DONOR NUMBERS FOR BINARY MIXTURES OF DIMETHYL SULFOXIDE WITH DIPOLAR APROTIC SOLVENTS

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Solvent effect on the visible absorption spectrum of (acetylacetonato)(N,N,N',N'-tetramethylethylene-diamine)copper(II) was applied to estimate D_N, the donor numbers of the binary mixtures of dimethyl sulfoxide with a series of other dipolar aprotic solvents. It was found that resulting D_N values may be treated as explanatory parameters in the description of the mixed solvent effect on the stability constants of complexes formed by some macrocyclic ligands with univalent cations.

Physicochemical properties of mixed solvents are interesting both from laboratory and industrial applications, because many reactions might be carried out advantageously in these media. However, theoretical description of solvation phenomena is often complicated: when the solute is dissolved in a mixed solvent, the solvation shell of the former need not have the same composition as the bulk solvent, but it may preferentially contain one component of the mixture. This is because the components compete for the environment of the ion, but this competition is not always forced into the narrow description of the coordinating molecules replacing each other. Therefore, in order to obtain even rudimentary understanding of reaction mechanisms, it is necessary to evaluate the relative solvating ability of the two solvents towards the reacting species.

Relative solvating abilities of pure solvents have been expressed by a variety of empirical scales[1–3]. An important contribution to preferential solvation arises from the donor–acceptor effects, therefore the Gutmann donicity scale[1] seems to be one of the most useful, particularly (but not only) in coordination chemistry. What is, however, the situation in binary solvent mixtures?

The studies of the Na^+ ion in selected mixed systems by ^{23}Na NMR technique[4,5] led to the estimation of appropriate donor number values[1], but such results are very scarce. It is also noteworthy that the β-scale[6] for hydrogen-bond-acceptance ability of pure

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solvents is linear with D_N to some extent. And, therefore, one should emphasize that β values were also reported for binary mixtures of selected organic solvents with methanol[7] and water[8]. To our knowledge, however, there are no any data for mixtures of two aprotic solvents.

(Acetylacetonato)(*N,N,N′,N′*-tetramethylethylenediamine)copper(II) perchlorate, abbreviated as [Cu(acac)(tmen)]ClO$_4$, is known to be strongly solvatochromic, owing to the structural changes caused by the solvation processes[9]. The chelate cation is axially solvated by electron donating solvents, so that the original square planar complex is transformed to a tetragonal and approximately octahedral configuration according to the strength of solvation. Consequently, the color of the solution follows the donor ability of the solvent, as it was quantitatively revealed by the linear relationship between the wave number of the maximum absorption band in the visible region and the solvent donor number[10]. This relationship was promoted to estimate easily the unknown D_N values[11,12] but it was more recently established that anomalies appear in very weak and very strong donating solvents[13].

We are currently interested in the solvation effects in the complexation of cations by macrocyclic ligands in binary solvent mixtures. Therefore it was of interest to us to estimate appropriate D_N parameters for the mixtures composed of two dipolar aprotic solvents. The individual solvents were selected so as to give a respectable range of donicities; as a consequence we report below the donor numbers for the mixtures of dimethyl sulfoxide (DMSO) with benzonitrile (BN), acetonitrile (ACN), acetone (AC), propylene carbonate (PC), γ-butyrolactone (BL), *N,N*-dimethylformamide (DMF) and hexamethylphosphoric triamide (HMPT).

EXPERIMENTAL

[Cu(acac)(tmen)]ClO$_4$ was prepared according to the procedure described in ref.[10]. The compound was recrystallized several times from ethanol of spectral grade purity, and then dried in vacuum dessicator over P$_2$O$_5$. The commercial solvents used in experiments were all dried and purified according to the literature[14,15].

The electronic absorption spectra were carried out using a Philips PU 8730 recording spectrophotometer cooperating with an IBM 386 computer. The blank solutions were identical in composition to each sample except for the absence of the solute compound. The accuracy of the assignment of the wavelengths of the maximum absorption and the reproducibility of the values determined in different experiments were in the range of ±1 nm.

RESULTS AND DISCUSSION

The present investigation is based on the difference of spectral properties of [Cu(acac)(tmen)]ClO$_4$ in various pure and mixed solvents. As it was many times reported in the literature[10–13], the wave number value at the maximum of the longwavelength band of this complex decreases on the addition of donor solvents. However, are the reasons to believe in the experimental homogeneity of the ν_{max} values from various

sources? We assume that unless careful standarization is carried out, the data for correlation analysis should be from one source only. Hence, we decide to reexamine the overall picture of the solvatochromism of [Cu(acac)(tmen)]ClO$_4$ in the solvents with D_N above 10 (cf. ref.[13]). The results obtained by us for 24 solvents are collected in Table I. Generally, these data agree satisfactorily with the already published ones (see e.g. Table I in ref.[12]), but in some cases the differences of several nm are observed. Of course, such discrepancies are important for the results of correlation analysis.

TABLE I
Wavenumbers, v_{max}, of the long-wavelength band of [Cu(acac)(tmen)]ClO$_4$ in various solvents and donor numbers, D_N, of these solvents

Solvent	D_N	v_{max}, cm^{-1}
Benzonitrile	11.9	17 540
Acetonitrile	14.1	17 350
Tetramethylene sulfone	14.8	17 790
Propylene carbonate	15.1	17 840
i-Butyronitrile	15.4	17 560
n-Butyronitrile	16.0	17 400
Propionitrile	16.4	17 480
Acetone	17.0	17 500
Ethyl acetate	17.1	17 300
Butanone-2	17.4	17 550
γ-Butyrolactone	17.8	17 790
Water	18.0	16 870
Methanol	19.1	16 960
1-Propanol	19.6	16 720
Tetrahydrofuran	20.0	17 270
Trimethyl phosphate	23.0	16 780
N,N-Dimethylformamide	26.6	16 580
N-Methylpyrrolidinone	27.1	16 440
N,N-Dimethylacetamide	27.8	16 380
Tetramethylurea	29.6	16 560
Dimethyl sulfoxide	29.8	16 250
N,N-Diethylformamide	30.9	16 070
N,N-Diethylacetamide	32.2	15 960
Hexamethylphosphoric triamide	38.8	15 610

As it can be seen, Table I contains ν_{max} values for a set of 21 dipolar aprotic solvents and for a group of 3 protic, highly structured ones (water, methanol and 1-propanol), for which appropriate donor numbers are known[16]. At the start we have considered both these series together. Regressing D_N against ν_{max}, we have obtained correlation equation in the following form

$$D_N = (-0.011 \pm 0.001)\, \nu_{max} + (202.2 \pm 27.8) \qquad (1)$$

with a correlation coefficient of $r = 0.9454$ and a standard deviation in D_N of $s = 2.3$ (errors were calculated at the confidence level of 0.95). Comparison of $(D_N)_{calc}$ with $(D_N)_{exp}$ indicates that the most serious deviations are with protic solvents, particularly with water and 1-propanol. If the protic liquids are excluded, the correlation is considerably improved

$$D_N = (-0.011 \pm 0.001)\, \nu_{max} + (206.2 \pm 22.4) \qquad (2)$$

with $r = 0.9695$ and $s = 1.8$. Thus we assume that Eq. (*2*) offers a suitable method for rapid estimation of the donor numbers of solvents for which the D_N values are still unknown. It is worthy to add, however, that the use of this expression gives reasonably good results for aprotic solvents only, for which the D_N lies between 10 and 40.

Next, visible absorption spectra of [Cu(acac)(tmen)]ClO$_4$ were studied in binary mixtures of DMSO with BN, ACN, PC, AC, BL, DMF and HMPT, respectively. Basing on the resulting ν_{max} and applying Eq. (*2*), we have calculated appropriate D_N values as a function of x_{DMSO}, the solvent mole fraction. The results are summarized in Table II. As an example, results obtained for DMSO–ACN, DMSO–DMF and DMSO–HMPT systems are shown in Fig. 1.

The dependences presented in this figure are typical. As it can be seen, the DMSO–DMF system behaves as a quite ideal mixture; the correlation between donicity parameter and solvent composition is close to linear. Such a dependence is expected for random, i.e. non-specific solvation of the solute by individual components of the mixture. In these terms the trend observed in Fig. 1, curve *2*, is not particularly surprising: the donicity of DMF is very close to that of DMSO, but both these solvents differ in their electric permittivities. It seems reasonable to assume that other mixtures of two dipolar aprotic solvents with approximately equal D_N values would behave similarly.

In all remaining solvent systems the plots of D_N vs x_{DMSO} show a pronounced curvature, indicating preferential solvation of the probe complex by one component of the mixture. This group of solvent systems can be divided into two types of behaviour; the first of these is represented by the DMSO–HMPT system. In this case, the curvature of

TABLE II
Donor numbers for the binary mixtures of dimethyl sulfoxide (DMSO) with various aprotic solvents.

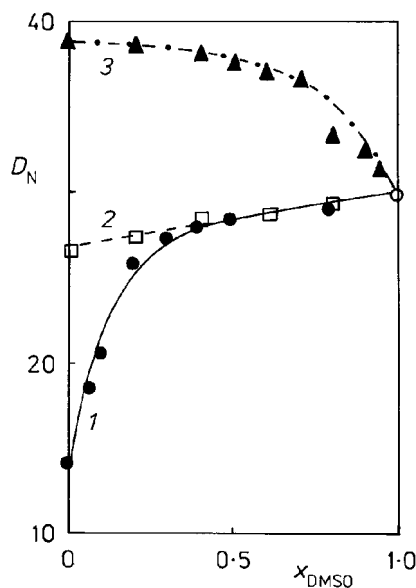| x_{DMSO}	Donor number						
	BN	ACN	PC	AC	BL	DMF	HMPT
0.0	11.9	14.1	15.1	17.0	17.8	26.6	38.8
0.05	17.5	18.5	18.5	20.6	20.7	–	–
0.1	22.5	20.5	20.2	21.8	22.2	–	–
0.2	26.3	25.8	22.4	23.5	24.0	27.3	38.5
0.3	28.0	27.2	24.1	24.8	25.6	–	–
0.4	28.7	28.0	25.3	26.2	27.0	28.0	38.0
0.5	29.2	28.2	26.0	27.3	28.0	–	37.7
0.6	–	28.5	26.6	27.8	28.6	28.5	37.0
0.7	–	–	27.3	–	29.0	–	36.5
0.8	29.8	29.0	28.0	28.6	–	29.2	33.2
0.9	–	–	–	29.0	–	–	32.5
0.95	–	–	–	–	–	–	31.4
1.0	29.8	29.8	29.8	29.8	29.8	29.8	29.8

Fig. 1
Donor numbers for binary mixtures of dimethyl sulfoxide with acetonitrile (1), N,N-dimethylform-amide (2) and hexamethylphosphoric triamide (3). Abscissa indicates mole fraction of DMSO

the plot (Fig. 1, curve *3*) decreases with increasing mole fraction of HMPT. The above is not large but indicates clearly the preferential solvation of [Cu(acac)(tmen)]$^+$ by HMPT. Of course, HMPT has higher donicity than DMSO. The second type of non-ideal behaviour is visualized by the DMSO–ACN system (Fig. 1, curve *1*). It should be noted that sometimes similar trends were observed for DMSO–BN, DMSO–AC, DMSO–PC and DMSO–BL mixtures, i.e. for the systems in which the co-solvent is a much weaker solvating agent than DMSO. Consequently, the preferential solvation by DMSO is characteristic for these mixtures.

From above data it is seen that the relative solvation ability of the binary systems towards [Cu(acac)(tmen)]$^+$ can be interpreted in terms of the Gutmann approach[1]. Therefore, taking into consideration the literature results, we tested the explanatory and predictive ability of the donor numbers presented in this communication. First attention was paid to the results of Popov and his school concerning to the preferential solvation of the Na$^+$ ion studied by determining the NMR chemical shift[4,5]. Correlating the data for the DMSO–ACN mixtures with our own D_N values, we obtained the equation

$$\delta^{23}Na^+ = (-0.451 \pm 0.035)\, D_N + (14.89 \pm 0.89) \tag{3}$$

with $r = 0.9977$ and $s = 0.1$; number of experimental points is $n = 7$. Similar tendency is also observed for the binary mixtures of DMSO with HMPT. Unfortunately, the numerical results of the NMR measurements for this solvent system are not available in the literature, but interpreting the $\delta^{23}Na^+$ chemical shifts from the graph (Fig. 3 in ref.[4]) we can estimate a correlation coefficient of $r > 0.97$ for $n = 10$.

TABLE III
Parameters of Eq. (*4*) for the complexation of the cesium ion by macrocyclic ligands in mixed solvents (log K_s values taken from refs[20,21])

Solvent	Ligand	α	β	n	r	s
DMSO–AC	DB21C7	−0.147 ± 0.010	6.54 ± 0.28	6	0.9986	0.03
	DB24C8	−0.167 ± 0.035	4.87 ± 0.21	6	0.9961	0.05
	[222]	−0.209 ± 0.018	7.15 ± 0.16	6	0.9954	0.09
DMSO–PC	DB24C8	−0.121 ± 0.033	5.30 ± 0.85	6	0.9806	0.12
	[222]	−0.185 ± 0.066	6.91 ± 1.67	6	0.9682	0.23
DMSO–ACN	DB24C8	−0.182 ± 0.050	7.14 ± 1.32	6	0.9819	0.16
	[222]	−0.252 ± 0.073	9.14 ± 1.92	6	0.9792	0.23

It is also assumed that the desolvation of the cation plays a decisive role in the complexation of alkali metal ions by macrocyclic ligands. Therefore in pure aprotic solvents the extent of complex formation usually varies inversely with D_N (refs[17,18]). In this context, it was interesting to analyse the data of Rounaghi and Popov[19,20] who determined K_S, the stability constants of the cesium complexes with cryptand-222 (ref.[20]) and coronands DB21C7 and DB24C8 (ref.[19]). Least-squares regression analysis was performed according to general equation

$$\log K_S = \alpha D_N + \beta \ . \tag{4}$$

As it can be seen from Table III, plots of $\log K_S$ against D_N give satisfactory linear relationships in all the systems considered. These confirms that the metal ion is partially or completely desolvated before a complex can be formed and documents forcibly that our D_N values may be treated as explanatory variables to describe the mixed solvent effect on the $\log K_S$ values. This problem will be also discussed in our forthcoming paper[21] considering the complexation equilibria of the thallium(I) ions by the monensin anion in binary solvent systems.

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