
CHAPTER 4: STUDY OF SOLUTE-SOLVENT AND SOLVENT-SOLVENT INTERACTIONS IN PURE AND MIXED BINARY SOLVENTS*

In the present work the solubility of a ketocyanine dye B (KCD B, figure 4.1) in fifteen different pure solvents and seven aqueous binary mixtures have been studied. Pure solvents include water, monoalcohols, nitrile, ketone, ester, ether and hydrocarbons. Cosolvents in the aqueous binary mixed solvent include methanol, ethanol, propan-1-ol, propan-2-ol, t-butanol, acetone and tetrahydrofuran. Results have been discussed in terms of solute-solvent and solvent-solvent interactions.

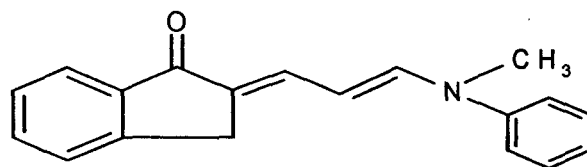


Figure 4.1: KCD B, the dye used in the present work

4.1 Results and Discussions

4.1.1 Pure solvent

Values of solubility (s) of the solute in the molar scale in different pure solvents have been listed in table 4.1. It is known that $\log s$ is related to the standard molar Gibbs energy of solvation [1]. We have studied the parallelism of $\log s$ with $E_T(30)$ value [2], a spectroscopic parameter representing solvent polarity on an empirical basis. Data points for aprotic solvents forms a separate group, which is distinctly different from the group of n-alkanols. For alcohols there exist strong solvent-solvent interaction due to hydrogen bonding and this explains the difference in behaviour for this class of solvents. In the normal alcohol series the solubility decreases as the number of CH_2 unit increases. Methanol,

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however, is an exception. Water does not fall in the line with the hydroxylic solvents. The low solubility of the dye in water is presumably due to the presence of the hydrophobic wing of the dye. Moreover, there is a tendency for water molecules to remain self-associated through hydrogen bonding. In order to study the role played by different modes of solvation interaction on solubility a multiple linear regression analysis (MLRA) involving various solvent parameters has been sought. In general, several independent modes of solute-solvent interaction have been characterized. It is customary to write any property linearly related to the Gibbs energy (XYZ) of a solute-solvent system in terms of linear free energy relationship LSER by the following equation [3, 4].

$$XYZ = XYZ_0 + \text{cavity formation energy} + \Sigma \text{ solute-solvent interaction energy} \quad (4.1)$$

The term XYZ_0 denotes a constant and depends only on the solute. The summation in the above equation extends over all the modes of solute-solvent interaction. Using Kamlet-Taft version of LSER [5], we can write

$$XYZ = XYZ_0 + m \delta_H^2 + p \pi^* + a \alpha + b \beta \quad (4.2)$$

In this equation the cavity term is written as a product of coefficient m and the Hildebrand solubility parameter, δ_H^2 , of the solvent. The solute-solvent interaction is written in terms of nonspecific dipolarity-polarisability interaction and specific interaction, e.g. hydrogen bond donation (HBD) and hydrogen bond acceptance (HBA). Empirical solvatochromic parameters π^* , α , β have been used as descriptors of dipolarity-polarisability, HBD, HBA respectively. Values of α , β , π^* , δ_H^2 for the solvents have been listed in table 4.1. Our results on solubility can be represented by the following equation.

$$\log s = -2.72 + 2.17 \alpha - 0.99 \beta + 3.91 \pi^* - 3.98 (\delta_H^2/1000); n=14, R^2=0.87, \sigma=0.0005 \quad (4.3)$$

The positive values of the regression coefficients of α and π^* indicate that solubility increases with increase in the value of these parameter. Thus, both HBD interaction of the solvent with the carbonyl group of the solute and dipolar solute - solvent interaction leads to an increase in solubility. The negative sign of the coefficient β indicates that HBA interaction of the solvent with the solute is unfavourable. Moreover, the magnitude of the

coefficient of β is relatively small compared to those of α and π^* indicating that solubility of the solute is less sensitive to a variation of β . We have tried the MLRA of $\log s$ with α , π^* and δ_H^2 . The result is hardly affected if the β is not used in the correlation equation. Thus.

$$\log s = -3.05 + 1.20 \alpha + 3.80 \pi^* - 3.54 (\delta_H^2 / 1000), n = 14, R^2 = 0.871, \sigma = 0.0002 \quad (4.4)$$

It appears from the above equations that solubility of the dye depends significantly on the Hildebrand parameter, δ_H^2 , representing the self-cohesiveness of the solvent. In this respect, the thermodynamic property, $\log s$, differs from the spectroscopic parameter viz, energy of maximum absorption / fluorescence of the dye [6]. The negative sign of the coefficient of δ_H^2 indicates the solubility decreases as the self-cohesiveness (or structuredness) of the solvent increases. Thus an increase in the solvent-solvent interaction inducing self-cohesiveness has unfavourable influence on the solubility of the solute.

4.1.2 Mixed binary solvents

Values of $\log s$ as a function of solvent composition in different binary aqueous mixtures have been listed in table 4.2. Figure 4.2 shows plots of $\log s$ versus the mole fraction of water (x_w). Note that $\log s$ is not a linear function of x_w . For all the mixtures data points for $\log s$ can be fitted satisfactorily with a polynomial cubic in x_w as given by the following equation.

$$\log s = A + B x_w + C x_w^2 + D x_w^3 \quad (4.5)$$

Best-fit values of A , B , C , and D have been listed in table 4.3. In equation 4.5, A represents the value of $\log s$ in the pure non-aqueous cosolvent. The agreement of A with the experimental value is good. In the event of ideal solvation the standard Gibbs energy of solution in a mixed binary solvent will be given by the mole fraction averaged value [7, 8] and the solubility in a binary solvent mixture, $\log s_{12}$, will be a linear function of mole fraction. The deviation from linearity of the plots of $\log s_{12}$ versus x_w over the entire composition range (figure 4.2) points to non-ideal solvation behaviour. The deviation from ideality can be compared for the solvent mixtures by defining the following dimensionless parameter.

Table 4.1. Values of solubility of the dye in different pure solvents

Sl. No.	solvent	$E_T(30)$	$\log s$	α	β	π^*	$(\delta_H^2/1000)/Jcm^{-3}$
1	water	63.1	-5.75	1.17	0.47	1.09	2.2940
2	methanol	56.3	-1.86	0.93	0.66	0.60	0.8585
3	ethanol	51.9	-1.72	0.83	0.75	0.60	0.6760
4	propan-1-ol	50.7	-2.00	0.78	0.80	0.52	0.5954
5	propan-2-ol	48.6	-2.23	0.76	0.84	0.48	0.5617
6	butan-1-ol	50.2	-2.56	0.79	0.82	0.47	0.5430
7	<i>t</i> -butanol	43.9	-3.00	0.68	0.93	0.41	0.4666
8	octan-1-ol	48.5	-3.29	0.4368
9	acetone	42.2	-1.56	0.08	0.48	0.71	0.4880
10	acetonitrile	46.0	-1.42	0.19	0.40	0.75	0.5810
11	dichloromethane	41.1	-0.78	0.30	0.00	0.82	0.4080
12	ethylacetate	38.1	-2.72	0.00	0.45	0.55	0.3310
13	benzene	34.5	-2.38	0.00	0.10	0.59	0.3534
14	tetrahydrofuran	37.4	-2.63	0.00	0.55	0.58	0.3610
15	n-hexane	31.0	-3.70	0.00	0.00	-0.08	0.2250

$$\delta = [\log s_{12} - (x_1 \log s_1 + x_2 \log s_2)] / [\log s_1 - \log s_2] \quad (4.6)$$

Values of δ for different solvent mixtures are given in table 4.2. Figure 4.3 shows variation of δ with x_w . For all the solvent mixtures plots of negative values of δ verses x_1 curve passes through a maximum. The maximum appears at $x_w > 0.5$ for the solvent mixtures except water + methanol. The nature of variation of δ with x_w can be represented by the following equation.

$$\delta = x_w (1 - x_w) (M + N x_w) \quad (4.7)$$

where M and N are constants depending on the solute-solvent system. The best fit values of M and N ($R^2 \approx 0.99$, $\sigma < 0.001$ for all the mixtures) are given in table 4.4. At this stage we classify the solvent mixtures in two classes depending on the variation of $\log s_{12}$ versus x_w curves.

Class a: For this class of mixtures the plot of $\log s_{12}$ verses x_w does not show any maximum, i.e., $\log s_2 > \log s_{12} > \log s_1$; the component 1 being water. Of the different mixtures, water + methanol, water + ethanol and water + acetone are in this category. Marcus has explained the nonlinear variation of $\log s$ with mole fraction as due to preferential solvation of the solute [1] when the local mole fraction of a component solvent (x_i^L) in the neighbourhood of the solute differs from the average value (x_i). The local x_i^L can be defined operationally according to Ben-Naim as follows [8]

$$\log s_{12} = x_1^L \log s_1 + x_2^L \log s_2 \quad (4.8)$$

Using the relation: $x_1^L + x_2^L = 1$, we get

$$x_1^L = (\log s_{12} - \log s_2) / (\log s_1 - \log s_2) \quad (4.9)$$

From equations (4.6) and (4.8) we have:

$$\delta = (x_1^L - x_1) \quad (4.10)$$

Thus the parameter, δ , defined by equation (4.6), represents the excess or deficit of the solvent component 1 in the local region. The negative value of δ as obtained for the three mixtures indicates that there is a deficit of the component 1 (water in the present case) in

Table 4.2. Values of $\log s$ and δ in mixed binary solvents

Sl. No.	cosolvent	values	x_w										
			0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
1	methanol	$-\log s$	1.86	1.93	2.12	2.29	2.61	3.03	3.38	4.04	4.74	5.21	5.75
		$-\delta$	0.08	0.13	0.19	0.21	0.20	0.21	0.14	0.06	0.04
		K_{ps}	0.16	0.27	0.26	0.29	0.30	0.26	0.24	0.19	0.10
2	ethanol	$-\log s$	1.72	1.95	2.07	2.13	2.19	2.31	2.54	2.94	3.57	4.49	5.75
		$-\delta$	0.04	0.11	0.20	0.28	0.35	0.40	0.40	0.34	0.21
		K_{ps}	0.51	0.35	0.24	0.17	0.15	0.14	0.13	0.11	0.08
3	acetone	$-\log s$	1.56	1.58	1.53	1.55	1.60	1.70	2.00	2.46	3.17	4.28	5.75
		$-\delta$	0.10	0.21	0.30	0.39	0.47	0.50	0.49	0.42	0.25
		K_{ps}	0.04	0.01	0.03	0.07	0.09	0.10	0.07
4	propan-1-ol	$-\log s$	2.00	2.01	1.83	1.56	1.21	1.16	1.48	1.62	2.29	3.75	5.75
		$-\delta$	0.10	0.25	0.42	0.61	0.73	0.74	0.80	0.72	0.43
5	propan-2-ol	$-\log s$	2.23	2.32	2.18	2.07	1.88	1.74	1.91	2.10	2.65	3.95	5.75
		$-\delta$	0.07	0.21	0.35	0.50	0.64	0.69	0.74	0.68	0.41
6	<i>t</i> -butanol	$-\log s$	3.00	3.05	2.77	2.66	2.41	2.07	2.12	2.18	2.59	3.89	5.75
		$-\delta$	0.08	0.28	0.42	0.61	0.83	0.92	0.99	0.95	0.57
7	tetrahydrofuran	$-\log s$	2.63	2.11	1.46	1.09	0.71	0.47	0.74	1.02	1.74	3.46	5.75
		$-\delta$	0.27	0.58	0.79	1.02	1.19	1.22	1.21	1.09	0.60

the local region around the solute relative to that in the bulk . Thus the organic cosolvent methanol, ethanol or acetone is preferred over water in the local region. This can be rationalized in terms of strong self-association of water molecules through hydrogen bonding. The solute, with its hydrophobic wing, cannot break the structure. Thus the percentage of free water molecules that take part in solvation decreases. Similar observation of preferential solvation of the solute by alcohols has been reported earlier using a spectroscopic parameter [6]. At this point we mention that the definition of x_1^L in terms of solubility is *ad hoc*. To check whether it has any general validity we have calculated the parameter using the solvent-sensitive spectroscopic property, namely, the energy of maximum absorption ($E(A)$) of the dye. Figure 4.4 shows the x_1^L values calculated using the two parameters for the solvent mixtures. Note that for the cosolvents methanol and ethanol, the values of x_1^L for a particular mole fraction, calculated using the two different parameters come as same within the experimental accuracy. For water + acetone mixture, however, the x_1^L values calculated using solubility differs from those obtained using spectroscopic parameter, although the general trend of variation of x_1^L versus x_1 are the same

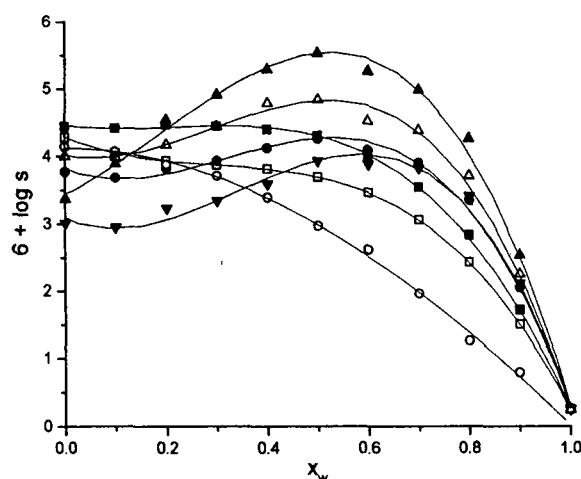


Figure 4.2: $\log s$ as a function of x_w for different aqueous organic mixed solvents. The organic cosolvents are methanol (○), ethanol (□), propan-1-ol (△), propan-2-ol (●), *t*-butanol (▼), acetone (■) and tetrahydrofuran (▲)

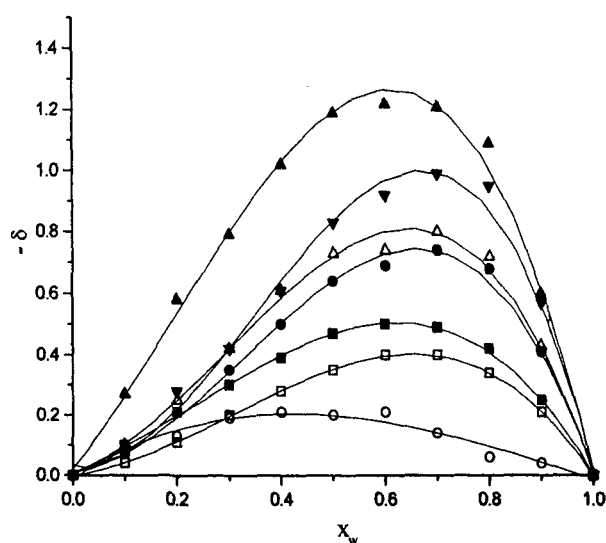
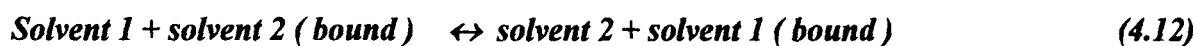


Figure 4.3: Plot of $-\delta$ as a function of solvent composition. Symbols for organic cosolvents are the same as in figure 4.2

in the two cases. According to the existing models, preferential solvation is often expressed by the parameter K_{ps} defined by equation (4.11) [9]

$$K_{ps} = [x_1^L (1 - x_1)] / [x_1 (1 - x_1^L)] \quad (4.11)$$

K_{ps} can be looked upon as the equilibrium constant representing the following solvent exchange process.



The term “*bound*” within the first bracket indicates the solvent i in the local zone. Values of K_{ps} have been calculated using x_1^L obtained from solubility data and listed in table 4.2. It appears that the values of K_{ps} are dependent on the composition of the solvent mixtures. For water + methanol system, however, K_{ps} is independent of the solvent composition. This means that methanol-methanol, water-water and water-methanol interactions are similar.

Class b: Mixtures in this category are characterized by the existence of a maximum in the $\log s_{12}$ versus x_w plot. In this case equation (4.8) is not valid. The nonlinear variation of $\log s_{12}$ with x_w cannot be explained by the idea of preferential solvation for this case. In this context it may be mentioned that equation (4.8) is not valid when strong solvent-solvent interactions are present [10]. The presence of maximum for an observed solute property at an intermediate solvent composition has also been reported by others and has been explained in terms of solvent-solvent interaction [11]. Existence of maximum or minimum of several properties for aqueous-organic binary mixtures also finds support from molecular simulation studies where strong water-cosolvent interaction has been identified [12-14]. Our results indicate that solvent-solvent interaction plays an important role in the case of aqueous tetrahydrofuran / propan-1-ol / propan-2-ol / *t*-butanol mixtures. In these aqueous binary mixtures the solubility at first increases as x_w increases, reaches a maximum and then decreases. Thus the whole composition range can be divided into at least two different regions. Water is highly structured solvent with a high self-cohesiveness and this property is expected to change as a cosolvent is added to it. As discussed in the previous section that $\log s$ depends on the self-cohesiveness of a solvent as described by δ_H^2 . It is known that the Stoke's shift (Δ) for a solute in a given solvent is dependent on solvent reorganization energy [15], which presumably depends on the self-cohesiveness of the solvent. We have sought a correlation of Δ with δ_H^2 for this solute in pure solvents. A fairly good correlation (equation 4.13) supports our supposition.

$$(\Delta / \text{kcal.mol}^{-1}) = 6.81 + 3.31 (\delta_H^2 / 1000); n = 20; R = 0.88; \sigma = 0.0002 \quad (4.13)$$

The positive slope indicates that solvent reorganization energy increases as the self-cohesiveness of solvent increases. Δ -values for the binary aqueous mixtures for the solute have also been determined as a function of solvent composition. Figure 4.5 shows plots of Δ versus x_w for some representative solvent mixtures. Note that except binary mixed aqueous solvents containing methanol and ethanol, the Δ versus x_w curve passes through a

Table 4.3. Values of A , B , C and D (equation 4.5) for mixed binary systems

Sl. No.	cosolvent	A	B	C	D
1	methanol	-1.90	0.49	-6.65	2.26
2	ethanol	-1.72	-3.10	8.61	-9.54
3	acetone	-1.55	-0.98	5.89	-9.11
4	propan-1-ol	-1.99	-1.44	14.59	-16.86
5	propan-2-ol	-2.19	-2.85	15.73	-16.39
6	<i>t</i> - butanol	-2.92	-3.20	19.25	-18.81
7	tetrahydrofuran	2.57	3.70	8.84	-15.64

Table 4.4. Values of M and N for mixed binary solvents

Sl. No.	cosolvent	M	N
1	methanol	1.06	-0.64
2	ethanol	0.24	2.36
3	acetone	0.81	2.16
4	propan-1-ol	0.58	4.69
5	propan-2-ol	0.28	4.71
6	<i>t</i> - butanol	0.04	6.87
7	tetrahydrofuran	2.33	5.12

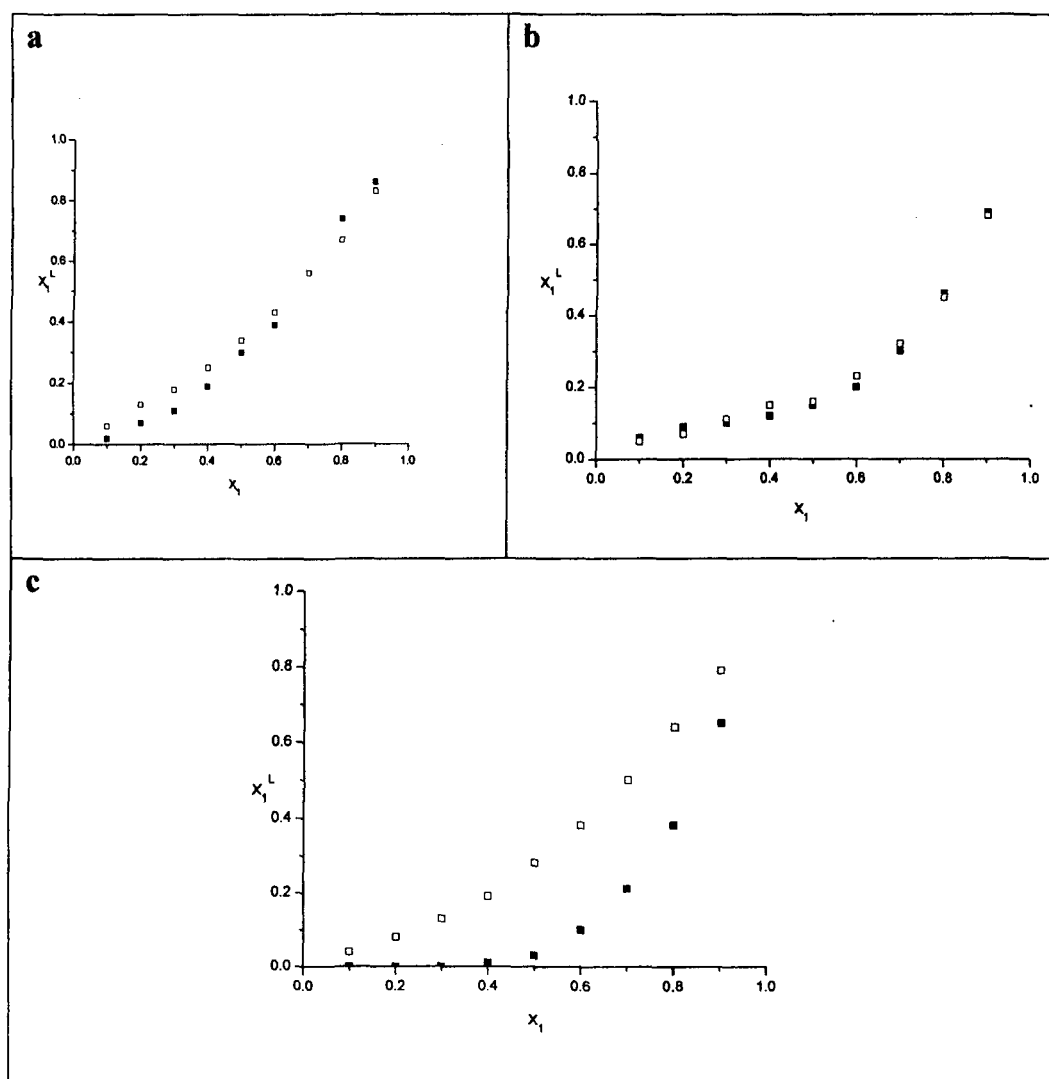


Figure 4.4: Plot of x_1^L calculated using solubility (■) and spectroscopic property, $E(A)$, (□) for mixed aqueous solvents containing methanol (a), ethanol (b) and acetone (c) as a function of x_1 .

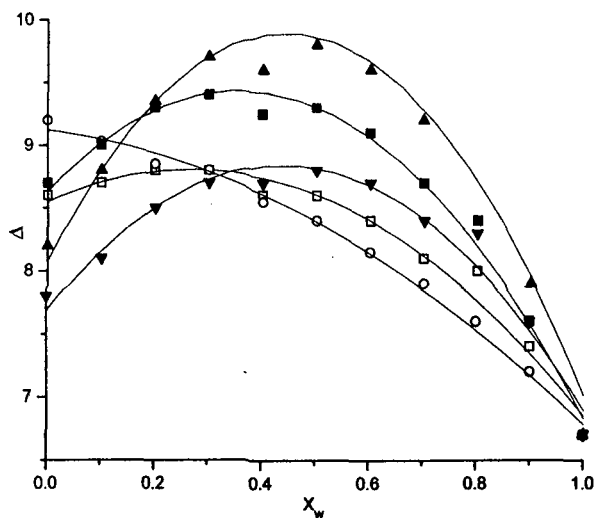


Figure 4.5: Plot of Δ versus x_w . Symbols for organic cosolvents are the same as in figure 4.2.

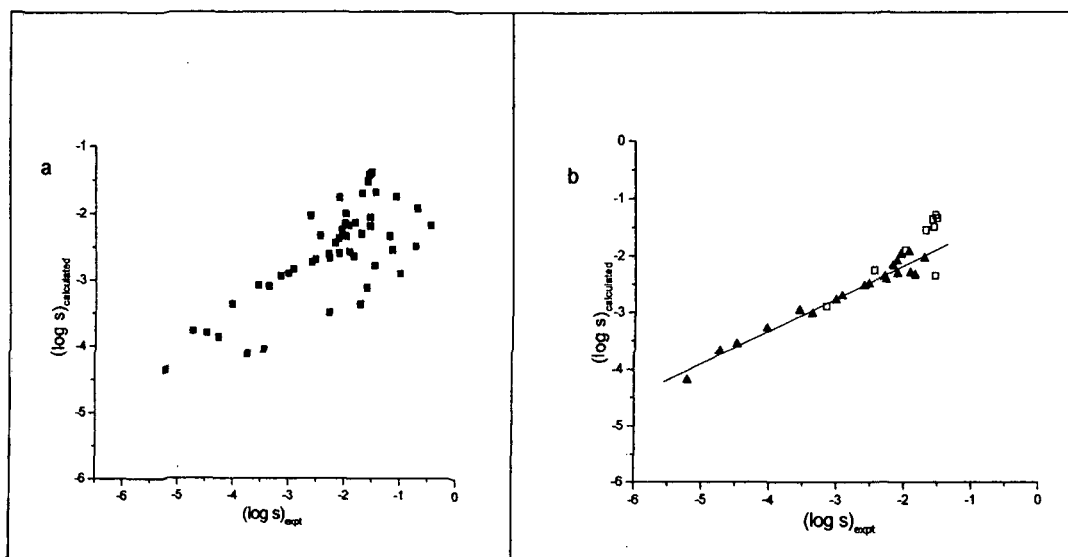


Figure 4.6: Plot of $(\log s)_{\text{calculated}}$ versus $(\log s)_{\text{expt}}$ (a): for all mixed aqueous solvents (except water + propan-2-ol and water + *t*-butanol) and (b): aqueous methanol, ethanol and acetone

maximum at an intermediate mole fraction of water. The negative slopes of Δ versus x_w for water + methanol and water + ethanol indicate that the value of Δ and hence δ_H^2 , decreases monotonically as x_w increases. But for other mixtures value of δ_H^2 at first increases, passes through a maximum and then decreases. The positions of maxima, however, do not coincide with those in δ versus x_w curves. This is presumably due to solvent-solute interaction. Thus we can conclude that self-cohesiveness of solvents, as represented by δ_H^2 has a predominant role in modifying solubility in the mixed solvents belonging to this class.

We have attempted correlation of solubility with the solvatochromic parameters (α, β, π^*) and the Hildebrand solubility parameter (δ_H^2) according to equation (4.3). Values of solvatochromic parameters of some of the systems studied are known [16] and values of δ_H^2 have been calculated for the binary mixtures from known enthalpies and volume of mixing and those quantities for neat solvents [7]. The calculated values of $\log s$ have been plotted against the observed $\log s$ values as shown in figure (4.6). Although the correlation is not very good when all the aqueous binary mixtures are included, there is a significant correlation when mixtures containing methanol, ethanol and acetone only considered. Thus for the solvent mixtures belonging to category b other modes of interaction besides those included in equation (4.3) are also important.

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