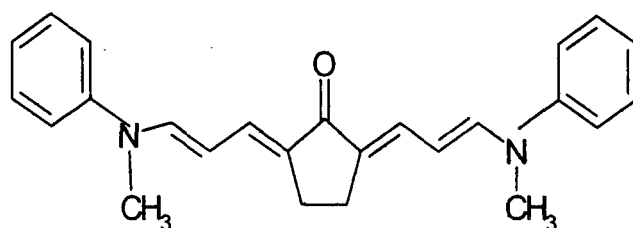
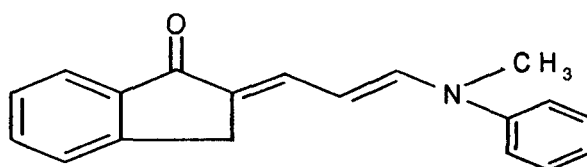

CHAPTER 6 : UV-VISIBLE SPECTROSCOPIC STUDY OF SOLVATION IN TERNARY SOLVENT MIXTURES. KETOCYANINE DYE IN METHANOL + ACETONE + WATER AND METHANOL + ACETONE + BENZENE *

A study of solvation characteristics of a solute in completely miscible ternary solvent mixtures using UV-Visible solvatochromic probes have been presented in this chapter. Ketocyanine dye B, KCD B, (figure 6.1) has been used as the solute. The solvent sensitive intra molecular charge transfer (ICT) absorption band of the solute has been monitored in the following ternary solvent mixtures as a function of solvent composition at a fixed temperature.

- (i) water + methanol + acetone
- (ii) methanol + acetone + benzene



KCD A



KCD B

Figure 6.1: Ketocyanine dyes used in the present study

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Solvation characteristics of the ketocyanine dye B in the binary solvent mixtures containing the solvents, viz., water + methanol, water + acetone, methanol + acetone, methanol + benzene and acetone + benzene, have also been studied as a function of solvent composition. A realistic model of solvation in a ternary solvent mixture has been discussed to interpret the results. Information about the knowledge of binary solvation has been utilized to analyze the results on ternary solvation using a two-phase model of solvation. To test the generality of results experiments were also performed in the two solvent mixtures using a structurally similar ketocyanine dye A (KCD A in figure 6.1).

6.1 Results

The ICT absorption band of the solutes in a mixed solvent appears broad and structureless. Solvatochromism of the ICT band is continuous reversible and independent of the concentration of the solute in the range studied. The bandwidth and shape practically remain unchanged and no isosbestic point is observed in the spectrum. All these facts indicate that the shift of band maximum is not caused by change of equilibria between different chemical species in solution. Figure 6.2 shows the experimental solvent compositions for the ternary solvent mixtures on triangular plot. Values of maximum energy absorption in a ternary solvent mixture, E_{123} , at various compositions at 298K for dye B have been listed in tables 6.1 and 6.2. For ideal solvation behavior the value of a solvent-sensitive property of a solute in a mixed solvent is supposed to be given by the mole fraction average of the property in pure component solvents [1, 2]. Thus the value of maximum energy of absorption in a ternary mixture in an ideal case will be given by the following equation.

$$E_{123} (ideal) = x_1 E_1 + x_2 E_2 + x_3 E_3 \quad (6.1)$$

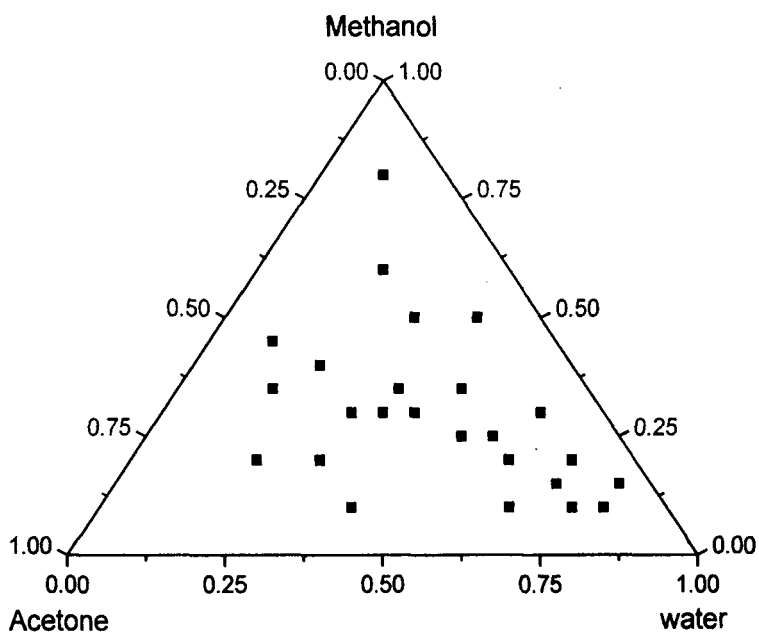
E_i and x_i in the above equation represent respectively the maximum energy of absorption and mole fraction of i -th solvent. Values of $E_{123} (ideal)$ and its difference from E_{123} ($\Delta = E_{123} - E_{123} (ideal)$) have been listed in tables 6.1 and 6.2. A significant deviation of E_{123} from the ideal value has been observed in all the cases. The deviation from the ideal value is always positive for methanol + water + acetone mixture while it is always negative for the methanol + acetone + benzene mixture. The following equation has been used in earlier studies to

represent the composition dependence of the solute property, E_{123} , in a ternary solvent mixture [3-6].

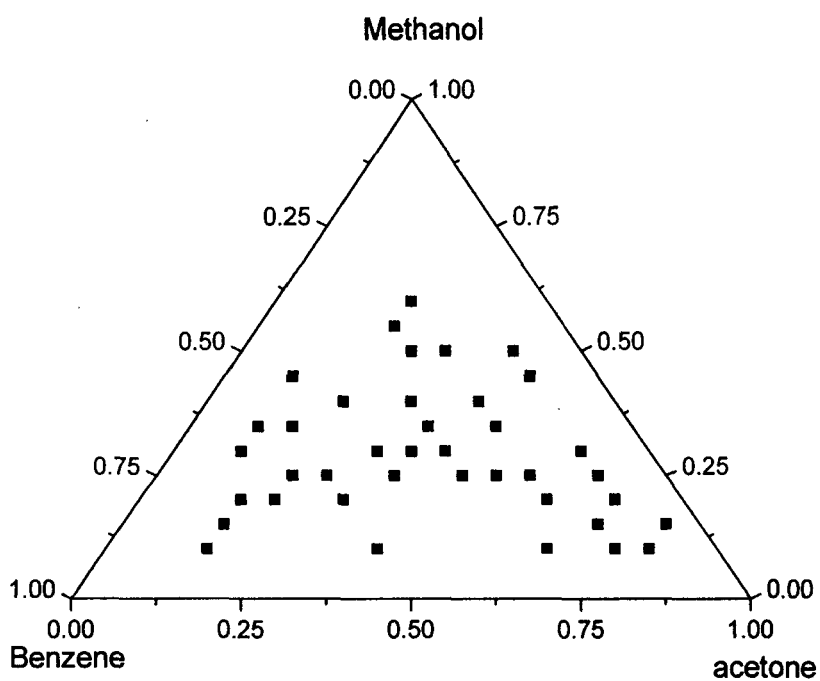
$$E_{123} = E_{123}(\text{ideal}) + x_1x_2x_3(A + Bx_1 + Cx_2) \quad (6.2)$$

where A , B and C are constants for a particular ternary mixture and the solute. It may be mentioned that similar expressions have been used earlier to describe the composition dependence of a solvent property in a ternary solvent mixture in absence of any solute [7-11]. In the present case also, equation (6.2) represents the experimental data points with the best-fit values of the coefficients A , B and C (within an uncertainty limit *ca.* 10%) as -31.3, 167.4 and -2.81 respectively for methanol + water + acetone mixture and -106.5, 84.8 and 120.2 for methanol + acetone + benzene mixture. Figure 6.3 shows the computed iso- Δ lines for the ternary systems. Note that iso- Δ lines are closed curves. The area enclosed by the curve decreases as the value of Δ increases. The estimated solvent composition, (x_1, x_2, x_3) , where the value Δ is maximum may be found as $(0.56, 0.22, 0.22)$ and $(0.25, 0.25, 0.50)$ respectively for the ternary mixture water (1) + methanol (2) + acetone (3) and methanol (1) + acetone(2) + benzene(3). In this context it may be noted that a study of excess properties of the binary solvent mixture shows that the maximum deviation from ideality is observed in approximately equimolar binary composition of acetone + methanol and this has been explained in terms hydrogen bond interaction between methanol and acetone [7]. In the case of a ternary solvation the maximum deviation is observed where the ratio of mole fraction of methanol and acetone is approximately unity. The ratio of mole fraction of methanol and acetone remains unchanged but the absolute value changes when water in the mixture water + methanol + acetone is replaced by benzene. This is because water and benzene interact differently with the cosolvents and also with the solute.

We have also studied the solvation characteristics of KCD B in the corresponding mixed binary solvents. Values of E_{12} , the energy of maximum absorption in a binary solvent mixture (1 + 2) are summarized in table 6.3. In the event of ideality the spectroscopic



(A)



(B)

Figure 6.2: Solvent composition used in the present study for methanol + acetone + water (A) and methanol + acetone + benzene (B)

property (E_{12}) will be given by the mole fraction average and equation 6.1 reduces to the following:

$$E_{12}(\text{ideal}) = x_1 E_1 + x_2 E_2 \quad (6.3)$$

Thus for ideal solvation in a binary solvent mixture a plot of the observed E_{12} values will be linear in mole fraction over the entire range. Figure 6.4 shows the plots of E_{12} as a function of mole fraction of a component solvent along with the ideal lines. It appears that the experimental data points deviates significantly from the ideal line for methanol + water, water + acetone and methanol + benzene mixtures. The deviation from ideality of the observed spectroscopic transition energy has often been explained in terms of preferential solvation (PS) of indicator solute by a component solvent [12-19]. The nature of deviation indicates that organic cosolvents are always preferred by dye B over water in an aqueous binary mixture. For methanol + benzene system the solute is preferentially solvated by the more polar component, namely, methanol. For methanol + acetone mixture there is a small deviation from ideal behavior. For acetone + benzene mixed solvent the cosolvents have E -values very close to each other and no appreciable deviation from ideal behavior is observed.

6.2 Discussions

In a mixed solvent system the indicator solute will be solvated by the component solvent molecules. Due to solute-solvent and solvent-solvent interaction the composition in the immediate neighbourhood of the solute may however differ from the bulk composition. The equilibrium composition in the immediate neighbourhood of the solute molecule will be determined by the criterion of minimum Gibbs free energy of the solute solvent system. Solvation in binary solvents has been extensively studied. In our earlier work with binary solvent systems we showed that a positive deviation of the measured spectroscopic transition energy (E) from the ideal line indicates PS of the solute by the solvent component having higher E -values and vice versa. Thus figure 6.4 indicates that the solute (KCD B) prefers methanol over benzene in methanol + benzene mixture. This is intelligible in terms of higher polarity of methanol. The preference of organic cosolvents by the solute in

Table 6.1. Energy of absorption band maximum of KCD B, E_{123} , and other related parameters as a function of solvent composition of the ternary solvent mixture water (1) + methanol (2) + acetone (3) at 298 K

x_1	x_2	$E_{123}^{a,b}$	$E_{123(id)}^{a,b}$	$\Delta^{a,b}$	$\delta_1^{a,b}$	$\delta_2^{a,b}$	$\delta_3^{a,b}$
0.60	0.20	64.23	63.32	0.91	-0.19	0.09	0.10
0.30	0.30	65.98	64.86	1.12	-0.22	0.09	0.14
0.40	0.30	65.07	64.28	0.79	-0.16	0.08	0.09
0.50	0.25	64.71	63.80	0.91	-0.19	0.09	0.10
0.30	0.20	65.69	65.06	0.63	-0.12	0.03	0.09
0.35	0.35	65.20	64.47	0.73	-0.15	0.08	0.08
0.45	0.35	64.51	63.89	0.62	-0.14	0.08	0.05
0.35	0.30	65.27	64.57	0.70	-0.14	0.06	0.08
0.55	0.25	64.46	63.51	0.95	-0.20	0.11	0.09
0.60	0.30	63.89	63.12	0.77	-0.18	0.13	0.05
0.65	0.10	64.64	63.23	1.41	-0.27	0.08	0.19
0.70	0.15	64.03	62.84	1.19	-0.25	0.12	0.12
0.70	0.20	63.69	62.74	0.95	-0.21	0.14	0.07
0.75	0.10	63.96	62.65	1.31	-0.26	0.11	0.16
0.80	0.10	63.48	62.36	1.12	-0.23	0.12	0.12
0.80	0.15	63.08	62.26	0.82	-0.19	0.14	0.05
0.20	0.40	65.69	65.24	0.45	-0.09	0.03	0.06
0.20	0.60	65.20	64.84	0.36	-0.08	0.06	0.03
0.30	0.50	64.99	64.46	0.53	-0.12	0.08	0.04
0.40	0.10	65.69	64.68	1.01	-0.18	0.03	0.16
0.40	0.50	64.44	63.88	0.56	-0.14	0.11	0.02
0.10	0.80	65.13	65.02	0.11	-0.03	0.02	0.01

^a kcalmol⁻¹, ^b Uncertainty in E_{123} , $E_{123(id)}$, Δ , $\delta = \pm 0.1, \pm 0.1, \pm 0.2, \pm 0.02$ respectively.

Table 6.2. Energy of absorption band maximum, E_{123} , of KCD B and other related parameters as a function of solvent composition of the ternary solvent mixture methanol (1) + acetone(2) + benzene(3) at 298 K

x_1	x_2	$E_{123}^{a,b}$	$E_{123(id)}^{a,b}$	$\Delta^{a,b}$	$\delta_1^{a,b}$	$\delta_2^{a,b}$	$\delta_3^{a,b}$
0.20	0.20	65.72	67.10	-1.38	0.46	0.48	-0.94
0.20	0.60	66.42	66.90	-0.48	0.11	0.42	-0.53
0.30	0.30	65.64	66.80	-1.16	0.38	0.40	-0.78
0.30	0.40	65.95	66.75	-0.80	0.25	0.36	-0.61
0.50	0.25	65.41	66.33	-0.92	0.33	0.18	-0.51
0.25	0.50	66.26	66.83	-0.57	0.16	0.36	-0.52
0.20	0.30	65.95	67.05	-1.10	0.33	0.54	-0.87
0.40	0.30	65.57	66.55	-0.98	0.34	0.27	-0.61
0.45	0.10	65.04	66.53	-1.49	0.57	0.13	-0.70
0.35	0.35	65.80	66.65	-0.85	0.28	0.30	-0.58
0.35	0.45	66.12	66.60	-0.48	0.15	0.22	-0.37
0.25	0.45	66.12	66.85	-0.73	0.21	0.43	-0.67
0.30	0.35	65.87	66.78	-0.91	0.29	0.37	-0.66
0.35	0.15	65.26	66.75	-1.49	0.55	0.24	-0.79
0.25	0.55	66.26	66.80	-0.54	0.14	0.37	-0.51
0.30	0.60	66.34	66.65	-0.31	0.08	0.21	-0.29
0.25	0.65	66.65	66.75	-0.10	0.02	0.11	-0.13
0.10	0.65	66.81	67.13	-0.32	0.04	0.45	-0.49
0.15	0.70	66.73	66.98	-0.25	0.04	0.31	-0.35
0.20	0.70	66.65	66.85	-0.20	0.04	0.22	-0.26
0.10	0.75	66.89	67.08	-0.19	0.01	0.32	-0.33
0.10	0.80	66.97	67.05	-0.08	-0.01	0.19	-0.18
0.15	0.80	66.89	66.93	-0.04	-0.01	0.11	-0.10
0.40	0.20	65.34	66.60	-0.26	0.46	0.24	-0.70
0.60	0.20	65.19	66.10	-0.91	0.34	0.12	-0.46
0.50	0.30	65.49	66.30	-0.81	0.29	0.18	-0.47
0.10	0.40	66.58	67.25	-0.67	0.13	0.67	-0.80
0.50	0.40	65.80	66.25	-0.45	0.15	0.14	-0.29
0.25	0.25	65.72	66.95	-1.23	0.41	0.43	-0.84
0.25	0.35	65.95	66.90	-0.95	0.29	0.44	-0.73
0.45	0.45	65.80	66.35	-0.55	0.18	0.20	-0.38
0.35	0.10	65.19	66.78	-1.59	0.60	0.18	-0.78
0.15	0.15	65.87	67.25	-1.38	0.46	0.48	-0.94
0.25	0.20	65.49	66.98	-1.49	0.51	0.43	-0.94
0.20	0.15	65.80	67.13	-1.33	0.46	0.36	-0.82
0.30	0.10	65.11	66.90	-1.79	0.67	0.22	-0.89
0.10	0.15	66.18	67.38	-1.20	0.36	0.58	-0.94
0.40	0.40	65.72	66.50	-0.78	0.26	0.28	-0.54
0.55	0.20	65.19	66.23	-1.04	0.39	0.14	-0.53

^a kcalmol⁻¹, ^b Uncertainty in E_{123} , $E_{123(id)}$, Δ , $\delta = \pm 0.1, \pm 0.1, \pm 0.2, \pm 0.02$ respectively

aqueous organic solvent mixture, however, needs special mention. In spite of greater polarity of water compared to that of methanol or acetone, the latter components are present in excess over water in the vicinity of the solute molecule. We have also observed similar preferential solvation behavior in these solvent mixtures by monitoring a different polarity (viz., solubility) of the indicator solute [20]. We have explained this behavior in terms of presence of hydrophobic wings in the molecule.

To describe solvation in a solvent mixture we have used the two-phase model of solvation. In this model solvent molecules are assumed to be partitioned in two regions. The region in the neighbourhood of the solute molecule, where the solvent molecules experience the field due to the solute, is the *local* region, while solvent molecules outside the local region are said to be in the *bulk*. If N_i^L and N_i are the number of solvent molecules of i th type in the local and the bulk region respectively, the Gibbs free energy, G , for the solute-solvent system is given by the following expression for a ternary solvent mixture.

$$\begin{aligned}
 G = & [N_1^L \epsilon_{s1}^L + N_2^L \epsilon_{s2}^L + N_3^L \epsilon_{s3}^L] + [N_1^L(N_1^L - 1) \epsilon_{11}^L / 2 + N_2^L(N_2^L - 1) \epsilon_{22}^L / 2 + \\
 & N_3^L(N_3^L - 1) \epsilon_{33}^L / 2 + N_1^L N_2^L \epsilon_{12}^L + N_3^L N_2^L \epsilon_{23}^L + N_1^L N_3^L \epsilon_{31}^L] + \\
 & [N_1(N_1 - 1) \epsilon_{11} / 2 + N_2(N_2 - 1) \epsilon_{22} / 2 + N_3(N_3 - 1) \epsilon_{33} / 2 + N_1 N_2 \epsilon_{12} \\
 & + N_2 N_3 \epsilon_{23} + N_3 N_1 \epsilon_{13}] - [kT \ln[(N_1^L + N_2^L + N_3^L)! / (N_1^L! N_2^L! N_3^L!)] + \\
 & kT \ln[(N_1 + N_2 + N_3)! / (N_1! N_2! N_3!)]] \quad (6.4)
 \end{aligned}$$

In the above equation ϵ_{si} and ϵ_{sj} are the energies of solute - i solvent and i solvent- j solvent interactions. The superscript L indicates the local phase. The first term in the square bracket on the right hand side of equation (6.4) represents solute-solvent interaction, the second and third term in bracket represent solvent-solvent interaction in the local and bulk region respectively. The fourth term represents the entropy term. N_i^L and N_i are related by particle number conservation as follows.

$$N_i^L + N_i = \text{total number of } i\text{-solvent molecule } (i = 1, 2, 3) \quad (6.5)$$

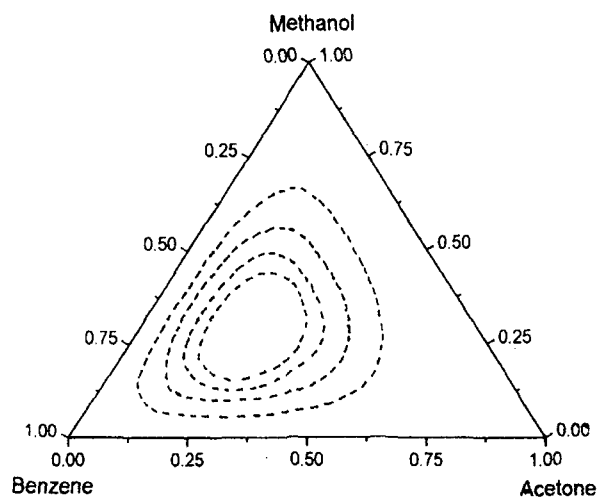
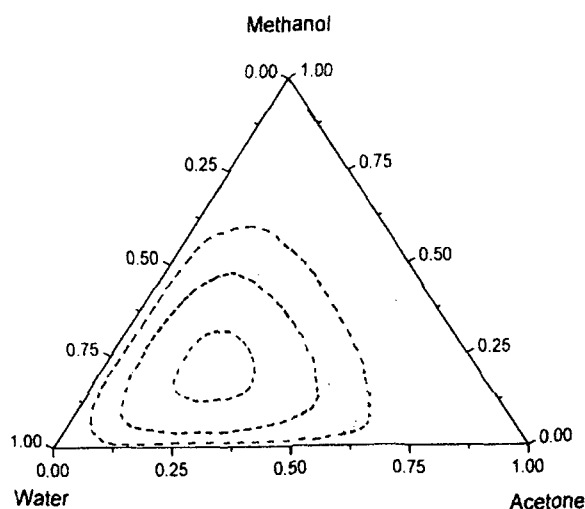


Figure 6.3: Curves of constant Δ -value for methanol + acetone + water (upper) and methanol + acetone + benzene (lower). Δ values in kcal mol⁻¹ for iso Δ curves (from outermost to innermost) are 0.3, 0.8 and 1.5 (upper) and - 0.6, -1.0, -1.3 and -1.45 (lower)

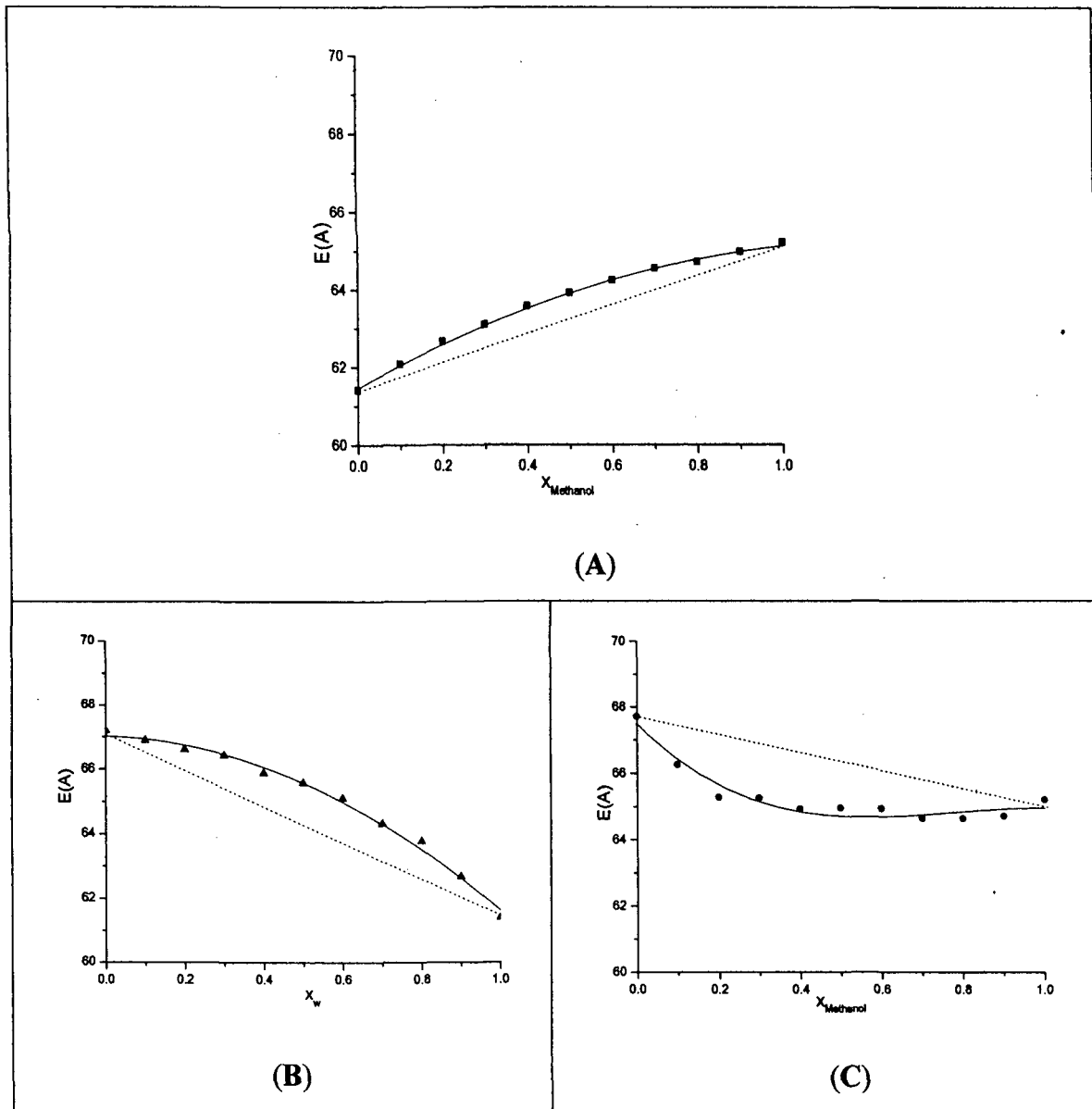


Figure 6.4: Plots of $E(A)$, the energy of maximum absorption of the ketocyanine dye B as a function of solvent composition in mixed binary solvents. (A): methanol + water, (B) : acetone + water, and (C) : methanol + benzene

Values of N_1^L , N_2^L and N_3^L vary with solvent composition. We assume that the total number of molecules in the local region (*cybotactic zone*), $(N_1^L + N_2^L + N_3^L)$ is constant. If we consider the first layer of solvent molecules as constituting local (*cybotactic*) region, the constancy of the total number of solvent molecules is valid when the molecules have the same size [19]. With this assumption the number of independent composition variables in the expression for G reduces to two. Values of N_i^L at equilibrium can be obtained by minimizing G with respect to the two independent variables. Thus taking N_1^L and N_2^L as two independent variables we get the following two conditions for equilibrium solvation.

$$\begin{aligned}
 kT \ln K_{13} = kT \ln [(N_1^L N_3)/(N_1 N_3^L)] = & [\epsilon_{83}^L - \epsilon_{81}^L] + [N_1 \epsilon_{11} - N_1^L \epsilon_{11}^L - N_3 \epsilon_{33} + \\
 & N_3^L \epsilon_{33}^L + (N_1^L - N_3^L) \epsilon_{31}^L - (N_1 - N_3) \epsilon_{31} + N_2 \epsilon_{12} - N_2^L \epsilon_{12}^L - N_2 \epsilon_{13} \\
 & + N_2^L \epsilon_{23}^L + (\epsilon_{11}^L - \epsilon_{33}^L)/2 - (\epsilon_{11} - \epsilon_{33})/2] \quad (6.6)
 \end{aligned}$$

and

$$\begin{aligned}
 kT \ln K_{23} = kT \ln [(N_2^L N_3)/(N_2 N_3^L)] = & [\epsilon_{83}^L - \epsilon_{82}^L] + [N_2 \epsilon_{11} - N_2^L \epsilon_{22}^L - N_3 \epsilon_{23} + \\
 & N_3^L \epsilon_{23}^L + (N_2^L - N_3^L) \epsilon_{32}^L - (N_2 - N_3) \epsilon_{32} + N_1 \epsilon_{12} - N_2^L \epsilon_{12}^L - N_1 \epsilon_{31} \\
 & + N_1^L \epsilon_{31}^L + (\epsilon_{22}^L - \epsilon_{33}^L)/2 - (\epsilon_{22} - \epsilon_{33})/2] \quad (6.7)
 \end{aligned}$$

The term K_{ij} , defined as $[(N_i^L N_j)/(N_i N_j^L)] = [(x_i^L x_j)/(x_i x_j^L)]$ may be looked upon as the equilibrium constant for the following solvent exchange equilibrium.



Where \bar{i} and \bar{j} represent component solvent molecules in the local region, while i and j represent those in the bulk. Equations (6.6) and (6.7) indicate that the value of K_{ij} is dependent on solute-solvent interaction and solvent-solvent interaction or solvent non-ideality effect (terms in the first and second square bracket respectively in the right hand side of equations 6.6 and 6.7). Moreover, the solvent-solvent interaction or the solvent non-ideality effect is dependent on the composition of the solvent mixture. When all the ϵ -values are equal and $\epsilon_{ij}^L = \epsilon_{ij}$, which is equivalent to ideality of the solvent behavior, terms in the second square bracket of equations (6.6) and (6.7) vanish. Similar expressions for the equilibrium constant for the solvent exchange equilibrium can be derived for binary solvation

Table 6.3. Energy of maximum absorption (kcal mol⁻¹) of the ketocyanine dye B in mixed binary solvents at 298K

solvent mixture	mole fraction of component 1											
	(1 + 2)	0. 0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
water + methanol		65.2	65.0	64.7	64.5	64.2	63.9	63.6	63.1	62.7	62.1	61.4
water + acetone		67.2	66.9	66.6	66.4	65.9	65.6	65.1	64.3	63.8	62.7	61.4
methanol + acetone		67.2	67.0	66.8	66.6	66.3	66.2	65.9	65.8	65.7	65.4	65.2
methanol + benzene		67.7	66.2	65.3	65.3	64.9	65.0	64.9	64.6	64.6	64.7	65.2
acetone + benzene		67.7	67.6	67.6	67.4	67.5	67.3	67.4	67.2	67.2	67.6	67.2

[21-23]. In that case the value of $K_{ij} \neq 1$ indicates that $x_i^L \neq x_i$, meaning that the composition of the solvent mixture in the local region is different from that in the bulk.

The maximum transition energy per mole, E , under these conditions, may be written as.

$$E = \frac{\sum N_i^L E_i}{\sum N_i^L} \quad (6.9)$$

In the above equation $\sum N_i^L$ represent the total number of solvent molecules in the local region and, for solvent molecules having almost equal size, may be assumed to be constant. Thus, defining the local mole fraction as $x_i^L = N_i^L / \sum N_i^L$; $i = 1, 2, 3$ we have the following.

$$E_{12} = x_1^L E_1 + x_2^L E_2 \quad : \text{ binary mixture} \quad (6.10)$$

$$E_{123} = x_1^L E_1 + x_2^L E_2 + x_3^L E_3 \quad : \text{ ternary mixture} \quad (6.11)$$

Note that according to equations 6.6 and 6.7 the value of x_i^L is in general different from that of x_i . This is because of differential solute-solvent interaction, and solvent-solvent interaction. To calculate the excess or deficiency of a solvent component in the cybotactic region over that in the bulk for a ternary solvent mixture we proceed as follows. From equations (6.1) and (16.11) we write.

$$\Delta = E_{123} - E_{123}(\text{ideal}) = \sum (x_i^L - x_i) E_i \quad (6.12)$$

Defining a quantity $\delta_i = (x_i^L - x_i)$, which is a measure of the excess or deficit of the i -solvent in the local region compared to that in the bulk and noting that $\sum \delta_i = 0$, we have.

$$\Delta = \delta_1(E_1 - E_3) + \delta_2(E_2 - E_3) \quad (6.13)$$

The component solvents of the ternary mixture in the present investigation have been chosen such that $E_1 > E_2 > E_3$. The overall sign of Δ thus depends on the sign of δ_1 and δ_2 . Equation (6.12) for a binary solvent mixture reduces to

$$\Delta = \delta_1(E_1 - E_2) \quad (6.14)$$

Note that, unlike the case of binary solvation, the apparent deviation from ideality, $\Delta = 0$, does not necessarily mean the equality of local and bulk mole fraction ($\delta_i = 0$). Rather, the local composition of all the components differ from that in the bulk in such a way that the value of the parameter E_{123} calculated according to equation (6.13) equals the ideal value. To calculate δ_1 and δ_2 we need another equation between δ_1 and δ_2 . From the definition of K_{12} it follows that $K_{12} = [(x_1 + \delta_1) x_2] / [x_1(x_2 + \delta_2)]$, which on rearrangement gives the following equation.

$$(\delta_1/x_1) - (\delta_2 K_{12})/x_2 = (K_{12} - 1) \quad (6.15)$$

Note that equations (6.13) and (6.15) indicate a relationship between Δ and K_{12} . Thus equations (6.2) and (6.4) are related in some way, indicating that the empirical parameters A , B , C are related to the model parameters. The actual relationship is not obtainable at the present state of development of the model. It appears from equations (15) and (17) that a knowledge of equilibrium constant for solvent exchange equilibrium, K_{12} (or in general, K_{ij}), would lead to evaluation of individual δ values. Values of K_{ij} cannot, however, be obtained from studies of solvation in a ternary solvent mixture. In our studies with binary solvent mixture it has been noted that electron spectroscopic studies provide a method for estimation of K_{12} . The local mole fraction of component solvents in a binary solvent mixture (1+2) is given by [21-23]:

$$X_1^L = (E_{12} - E_2) / (E_1 - E_2) \quad (6.16)$$

and

$$K_{12} = ((E_{12} - E_2) / (E_1 - E_2)) \cdot (x_2 / x_1) \quad (6.17)$$

We have calculated K value for methanol + acetone system for KCD B at various compositions. As discussed earlier, solvation in this mixture shows only small deviation from ideality. Thus K_{12} values for the binary solvent mixture are close to unity. It has been found that K_{12} values are smooth functions of the ratio of mole fraction of solvent components, x_1 / x_2 . $K_{12} = 0.997 - 0.0295 (x_1 / x_2)$, where the suffix 1 and 2 represent acetone and methanol respectively. We have assumed that the preferential solvation parameter K_{12} (which is a measure of excess solute property) obtained in binary solvent mixture is transferable to ternary solvation for the same solute. Similar procedure for explaining excess solvent properties in a ternary mixture has been reported in the literature [7-9]. In our present work we have assumed that the value of K_{12} in a ternary solvent mixture depends similarly on the ratio of mole fraction of acetone and methanol as that observed for binary solvation of the solute involving solvents. Thus, in our calculation for a particular ternary solvent composition (x_1, x_2, x_3) we have taken the value of K_{12} as obtained from the binary solvation of the solute for the same (x_1 / x_2) ratio. Values of δ_1, δ_2 were then calculated using equations (6.13) and (6.15). The values have been listed in tables 6.1 and 6.2. For the two solvent mixtures the value of δ for methanol and acetone are positive while

those of water and benzene are negative. The negative value of δ for a solvent component indicates that the local region is deficient with respect to that component relative to the average composition. Thus results in the present case indicate that methanol and acetone are preferred over benzene or water in the local region. Benzene and acetone have similar value of spectroscopic transition energy and the preference of acetone over benzene cannot be explained in terms of solute-solvent interaction. On the other hand benzene-methanol and benzene-acetone interaction is weaker than methanol-acetone interaction. Deficiency of benzene possibly arises due to differential solvent-solvent interaction. In the case of ternary mixtures of methanol and acetone containing water the deficiency of water is intelligible in terms of strong water-water interaction due to hydrogen bond formation. Moreover the presence of hydrophobic wing in the solute molecule repels water molecules in the local region. As a result water remains self associated and the number of water molecules in the local region is less than

Table 6.4. Energy of absorption band maximum E_{123} of the indicator dye KCD A in the ternary solvent mixture methanol (1) + acetone (2) + benzene(3) at 298 K

x_1	x_2	$(E_{123})_{observed}^{a,b}$	$(E_{123})_{calculated}^{a,b,*}$
0.20	0.20	57.9	57.8
0.50	0.25	57.4	57.2
0.35	0.35	57.9	58.0
0.25	0.55	58.9	58.9
0.20	0.70	59.8	59.7
0.25	0.35	58.3	58.3
0.20	0.15	58.1	58.0
0.55	0.20	56.7	56.8

^a kcalmol⁻¹, ^b Uncertainty in $(E_{123})_{observed} = \pm 0.1$

* calculated using equation (6.18); $E_1 = 56.9$, $E_2 = 60.9$, $E_3 = 62.2$

Table 6.5. Energy of absorption band maximum E_{123} of the indicator KCD A in the ternary solvent mixture water (1) + methanol (2) + acetone(3) at 298 K

x_1	x_2	$(E_{123})_{observed}^{a,b}$	$(E_{123})_{calculated}^{a,b,*}$
0.60	0.20	56.3	56.2
0.30	0.30	59.1	59.3
0.15	0.35	58.4	58.4
0.20	0.60	57.6	57.8
0.40	0.50	56.0	55.6

^a kcalmol⁻¹, ^b Uncertainty in $(E_{123})_{observed} = \pm 0.1$

* calculated using equation (6.18); $E_1 = 52.3$, $E_2 = 56.9$, $E_3 = 60.9$

the average value. The obtained δ values have been used to fit experimental data on E_{123} ($(E_{123})_{obs}$) in the studied solvent mixtures with a structurally similar probe (dye B, figure 6.1) having similar properties [24]. Thus, we have calculated E_{123} values according to the following equation.

$$(E_{123})_{calculated} = (x_1 + \delta_1)E_1 + (x_2 + \delta_2)E_2 + (x_3 + \delta_3)E_3 \quad (6.18)$$

The observed and calculated values are given in tables 6.4 and 6.5. Note that the calculated values of E_{123} for the KCD A using the δ -values for the KCD B agree well with the experimentally observed values.

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