size of the solvent molecules. In such a situation the observed parameter  $E_{12}$  should be written as

$$E_{12} = \phi_1 E_1 + \phi_2 E_2$$

where  $\phi_i$  is volume fraction of *i*th solvent. The above equation may be written as

$$E_{12} = x_1 E_1 + x_2 E_2 + (\bar{V}_1 - \bar{V}_2)(E_1 - E_2) x_1 x_2 / (\bar{V}_1 x_1 + \bar{V}_2 x_2)$$
(18)

That is,  $E_{12}$  would deviate from linearity. The extent of deviation as measured by  $(E_{12} - x_1E_1 + x_2E_2)/(E_1 - E_2)$  would depend on  $(\bar{V}_1 - V_2)$ . Thus one can make the required correction for the size effect and get corrected  $x_1^L$  and hence  $K_{PS}$  and  $K'_{PS}$ . But in no case is  $K_{PS}$  (or  $K'_{PS}$ ) found to be constant. Thus solventsolvent interaction rather than the size effect plays an important role in the PS of NAPI.

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