UV-visible spectroscopic study of preferential solvation of N-alkylpyridinium iodides in mixed binary solvents containing benzene

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Received 11 August 1994; accepted 28 December 1994

The UV-visible absorbance wavelength maximum of N-ethyl-4-cyanopyridinium iodide and N-ethyl-pyrazinium iodide has been utilised to investigate the solvation characteristics of the solute in fourteen binary mixed solvents containing benzene. The observed preferential solvation (PS) of the indicator solute by the polar cosolvents has been explained in terms of various interactions present in the system using the existing models for PS. The PS parameters characterising various interactions have been calculated.

Solvation of a solute depends on interactions of solute with solvent molecules and on how these interactions modify the interactions between the solvent molecules in the vicinity of the solute. The use of mixed binary solvent provides a means of varying the solvent-solvent interaction. The present paper addresses the problem of preferential solvation (PS) of the solute in relation to various interactions present in the solution. It has been known that N-alkylpyridinium iodide provides a suitable system for studying the solute-solvent interaction using UV-visible spectroscopic techniques. In this work the PS characteristics of N-alkylpyridinium iodide and N-alkylpyrazinium iodide have been studied in mixed binary solvents containing benzene. The cosolvents used are alcohols (methanol, ethanol, 2-propanol and t-butanol), nitriles (acetonitrile, propionitrile, butyronitrile and benzonitrile), ketones (aceton, butan-2-one, cyclopentanone and cyclohexanone) and dichloroethane. Some work has also been done using cyclohexane in place of benzene. The experimental results have been analysed by using the existing models of PS.

Materials and Methods
The solutes were prepared by a procedure discussed previously and crystallised using ethanol + benzene. All the solvents were purified and dried by standard procedures. Traces of oxidising agents present in the solvents were removed by treatment with calcium hydride and subsequent distillation prior to use. Mixed solvents were prepared by carefully mixing the solvents, avoiding contamination by moisture.

Spectrophotometric measurements were done using a Shimadzu spectrophotometer (UV 160A) provided with a peak detection algorithm. For a particular solution the wavelength corresponding to the absorption maximum \( \lambda_{\text{max}} \) was determined several times and a mean value was taken. This enabled us to measure the \( \lambda_{\text{max}} \) value within ±1 nm. The total concentration of the solute varied in the range \( 10^{-3} \) to \( 10^{-4} \) mol dm\(^{-3}\) according to the solvent composition.

Theoretical background
Two different approaches are adopted to quantify the extent of PS. In the first approach the 'local' excess or deficiency of the ith solvent component over the bulk composition, as measured by
\[
\delta_i = x_i^L - x_i
\]
where \( x_i^L \) and \( x_i \) are the local and bulk mole fraction of the ith solvent component, is used to describe PS. In the second, the parameter
\[
K_{ps} = \frac{(x_i^L x_j^B)}{(x_i x_j^L)}
\]
is used. The parameter \( K_{ps} \) is related to \( \delta_i \) as
\[
\delta_i = - \frac{x_i (1-x_i)}{K_{ps} - 1} \quad \text{or} \quad K_{ps} = 1 + \delta_i \frac{1}{x_i (1-x_i-\delta_i)}
\]
Several theoretical approaches to the problem of PS in a three component system are found in the literature. Covington et al. has given a thorough thermodynamic treatment of PS of solute S in a mixture of solvents A (component 1) and B (component 2) in terms of the stepwise solvent exchange (SSE) equilibria:
\[
SA_{i-1}B_{i+1} + A \quad K_i \quad SA_iB_i + B; \quad i = 1, ..., n; \quad i+j = n
\]
The constant $K_i$ depends on the state of solvation of $S$ (i.e., the value of $i$) and under the condition that the change of enthalpy accompanying the substitution of one molecule of $B$ by one molecule of $A$ is equal for all the equilibria and entropic terms are related statistically, one has:

$$K_i = K^{1/n} [(n-i+1)/i]$$  \(\ldots \) (3)

Where $K$ is the equilibrium constant for the overall process:

$$S B_n + A \leftrightarrow S A_n + B$$  \(\ldots \) (4)

The above relation (3) assumes ideal mixing of solvent components in the solvation shell. If solvent nonideality is taken into account, one has the following relation:

$$K_i = K^{1/n} [\exp(-\Delta g_i^E/RT)]$$  \(\ldots \) (5)

For relatively simple type of interaction it is possible to express $\Delta g_i^E$ as:

$$\Delta g_i^E = (n-2i+1)h/2$$  \(\ldots \) (6)

The interaction parameter $h$ may be looked upon as the enthalpy change for consecutive values of $i$.

$$K_{ps} = K^{1/n}$$  \(\ldots \) (7)

Introduction of solvent nonideality (Eq. 5) gives the expression (8):

$$K_{ps} = K^{1/n} \sum_{i=1}^{n} \frac{(n-1)!}{(i-1)!(n-i)!} \left[K^{(n-i)/n} Y^{i-1} \right] \frac{\exp(-\Delta g_i^E/RT)}{\left[1 + \sum_{i=1}^{n} \frac{(n-1)!}{(i-1)!(n-i)!} \frac{(n-1)!}{i} \left[K^{(n-i)/n} Y^{i-1} \exp(-\Delta g_i^E/RT)\right]\right]}$$  \(\ldots \) (8)

where $Y = x_1/x_2$

Equation (8) may be simplified by using Eq. (6) as:

$$K_{ps} = K^{1/n} \sum_{i=1}^{n} \frac{(n-1)!}{(i-1)!(n-i)!} \exp[-i(n-i)h/RT]$$

$$\sum_{i=1}^{n} \frac{(n-1)!}{(i-1)!(n-i)!} \exp[-i(n-i)h/RT]$$  \(\ldots \) (8a)

The quasi-lattice quasi-chemical (QLQC) approach of Marcus uses a lattice theory of solution and attempts to calculate the extent of PS in terms of nearest neighbour interactions. The local excess or deficiency of the component $1$, as measured by $\delta_{s1}$ is given by Eq. (9):

$$\delta_{s1} = x_1 - x_1 = [(1-x_1)(1-y \exp\Delta/2)]/\left[1 + (1-x_1)(1-y \exp\Delta/2)\right]$$  \(\ldots \) (9)

where $y$ depends on the ratio of self preference of the solvents over their mutual interaction and is independent of the nature of the solute but depends on the solvent composition, and

$$\Delta = [(\varepsilon_{ss} + \varepsilon_{11} - 2\varepsilon_{s1}) - (\varepsilon_{ss} + \varepsilon_{22} - 2\varepsilon_{s2})]/kT$$

$\varepsilon_{ij}$ is the pair interaction energy between the species $i$ and the species $j$. The QLQC expression for $\delta_{s1}$ may be used to get the value of $K_{ps}$. Thus according to the QLQC theory

$$\ln K_{ps} = -\ln y - \Delta/2$$

$$= [-\ln y + (\varepsilon_{11} - \varepsilon_{22})/2kT] + (\varepsilon_{s2} - \varepsilon_{s1})/kT$$  \(\ldots \) (10)

Recently we have developed a model for describing PS in terms of various interactions present in a solution. Here the descriptor of PS, $K_{ps}$, is given by

$$kT \ln K_{ps} = \varepsilon_{s1} - \varepsilon_{s2} + \varepsilon_{11} - \varepsilon_{22} - \varepsilon_{12}$$

$$- N_{1}e_{11}^{1} - N_{2}e_{22}^{1} + N_{1}e_{11}^{2} + N_{2}e_{22}^{2}$$  \(\ldots \) (11)

Here $\varepsilon_{s1}$ and $\varepsilon_{ij}$ has the same significance as in the QLQC theory, the superscript 'L' denotes the local phase, and $N_{1}^L$ and $N_{1}^B$ are the number of molecules of $i$th solvent component in the local and the bulk phase. The term inside the square brackets arises due to solvent-solvent interaction. Note that the contribution of the solute-solvent interaction towards $\ln K_{ps}$ viz. $(\varepsilon_{s2} - \varepsilon_{s1})/kT$ is the same in Eqs (10) and (11).

Thus the theories describe the PS characteristics of a solute in a mixed binary solvent in terms of solute-solvent and solvent-solvent interaction. Realistic solvent behaviour has been built into the theories at the expense of more complexity. Such theories involve three adjustable parameters viz. (a) one indicating solute-solvent interaction ($K^{1/n}$ in the SSE model or $\Delta$ in the QLQC model), (b) one representing solvent-solvent interaction e.g. $h$ in the Covington model, and (c) the coordination number $n$. 
Results
The CT band in both the solutes appears as broad and structureless and shifts continuously to the red as percentage of benzene in the mixed binary solvent is increased. The band width and shape, however, remains practically unaltered. This suggests that the band shift is not due to a modification of the equilibria between the solute subspecies as the dielectric constant of the medium changes. The position of the band maximum does not depend on the concentration of the solute in the concentration range studied. The overall intensity, however, changes. The transition energy corresponding to the maximum absorption, $E_{12}$, in various binary mixtures as a function of bulk solvent composition has been shown in Fig. 1. It appears that $E_{12}$ is not a linear function of $x_1$, the bulk mole fraction of the cosolvent (component 1) for all the systems. The experimental $E_{12}$ values for any binary mixture may be represented within experimental accuracy by a polynomial in $x_1$, containing terms up to $x_1^3$ (Eq. 12)

$$E_{12} = A_0 + A_1 x_1 + A_2 x_1^2 + A_3 x_1^3$$

... (12)

The value of $A_0$ represents the value of transition energy maximum for pure benzene. The transition energy in pure benzene could not be determined experimentally due to insolubility of the compounds in benzene. The best-fit value of $A_0$ obtained by using different binary mixtures containing benzene comes out to be the same (except benzene + alcohol solvents) e.g. 54 kcal mol$^{-1}$ for N-ethyl-4-cyanopyridinium iodide and 56 kcal mol$^{-1}$ for N-ethylpyrazinium iodide. This value is also obtained by smooth extrapolation of $E_{12}$ versus $x_1$ curves to $x_1 = 0$. For benzene + alcohols there is sharp variation of $E_{12}$ with $x_1$ in the limit $x_1 \rightarrow 0$ and hence extrapolation has not been attempted. A non-linear variation of the UV-visible spectroscopic parameter, $E_{12}$ versus $x_1$, has often been explained as due to a preferential solvation of the indicator solute in a binary solvent mixture. In our earlier communications we have shown that the PS characteristics of the CIP species may be obtained from UV-visible spectroscopic studies and the index of preferential solvation, $\delta_{PS}$, may be obtained from the experimental $E_{12}$ values as

![Figure 1](image-url)
Table 1—PS parameter, $\delta_{s1}$, for N-ethyl-4-cyanopyridinium iodide in several mixed binary solvents containing benzene as a function of solvent composition

<table>
<thead>
<tr>
<th>Mole fraction</th>
<th>Cosolvents</th>
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<tbody>
<tr>
<td>0.10</td>
<td>Methanol</td>
</tr>
<tr>
<td>0.20</td>
<td>Ethanol</td>
</tr>
<tr>
<td>0.30</td>
<td>1-Propanol</td>
</tr>
<tr>
<td>0.40</td>
<td>1-Butanol</td>
</tr>
<tr>
<td>0.50</td>
<td>2-Propanol</td>
</tr>
<tr>
<td>0.60</td>
<td>t-Butanol</td>
</tr>
<tr>
<td>0.70</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>0.80</td>
<td>Propionitrile</td>
</tr>
<tr>
<td>0.90</td>
<td>Butyronitrile</td>
</tr>
<tr>
<td></td>
<td>Benzonitrile</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
</tr>
<tr>
<td></td>
<td>2-Butanone</td>
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<tr>
<td></td>
<td>Cyclopentanone</td>
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<tr>
<td></td>
<td>Dichloroethane</td>
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</tbody>
</table>

$\delta_{s1} = (E_{12} - x_1 E_1 - x_2 E_2)/(E_1 - E_2)$ \hspace{1cm} \ldots (13)

where $E_1$ and $E_2$ are the transition energy in pure solvent 1 and solvent 2 respectively. The parameter $K_{ps}$ may also be obtained from the spectral data. Thus

$K_{ps} = [x_2 (E_{12} - E_2)]/[x_1 (E_1 - E_{12})]$ \hspace{1cm} \ldots (14)

A positive value of $\delta_{s1}$ or $\ln K_{ps}$ would indicate PS by the component 1. Table 1 lists the PS parameter $\delta_{s1}$ for the binary mixtures. It may be seen that cosolvents are always preferred by the solute over benzene. Figures 2 and 3 represent the variation of $\delta_{s1}$ and $K_{ps}$ respectively with the solvent composition. Alcohols are characterised by a high positive value of $\delta_{s1}$ and also a sharp variation of $K_{ps}$ with $x_1$. A very steep decrease of $E_{12}$ values in the range $0.0 < x_{alcohol} < 0.1$. Possibly in this region every alcohol molecule solvates the CIP species through hydrogen bonding interaction and the conventional theories do not work. Beyond this range the extent of PS follows the order alcohols $\gg$ nitriles $>$ ketones $= \text{dichloroethane}$.

Fig. 2—Representative plots of $\delta_{s1}$ versus the mole fraction of cosolvents: ethanol (a), acetonitrile (b) acetone (c) and dichloroethane (d). Experimental points, continuous lines represent the values calculated according to Eq. (8a) with $K^{1/\alpha}$ and $h$ as 15.5 and $-0.30$ for (a), 2.38 and $-0.06$ for (b), 1.55 and 0.06 for (c) and 1.60 and 0.08 for (d). $Z=8$ for all the cases. Solute: N-ethyl-4-cyanopyridinium iodide.

Fig. 3—Representative plot of $K_{ps}$ versus the mole fraction of cosolvents: alcohols (a), nitriles (b) and ketones (c). Solute: N-ethyl-4-cyanopyridinium iodide.
Discussion

In the present study the two solutes used are similar in nature but the extent of interaction of the solutes with the component solvents are different. It has been pointed out that due to a difference in the non-specific interaction of the two solvents, the solvent with higher dielectric constant ($\varepsilon$) would be preferred near a polar solute\textsuperscript{16}. But the fact that an alcohol having comparable value of $\varepsilon$ as a nitrile or a ketone is more preferred by the solute indicates that other modes of interaction (e.g. specific solute-solvent interaction) play a significant role in the PS by alcohol solvent. It has been found that the solute-solvent interaction as measured by the transition energy of N-alkylpyridinium iodide depends to a large extent (ca. 65%) on the H-bond donating (HBD) ability of the solvents besides the H-bond accepting (HBA) and long range non-specific dipolar interactions\textsuperscript{17}. Thus for protic solvents (alcohols) the PS characteristics of the solute is determined both by the specific hydrogen bonding ability of the solvent and the non-specific interactions. For aprotic solvents the observed PS is due to a difference in the HBA interactions and/or non-specific interactions of the component solvents. The two indicator solutes e.g. N-ethyl-4-cyanopyridinium iodide and N-ethylpyrazinium iodide show similar PS characteristics in a particular binary mixture and this indicates that the HBD interaction with the iodide ion plays a significant role. From Eq. (10) or Eq. (11) the parameter $K_{ps}$ may be written as

$$\ln K_{ps} = \varepsilon_{s2} - \varepsilon_{s1} + \text{solvent-solvent interaction terms} \ldots (15)$$

$\varepsilon_{s1}$ representing energy for the solute-ith solvent interaction. Thus $\ln K_{ps}$ in the present case would depend on $\varepsilon_{s2} - \varepsilon_{s1}$ for a class of cosolvents (component 1) for which the solvent-solvent interaction is practically constant. For a series of monohydroxy alkanols as cosolvents, the cosolvent-benzene interaction may be assumed to be constant and $\varepsilon_{s1}$, the cosolvent-solute interaction is determined largely by the HBD interaction. Thus in such a case $\ln K_{ps}$ is expected to be correlated with HBD interaction represented by Kamlet Taft $\alpha$ parameter\textsuperscript{18}. As the parameter $K_{ps}$ is dependent on the solvent composition we have chosen the value of $K_{ps}$ at the equimolar bulk mixture (i.e. $x_1 = 0.5$). Figure 4 shows a plot of $\log K_{ps}$ values (at $x_1 = 0.5$) versus the $\alpha$ parameters of the cosolvents indicating a good correlation. Plots of $\delta_{s1} (x_1 = 0.5)$ versus $\alpha$ or $\beta$ values are shown in the Fig. 5. The figure indicates that for a class of solvents characterised by little or zero $\alpha$ value, $\delta_{s1} (x_1 = 0.5)$ are correlated with $\beta$ values, while

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Fig. 4—log $K_{ps} (x_1 = 0.5)$ versus $\alpha$ of cosolvents; N-ethyl-4-cyanopyridinium iodide as indicator solute. The numbers have the same significance as in Fig. 1.

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Fig. 5—$\delta_{s1}$ versus $\alpha$ or $\beta$ for N-ethyl-4-cyanopyridinium iodide in mixed solvents containing benzene.
for the alcohols with high $\alpha$ value a straight line parallel to the $\beta$ axis is obtained indicating that in these cases the $\alpha$ value mostly governs the solute-solvent interaction. At this point it is interesting to note the significance of $\delta_{s1}$ ($x_1 = 0.5$). According to Ben-Naim$^{19}$ the parameter $\delta_{s1}$ is given by

$$\delta_{s1} = (G_{s1} - G_{s2})x_1 x_2 / (x_1 G_{s1} + x_2 G_{s2} + V_c) \quad \ldots (16)$$

where $G_{s1}$ and $V_c$ represent the Kirkwood-Buff (KB) parameters$^{20}$ and the correlation volume$^{19}$ respectively. Equation (16) may be rearranged as

$$\frac{\delta}{x_1 + 1} = \frac{G_{s1} + V_c}{x_1 G_{s1} + x_2 G_{s2} + V_c} \quad \ldots (17)$$

Making use of the fact that $x_1 G_{s1} + x_2 G_{s2} \ll V_c$ (ref. 21) we may have the following relations.

$$G_{s1} / V_c = \delta_{s1} / x_1; \quad G_{s2} / V_c = - \delta_{s1} / x_2 \quad \ldots (18)$$

Thus the parameter $\delta_{s1}$ ($x_1 = 0.5$) is a measure of solute-solvent KB parameter at equimolar bulk composition i.e. $G_{s1}$ ($x_1 = 0.5$). It is worthwhile to compare the results obtained for cyclohexane + ethanol with those for benzene + ethanol system (Fig. 1). It appears that due to the addition of cyclohexane the transition energy changes very little indicating that cyclohexane molecules are not as effective as benzene in removing ethanol molecules from the immediate neighbourhood of the solute. Both cyclohexane and benzene have insignificant dipolar and specific interaction with the solute but benzene with its $\pi$-electron density is expected to interact with the solute to a small extent. Thus with an increase in the percentage of benzene in the solvent composition some benzene molecules may be found in the cybotactic region while cyclohexane is almost totally rejected by the solute. Thus in a non-polar solvent where other modes of interaction are absent, the polarisability may become significant in modifying the solvation. This conclusion has also been obtained from multiple linear regression analysis studies$^{17}$.

In the Covington approach the PS characteristics is explained in terms of $K^{1/n}$, a parameter representing solute-solvent interaction, $h = h/RT$, representing solvent-solvent interaction or solvent nonideality and $n$, the coordination number. The parameter $K_{ps}$ may be calculated using these parameters from Eq. 8(a), $\delta_{s1}$ values may then be obtained from the $K_{ps}$ values [Eq. (1)]. We have found that the values of $K^{1/n}$, $h$ and $n$ as given in Table 2 reproduce the experimental $\delta_{s1}$ versus $x_1$ curves (Fig. 2) for the case of N-ethyl-4-cyanopyridinium iodide. It may be observed that the cosolvent-solute interaction as reflected from the parameter $K^{1/n}$ increases in the order dichloroethane $\approx$ acetonitrile $< \approx$ alcohols. This is in accordance with strong HBD interaction of alcohols with iodide ion, the anion of the CIP species through HBD interaction$^{22}$. The observed skewness of the $\delta_{s1}$ versus $x_1$ curves is determined mostly by the parameter $h'$. For the binary mixture containing alcohols and nitriles $h'$ comes as negative (alcohols $\gg$ nitriles) and the mixed solvents with ketones and dichloroethane are characterised by zero and a small positive value respectively.

At this point it is worthwhile to discuss the observed skewness of the $\delta_{s1}$ versus $x_1$ curves. From the relation of $K_{ps}$ and $\delta_{s1}$ (Eq. 1) we may write for the mole fraction $\langle X \rangle$ for which $\delta_{s1}$ is maximum as

$$X_1 = 0.5 - \frac{[\delta_{s1} / [2(K_{ps} - 1)]]}{[X_1 (1 - X_1) dK_{ps} / dx] / [2(K_{ps} - 1)]} \quad \ldots (19)$$

Thus even for ideal solvent-solvent interaction characterised by $K_{ps} = K^{1/n}$ and $h = 0$ in the Covington model, i.e., $dK_{ps} / dX = 0$, we have $X_1 < 0.5$, i.e. the maximum would lie towards the non-polar end. This effect will be enhanced if $dK_{ps} / dX$ is negative. It follows from our calculation that a negative value of $dK_{ps} / dX$ also means a negative value of $h$, meaning an increased stability of $SA_i B_j$ over $SA_{i-1} B_{j+1}$ (Eq. 2)$^{12}$ compared to the situation of solvent ideality ($h' = 0$). In the present case this indicates that the stability of the mixed solvates with benzene increases in the order alcohol $\gg$ nitrile $> \approx$ ketone $> \approx$ dichloroethane. The strong nonideality of binary mixtures of benzene

<table>
<thead>
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<tr>
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and alcohols is intelligible in terms of stronger alcohol-alcohol association through H-bonding compared to very weak alcohol-benzene interaction. Thus a study of optical response of a suitable indicator solute may provide information about solvent-solvent interaction in a binary mixture.

Acknowledgement
The authors thank the CSIR, New Delhi and Burdwan University for financial support.

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