trazoline-5-thione (**2a, R_2=allyl**)[12] (334 mg, 83%, based on 1-methyltetrazoline-5-thione) and of 1-methyl-5-allylthiotetrazole (**3a, R_2=allyl**)[12] (54 mg, 13%) as oils.

Method B. To a solution of allyl bromide (1.56g, 12.9 mmol) in dry propionitrile (15 m*l*) is added potassium iodide (2.07g, 12.9 mmol), 1-methyltetrazoline-5-thione (**1c**) (300 mg, 2.58 mmol), and trimethylsilyl iodide (51.6 mg, 0.25 mmol). The reaction mixture is heated at reflux for 13 h after which it is cooled to room temperature and concentrated. The same workup procedure followed by purification as described in the preceding procedure furnished 1-methyl-4-allyltetrazoline-5-thione (242 mg, 60%) and of 1-methyl-5-allylthiotetrazole (121 mg, 30%) as oils.

Method C. To a mixture of 1-methyltetrazoline-5-thione (300 mg, 2.58 mmol) in allyl bromide (1.56g, 12.91 mmol) is added trimethylsilyl iodide (51.6 mg, 0.25 mmol). The mixture was heated at 85-90 °C for 4 h after which it is cooled to room temperature. The same workup procedure followed by purification as described in the procedure A afforded 1-methyl-4-allyltetrazoline-5-thione (314 mg, 78%) and 1-methyl-5-allylthiotetrazole (62 mg, 15%) as oils.

Acknowledgement. The financial support of the Ministry of Science and Technology, Korea is gratefully appreciated.

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The Measurement of Transfer Enthalpy in Mixed Solvent (Part I). Enthalpies of Solution of Aniline, Pyridine and Benzylamine in the Isodielectric Binary Mixtures of Methanol with Acetonitrile, Nitrobenzene and Nitromethane

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Enthalpies of solution of aniline, pyridine and benzylamine in iso-dielectric mixtures of methanol with acetonitrile (AN), nitrobenzene (NB) and nitromethane (NM) have been measured calorimetrically. The solute-solvent interaction was analyzed using a model developed by Waghorne *et al.* and found that the relatively weak base, aniline, tended to behave anomalously, especially in the NB and NM binary systems by forming bidentate hydrogen bonds between the two $-NH_2$ hydrogens and the two $-NO_2$ oxygens. Pyridine and benzylamine were found to be preferentially solvated by methanol in all the binary mixtures.

Introduction

Thermodynamics of solvation of organic non-electrolytes has attracted considerable interest in the elucidation of organic reaction mechanism. Information on the variation of the transition state(TS) structure with solvent changes can be obtained from the enthalpies of solution of reactants in a series of solvent together with the enthalpies of activation.[1-4]

Recently[5] we have been interested in the solvent effects on the mechanisme of S_N2 type reactions, especially involving with isodielectric binary solvent systems of methanol-acetonitrile(MeOH-AN), methanol-nitrobenzene (MeOH-NB) and methanol-nitromethane (MeOH-NM) binary systems. In a previous work,[6] we reported on the relative partial

Table 1. Heats of Solution, (ΔH^{X}_{MS}) (kJ·mol^{-1}), of Amines (M= An, Py and Ba) in Binaries Mixed Solvents at 25.0 °C.

MeOH	MeOH-AN			MeOH-NM			MeOH-NB		
v/v%	An	Py	Ba	An	Py	Ba	An	Py	Ba
100	-2.54	-3.98 (-4.06)[a] (-3.96)[b]	-11.51	-2.54	-3.98	-11.51	-2.54	-3.98	-11.51
90	-2.71	-4.19	-11.64	-2.04	-4.70	-12.25	-2.17	-4.59	-11.67
80	-2.66	-4.21	-12.14	-1.52	-5.14	-12.79	-1.83	-5.19	-12.33
70	-2.56	-4.27	-12.29	-1.04	-5.75	-13.17	-1.57	-5.76	-12.56
50	-2.16	-4.21	-12.60	-0.29	-6.18	-13.45	-0.94	-6.63	-12.92
30	-1.68	-3.86	-12.15	0.31	-6.70	-14.25	-0.79	-7.50	-13.91
10	-0.76	-1.62	-7.74	1.54	-5.14	-12.20	0.21	-7.43	-14.24
5	-0.41	-0.27	-4.29	—	—	—	0.59	-6.64	-12.57
0	0.11	1.67 (1.64)[a]	1.83	3.27	1.99	2.14	1.95	0.39	1.12

[a] Reference 8, [b] Reference 9.

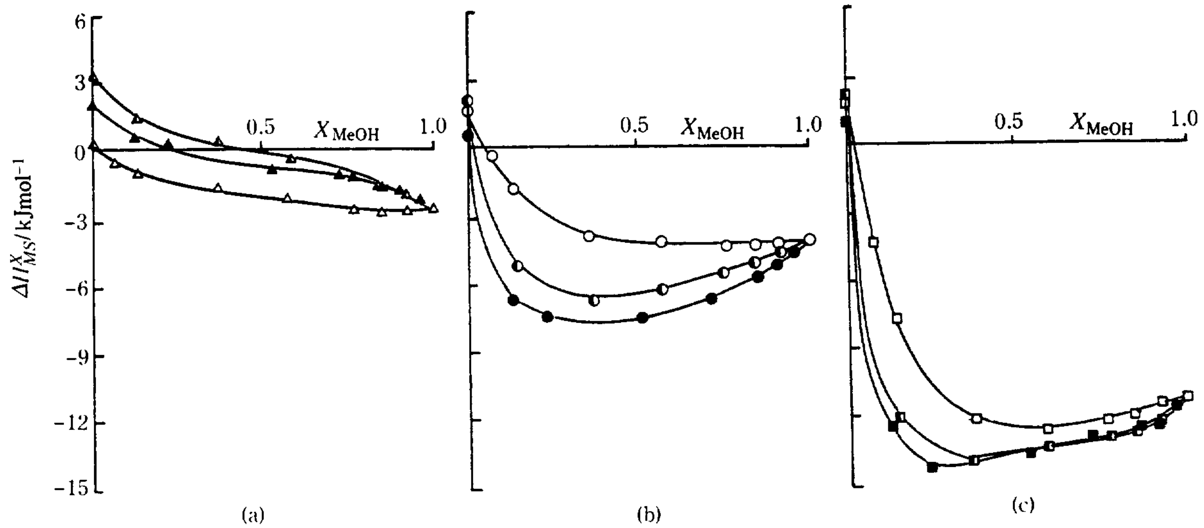


Figure 1. a) Plots of heats of solution of aniline ($\Delta H^{X}_{An\cdot S}$) *versus* MeOH mole fraction (X_{MeOH}) in binary mixtures (△MeOH-AN; ▲MeOH-NM; ▲MeOH-NB) at 25.0 °C. b) Plots of heats of solution of pyridine ($\Delta H^{X}_{Py\cdot S}$) *versus* MeOH mole fraction (X_{MeOH}) in binary mixtures (○MeOH-AN; ◑MeOH-NM; ●MeOH-NB) at 25.0 °C. c) Plots of heats of solution of benzylamine ($\Delta H^{X}_{Ba\cdot S}$) *versus* MeOH mole fraction (X_{MeOH}) in binary mixtures (□MeOH-AN; ◨ MeOH-NM; ■MeOH-NB) at 25.0 °C.

molal enthalpies of component solvents, ΔH^{*}_{CS} and ΔH^{*}_{MeOH}, in these binary mixtures. We found that these binary systems exhibit non-regular behavior with deviation from the regularity increasing in the order MeOH-AN<MeOH-NB<MeOH-NM.

In this work, we have determined calorimetrically heats of solution of three neutral bases, aniline, pyridine and benzylamine, in the three isodielectric binary systems and transfer enthalpies of these bases are discussed in terms of specific and non-specific solute-solvent interactions.[7]

Experimental

Materials. Solvents were purified by standard methods as described previously.[6] Aniline(Aldrich, ACS grade) was treated with HCl and the salt solution was extracted with ethyl ether. After treating with a base, aniline was dried over KOH and distilled under reduced pressure. Pyridine (Tedia, ACS grade) was dried over KOH and distilled from molecular sieve (Linde type 5A). Benzylamine (Fluka, puriss) was used without further purification. G.l.c analyses indicated reagents purifities of over 99.8 mole%.

Calorimetric Measurements. Heats of solution were measured as described previously[6] using LKB-2277 TAM(Sweden, twin isoperibol calorimeter) at $25.0 \pm 2 \times 10^{-4}$ °C. Final concentrations of neutral bases were $1.2 \times 10^{-2} \sim 2.1 \times 10^{-2}$ mol dm^{-3} and all calorimetric measurements were carried out more than three times with variation in the base concentration under no stirring condition. The measured heats of solution were within ±2% of the average value reported.

Results and Discussion

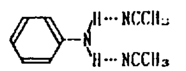
The enthalpies of solution (ΔH^{X}_{MS}), determined are summarized in Table 1, and graphically presented in Figure 1.

Table 2. Solvatochromic Parameters, Hydrogen Bond Acidity α_s, Hydrogen Bond Basicity β_s, Dipolarity π_s^* and Cohesive Energy Density $\delta_H^2/100$, for Solvents[17,18]

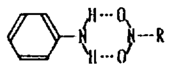
Solvent	α_s	β_s	π_s^*	$\delta_H^2/100$
Methanol (MeOH)	0.93	0.62	0.60	2.052
Acetonitrile (AN)	0.19	0.37	0.75	1.378
Nitrobenzene (NB)	0.0	0.30	1.01	1.222
Nitromethane (NM)	0.22	0.25	0.85	1.585

The enthalpies of solution of pyridine in MeOH, $(\Delta H^o_{Py\cdot S})_{MeOH}$, and in acetonitrile, $(\Delta H^o_{Py\cdot S})_{AN}$, agree quite well with those of the literature values.[8,9] The enthalpies of solution of the three neutral bases, M = aniline (An), pyridine (Py) and benzylamine (Ba), are all positive in pure cosolvents ($(\Delta H^o_{MS})_{CS} > 0$ for CS = AN, NB and NM), but are negative in pure methanol ($(\Delta H^o_{MS})_{MeOH} < 0$), the exothermicity being proportional to the basicities of base[10] (pK_a values are 4.60, 5.17 and 9.35 for aniline,[11] pyridine[12] and benzylamine[12] in water at 25.0 °C, respectively). We note that aniline (Figure 1a) exhibits somewhat different behavior from the other two (Figures 1b and 1c) in variations of $(\Delta H^X_{An\cdot S})$ *vs* X_{MeOH}.

Reference to Figure 1a reveals that in the cosolvent rich region ($X_{MeOH} < 0.5$) the $(\Delta H^X_{An\cdot S})$ values are positive in the MeOH-NM and MeOH-NB systems whereas they are negative in the MeOH-AN system. Upon entry of aniline into the pure cosolvents, two processes will compete: endoergic cavity formation[13] and exoergic solute-solvent hydrogen-bond interaction.[14] Since the former will be in the order of cohesive energy dnesity, $\delta_H^2/100$,[15] and the latter could be either in the order of the solvent hydrogen bond acidity, α_s, or the hydrogen bond basicity, β_s, scale[16] in Table 2, our observed order of $(\Delta H^X_{An\cdot S})$, NM>NB>AN, suggests that the cosolvent hydrogen-bond basicity (β_s) is more important in determining the $(\Delta H^o_{An\cdot S})_{CS}$ values. This means that the aniline-cosolvent interaction is of the form (Ia) or (Ib) rather than (II), which is reasonable since the bidentate forms of H-bonding, (I), will be stronger than single H-bond formed with weak H-bond acidity (α_s) bases, especially for NB this form, (II), is not possible. Since in the cosolvent rich region the relatively weak aniline-cosolvent interaction will be gradually replaced by the more exoergic aniline-MeOH interaction, which will be of the type II, all the three $(\Delta H^X_{An\cdot S})$ *vs* X_{MeOH} curves show nearly parallel downward drifts. In the MeOH rich region ($X_{MeOH} > 0.75$), however, the two curves for the NM and NB binaries almost coalesce while the AN binary curve diverges from these two. In this region, the polymer chain structure of MeOH will be further broken by the entry of aniline in addition to the already broken chain by the cosolvent molecules. Since the chain breaking by NM and NB will be less efficient due to the low β_s values, scavenging less amount of $(OH)_{free}$ groups of MeOH,[19,20] than by AN the aniline-MeOH interaction should be less favored in the NM and NB binary systems than in the AN binary system. In other words, there will be more free NM and NB molecules available together with relatively extensive MeOH polymer chain in the NM and NB binary systems, whereas more AN will be bound to MeOH and hence relatively less extensive MeOH polymer chain will be present in the AN binary system. Thus the entry of aniline requires additional chain breaking (endoergic) in the former binary systems (NB and NM) in forming hydrogen-bond complex between aniline and MeOH (exoergic) and there will be relatively extensive hydrogen bond formation between aniline and cosolvent (NM or NB) of the type (Ib) which is less exoergic than that of the aniline-MeOH complex, (II), while the reverse situation will hold in the latter binary (AN) system, i.e., relatively more extensive aniline-MeOH complex, (II), will be formed than the aniline-AN type complex, (Ia). As a result, the AN curve exhibits continuous downward drift with a small minimum indicating further endoergic MeOH-chain breaking requried by the solute in the nearly pure MeOH solvent, whereas the less exoergic NM and NB $(\Delta H^X_{An\cdot S})$ curves level off at $\sim X_{MeOH} = 0.5$ and then rapidly drift downward as the binary mixtures approach to $X_{MeOH} = 1.0$.

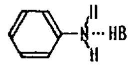


(Ia)



R=CH₃ or C₆H₅

(Ib)



HB=solvent (base)

(II)

On the other hand, the enthalpies of solution of pyridine, $(\Delta H^X_{Py\cdot S})$, and benzylamine, $(\Delta H^X_{Ba\cdot S})$, exhibit entirely different behavior (Figures 1b and 1c). In pure cosolvents, the $(\Delta H^X_{Py\cdot S})$ values are more positive in the order NB< AN<NM. Since pyridine has no acidic hydrogen in addition to the greater basicity, only the type (II) hydrogen bond will be possible; we note in Table 2 that the hydrogen bond acidity, α_s, of the cosolvents is small and the endoergic $(\Delta H^X_{Py\cdot S})$ values expected from the type (II) H-bonding will be in a reverse order of the observed one. Thus we can rationalize the order of $(\Delta H^X_{Py\cdot S})$ in pure cosolvents only with endoergic cavity formation term as represented by the solvent cohesive energy density, $\delta_H^2/100$, in Table 2.

The enthalpies of solution of benzylamine, $(\Delta H^X_{Ba\cdot S})$, in the three binary mixtures (Figure 1c) behave similarly with those of pyridine (Figure 1b), the main difference being the stronger solute-solvent interaction due to the stronger basicity of benzylamine. Thus the well depths for benzylamine in the three binary systems are deeper than those for pyridine but their order is kept the same for the two solutes.

We have subjected the heats of solution, (ΔH^X_{MS}), in Table 1 to the type of model analysis developed by Waghorne *et al.*[21,22] with some modifications.

In this model, a solute, M, occupies a cavity in which n solvent molecules form its nearest neighbours, and on average N solvent molecules which are further away from the nearest neighbours are affected giving rise to an increase in enthalpy $-n\alpha\Delta H^*$ and $-N\beta\Delta H^*$ respectively, where α is the fraction of the molar enthalpy of solvent-solvent bonding, ΔH^*, associated with the broken bond and β the average proportionality constant for the different modified bonds. The solute, M, interacts with the modified solvent, A resulting in an enthalpy change of $(\Delta H_M)_A$.

We can arrive at an expression, (1), for the enthalpy of solution of a solute, M, in a binary solvent AB, $(\Delta H^X_{MS})_{AB}$, in which mole fractions x_{MA} of A and x_{MB} of B are solvating M(See Appendix for the derivation).

$$(\Delta H^X_{MS})_{AB} = x_{MA}(\Delta H^\circ_{MS})_A + x_{MB}(\Delta H^\circ_{MS})_B - (\alpha n_A + \beta N_A)$$

$$\Delta H^*_A(X) - (\alpha n_B + \beta N_B)\Delta H^*_B(X) \qquad (1)$$

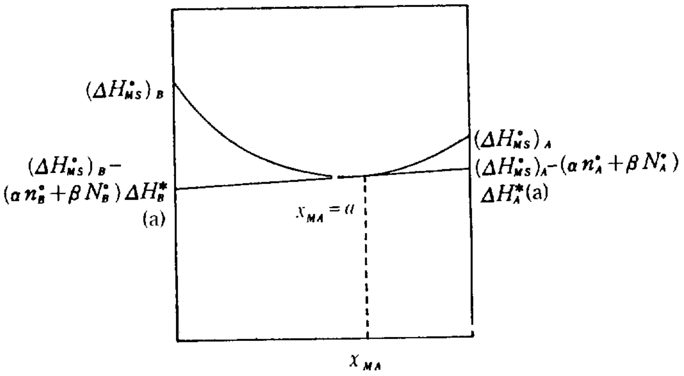


Figure 2. Plots of $(\Delta H^{X}_{MS})_{AB}$ *vs* x_{MA}, demonstrating the significance of eq. (3).

where $(\Delta H^{o}_{MS})_A$ and $(\Delta H^{o}_{MS})_B$ are the enthalpies of solution of solute M in pure solvents A and B respectively.
Assuming that

$$x_{MA}(\alpha n^{\circ}_A+\beta N^{\circ}_A)=(\alpha n_A+\beta N_A) \qquad (2)$$
$$x_{MB}(\alpha n^{\circ}_B+\beta N^{\circ}_B)=(\alpha n_B+\beta N_B)$$

equation (1) can be modified into

$$(\Delta H^{x}_{MS})_{AB}=x_{MA}[(\Delta H^{\circ}_{MS})_A-(\alpha n^{\circ}_A+\beta N^{\circ}_A)\Delta H^{*}_A(X)] + x_{MB}[(\Delta H^{\circ}_{MS})_B-(\alpha n^{\circ}_B+\beta N^{\circ}_B)\Delta H^{*}_B(X)] \qquad (3)$$

The two quantities in brackets on the right side of eq. (3) represent partial molal enthalpies of solute M in A and B, and can be obtained as intercepts of a tangential line at x_{MA} = a in Figure 2.
Introducing a preferential solvation fractor p, we obtain

$$x_{MA}=\frac{X_A}{X_A+pX_B} \text{ and } x_{MB}=\frac{pX_B}{X_A+pX_B} \qquad (4)$$

Substituting eqs. (4) into (3) we get

$$(\Delta H^{x}_{MS})_{AB}=\frac{X_A}{X_A+pX_B}[(\Delta H^{\circ}_{MS})_A-(\alpha n^{\circ}_A+\beta N^{\circ}_A)\Delta H^{*}_A(X)] + \frac{pX_B}{X_A+pX_B}[(\Delta H^{\circ}_{MS})_B-(\alpha n^{\circ}_B+\beta N^{\circ}_B)\Delta H^{*}_B(X)] \qquad (5)$$

Differentiating eq. (3) with respect to X_{MA} we obtain

$$\left(\frac{\partial(\Delta H^{x}_{MS})_{AB}}{\partial x_{MA}}\right)=(\Delta H^{\circ}_{MS})_A-(\Delta H^{\circ}_{MS})_B-(\alpha n^{\circ}_A+\beta N^{\circ}_A)\Delta H^{*}_A(X)+(\alpha n^{\circ}_B+\beta N^{\circ}_B)\Delta H^{*}_B(X) \qquad (6)$$

At $x_{MA}=X_A=1$, $\Delta H^{*}_A=0$ and we get

$$\left(\frac{\partial(\Delta H^{x}_{MS})_{AB}}{\partial x_{MA}}\right)_{X_A=1}=(\Delta H^{\circ}_{MS})_A-(\Delta H^{\circ}_{MS})_B+(\alpha n^{\circ}_B+\beta N^{\circ}_B)\Delta H^{*}_B(X_A=1) \qquad (7)$$

Table 3. Summary of the Best Fitting Values for p, $(\alpha n^{o}_A+\beta N^{o}_A)$ and $(\alpha n^{o}_B+\beta N^{o}_B)$

Solute	Solvent	p	$(\alpha n^{o}_A+\beta N^{o}_A)$	$(\alpha n^{o}_B+\beta N^{o}_B)$
Aniline	MeOH-AN	1.0	0.70	1.0
(An)	MeOH-NB	0.95	2.6	-1.4
	MeOH-NM	0.95	2.0	-0.50
Pyridine	MeOH-AN	0.58	2.6	2.1
(Py)	MeOH-NB	0.37	2.7	9.1
	MeOH-NM	0.16	1.0	13
Benzylamine	MeOH-AN	0.15	1.2	12
(Ba)	MeOH-NB	0.12	1.7	18
	MeOH-NM	0.11	1.5	20

Likewise at $x_{MA}=X_A=0$, $\Delta H^{*}_B=0$ and we get

$$\left(\frac{\partial(\Delta H^{x}_{MS})_{AB}}{\partial x_{MA}}\right)_{XA=0}=(\Delta H^{\circ}_{MS})_A-(\Delta H^{\circ}_{MS})_B-(\alpha n^{\circ}_A+\beta N^{\circ}_A)\Delta H^{*}_A(X_A=0) \qquad (8)$$

Since $x_{MA}=\dfrac{X_A}{X_A+p(1-X_A)}$,

$$\frac{\partial x_{MA}}{\partial X_A}=\frac{p}{[X_A+p(1-X_A)]^2} \qquad (9)$$

and hence

$$\left(\frac{\partial x_{MA}}{\partial X_A}\right)_{X_A=1}=p \text{ and } \left(\frac{\partial x_{MA}}{\partial X_A}\right)_{X_A=0}=\frac{1}{p} \qquad (10)$$

Using these relations,

$$\left(\frac{\partial(\Delta H^{x}_{MS})_{AB}}{\partial x_{MA}}\right)_{X_A=1}=\left[\frac{\partial(\Delta H^{x}_{MS})_{AB}}{\partial X_A}\cdot\left(\frac{\partial X_A}{\partial x_{MA}}\right)\right]_{X_A=1}$$
$$=\left(\frac{\partial(\Delta H^{x}_{MS})_{AB}}{\partial X_A}\right)_{X_A=1}\cdot\frac{1}{p} \qquad (11)$$

Likewise

$$\left(\frac{\partial(\Delta H^{x}_{MS})_{AB}}{\partial x_{MA}}\right)_{X_A=0}=\left(\frac{\partial(\Delta H^{x}_{MS})_{AB}}{\partial X_A}\right)_{X_A=0}\cdot p \qquad (12)$$

We can estimate the slope of tangential lines at $X_A=1$ and $X_A=0$ *i.e.*, $\left(\frac{\partial(\Delta H^{x}_{MS})_{AB}}{\partial X_A}\right)_{X_A=1}$ and $\left(\frac{\partial(\Delta H^{x}_{MS})_{AB}}{\partial X_A}\right)_{X_A=0}$ from Figures 1a~1c, and substitution of the values into eqs. (11) and (12) will give us the quantities on the left side of eqs. (6) and (7) in terms of an unknown factor p.
At the extremum point X_e,

$$\left(\frac{\partial(\Delta H^{x}_{MS})_{AB}}{\partial x_{MA}}\right)_{XA=XF}=0=(\Delta H^{\circ}_{MS})_A-(\Delta H^{\circ}_{MS})_B-(\alpha n^{\circ}_A+\beta N^{\circ}_A)\Delta H^{*}_A(X_A=X_e)+(\alpha n^{\circ}_B+\beta N^{\circ}_B)\Delta H^{*}_B(X_A=X_e) \qquad (13)$$

With equations (7), (8), (11), (12) and (13), we can determine three unknowns, p, $(\alpha n^{o}_A+\beta N^{o}_A)$ and $(\alpha n^{o}_B+\beta N^{o}_B)$ using

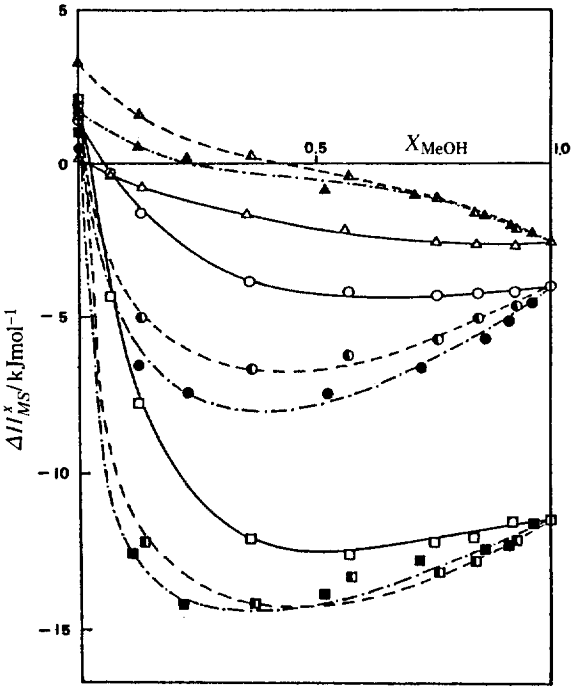


Figure 3. Plots of $(\Delta H^X_{MS})_{AB}$ for M= aniline (△), pyridine (○) and benzylamine (□) against mole fraction of MeOH for MeOH-AN (—), MeOH-NM (--) and MeOH-NB (—-). Points and curves represent experimental and calculated data.

experimentally observed values of $(\Delta H^o_{MS})_A$, $(\Delta H^o_{MS})_B$ and $\Delta H^*_t(X)$.[6]
The results are summarized in Table 3. Using these three determined values, we have back calculated the $(\Delta H^X_{MS})_{AB}$ values from eq. (5). The agreement between the observed and calculated values were very good with correlation coefficients between 0.997 and 0.999. The maximum deviation was 0.4 kJ·mol^{-1} and average deviation was 0.1 kJ·mol^{-1}. The observed (full line) and calculated (points) values are compared in Figure 3.

We note in Table 3 that the values determined reflect quite reasonable trends of solvation phenomena in the binary system for the three nitrogen bases. Aniline being a weak base, preferential solvation of MeOH (p<1) is not so conspicuous compared to the other two nitrogen bases, pyridine and benzylamine. Methanol is shown to be more and more preferentially solvated as the basicity of the base increases from aniline to benzylamine. Furthermore the preferential solvation of methanol is seen to be enhanced as the hydrogen bond basicity (β_s) of the cosolvent decreases from acetonitrile (β_s=0.37) to nitromethane (β_s=0.25) (Table 2). This suggests that the solute base competes with the cosolvent for the methanolic hydrogen and the hydrogen bond acidities (α_s) of the cosolvents are so low that the cosolvent acts as a very poor hydrogen bond donor compared with MeOH.

Large cosolvent structure breaking is also noted in Table 3 with large $(\alpha n^o_B + \beta N^o_B)$ factor for the two strong bases, pyridine and benzylamine; this is in line with large endoergic cavity formation energy for the cosolvents. It is interesting to find that for aniline the cosolvents NB and NM are structure forming, $(\alpha n^o_B + \beta N^o_B)<0$; this may be due to relatively extensive hydrogen bond formation between aniline and cosolvent (NM or NB) of the type (Ib).

Conclusions

Three nitrogen bases, aniline, pyridine and benzylamine, are preferentially solvated by methanol especially when the basicity of the base is greater and the hydrogen bond basicity of the cosolvent is weaker.

The enthalpies of solution of the bases in the methanol binary mixtures with the cosolvents, acetonitrile, nitrobenzene and nitromethane can be accounted for satisfactorily by the two state model developed by Waghorne *et al.*

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Appendix.

Derivation of eq. (1).

The model adeopted is in general the same as that of Waghorne *et al.*[21,22], but we introduced slightly different notations and some modifications.

$(\Delta H^o_{MS})_A$: heat of solution of a solute, M, in pure A.
$(\Delta H^o_M)_A$: net solvation enthalpy of a solute, M, in pure A.
n^o_{AA} : number of molecules of A formaed by breaking solvent–solvent bonds for cavity formation in pure A.
α^o_{AA} : fraction of the molar enthalpy of solvent–solvent bonding ($\bar{H}^o_{AA}$) associated with the broken bonds in pure A.
N^o_{AA} : average number of non–nearest neighbour molecules of A that are affected by a solute in pure A.
β^o_{AA} : average proportionality constant for the different modified bonds in pure A.
$\bar{H}^o_{AA}$: molar enthalpy of solvent-solvent bonding in pure A
$\bar{H}^o_{AB}(X)$: molar enthanlpy of solvent (A)–solvent (B) bonding in a binary mixture AB with a mole fraction X of A.

Other notations have obvious meanings.
For pure A,

$$(\Delta H^\circ_{MS})_A = (\Delta H^\circ_M)_A - (\alpha^\circ_{AA} n^\circ_{AA} + \beta^\circ_{AA} N^\circ_{AA}) \bar{H}^\circ_{AA} \tag{A1}$$

Similarly for pure B,

$$(\Delta H^\circ_{MS})_B = (\Delta H^\circ_M)_B - (\alpha^\circ_{BB} n^\circ_{BB} + \beta^\circ_{BB} N^\circ_{BB}) \bar{H}^\circ_{BB} \tag{A2}$$

In a binary mixture AB of a mole fraction X of A,

$$\begin{aligned} (\Delta H^x_{MS})_{AB} = (\Delta H^x_M)_A &- (\alpha_{AA} n_{AA} + \beta_{AA} N_{AA}) \bar{H}_{AA}(X) \\ &- (\alpha_{AB} n_{AB} + \beta_{AB} N_{AB}) \bar{H}_{AB}(X) + (\Delta H^x_M)_B \\ &- (\alpha_{BB} n_{BB} + \beta_{BB} N_{BB}) \bar{H}_{BB}(X) \\ &- (\alpha_{BA} n_{BA} + \beta_{BA} N_{BA}) \bar{H}_{BA}(X) \end{aligned} \tag{A3}$$

Let x_{MA} ($\equiv 1-x_{MB}$) be a mole fraction of A solvating solute M, then

$$\begin{aligned} (\Delta H^x_M)_A &= x_{MA} (\Delta H^\circ_M)_A \\ (\Delta H^x_M)_B &= x_{MB} (\Delta H^\circ_M)_B \end{aligned} \tag{A4}$$

Substitution of eqs. (A1), (A2) and (A4) into (A3) gives,

$$\begin{aligned}(\Delta H^{x}_{MS})_{AB}=x_{MA}[(\Delta H^{\circ}_{MS})_{A}&+(\alpha^{\circ}_{AA}n^{\circ}_{AA}+\beta^{\circ}_{AA}N^{\circ}_{AA})\bar{H}^{\circ}_{AA}]\\&-(\alpha_{AA}n_{AA}+\beta_{AA}N_{AA})H_{AA}(X)\\&-(\alpha_{AB}n_{AB}+\beta_{AB}N_{AB})H_{AB}(X)+x_{MB}[(\Delta H^{\circ}_{MS})_{B}\\&+(\alpha^{\circ}_{BB}n^{\circ}_{BB}+\beta^{\circ}_{BB}N^{\circ}_{BB})\bar{H}^{\circ}_{BB}]\\&-(\alpha_{BB}n_{BB}+\beta_{BB}N_{BB})\bar{H}_{BB}(X)\\&-(\alpha_{BA}n_{BA}+\beta_{BA}N_{BA})\bar{H}_{BA}(X)\end{aligned}\tag{A5}$$

This equation can be simplified with the following assumptions,

$$\begin{aligned}x_{MA}N^{\circ}_{AA}&=N_{AA}+N_{AB}=N_{A}\\x_{MB}N^{\circ}_{BB}&=N_{BB}+N_{BA}=N_{B}\end{aligned}\tag{A6}$$

$$\begin{aligned}x_{MA}n^{\circ}_{AA}&=n_{AA}+n_{AB}=n_{A}\\x_{MB}n^{\circ}_{BB}&=n_{BB}+n_{BA}=n_{B}\end{aligned}\tag{A7}$$

$$\begin{aligned}\alpha^{\circ}_{AA}&=\alpha^{\circ}_{BB}=\alpha_{ij}=\alpha\\\beta^{\circ}_{AA}&=\beta^{\circ}_{BB}=\beta_{ij}=\beta\end{aligned}\tag{A8}$$

$$\begin{aligned}(\Delta H^{x}_{MS})_{AB}=x_{MA}(\Delta H^{\circ}_{MS})_{A}&+x_{MB}(\Delta H^{\circ}_{MS})_{B}\\&-(\alpha n_{AA}+\beta N_{AA})[\bar{H}_{AA}(X)-\bar{H}^{\circ}_{AA}]\\&-(\alpha n_{AB}+\beta N_{AB})[\bar{H}_{AB}(X)-\bar{H}^{\circ}_{AA}]\\&-(\alpha n_{BB}+\beta N_{BB})[\bar{H}_{BB}(X)-\bar{H}^{\circ}_{BB}]\\&-(\alpha n_{BA}+\beta N_{BA})[\bar{H}_{BA}(X)-\bar{H}^{\circ}_{BB}]\end{aligned}\tag{A9}$$

We now introduce the following approximations.

$$\begin{aligned}\frac{N_{AB}}{N_{AA}}=\frac{n_{AB}}{n_{AA}}=\frac{X_B}{X_A}&\exp\{-[(-\bar{H}_{AB}(X)-(-\bar{H}_{AA}(X))]/RT\}\\&=\frac{X_B}{X_A}\exp\{\bar{H}_{AB}(X)-\bar{H}_{AA}(X))]/RT\}=\frac{p_BX_B}{X_A}\end{aligned}\tag{A10}$$

where $$p_B=\exp\{[\bar{H}_{AB}(X)-\bar{H}_{AA}(X))]/RT\}\tag{A11}$$

Thus
$$\begin{aligned}N_{AA}&=\frac{X_A}{X_A+p_BX_B}N_A\\N_{AB}&=\frac{p_BX_B}{X_A+p_BX_B}N_A\end{aligned}\tag{A12}$$

$$\begin{aligned}n_{AA}&=\frac{X_A}{X_A+p_BX_B}n_A\\n_{AB}&=\frac{p_BX_B}{X_A+p_BX_B}n_A\end{aligned}\tag{A13}$$

Likewise
$$\begin{aligned}N_{BB}&=\frac{X_B}{X_B+p_AX_A}N_B\\N_{BA}&=\frac{p_AX_A}{X_B+p_AX_A}N_B\end{aligned}\tag{A14}$$

$$\begin{aligned}n_{BB}&=\frac{X_B}{X_B+p_AX_A}n_B\\n_{BA}&=\frac{p_AX_A}{X_B+p_AX_A}n_B\end{aligned}\tag{A15}$$

New eq. (A9) can be simplified into (A16).

$$\begin{aligned}(\Delta H^{x}_{MS})_{AB}=x_{MA}(\Delta H^{\circ}_{MS})_{A}&+x_{MB}(\Delta H^{\circ}_{MS})_{B}\\&-(\alpha n_{A}+\beta N_{A})\{\frac{X_A}{X_A+p_BX_B}[\bar{H}_{AA}(X)-\bar{H}^{\circ}_{AA}]\\&+\frac{p_BX_B}{X_A+p_BX_B}[\bar{H}_{AB}(X)-\bar{H}^{\circ}_{AA}]\}\\&-(\alpha n_{B}+\beta N_{B})\{\frac{X_B}{X_B+p_AX_A}[\bar{H}_{BB}(X)-\bar{H}^{\circ}_{BB}]\\&+\frac{p_AX_A}{X_B+p_AX_A}[\bar{H}_{BA}(X)-\bar{H}^{\circ}_{BB}]\}\end{aligned}\tag{A16}$$

Substitution of $\frac{X_A}{X_A+p_BX_B}[\bar{H}_{AA}(X)-\bar{H}^{\circ}_{AA}]+\frac{p_BX_B}{X_A+p_BX_B}[\bar{H}_{AB}(X)-\bar{H}^{\circ}_{AA}]=\Delta H^{*}_{A}(X)$ and $\frac{X_B}{X_B+p_AX_A}[\bar{H}_{BB}(X)-\bar{H}^{\circ}_{BB}]+\frac{p_AX_A}{X_B+p_AX_A}[\bar{H}_{BA}(X)-\bar{H}^{\circ}_{BB}]=\Delta H^{*}_{B}(X)$ into (A16) leads to eq. (1) in the text.

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Luminescence Quenching of Tris(2,2′-bipyridine) Ruthenium(II) Complex by Viologens in Anionic Micellar and Polyelectrolyte Solutions: Variation with Alkyl Chain of Viologens

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Luminescence quenching reactions of photoexcited tris(2,2′-bipyridine)ruthenium (II) complex cation, $Ru(bpy)_3^{2+}$, by dialkylviologens (dimethyl, dioctyl, dibenzyl, methyloctyl, methyldodecyl, and methylbenzyl) were studied in sodium dodecyl sulfate (SDS), poly(styrenesulfonate) (PSS), and poly (vinylsulfonate) (PVS) solutions. The relative quenching rate varies widely with the microheterogeneous media employed: the highest quenching rate is observed for methyldodecylviologen in homogeneous aqueous medium, dibenzylviologen in SDS and PVS solutions, and dimethylviologen in PSS solution; the lowest rate is found for dimethylviologen in homogeneous medium and SDS solution, methyldodecylviologen in PSS and PVS solutions. These results were interpreted in terms ot reduction potential of viologens, affinity of $Ru(bpy)_3^{2+}$ and viologens to the microparticles, and the structures of the viologen-colloid complexes.

Introduction

Micelles, polyelectrolytes, and other microheterogeneous systems are increasingly used to control physico-chemical properties and reaction kinetics of substrates.[1–] Photosensitized electron-transfer reactions in microheterogeneous media have been an active research area with goal of achieving efficient solar energy conversion systems and, more recently, with emphasis on using the photoredox systems as probes for microheterogeneous environments.[2,3] Tris(2,2′-bipyridine)ruthenium (II) ($Ru(bpy)_3^{2+}$/4,4′-bipyridinium salts (viologens) photoredox couple has been recognized as one of the most promising systems for the former purpose.[2b,4–6] Much of works have been carried out with dimethylviologen (1,1′-dimethyl-4,4′-bipyridinium). The photoinduced electron-transfer reaction between $Ru(bpy)_3^{2+}$ and viologens are usually followed by the luminescence quenching of the photosensitizer by the electron acceptors. The presence of anionic micelles and polyelectrolytes remarkably enhances the rate of the quenching reactions.[7] This was attributed to the condensation of the reacting pair in the potential field of the anionic micelles and polyanions by the coulombic interaction.

Viologens, especially those with long alkyl chain, interact with microphase particles by hydrophobic interaction as well as coulombic force. It was demonstrated that use of dialkylviologens with long alkyl chains results in enhanced quantum yield in Ru(II) complex photosensitized reduction of the viologens in micelle.[8] reversed micelle[9] and water-in-oil microemulsion,[10] due to the stabilization of the photoproducts against the recombination reaction involving back-electron transfer. Electron spin echo modulation (ESEM) spectroscopy[11] and ESR[12] studies on the dialkylviologens in sodium dodecyl sulfate (SDS) micelle and dihexadecyl phosphate (DHP) vesicle revealed that the degree of embedment of viologen in the microphase particles depends on the alkyl chain length of the viologens. This lead to the variation of quenching rate with the alkyl chain of viologens in the microheterogeneous systems.[13] The reduction potential of viologen varies with alkyl chain,[14] and changes upon the presence of microphase particles such as micelles and vesicles.[14a,15] Anionic polyelectrolytes interact with Ru(II) complex cation and viologens and affect the photochemical electron-transfer reaction between them in similar fashion to the anionic micelles.[16] Thus the dependence of the rate of the quenching reaction on the alkyl chains of viologens are also expected in polyelectrolyte solutions.

In our laboratory, we have undertaken a series of studies on interactions of dimethylviologen and its reduced cationicradical with SDS,[17] Ru(II) photosensitizers with anionic surfactants,[18] and on kinetics of the quenching of luminescence from photoexcited $Ru(bpy)_3^{2+}$ by cationic quenchers including dimethylviologen.[16] In this paper, we report the results of the kinetic studies for electron-transfer quenching reactions of $Ru(bpy)_3^{2+}$ by various symmetric and asymmetric viologens **1-6** in SDS micellar, and poly(styrenesulfonate) (PSS) and poly(vinylsulfonate) (PVS) polyelectrolyte solutions. We discuss the influence of alkyl chain of the violo-