
CHAPTER 7: USE OF A SOLVATOCHROMIC DYE FOR STUDY OF SOLVATION IN TERNARY SOLVENT MIXTURES IN WHICH ONE OF THE PAIRS ARE PARTIALLY MISCIBLE

An interesting way of analyzing the local environment around a solute in a ternary solvent mixture by using electronic absorption spectroscopy has been presented in this chapter. The ICT band of a ketocyanine dye B (figure 7.1) has been studied in two ternary solvent mixtures in which one of the pairs are partially miscible. Solvent mixtures include the following:

- (i) water + ethanol + benzene
- (ii) water + ethanol + cyclohexane

Investigations have been done in the completely miscible region of the ternary system including the binodal curve. The solvation characteristics in the corresponding binary solvent mixtures (viz., water + ethanol, ethanol + benzene and ethanol + cyclohexane) have also been studied. Information about the knowledge of binary solvation has been utilized to analyze the results on ternary solvation.

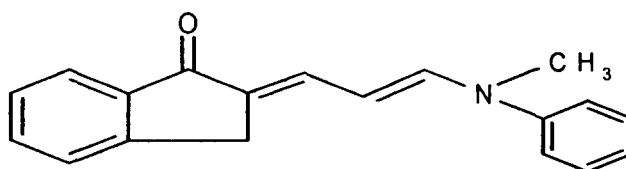


Figure 7.1: Ketocyanine dye B (KCD B) used in the present study

7.1 Results

The ICT absorption band of the solute 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. Figures 7.2 and 7.3 show the experimental solvent compositions for the ternary solvent mixtures on triangular plot. Values of maximum energy of absorption in a ternary solvent mixture, E_{123} , at various compositions at 298K have been listed in tables 7.1 and 7.2. 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.

$$E_{123} \text{ (ideal)} = x_1 E_1 + x_2 E_2 + x_3 E_3 \quad (7.1)$$

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 $E_{123} \text{ (ideal)}$ and its difference from E_{123} ($\Delta = E_{123} - E_{123} \text{ (ideal)}$) have been listed in tables 7.1 and 7.2. A significant deviation of E_{123} from the ideal value has been observed in all the cases. The binodal curves for the two mixtures have been indicated by XYZ and QRS in figures 7.2 and 7.3 respectively. Both positive and negative deviation from ideality occurs along the binodal curve. The point Y in figure 7.2 represents a composition for which the value of Δ is zero for water(1) + ethanol(2) + benzene(3) system. This corresponds to a composition : $x_1 = 0.31$, $x_2 = 0.47$ and $x_3 = 0.22$. Positive values of Δ have been obtained in the composition range represented by points on XY where the mole fraction of water is high. On the other hand, solvent composition having lower mole fraction of water (points on YZ) are characterized by negative values of Δ . In the completely miscible range, we have an interesting situation. Solvent compositions indicated by the line joining the ethanol end of ternary system (E) and the point Y on the binodal curve as indicated in the figure 7.2 corresponds to $\Delta \cong 0$. Thus $\Delta \cong 0$ is indicated for solvent composition, where $x_{\text{water}} : x_{\text{benzene}}$ is fixed (~ 1.4). Solvent compositions for which the ratio is less than the fixed ratio (indicated by the region N in the figure 7.2) shows uniformly a negative value of Δ , while a positive value is shown when the ratio is greater than the fixed value (region P in the figure 7.2). Similar observations have been found when benzene in the ternary mixture is replaced by cyclohexane. Thus in Figure 7.3 compositions represented by

the point R on the binodal line (QRS) and the line ER are characterized by almost zero value of Δ . Thus the points where $x_{water} : x_{cyclohexane}$ is ~ 1.08 are characterized by almost zero Δ value. Points in the region P (bounded by the lines ER and RS) have positive Δ values while those in the region N (bounded by the lines ER and QR) are characterized by negative values of Δ .

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].

$$E_{123} = E_{123}(\text{ideal}) + x_1 x_2 x_3 (A + Bx_1 + Cx_2) \quad (7.2)$$

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 (7.2) represents the experimental data points on E values (solute property) with the best-fit values of the coefficients A , B and C (within an uncertainty limit *ca.* 10%) as -245.14, 433.4 and 228.6 respectively for water + ethanol + benzene mixture and - 814.8, 1193.8 and 867.9 for water + ethanol + cyclohexane mixture. Solvation characteristics of the indicator solute in the corresponding mixed binary solvents have also been studied. Values of E_{12} , the energy of maximum absorption in a binary solvent mixture (1 + 2), are summarized in table 7.3. In the event of ideality the spectroscopic property (E_{12}) will be given by the mole fraction average and equation (7.1) reduces to the following.

$$E_{12}(\text{ideal}) = x_1 E_1 + x_2 E_2 \quad (7.3)$$

Thus ideal solvation in a binary solvent mixture will be characterized by a linear plot of the observed E_{12} values with mole fraction over the entire range. Figure 7.4 shows the plots of

Table 7.1. Energy of absorption band maximum of the indicator KCD B, E_{123} and other related parameters as a function of solvent composition of the ternary solvent mixture water (1) + ethanol (2) + benzene (3) at 298 K. Serial number 1 – 16 represents data points in the miscible range and serial number 17 – 28 represents data points on binodal curve

Sl. No.	x_1	x_2	$E_{123}^{a,b}$	$E_{123}(id)^{a,b}$	Δ
1	0.06	0.91	64.86	64.96	-0.10
2	0.17	0.79	64.71	64.58	0.13
3	0.40	0.56	64.51	63.72	0.79
4	0.22	0.58	64.51	64.81	-0.30
5	0.04	0.78	64.79	65.42	-0.63
6	0.08	0.47	64.36	65.97	-1.61
7	0.30	0.65	64.79	64.12	0.67
8	0.35	0.55	64.71	64.07	0.64
9	0.25	0.65	64.79	64.44	0.35
10	0.35	0.50	64.64	64.20	0.44
11	0.15	0.55	64.84	65.33	-0.49
12	0.15	0.60	64.71	65.20	-0.49
13	0.05	0.65	64.99	65.70	-0.71
14	0.10	0.55	64.84	65.64	-0.80
15	0.46	0.45	64.57	63.63	0.94
16	0.80	0.47	64.79	64.08	0.71
17	0.05	0.20	64.92	66.87	-1.95
18	0.09	0.30	64.79	66.35	-1.56
19	0.16	0.42	64.79	65.60	-0.81
20	0.25	0.46	64.64	64.93	-0.29
21	0.34	0.46	64.44	64.36	0.08
22	0.38	0.46	64.36	64.11	0.25
23	0.36	0.46	64.36	64.24	0.12
24	0.34	0.46	64.02	64.36	-0.34
25	0.38	0.45	64.36	64.14	0.22
26	0.57	0.36	64.23	63.17	1.06
27	0.53	0.38	64.36	63.37	0.99
28	0.44	0.43	64.48	63.81	0.67

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

Table 7.2. Energy of absorption band maximum of the indicator KCD B, E_{123} and other related parameters as a function of solvent composition of the ternary solvent mixture water (1) + ethanol (2) + cyclohexane (3) at 298 K. Serial number 13 - 17 represents data points in the miscible range and serial number 1 -12 represents data points on binodal curve

Sl. No.	x_1	x_2	$E_{123}^{a,b}$	$E_{123}(id)^{a,b}$	Δ
1	0.49	0.49	64.43	63.39	1.04
2	0.44	0.54	64.57	63.57	1.00
3	0.38	0.59	64.71	63.85	0.86
4	0.32	0.62	64.79	64.22	0.57
5	0.20	0.70	64.98	64.87	0.11
6	0.15	0.72	65.06	65.21	-0.15
7	0.14	0.72	65.13	65.30	-0.17
8	0.09	0.71	65.27	65.79	-0.52
9	0.09	0.70	65.20	65.84	-0.64
10	0.08	0.71	65.27	65.88	-0.61
11	0.17	0.71	65.06	65.08	-0.02
12	0.03	0.55	64.64	67.13	-2.49
13	0.09	0.85	64.98	65.07	-0.09
14	0.16	0.80	65.07	64.71	0.36
15	0.22	0.74	65.08	64.49	0.59
16	0.05	0.80	65.32	65.68	-0.36
17	0.04	0.77	65.34	65.92	-0.58

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

E_{12} as a function of mole fraction of a component solvent. The ideal lines have also been shown in the figure. It appears that the experimental data points deviate significantly from the ideal line for all the solvent mixtures. The deviation from ideality of the observed spectroscopic transition energy has often been explained in terms of preferential solvation of indicator solute by a component solvent [12-18]. The nature of deviation indicates that ethanol is always preferred by the solute over water, benzene or cyclohexane in a binary mixture containing ethanol.

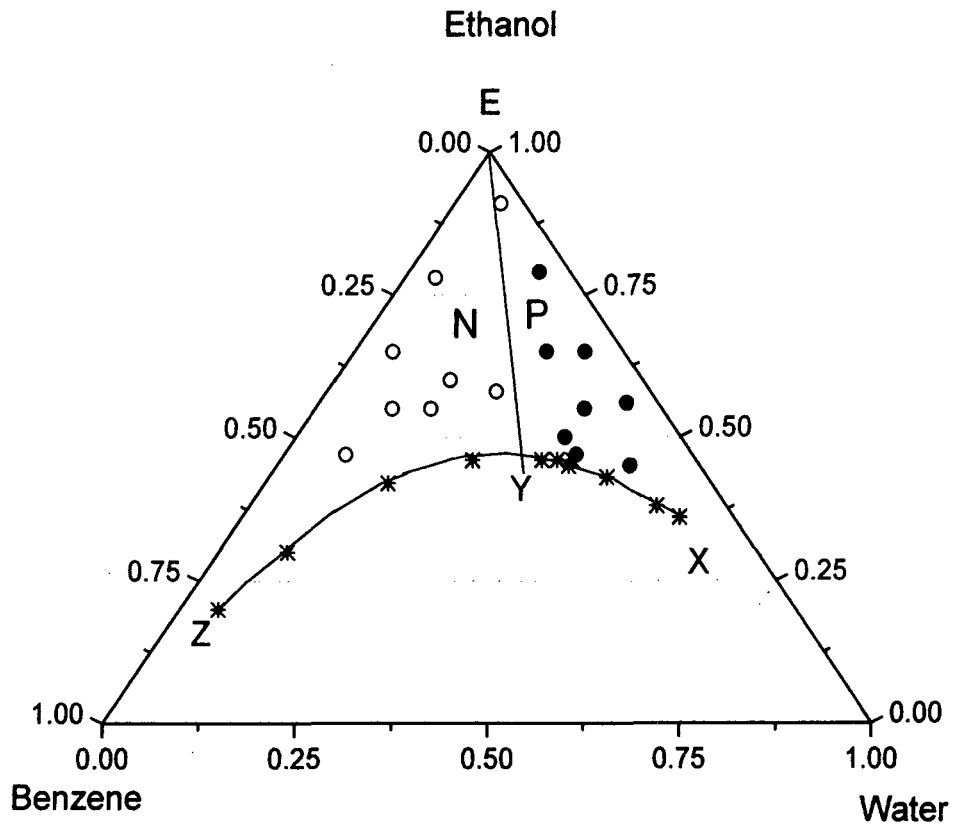


Figure 7.2: Solvent composition used in the present study for water + ethanol + benzene in the miscible composition and the binodal curve XYZ. Points on the line EY are characterized by $\Delta = 0$ and those in regions P (filled circle) and N (open circle) are characterized respectively by positive and negative Δ values

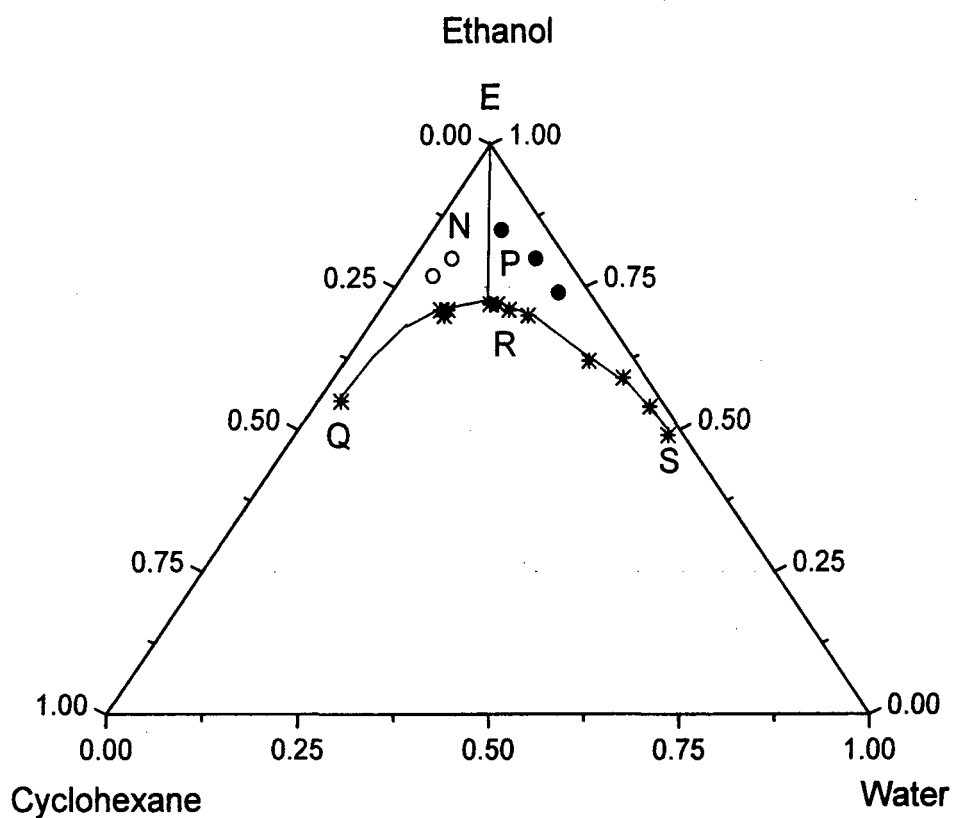


Figure 7.3: Solvent composition used in the present study for water + ethanol + cyclohexane in the miscible composition and the binodal curve QRS. Points on the line ER are characterized by $\Delta = 0$ and those in regions P (filled circle) and N (open circle) are characterized respectively by positive and negative Δ values

7.2 Discussion

In a mixed solvent (binary or ternary) a molecule of the indicator solute will be solvated by the molecules of the component solvents. Let N_i represent the number of solvent molecules of the i -th type around the solute. The maximum transition energy per mole, E , under these conditions, may be written as [3].

$$E = \sum N_i^L E_i / \sum N_i^L \quad (7.4)$$

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. The local mole fraction can be defined as $x_i^L = N_i^L / \sum N_i^L$; $i=1,2,3$ for a ternary mixture and $i = 1, 2$ for a binary mixture. Thus we have the following.

$$E_{12} = x_1^L E_1 + x_2^L E_2 \quad : \text{binary mixture} \quad (7.5)$$

$$E_{123} = x_1^L E_1 + x_2^L E_2 + x_3^L E_3 \quad : \text{ternary mixture} \quad (7.6)$$

Due to differential solute-solvent and solvent-solvent interaction the value of x_i^L is in general different from that of x_i . To study the deviation from ideality we proceed as follows. From equations (7.1) and (7.5) we write for a mixed binary solvent.

$$\Delta = E_{12} - E_{12}(\text{ideal}) = \sum (x_i^L - x_i) E_i \quad : i=1, 2 \quad (7.7)$$

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 $\delta_1 + \delta_2 = 0$, we have.

$$\Delta = \delta_1 (E_1 - E_2) \quad (7.8)$$

Thus for a binary solvent mixture $\Delta = 0$ implies $\delta_1 = 0$, that is, the local and the bulk mole fraction are equal and an ideal situation is obtained. On the other hand, for a ternary mixture we have.

$$\Delta = E_{123} - E_{123}(\text{ideal}) = \sum (x_i^L - x_i) E_i \quad : i=1, 2, 3 \quad (7.9)$$

Noting that $\sum \delta_i = 0$, we have for this system.

$$\Delta = \delta_1 (E_1 - E_3) + \delta_2 (E_2 - E_3) \quad (7.10)$$

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

Table 7.3. Energy of maximum absorption (kcal mol⁻¹) of the KCD B in mixed binary solvents at 298K

solvent mixture (1 + 2)	mole fraction of component 1										
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
water + ethanol	65.1	64.9	64.8	64.7	64.6	64.5	64.2	63.9	63.4	62.6	61.4
ethanol + benzene	67.7	65.8	65.0	64.8	64.9	65.2	64.0	64.3	64.7	64.9	65.1
ethanol + cyclohexane	70.2	65.9	65.7	65.6	65.5	65.3	65.3	65.1

value of the parameter E_{123} calculated according to equation (7.10) equals the ideal value.

It appears that the overall sign of Δ thus depends on the sign of δ_1 and δ_2 . We first discuss the case when $\Delta = 0$ (apparent ideal behavior). For such a case we write from equation (7.10) the following.

$$\delta_1 / \delta_2 = - (E_2 - E_3) / (E_1 - E_3) \quad (7.11)$$

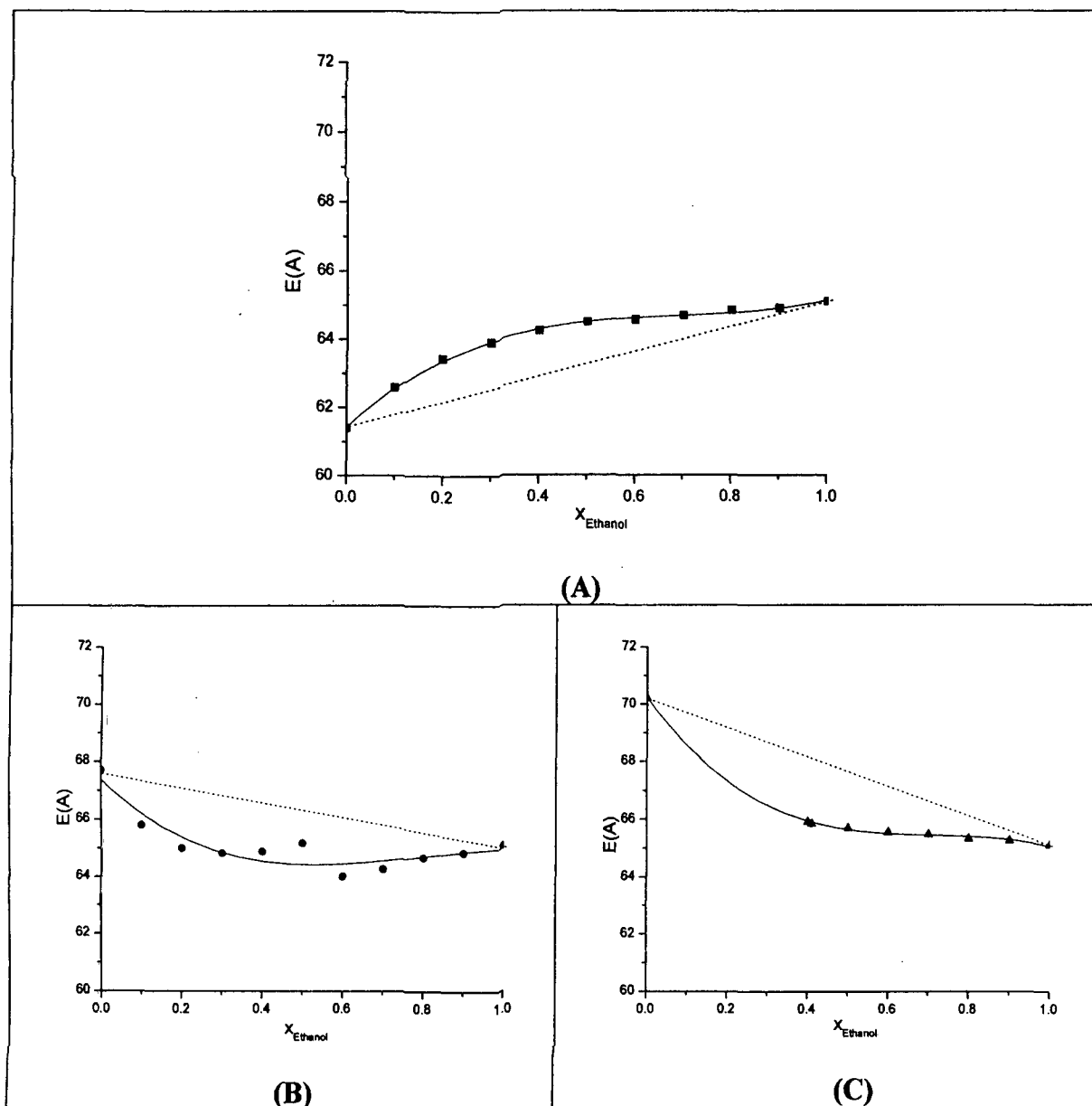


Figure 7.4: Plots of $E(A)$, the energy of maximum absorption of the KCD B as a function of solvent composition in mixed binary solvents. (A): ethanol + water, (B): ethanol + benzene, and (C): ethanol + cyclohexane

In the studied solvent mixtures, namely water (1) + ethanol(2) + benzene / cyclohexane (3) we have $E_1 < E_2 < E_3$. Thus from equation (7.10) we conclude that δ_1 and δ_2 are of different sign. Similar analysis shows that δ_1 and δ_3 are of same sign. A positive value of δ_i means that there is an excess concentration of the i -th component in the local region over that in the bulk. Our results with the mixed binary solvents indicate that ethanol is preferred by the dye in its local environment over cyclohexane, benzene or water. Thus in the present case the possibility, that δ_2 is positive while δ_1 and δ_3 are negative, is most likely. Thus we can conclude that even when the experimental value E_{123} equals the mole fraction averaged value, $E_{123}(\text{ideal})$ e.g. (solvent compositions at the point Y (or R), or, on the line EY (or ER) in figures 7.2 and 7.3, the solute prefers the ethanol molecules in its neighbourhood over water or benzene. For higher mole fraction of water a positive value of Δ has been obtained. This is intelligible in terms of self-association of water through hydrogen bonding in this region. Thus the local mole fraction of free water molecule is relatively small and δ_1 assumes a more negative value. The first term in equation (7.10) exceeds the second term. Thus the value of Δ , as given by the equation (7.10) comes as positive. With a decrease in mole fraction of water, however, the self-associated structure of water gradually breaks and δ_1 becomes less negative and the positive value of Δ decreases and ultimately becomes negative (as for the solvent compositions in the region YZ). The condition $\Delta = 0$ is satisfied for a fixed value of water : benzene ratio (~ 1.4). The value of the ratio (water : organic solvent) however changes if the cosolvent benzene is replaced by cyclohexane. The ratio also depends on the nature of the solute. Thus, similar behavior has been observed for these solvent mixtures using the Reichardt's $E_T(30)$ dye. The condition of apparent ideality ($\Delta = 0$) in that case appeared at composition with fixed ratio ($\sim 1:1$) of mole fraction of benzene and water [3].

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