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Strong Thermochromic and Solvatochromic Effects of Ni(II) and Cu(II) Complexes in DMF/Nitromethane Mixtures: A Probe for Investigation of Binary Solvents

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Thermochromic and solvatochromic equilibria involving the ions $[Ni(tmen)(acac)]^+$ and $[Cu(tmen)(acac)]^+$ respectively are highly sensitive to the polarity of the solvent. These probes are thus suited for the study of binary mixtures. In nitromethane (NM)/dimethylformamide (DMF) binary solvent the Ni(II) complex displays strong thermochromism in a zone of low DMF concentration. This result is surprising because neither of the two solvents are intrinsically thermochromic since NM is a weak donor while DMF is a strong donor. NM/DMF binary mixtures behave like solvents with intermediate donor properties. In the same solvent mixtures (low DMF concentration), the solvatochromic behavior of the Cu(II) complex is reflected by a large shift in the maximum absorption of more than 70 nm. This was accounted for by the considerable variation in donor power of the solvent mixture in this concentration range. Quantitative analysis of the thermochromic and solvatochromic equilibria as a function of DMF concentration in NM indicated the existence of self-associations of DMF. The relatively small effects of dilution of DMF on the donor properties of the solvent mixture was explained in terms of the discharge of free DMF from self-associations with increasing dilution. In DCE, DMF self-associates to a greater extent than in NM.

Thermochronism and solvatochromism are observed as a change in color either with temperature or with solvent.[1–2] These two processes lead to homogeneous equilibria in solution.[3–5] With Ni(II), there is the following thermochromic equilibrium:[6]

$$\underset{\text{red, square planar}}{[Ni(tmen)(acac)]^+} + 2S \leftrightarrows \underset{\text{green, octahedral}}{[Ni(tmen)(acac)S_2]^+} \quad (1)$$

where tmen is the ligand tetramethylethylenediamine and acac the acetylacetonate ion. S is a donor solvent in the Lewis sense, and is characterized by the Gutmann parameter D_N.[7] For weak donor solvents ($D_N<10$), the above equilibrium is shifted strongly towards the red complex (λ_{max}=488 nm), which is the case in nitromethane NM (D_N=2.7). For strong donor solvents ($D_N>25$), the equilibrium is shifted towards the green complex (625 nm). This is the case for DMF (D_N=26.6). In thermochromic solvents with values of D_N ranging from 10 to 25, there is a reversible color change close to ambient temperature:[8] high temp., red; low temp., green. Thus neither NM nor DMF are thermochromic solvents, but NM/DMF binary mixtures behave like solvents with intermediate donor properties. With the same ligands, Cu(II) gives solvatochromic complexes in the equilibrium reaction:[9]

$$\underset{\substack{\text{color 1 (low } \lambda_{max}) \\ \text{octahedral with strong} \\ \text{tetragonal distortion}}}{[Cu(tmen)(acac)S_2']^+} + 2S'' \leftrightarrows \underset{\substack{\text{color 2 (high } \lambda_{max}) \\ \text{octahedral with weak} \\ \text{tetragonal distortion}}}{[Cu(tmen)(acac)S_2'']^+} + 2S' \quad (2)$$

S′ and S″ are donor solvents, S″ being a stronger donor than S′. With NM as S′ and DMF as S″ the absorption peaks of the two complexes are 536 nm for the violet complex (NM) and 606 nm for the blue complex (DMF), which is in agreement with other studies.[10] These complexes are highly sensitive to the polarity of the medium and are thus well suited for study of the properties of pure solvents or mixtures of solvents.[11] In binary solvent mixtures, the apparent donor power can be adjusted to any value between those of the two pure solvents. Therefore, the aim of the present study was as follows: (1) to demonstrate the behavior of these probe complexes in the binary solvent mixture NM/DMF, (2) to use the properties of these thermochromic and solvatochromic probes to analyze molecular associations in binary mixtures.

Experimental

1) Synthesis of the Complexes. Crystalline $[Ni(tmen)(acac)]^+ ClO_4^-$ and $[Cu(tmen)(acac)]^+ ClO_4^-$ were synthesized using the methods described by Fukuda and Sone.[12–14] Anal. ($C_{11}H_{23}N_2O_6ClNi$) C, H, N, Cl, Ni, Anal. ($C_{11}H_{23}N_2O_6ClCu$) C, H, N, Cl, Cu. The counter ion ClO_4^- was used for both the $[Ni(tmen)(acac)]^+$ and $[Cu(tmen)(acac)]^+$ complexes in order to favor complex/solvent interactions, and prevent formation of pentacoordinated complexes.[15]

2) Solvents. All solvents of Puriss grade were kept on molecular sieves. Pure solvent concentrations were taken as: $[DMF]_{max}$=12.98 M, (M=mol dm^{-3}), $[NM]_{max}$=18.46 M and $[DCE]_{max}$=12.66 M. The binary mixtures were obtained by mixing two solutions which contained equal concentrations of the complex under study. The solutions were prepared using either pure solvent (NM, DCE, or DMF) or a previously prepared binary mixture (NM/DMF or DCE/DMF). The latter procedure was employed to explore the zone with very low concentrations of DMF in more detail.

3) UV/Visible Spectroscopy. The spectroscopic data were recorded on a diode array UV/visible spectrophotometer equipped with a Peltier effect thermostated sample holder. Temperature could be programmed accurately by computer to record spectra at defined temperature intervals.

For the thermochromic study, the temperature ranged from −5 °C to +80 °C. Slow changes in temperature (1 °C per min) could be obtained with the Peltier effect system. This rate of change is designed to prevent departure from equilibrium conditions. The accuracy of the temperature measurements was around 0.1 °C. To avoid condensation, a jet of dry nitrogen was directed continuously on the optical faces of the sample cuvettes. The solutions were homogenized using a magnetic stirrer. Solvatochromic effects were studied at 20 °C.

Results and Discussion

(A) The Thermochromic Equilibrium. Experimental Results. Certain binary mixtures of DMF/MN behave like pure thermochromic solvents towards the $[\mathrm{Ni(tmen)(acac)}]^+$ ion (Fig. 1). The intensity of the thermochromism depends on the molar ratio of the two solvents. The amplitude of the thermochromism was expressed in terms of an arbitrary unit, *Th* (in K^{-1}) referred to as the thermochromic index:[16]

$$Th=100\cdot(A_{\max}-A_{\min})/(A_{\mathrm{isos}}\Delta T),$$

where $A_{\max}-A_{\min}$ is the absolute amplitude of the thermochromic effect for a temperature interval ΔT. A_{isos} is the optical density at the isosbestic point, which corrects for concentration. It can be seen from Fig. 2 that thermochromism appears over a relatively narrow range of DMF concentration, $5\times10^{-3}\ \mathrm{M}<[\mathrm{DMF}]<0.4\ \mathrm{M}$ or $-3.5<\log([\mathrm{DMF}]/[\mathrm{DMF}]_{\max})<-2.5$. A scale displaying the logarithm of the normalized concentration ($[\mathrm{DMF}]/[\mathrm{DMF}]_{\max}$) is used to spread this phenomenon. Then, in this particular case, DMF acts as a solute, and one can characterize binary mixtures in terms of their DMF content. The result shown in Fig. 2 confirms the conclusions of Ouchi and Taminaga,[17] who observed an amplification of the thermochromism of complexes of Ni(II) in binary mixtures of piperidine and DMF at low DMF concentrations. The continuous change in thermochromism around this extremum corresponds to a variation in the thermodynamic parameters of the equilibrium (1). These values were determined by computerized processing of data obtained for each binary mixture. The method of computation has been described elsewhere.[18] The results are listed in Table 1. On the basis of these results, all the binary mixtures could be located on an enthalpy-entropy diagram at 300K. (Fig. 3). The representative point of mixture 4 (maximal thernochromism) is close to the sensitive color (equal concentrations of red and green species). For binary mixtures with low DMF contents (Nos. 1 and 2), the shift is almost vertical ($\Delta H^\circ/300\mathrm{R}$ constant) and essentially entropic; whereas, for higher concentrations of DMF (Nos. 6—8), the shift is almost horizontal ($\Delta S^\circ/\mathrm{R}$ constant) and mainly enthalpic. The location of DMF/NM binary mixtures are compared with those of some pure thermochromic solvents.

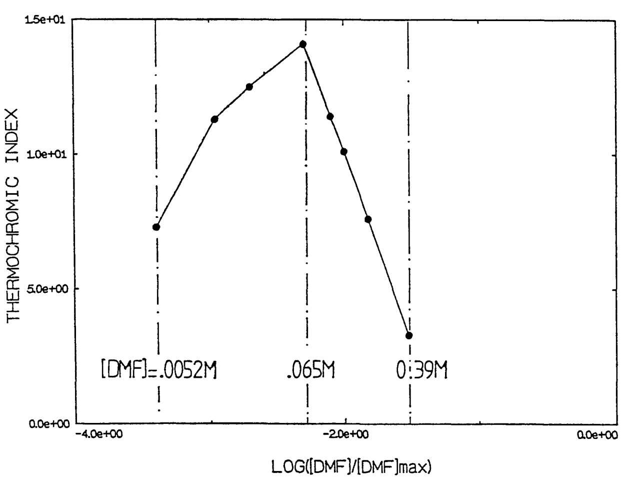

Fig. 2. Plot of thermochromic index *Th* against logarithm of the normalized concentration of DMF ($[\mathrm{DMF}]/[\mathrm{DMF}]_{\max}$) in the binary mixture NM/DMF. The maximum value is at $\log([\mathrm{DMF}]/[\mathrm{DMF}]_{\max})=-2.3$: $[\mathrm{DMF}]=6.5\times10^{-2}$ M. It can be seen that the thermochromic probe $[\mathrm{Ni(tmen)(acac)}]^+$ is sensitive to concentrations where $\log[\mathrm{DMF}]/[\mathrm{DMF}]_{\max}<-3.2$: $[\mathrm{DMF}]<1\times10^{-2}$ M in NM.

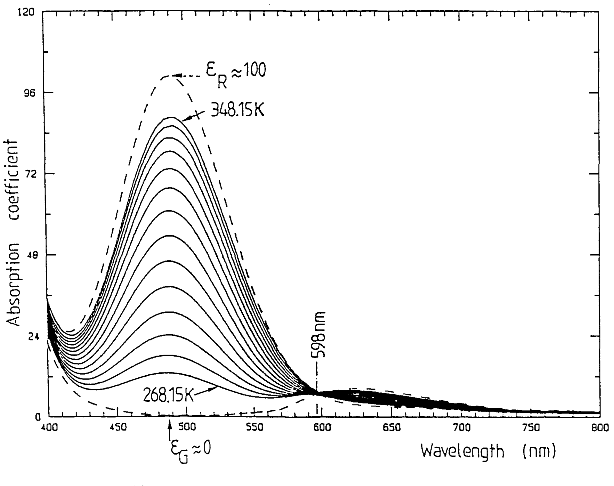

Fig. 1. Effect of temperature in the range 268.15—348.15 K (6.15 K temp interval) on the UV/visible spectrum of a 2×10^{-2} M solution of $[\mathrm{Ni(tmen)(acac)}]^+$ in a binary mixture of NM/DMF (99.64%/0.36% in moles); $[\mathrm{DMF}]=6.5\times10^{-2}$ M. An isosbestic point at 598 nm can be observed, which shows the existence of a single eguilibrium between the colored species. The binary mixture NM/DMF was adjusted for maximal thermochromism. The spectra shown in dotted lines were mathematically reconstructed, and correspond to spectra of the pure red and green species.

Interpretation. Qualitatively, the occurrence of thermochromism of $[\mathrm{Ni(tmen)(acac)}]^+$ in binary solvents can be interpreted in terms of the large difference in donor power between NM and DMF. By diluting DMF in NM, mixtures can be obtained which behave towards $[\mathrm{Ni(tmen)(acac)}]^+$ like thermochromic solvents. The thermochromic effect can thus be optimi-

Table 1. Thermochromic Index *Th* and Thermodynamic Parameters Derived from Results on Thermochromic Equilibrium of $[Ni(tmen)(acac)]^+$ in Various Binary Mixtures of NM/DMF

No.	[DMF]	$\log[DMF]/[DMF]_{max}$	*Th*	$\Delta H°/R$	$\Delta S°/R$
	M		K^{-1}	K	a)
1	.0052	−3.40	7.3	−4461	−17.2
2	.0142	−2.96	11.3	−4448	−16.7
3	.026	−2.70	12.5	−4488	−16.2
4	.0649	−2.30	14.1	−4626	−15.2
5	.103	−2.10	11.4	−4795	−14.7
6	.130	−2.00	10.1	−4859	−14.5
7	.195	−1.82	7.6	−5093	−14.6
8	.390	−1.52	3.3	−5183	−14.0

a) Dimensionless.

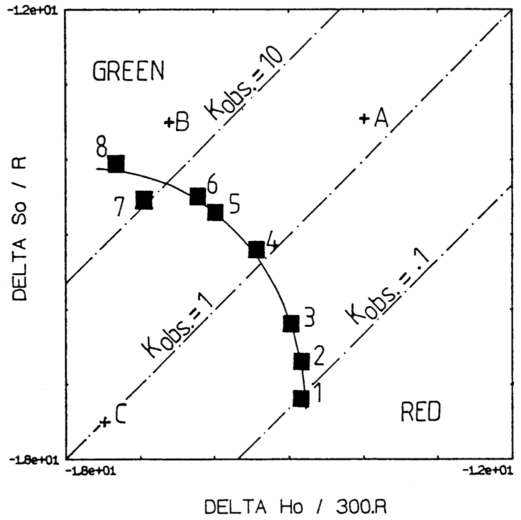

Fig. 3. Dimensionless entropy-enthalpy diagram at 300 K ($\Delta S°/R$ as a function of $\Delta H°/300R$) showing that the thermochromism is maximum when K_{obs} is close to unity. Predominantly green (high K_{obs}) and red (low K_{obs}) are situated on either side of the line $K_{obs}=1$. The representative points of binary NM/DMF solvents are numered as a function of increasing DMF concentration (see Table 1), those marked with a (+) correspond to pure thermochromic solvents (A: benzyl alcohol; B: 1-propanol; C: 2-propanol).

zed by adjusting the concentration of DMF in NM. From a quantitative point of view, the thermochromic equilibrium is principally influenced by molecular interactions involving DMF. These interactions reduce the capacity of DMF to complex with $[Ni(tmen)(acac)]^+$.

Two main types of interaction may occur:[19] DMF-DMF[20–22] and NM-DMF. The latter are exemplified by the exothermicity of mixing equal volumes of NM and DMF. In principle, both types of interaction could influence the thermochromic equilibrium, although in practice they do not have equal effects. In the concentration range shown in Fig. 2, DMF-DMF self-associations appear to have the major influence. [DMF] varies in a 1 to 75 ratio, whereas [NM] hardly changes. Variations in [DMF] have much greater effects on the self-associations of DMF than on the NM-DMF association.

The thermochromic equilibrium (1) can be schematized as follows:

$$R+2S \leftrightarrows G.$$

R is the square-planar complex (red), and G the octahedral complex (green) which is solvated by two molecules of free DMF (S). Taking account of solvation and self-associations:

$$[G]=\alpha[C_0],\ [R]=(1-\alpha)[C_0], \tag{3}$$

and

$$[S]=[S_0]-2\alpha[C_0]-[X], \tag{4}$$

where [S] is the concentration of free DMF, $[S_0]$ the total concentration of DMF, α the proportion of the solvated $[Ni(tmen)(acac)S_2]^+$ complex, $[C_0]$ the total concentration of the $[Ni(tmen)(acac)]^+$ and $[Ni(tmen)(acac)S_2]^+$ complexes, and [X] the concentration of DMF-DMF self-associated species.

$$\begin{aligned} K_{DMF} &= [G]/[R][S]^2=\alpha/\{(1-\alpha)([S_0]-2\alpha[C_0]-[X])^2\} \\ &= K_{obs}/([S_0]-2\,\alpha[C_0]-[X])^2, \end{aligned} \tag{5}$$

with

$$K_{obs}=\alpha/(1-\alpha). \tag{6}$$

For each mixture, α can be derived from the experimental results from:

$$\alpha=(\varepsilon_R-\varepsilon)/(\varepsilon_R-\varepsilon_G),$$

where ε is the apparent molar extinction coefficient, ε_G is the molar extinction coefficient of the solvated green form and ε_R that of the non-solvated red form. In theory, this can be determined at all wavelengths, although in practice it is more accurately determined at 488 nm (λ_{max} for the red complex: $\varepsilon_R=100$ and $\varepsilon_G=0$; see Fig. 1). To determine K_{DMF}, the proportion of self-associated DMF $[X]/[S_0]$ must be estimated. This is based on the assumption that this proportion is negligible at low DMF concentrations. Another argument is that a large proportion of this solvent is complexed with the Ni(II) at low DMF concentrations. For binary mixture No. 1, K_{DMF} can be estimated assuming [X]=0 in relationship (5):

$$K_{\mathrm{DMF}}=2.9\times10^{4}\ \mathrm{M}^{-2}\ \text{at } 293\ \mathrm{K}.$$

From this value of K_{DMF}, the relative proportion of self-associated DMF is calculated for the other binary mixtures:

$$[\mathrm{X}]/[\mathrm{S_0}]=1-2\alpha[\mathrm{C_0}]/[\mathrm{S_0}]-[(K_{\mathrm{obs}}/K_{\mathrm{DMF}})^{1/2}]/[\mathrm{S_0}]. \quad (8)$$

The results of these calculations are listed in Table 2. It can be seen that the self-associations of DMF ([X]/[S$_0$]) increases rapidly with its concentration. Such self-associations are independent of the probe employed (thermochromic or solvatochromic). This was demonstrated with the study of the solvatochromism of the [Cu(tmen)(acac)]$^+$ complex ion.

Table 2. Equilibrium Position and Estimation of the Relative Proportions of Self-Associated DMF as a Function of DMF Content in Binary Mixtures of NM/DMF Using the Thermochromic Probe [Ni(tmen)(acac)]$^+$ at 293 K

No.	α(293K)	$(K_{\mathrm{obs}}/K_{\mathrm{DMF}})^{1/2}$ M	$[\mathrm{S_0}]-2\alpha[\mathrm{C_0}]$ M	[X]/[S$_0$]
1	.085	.0018	.0018	—
2	.181	.0028	.0070	.29
3	.299	.0038	.0140	.39
4	.611	.0082	.0405	.50
5	.844	.0137	.0692	.54
6	.902	.0179	.0939	.58
7	.949	.0254	.1570	.67
8	.970	.0336	.3510	.81

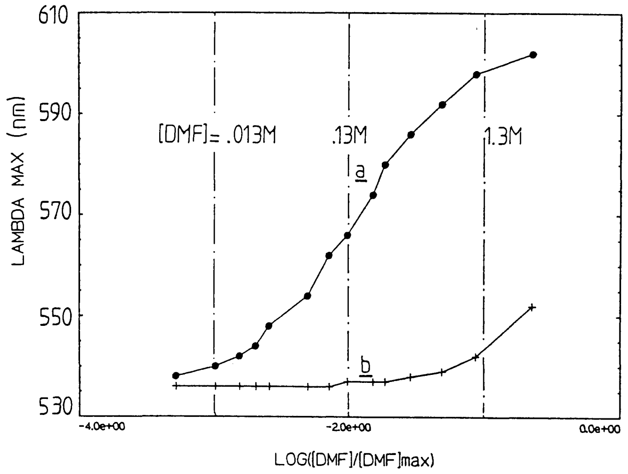

Fig. 4. Wavelength of the maximum absorption peak of the complex ion [Cu(tmen)(acac)]$^+$ (5.3×10^{-3} M) in various binary mixture of NM/DMF as a function of log([DMF]/[DMF]$_{\mathrm{max}}$). a) Experimental data showing that a small change in DMF concentration led to a very marked shift in the absorption band. b) Calculated data assuming a linear relationship between the wavelength of the maximum absorption peak and the concentration of DMF.

(B) The Solvatochromic Equilibrium. Experimental Results. The solvatochromic complexes of Cu(II) are relatively insensitive to changes in temperature, although they are highly sensitive to the nature of the solvent. Both strong and weak donor solvents bind to [Cu(tmen)(acac)]$^+$. Figure 4 shows that the shift of the absorption band of the solvated copper complex in the binary mixture NM/DMF extended from 536 nm to 606 nm. The phenomenon was observed over a narrow range of concentration, and a small change in DMF concentration led to a very marked shift in the absorption band. Similar observations have been made for mixtures containing low concentrations of a polar solvent in a less polar solvent.23) For each mixture, determination of λ_{max} defines a ratio β which characterizes the progress of the equilibrium (2):

$$\beta=(\lambda_{\mathrm{max}}-536)/(606-536). \quad (9)$$

In pure NM, λ_{max}=536 nm and β=0; in pure DMF, λ_{max}=606 nm and β=1. K_{obs}' can be estimated from the relationship:

$$K_{\mathrm{obs}}'=\beta/(1-\beta). \quad (10)$$

At concentrations of DMF around 3M, the peak absorption of the complex of Cu(II) is very close to that observed in pure DMF (602 versus 606 nm). Moreover, the inversion point of the solvatochromic equilibrium (λ_{max}=571 nm; β=0.5; K_{obs}'=1) is found in a zone of concentration where [DMF]=1.70×10^{-1} M and [NM]=18.2 M (ratio≈100). These results illustrate the fact that DMF is a much stronger solvating agent than NM.

Interpretation. Assuming that the solvatochromic equilibrium (2) does not affect the concentration of NM which is always in large excess, and taking into account that DMF solvates the complex and self-associates, the constant of equilibrium (2) is expressed as:

$$\begin{aligned} K' &= ([\mathrm{Cu(tmen)(acac)DMF_2}]^+)([\mathrm{NM}]^2)/([\mathrm{Cu(tmen)(acac)NM_2}]^+)([\mathrm{DMF}]^2)\\ &=(\beta/(1-\beta))[\mathrm{NM}]^2/([\mathrm{S_0}]-2\beta[\mathrm{C_0}]-[\mathrm{X}])^2\\ &=K_{\mathrm{obs}}'[\mathrm{NM}]^2/([\mathrm{S_0}]-2\beta[\mathrm{C_0}]-[\mathrm{X}])^2. \quad (11) \end{aligned}$$

As for thermochromism, the value of K' can be estimated from mixtures with low concentrations of DMF in which self-associations can be neglected ([X]=0). Thus:

$$K'=5.6\times10^{4}.$$

From K', the relative proportion of self-associated DMF in the other binary mixtures is obtained from relationship (12):

$$[\mathrm{X}]/[\mathrm{S_0}]=1-2\beta[\mathrm{C_0}]/[\mathrm{S_0}]-[(K_{\mathrm{obs}}'/K')^{1/2}][\mathrm{NM}]/[\mathrm{S_0}]. \quad (12)$$

The results of these calculations are listed in Table 3. As in the case of thermochromism, it can be seen that the higher the concentration of DMF the higher the

Table 3. Wavelength of the Maximum Absorption Peak, Equilibrium Position and Estimation of the Relative Proportions of Self-Associated DMF as a Function of DMF Content in Binary Mixtures of NM/DMF from the Study of Solvatochromism of the Complex $[Cu(tmen)(acac]^+$

No.	[DMF] / M	$\log \frac{[DMF]}{[DMF]_{max}}$	[NM] / M	λ_{max} / nm	β	$[NM](K'_{obs})^{1/2}$ / M	$[S_0]-2\beta[C_0]$ / M	$[X]/[S_0]$
9	.0066	−3.29	18.5	538	.029	1.49	.0063	—
10	.0131	−3.00	18.5	540	.057	4.55	.0125	—
11	.0196	−2.82	18.5	542	.086	5.66	.0187	—
12	.0261	−2.70	18.5	544	.114	6.63	.0249	—
13	.0324	−2.60	18.5	548	.171	8.38	.0306	—
14	.0633	−2.31	18.4	554	.257	10.8	.0606	.35
15	.0927	−2.15	18.4	562	.371	14.1	.0888	.41
16	.126	−2.01	18.3	566	.429	15.9	.121	.51
17	.197	−1.82	18.2	574	.544	19.9	.191	.61
18	.243	−1.73	18.1	580	.628	23.5	.236	.63
19	.377	−1.54	17.9	586	.714	28.3	.369	.71
20	.631	−1.31	17.6	592	.800	35.2	.623	.79
21	1.141	−1.06	16.8	598	.885	46.6	1.13	.85
22	2.978	−.64	14.2	602	.940	56.2	2.97	.93

Table 4. Experimental Results for Solvatochromism of the Complex $[Cu(tmen)(acac]^+$ (1.69×10^{-3} M). Estimation of the Relative Proportions of Self-Associated DMF as a Function of DMF Content in Binary Mixtures of DCE/DMF Taking $K'_{DMF}=4.77\times10^8$

No.	[DMF] / M	$\log[DMF]/[DMF]_{max}$	[DCE] / M	λ_{max} / nm	β	$[DCE](K'_{obs})^{1/2}$ / M	$[S_0]-2\beta[C_0]$ / M	$[X]/[S_0]$
23	.0013	−4.00	12.66	556	.129	4.87	.000654	.50
24	.0053	−3.39	12.65	562	.226	6.84	.00454	.80
25	.0134	−2.99	12.65	578	.484	12.25	.0118	.84
26	.0372	−2.54	12.62	591	.694	19.01	.0349	.91
27	.110	−2.07	12.55	601	.887	35.16	.107	.97

degree of self-associations.

(C) Comparison of Thermochromism and Solvatochromism. The two independent investigations (thermochromism and solvatochromism) demonstrated the existence of self-associations of DMF in NM. To check that this phenomenon was arizing from the same origin in both cases, the proportion of self-associated DMF was plotted as a function of the logarithm of the normalized concentration ($[DMF]/[DMF]_{max}$) of DMF in the NM/DMF binary mixtures (cf. Fig. 5). It can be seen that points from comparable measurements lie in similar positions on the curve, indicating that the same process of self-association is observed by thermochromism and solvatochromism.

However, a small amount of NM-DMF association probably also occurs. This effect was assessed by replacing NM with 1,2-dichloroethane (DCE).[24] In DCE,[25] only DMF-DMF interactions take place, as DCE-DMF interactions are negligible in view of the chemical inertness of DCE. In this solvent, the inversion point of the equilibrium is observed at $[DMF]=1.77\times10^{-2}$ M, which is 10-fold less than in NM. The order of complexation power is thus: DCE$<$NM$\ll$DMF. This order is in agreement with the order of the Gutmann parameters[26] and other scales of donor solvents.[27] Study of the solvatochromism of $[Cu(tmen)(acac)]^+$ in the binary mixture

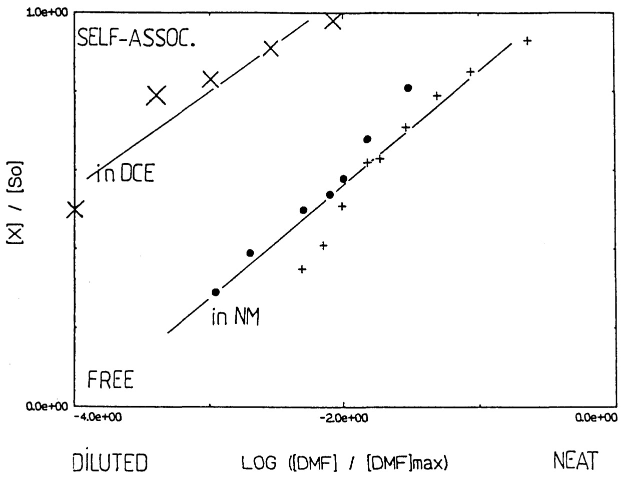

Fig. 5. a) Self-associated fraction $[X]/[S_0]$ of DMF in various binary mixtures of NM/DMF determined by: — thermochromism of $[Ni(tmen)(acac)]^+$ (●), — solvatochromism of $[Cu(tmen)(acac)]^+$ (+). b) Self-associated fraction $[X]/[S_0]$ of DMF in various binary mixtures of DCE/DMF observed by solvatochromism of $[Cu(tmen)(acac)]^+$ (×).

DCE/DMF allows us to estimate the fraction of DMF associated in DCE. We used an identical method of calculation to that temployed for NM/DMF. The results shown in Table 4, demonstrate that there is a greater tendency for self-associations of DMF in DCE than in MM (cf. Fig. 5).

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