Solubility and solvation interaction in neat and mixed binary solvents

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Solubilities of 1-ethyl-4-cyanopyridinium iodide and two ketocyanine dyes have been determined in various neat and mixed binary solvents. A multiple linear regression analysis for neat solvents indicates that the solubility depends on various modes of solute-solvent interaction and also on the Hildebrand solubility parameter representing the cohesive energy density of the solvent. Data in mixed binary solvents point to a deviation from ideal solution behaviour. The results have been explained in terms of solvent-solvent interaction as well as a difference in solute-solvent interaction for the component solvents.

It is well-known that the kinetic, spectroscopic or thermodynamic properties of a solute in solution depend largely on solvation interactions and a systematic study of properties of solute in various media provides information regarding such interactions. In general a neat solvent is characterised by many parameters like dipolarity and polarisability, hydrogen bond donation or acceptance, structuredness etc. which represent various modes of interaction with a solute. It has been found that the free energy change ($\Delta G$) of solvation of a solute in a neat solvent is described by linear solvation energy relationship (LSER):

$$\Delta G = A_0 + \sum A_i P_i$$

where $A_0$ and $A_i$'s are terms dependent only on the solute, and $P_i$'s are solvent properties pertinent to i-type interactions. It is instructive to study whether similar information about solute-solvent and solvent-solvent interactions is obtained when one analyses the dependence of $\Delta G$ for different processes involving a particular solute. Equation (1) does not hold good in mixed solvents. On the other hand mixed binary solvents provide a system where it is possible to vary the solvent-solvent interaction and studies in these media throw light on the role of such interactions on the solvation process. Depending on the specificities of interaction with component solvent, the local solvent composition around the solute may be significantly different from that in the bulk. The phenomenon, known as preferential solvation, has been found to depend on solute-solvent and solvent-solvent interaction. In our laboratory we have extensively investigated the solvation characteristics of 1-ethyl-4-cyanopyridinium iodide in various neat and mixed binary solvents by spectroscopic procedures. The objective of the present paper is to study the solvation characteristics of the solute in neat and mixed binary solvents by measuring the solubility and to compare the results with those obtained from the light absorption data. In order to investigate the role of the solute in determining the solvation characteristics, solubility measurements in neat and mixed binary solvents have been carried out with 1-ethyl-4-cyanopyridinium iodide and two ketocyanine dyes (Fig. 1). These dyes show solvent sensitive fluorescence and have been found to be good reporters of solvation interaction.

Materials and Methods

Preparation of solutes

1-Ethyl-4-cyanopyridinium iodide was prepared by quaternising 4-cyanopyridine (Koch-Light) with iodoethane in the dark. The compound was purified by repeated crystallisation from dry ethanol, and the purity was checked by noting physical properties; melting point (found 140°C, lit. 140-141°C), longest wavelength band maxima, $\lambda_{\text{max}}$ (found 484 nm; lit. 482 nm) and corresponding values of $\varepsilon$ (found 1210 dm$^3$mol$^{-1}$cm$^{-1}$; lit. 1200 dm$^3$mol$^{-1}$cm$^{-1}$ in CH$_2$Cl$_2$).

Ketocyanine dyes (Fig. 1) were synthesized as described in the literature. Indoline (for Dye I), N-methylaniline (for Dye II), 1,1,3,3-tetramethoxypropane and cyclopentanone (Sigma Chemicals, USA) were used as received. Purity of the prepared compounds was
checked by IR spectral data [1R bands obtained in KBr disc: 1622, 1578, 1485, 1390 cm⁻¹; lit. 1620, 1580, 1485, 1400 cm⁻¹ (Dye I) and 1608, 1570, 1490 cm⁻¹; lit. 1610, 1570, 1490 cm⁻¹ (Dye II)] and absorption and fluorescence spectral data [Amax(abs) = 524 nm (lit. 525 nm), A(FL) = 622 nm (lit. 622 nm.) in ethanol for Dye I and Amax(abs) = 503 nm (lit. 505 nm), A(FL) = 589 nm (lit. 590 nm.) in ethanol for Dye II]. Solvents used were ethanol, propan-1-ol, propan-2-0I, butan-1-ol, diethyl ether, acetonitrile, propionitrile, acetone, 1,2-dichloroethane, chloroform, dichloromethane, tetrahydrofuran, benzene, methylformate and n-hexane. All the solvents were purified and dried by standard procedures and distilled over CaH₂. Mixed solvents were prepared by mixing the components by volume. Care was taken to avoid contamination of moisture during mixing. The empirical solvent polarity parameter, E(30) for the neat solvents were taken from the literature. Values for the mixed binary solvents were determined from the λmax of the indicator dye, viz, N-phenyl pyridinium betaine in the solvent according to the relation

\[ E(30)/\text{kcal mol}^{-1} = 28590(\lambda_{\text{max}}/\text{nm}) \] ...

Solubility measurements

Saturated solutions of solutes were prepared by agitating the closed flask containing a solute and a solvent in a thermostat kept at 298 ± 0.5 K for long time (at least 24 h) till equilibrium was attained. For 1-ethyl-4-cyanopyridinium iodide the concentrations were determined by adding excess water and then titrating the iodide conductometrically against silver nitrate solution. For the ketocyanine dyes the concentration in a particular solvent was determined spectrophotometrically after proper dilution with that solvent. Spectrophotometric measurements were done in a Shimadzu spectrophotometer [UV 2101 PC].

Results and Discussion

Neat solvents

Solubilities in the molar scale (sₘ) and also in the mole fraction scale (sₐ) of 1-ethyl-4-cyanopyridinium iodide in various neat solvents have been listed in Table I. It is known that log sₐ or log sₘ is related to the standard molar Gibbs energy of solution (ΔG°) at 10. Figure 2(a) shows a plot of log sₐ versus Eₐ(30) for 1-ethyl-4-cyanopyridinium iodide. A linear plot is obtained for aprotic solvents. Data points for alcohol solvents, however, form a separate line. The results indicate that for non-alcoholic solvents the local parameter Eₐ(30) correlates well with a bulk thermodynamic parameter (e.g. sₐ). For alcohols there exists strong solvent-solvent hydrogen bond interaction in the bulk and this explains the different line obtained for these solvents. Observations of earlier workers also support this view. In order to study the dependence of solubility on various specific and non-specific modes of solvation, a multiple linear regression analysis (MLRA) involving various solvent properties was performed. In general several independent modes of solute-solvent interaction have been characterised. These include the non-specific dipolarity and polarisability interactions and specific interactions e.g. hydrogen bond donation (HBD) and hydrogen bond acceptance (HBA). Empirical solvatochromic parameters α, β, and π introduced by Taft, Kamlet and others have been found to represent the dipolarity-polarisability, HBD and HBA interaction respectively. MLRA of log sₐ with the parameters α, β, and π shows a correlation coefficient of ~0.8. Thus an additional interaction term for the formation of solute cavity in a solvent is also important for describing solubilities. It has been recognised that the square of the Hildebrand solubility parameter (Δh²) is appropriate for this mode of interaction. It has been found by other workers that solubility in neat solvents can be described by LSER. Hence a linear correlation of log sₐ and log sₘ with the solvent parameters π, α, β and Δh² was sought. The final equation is

\[ \log sₐ = -3.47 - 2.92α - 1.29β - 3.94π + 10.09(Δh²/10000) \] ...

\[ \log sₚ = -4.59 - 2.46α - 1.98β - 3.42π + 13.79(Δh²/10000) \] ...
Table 1: Values of solubilities for 1-ethyl-4-cyanopyridinium iodide in various neat solvents at 298K

\[ s_m = \text{solubility} / \text{mol dm}^{-3}; \ s_s = s_m \times \text{molar volume of solvent} / \text{dm}^3\text{mol}^{-1} \]

<table>
<thead>
<tr>
<th>Solvent</th>
<th>log ( s_m )</th>
<th>log ( s_s )</th>
<th>( E_t(30) )</th>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>( \pi^* )</th>
<th>( (\delta_m/1000)^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>-0.955</td>
<td>-2.186</td>
<td>52.1</td>
<td>0.83</td>
<td>0.75</td>
<td>0.54</td>
<td>0.676</td>
</tr>
<tr>
<td>Propan-1-ol</td>
<td>-1.651</td>
<td>-2.777</td>
<td>50.7</td>
<td>0.78</td>
<td>0.80</td>
<td>0.52</td>
<td>0.595</td>
</tr>
<tr>
<td>Propan-2-ol</td>
<td>-1.959</td>
<td>-3.075</td>
<td>48.6</td>
<td>0.76</td>
<td>0.84</td>
<td>0.48</td>
<td>0.562</td>
</tr>
<tr>
<td>Butan-1-ol</td>
<td>-2.154</td>
<td>-3.193</td>
<td>50.2</td>
<td>0.79</td>
<td>0.82</td>
<td>0.47</td>
<td>0.543</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>-0.085</td>
<td>-1.367</td>
<td>46.0</td>
<td>0.19</td>
<td>0.31</td>
<td>0.75</td>
<td>0.581</td>
</tr>
<tr>
<td>Propionitrile</td>
<td>-0.844</td>
<td>-1.991</td>
<td>43.7</td>
<td>0.00</td>
<td>0.37</td>
<td>0.71</td>
<td>0.475</td>
</tr>
<tr>
<td>Acetone</td>
<td>-1.007</td>
<td>-2.141</td>
<td>42.2</td>
<td>0.08</td>
<td>0.48</td>
<td>0.71</td>
<td>0.488</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>-2.698</td>
<td>-3.802</td>
<td>41.9</td>
<td>0.00</td>
<td>0.00</td>
<td>0.81</td>
<td>0.400</td>
</tr>
<tr>
<td>Chloroform</td>
<td>-2.097</td>
<td>-3.194</td>
<td>39.1</td>
<td>0.44</td>
<td>0.00</td>
<td>0.58</td>
<td>0.38</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>-1.959</td>
<td>-3.152</td>
<td>41.1</td>
<td>0.13</td>
<td>0.10</td>
<td>0.82</td>
<td>0.404</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>-3.000</td>
<td>-4.091</td>
<td>37.4</td>
<td>0.00</td>
<td>0.55</td>
<td>0.58</td>
<td>0.361</td>
</tr>
<tr>
<td>Methyl formate</td>
<td>-0.617</td>
<td>-1.850</td>
<td>45.0</td>
<td>0.00</td>
<td>0.37</td>
<td>0.62</td>
<td>****</td>
</tr>
</tbody>
</table>

* kcal mol\(^{-1}\)  
* J cm\(^{-1}\)

Fig. 2: (a) Plot of log \( s_m \) versus \( E_t(30) \) in mixed binary solvents with 1-ethyl-4-cyanopyridinium iodide as solute. The numbers are the serial numbers of the solvents in the Table 1. Solid lines represent correlation lines for protic and aprotic solvents; (b) Plot of log \( s_s \) versus \( E_t(30) \) in mixed binary solvents: 1-ethyl-4-cyanopyridinium iodide in acetone + tetrahydrofuran (●) and acetone + ethanol (×), ketocyanine dye(1) in benzene + n-hexane (●) and ethanol + acetone (△).
with eleven solvents. The correlation coefficients found were greater than 0.90 in both the cases. It appears from the above equation that the solubility parameter representing the self-cohesiveness of the solvent plays a significant role in determining the solubility of 1-ethyl-4-cyanopyridinium iodide. In this respect the thermodynamic parameter, log \( s_m \), differs from the spectroscopically determined solvation parameter viz. energy of maximum absorption (\( E_{\lambda_{\max}} \)) which shows no correlation with \( \delta_{(\text{H})}^2 \)-parameter\(^{15}\). It appears from our result that apart from the self-cohesiveness of solvents, the solubility is also determined by the dipolarity-polarisability interaction (\( \pi^* \)) and the HBD interaction(\(\alpha\)) of the solvent with the reference solute. The coefficients of the \( \delta_{(\text{H})}^2 \) term are positive. This indicates the endothermic nature of cavity formation. An important point to note is that Eq. (3) will apply to cases where other specific modes of interaction e.g. complexation is absent. Thus one can calculate a value of \( s_m/\text{mol dm}^{-3} = 0.14 \) for dimethylformamide (DMF) by using (3) which is too low compared to the value obtained by others\(^9\), DMF is known to form solvation complex with the anion\(^{16}\) and this may explain the discrepancy in DMF.

**Mixed binary solvents**

(a) 1-Ethyl-4-cyanopyridinium iodide

Figure 2(b) shows plots of log \( s_m \) versus \( E_{\lambda_{(30)}} \) for representative solvent mixtures. For mixed aprotic solvents this plot is linear while for alcohol + acetone mixture a curve passing through a maximum (at \( E_{\lambda_{(30)}} \sim 51 \)) is obtained. In the earlier section we noted that \( E_{\lambda_{(30)}} \) vs log \( s_m \) is linear for neat solvents, alcohols forming a separate group. The non-linear curve for alcohol + acetone may be intelligible in view of a difference in the nature of solvent-solvent interaction in two component solvents. Values of log \( s_m \) in mixed binary solvents containing acetone are shown in the Fig.3 as a function of \( x_1 \), the mole fraction of acetone. It appears that the plot of log \( s_m \) versus the mole fraction of acetone is linear (within experimental error) for acetone + acetonitrile mixture. For other two binary mixtures non-linear plots are obtained, indicating a non-ideal solvation behaviour in these cases. The case of acetone + ethanol mixture is interesting. Here the curve passes through a maximum, i.e., the solubilities at intermediate compositions are greater than the solubility in component solvents.

A linear relationship between log \( s_m \) and mole fraction (i.e., ideal solvation behaviour) is expected when the two component solvents have similar solvation interaction with the solute\(^{10}\). The present results indicate that the solute-acetonitrile and solute-acetone interactions are almost similar. A non-linear log \( s_m \) versus mole fraction plot has been explained by Marcus\(^{10}\) by postulating preferential solvation of the solute. Thus we may explain the results obtained for acetone + tetrahydrofuran mixture as due to preferential solvation of the solute.

The nature of the log \( s_m \) versus x plot in the present case indicates that acetone is relatively preferred over tetrahydrofuran by the solute. The two component solvents as mentioned above differ with respect to interaction with the solute. A relative preference in the cybotactic region of the component having higher solute-solvent interaction (i.e., acetone) may thus be qualitatively understood. The local mole fraction of acetone (component 1) may be calculated using the relation\(^4,17,18\)

\[
x_{1'} = \frac{(P_{12} - P_2)}{(P_1 - P_2)}
\]

where \( P \) is an observed property, in this case log \( s_m \); the subscripts 1, 2 and 12 represent component solvents and their binary mixture respectively. The extent of preference\(^{19}\) of component 1, as expressed by \( \delta_{1a} = x_{1'} - x_1 \), may also be calculated. Table 2 lists the \( x_{1'} \) values. A positive value of \( \delta_{1a} \) indicates that the solute is preferentially solvated by the component 1, i.e. acetone. The \( \delta_{1a} \) values are related to the parameter \( K_m \) representing an index of preferential solvation\(^{17}\) as,

\[
K_m = \frac{(x_1' - x_1)}{(x_1 - x_1') \delta_{1a}} = 1 + \frac{\delta_{1a}}{[x_1(1-x_1) - \delta_{1a}]} \]

**Table 2 - Parameters representing preferential solvation in mixed binary solvents for 1-ethyl-4-cyanopyridinium iodide.**

<table>
<thead>
<tr>
<th>Solvent mixtures (1 + 2)</th>
<th>( x_1 )</th>
<th>( x_1' )</th>
<th>( \delta_{1a} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( s_m )</td>
<td>spectroscopy</td>
<td>method</td>
</tr>
<tr>
<td>0.1</td>
<td>0.20</td>
<td>0.24</td>
<td>0.10</td>
</tr>
<tr>
<td>0.2</td>
<td>0.38</td>
<td>0.40</td>
<td>0.18</td>
</tr>
<tr>
<td>0.3</td>
<td>0.48</td>
<td>0.48</td>
<td>0.18</td>
</tr>
<tr>
<td>0.4</td>
<td>0.58</td>
<td>0.56</td>
<td>0.18</td>
</tr>
<tr>
<td>0.5</td>
<td>0.66</td>
<td>0.64</td>
<td>0.16</td>
</tr>
<tr>
<td>(Acetone + Tetrahydrofuran)</td>
<td>0.6</td>
<td>0.75</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>0.81</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>0.95</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

\(^{15}\) This work.

\(^{17}\) Ref. 22
and \[ \delta_{1x_i} = x_i (1 - x_i) \frac{(K_{p_1} - 1)^2}{1 + x_i (K_{p_2} - 1)} \] ... (6)

The parameter \( K_p \) is associated with the solvent exchange equilibrium \(^7\)

\[ \text{Solv}_1 + \text{Solv}_2 (\text{bound}) \rightleftharpoons \text{Solv}_1 + \text{Solv}_2 (\text{bound}) \] ... (7)

According to the existing model of preferential solvation, the parameter \( K_p \) is given by \(^7\) \( K_p = K^{\text{op}}f(y) \)

\[
\begin{align*}
\frac{f(y)}{\sum i (z - 1)^i} & \left[ \frac{(i - 1)^i}{(z - 1)^i} \right] \\
\times \left( K^{\text{op}}y \right)^{-i} \exp \left[ -i h/RT \right] \\
\sum i (z - 1)^i & \left[ \frac{(i - 1)^i}{(z - 1)^i} \right] \\
\times \left( K^{\text{op}}y \right)^{-i} \exp \left[ -i (z - 1)h/RT \right] \\
y = x_i/k_i
\end{align*}
\] ... (8)

In the above equation preferential solvation is described in terms of three parameters, viz, \( K, h \) and \( z \). \( K \) is determined by a difference in solute-solvent interaction energies of the two solvents, \( K = 1 \) represents the case when the two solvent components have equal solute-solvent interaction. The parameter \( h \) represents the solvent non-ideality. \( z \) is the total number of solvent molecules around the solute. The experimental data in the present case are well-represented by \( K = 2.15, h = -0.035 \) and \( z = 6 \) for the acetone + tetrahydrofuran mixture. The results are shown in Fig. 3(b). A value of \( K > 1 \) indicates that the interaction energy with solute is greater for acetone than for tetrahydrofuran. A small value of \( h \) indicates that the effect of solvent non-ideality is not large. A negative value of \( h \) indicates that the solvent components repel each other \(^7\).

It may be emphasized at this point that Eq.(4) provides an 'operational definition' of the local mole fraction \(^2\) and the quantity \( x_i^L \) should be independent of the particular property measured. Our earlier spectroscopic studies indicated an almost ideal solvation in the case of the acetone + acetonitrile mixture \(^4\), while in the acetone + tetrahydrofuran mixture the solute was found to be solvated preferentially by acetone, the preference of acetone over tetrahydrofuran being rationalisable in view of the greater acetone-solute interaction. Thus the solubility measurements give similar results as obtained from spectroscopic studies for these two binary mixtures. The values of \( x_i^L \) for the acetone + tetrahydrofuran system obtained from spectroscopic studies are also given in Table 2. The agreement is quite good.

Mixed binary solvents of acetone with alcohols differ from other binary mixtures. The maximum in the log \( s_m \) versus mole fraction plot indicates that the solvent-
solvent interaction may play an important role. The plot of log $s_n$ versus $E(30)$ in the acetone + ethanol mixture passes through a maximum at $E(30) \approx 51$ corresponding to a mole fraction of ethanol $= 0.45$. This value also corresponds approximately to the maximum in the log $s_n$ versus mole fraction curve. Alcohols are highly structured solvents with high self-cohesiveness and this property is expected to change as another solvent component is added to it. Our experimental findings indicate that in the range $0.45 < x > 1$ the self-cohesiveness of alcohol increases. Such an observation of increase in self-association in water and ethanol has also been reported earlier. Unlike a spectroscopic parameter solubility reflects only the ground state characteristics of the solute and as such will depend very much on the self-cohesiveness of the solvent. It may be pointed out in this context that spectroscopic transition energy of 1-ethyl-4-cyanopyridinium iodide in acetone + alcohol mixture does not pass through a maximum as composition is varied.

(b) Ketoncyanine dyes

Solubilities of ketocyanine dyes (non-electrolyte solute) have been studied in mixed binary solvents containing acetone. The co-solvents are ethanol (o), propanol-2-ol (●), dichloroethane (□) and diethyl ether (φ); (b) data points for dye (II), legends for solvent mixtures are the same as in (a); (c) Plot of log $s_n$ versus the mole fraction of n-hexane ($x_{n-h}$) for ketocyanine dye (II) in mixed solvents containing n-hexane. Co-solvents are 1,2-dichloroethane (φ), ethanol (o), and benzene (x).

The case of n-hexane + ethanol is particularly interesting. Here the log $s_n$ versus $x_{n-h}$ ($x_{n-h}$ is the mole fraction of n-hexane) curve is almost parallel to mole fraction axis in the range $0.0 < x_{n-h} < 0.7$ indicating that solute has mostly the ethanol environment in this range.
This is presumably due to a strong hydrogen bonded interaction of the solute, i.e., the ketocyanine dye and alcohol.

Plots of log $s$ versus mol fraction for mixed solvents of acetone containing alcohols for these solutes also pass through a maximum indicating non-ideal solvation behaviour originating due to a difference in the nature of solvent-solvent interaction in alcohol and acetone (vide supra). But in this case the difference between the maximum value of solubility and the solubility in alcohol (or acetone) is not large compared to the case of 1-ethyl-4-cyanopyridinium iodide (Fig. 3a). This may be due to an increase in the dissociation of the solute in the intermediate solvent composition for 1-ethyl-4-cyanopyridinium iodide.

To conclude (i) solubility of a solute may provide a suitable parameter for indicating solvation interaction, but unlike spectroscopic parameter, solubility depends on the self-cohesiveness of the solvent as represented by $\delta_1^2$; (ii) in mixed binary solvents when solvation interactions differ, the solute shows preferential solvation; (iii) the parameters representing preferential solvation are the same whether one uses solubility parameter or a spectroscopic parameter; and (iv) similar solvation characteristics are obtained from solubility measurement involving different solutes.

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References