ACCEPTOR NUMBERS FOR BINARY MIXTURES OF DIPOLAR APROTIC SOLVENTS WITH METHANOL

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Using bis(cyano)bis(9,10-phenanthroline)iron(II) as solvatochromic indicator, the acceptor numbers, A_N, were determined for binary mixtures of benzene, benzonitrile, acetonitrile, acetone, N,N-dimethylformamide, dimethyl sulfoxide and hexamethylphosphoric triamide with methanol. Deviations from linearity of the plots of A_N values against the molar fraction of the components were interpreted both in terms of changes in solvent liquid structure and in cathegories of preferential solvation.

The influence of solvent properties on the kinetic and thermodynamic parameters of chemical reactions is a large area of scientific research. In pure solvents the donor–acceptor approach[1] is of great importance. According to this, numerous quantities that relate to the electron pair donation and acceptance abilities of solvents can be elucidated by the use of many empirical parameters which are derived from carefully selected solvent-dependent reference processes[1–3]. Of the parameters that are of especial importance in coordination chemistry are the donor and acceptor numbers introduced by Gutmann and his school[1]. Therefore, in the context of our studies on the complexation of metal ions by coronands[4,5], it was of interest to us to know the D_N and A_N values for binary solvent mixtures.

Corresponding data are rather scarce in the literature. To our knowledge the only donor numbers were estimated for mixtures of dimethyl sulfoxide and pyridine with acetonitrile (cf. Chap. 9 in ref.[1]). It is noteworthy, however, that the β-scale[3] for hydrogen bond-acceptance ability of pure solvents is linear with D_N to some extent[6]. And, therefore, one should emphasize that β, the Kamlet and Taft basicity parameters, were also reported for binary mixtures of selected organic solvents with methanol[7] and water[8]. Next, the acceptor numbers for aqueous–non aqueous solvent systems were measured basing on the ^{31}P NMR shift in triethylphosphine oxide[9] which was originally

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applied in establishing of the A_N-scale for pure solvents. It has been shown that the A_N values are not related to the composition of a given mixture in a simple manner but are highly influenced by water–solvent interactions[10]. An empirical two-parameter relation between E_T, the other electron pair acceptance index[2], and the concentration of the more polar component of the mixtures was analyzed by Langhals[11]. More recently a preferential solvation equation simpler than that proposed by this author was derived by Bosch and Roses[12]. It should be noted that E_T values are presently known for numerous mixed solvent systems[2,11–15]. It is seen, however, that the two measures do not agree well, even though for pure solvents the linear regression between A_N and E_T is acceptable[2].

Bis(cyano)bis(9,10-phenanthroline)iron(II), abbreviated as $Fe(CN)_2(phen)_2$, is known to be strongly solvatochromic. The coordination center which determines the position of the visible charge transfer band ($t_{2g} \rightarrow \pi^*$) is extremely sensitive to electrophilic solvent attack. This fact led to the proposal to use the complex as a color indicator for solvent acidity, which is expressed in acceptor number scale[16,17]. The procedure has been tested for pure solvents[16,18]. In the previous paper[18] we have discussed the relationship expressing the solvent acceptor numbers as a function of the position of the long-wavelength band of $Fe(CN)_2(phen)_2$. For a set of 18 solvents (including dipolar aprotic solvents, alcohols and water) the following correlation equation can be written[18]

$$A_N = 0.013 \, \nu_{max} - 192.1 , \qquad (1)$$

which holds with a correlation coefficient of $r = 0.9906$ and a standard deviation of the fit of $s = 1.7$. Thus, the use of this complex to estimate unknown A_N values appropriate for pure solvents gives reasonably good results when the A_N lies between 10 and 55. However, is Eq. (1) also valid for binary solvent mixtures? The problem is discussed in this communication.

EXPERIMENTAL

The solvents *N,N*-dimethylformamide and dimethyl sulfoxide (both from Reakhim, Russia), acetone, methanol and benzene (all from POCh, Poland) as well as benzonitrile, acetonitrile and haxamethylphosphoric triamide (all from Fluka) were carefully dried and purified according to the earlier described procedures[19]. The $Fe(CN)_2(phen)_2$ complex (Alfa Ventron) was used without additional purification. The electronic spectra were recorded using a Philips PU 8730 spectrophotometer with data station based on IBM 386 computer at a temperature 23 ± 0.2 °C. The blank solutions were identical in composition to each sample except for the absence of the solute complex. 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

To verify the validity of Eq. (*1*) for binary solvent mixtures we have undertaken a series of experiments emploing the measurements of the acceptor numbers of the mixtures of methanol, ethanol, *N,N*-dimethylformamide, acetonitrile and dimethyl sulfoxide with water. The results presented in Fig. 1 indicate convincingly that our data obtained on the basis of Eq. (*1*) are fully consistent with those reported earlier by Mayer et al.[10]. Comparing our results with those described in ref.[10] we have found that the correlation coefficients between them are as follows: 0.974 in MeOH–H_2O, 0.980 in EtOH–H_2O, 0.962 in *N,N*-dimethylformamide–H_2O, 0.969 in acetonitrile–H_2O and 0.982 in dimethyl sulfoxide–H_2O systems. One may assume, therefore, that the $Fe(CN)_2(phen)_2$ complex can be used as a suitable probe substance for assessing the acceptor properties of mixed solvents.

Taking into account this finding we have determined the A_N values for the mixtures of benzene (Bz), benzonitrile (BN), acetonitrile (ACN), acetone (AC), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and hexamethylphosphoric triamide (HMPT) with methanol; the solvents were selected to give a range of Lewis acid–base properties. The results are given in Table I; appropriate A_N values for pure liquids were taken from ref.[9]. Typical variations of the acceptor number with the mole fraction of the components are illustrated in Fig. 2 for three selected systems. The isosolvation points, χ_{iso}, are collected in Table II; the estimated error is ±0.03. Note that χ_{iso} values correspond to the mixture composition at which the acceptor number lies midway be-
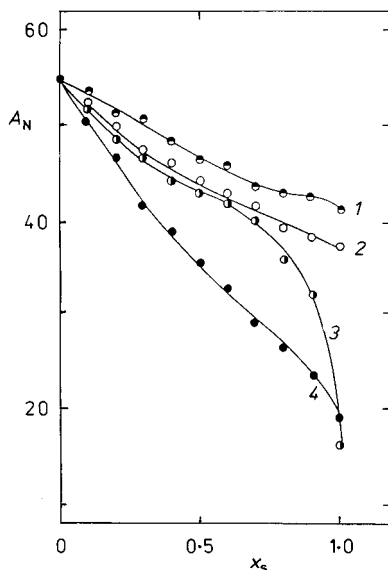

Fig. 1
Acceptor numbers for binary mixtures of water with methanol (*1*), ethanol (*2*), acetonitrile (*3*) and dimethyl sulfoxide (*4*). Experimental points of this work are indicated by the circles; the lines were depicted using the data of Mayer[10]. Abscissa indicates molar fraction of organic solvent component

tween those of the pure solvent components. According to that, isosolvation points and their deviations were estimated from graphs of the type reproduced in Fig. 2.

Even superficial inspection of the data collected in Table II indicates that the relative ability of the studied solvents towards the $Fe(CN)_2(phen)_2$ complex increases with their donor numbers.

TABLE I

Acceptor numbers, A_N for binary mixtures of methanol with various aprotic solvents

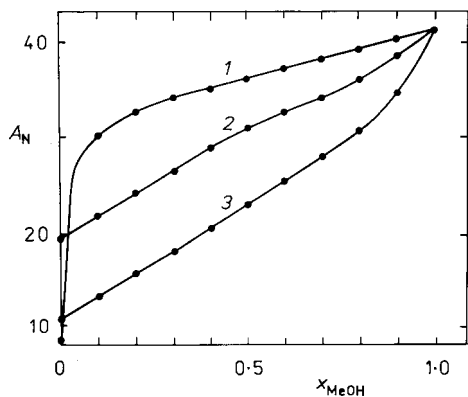| χ_{MeOH}	A_N						
	Bz	BN	ACN	AC	DMF	DMSO	HMPT
0.0	8.2	15.5	18.9	12.5	16.0	19.3	10.6
0.1	30.2	23.3	27.5	22.3	21.6	21.9	13.1
0.2	32.5	29.7	32.9	28.7	24.4	24.2	15.5
0.3	34.0	32.3	35.1	31.6	26.3	26.4	17.8
0.4	34.8	33.7	36.3	32.7	28.2	28.7	20.5
0.5	35.6	34.8	37.4	33.9	30.3	30.8	22.8
0.6	36.8	35.6	38.5	35.7	31.7	32.4	25.4
0.7	37.8	36.7	39.4	37.1	34.1	34.0	27.5
0.8	38.4	37.9	40.1	38.7	36.2	36.0	29.8
0.9	39.4	39.4	40.7	39.7	38.4	38.9	33.9
1.0	41.3	41.3	41.3	41.3	41.3	41.3	41.3

FIG. 2

Acceptor numbers for binary mixtures of methanol with benzene (*1*), dimethyl sulfoxide (*2*) and hexamethylphosphoric triamide (*3*)

A relationship between χ_{iso} and D_N is evidenced by Eq. (*2*) which holds with $r = 0.9760$ and $s = 0.048$ ($n = 8$)

$$\chi_{iso} = 0.018 \, D_N - 0.059 \ . \tag{2}$$

An error of free term (± 0.099 at the confidence level of 0.95) indicates that the regression line pass, in reality, through the origin so that the isosolvation points for low donating second component are not practically measurable.

It is worthy to add that a similar correlation was observed for the mixtures of organic solvents with water[10] and this finding was attributed to the specific donor–acceptor interactions between water and co-solvent. Certainly such interactions change a solvent structure from that a pure liquids and these changes contribute to the observed variation of the acceptor number with the solvent composition. It can be seen from Eq. (*2*) that the strength of the co-solvent–MeOH interaction increases with the donor number of the former. Add in this place that D_N values of aprotic solvents (Table II) were extracted from ref.[1].

Figure 2 documents that the A_N values of solvent mixtures can change on three different ways depending on the molar fraction of the components. First of all, nearly linear relationships between A_N and χ_{MeOH} (Fig. 2, curve *2*) are observed for DMF–MeOH and DMSO–MeOH systems. Such dependences should be expected for random, i.e. non specific solvation of $Fe(CN)_2(phen)_2$ by the components of the binary solvent mixture. In fact both these systems are characterized by roughly equimolar isosolvation

Table II
Isosolvation points of $Fe(CN)_2(phen)_2$ in binary solvent mixtures

Solvent mixture (I) (II)	χ_{iso}	$D_N(I)$	$A_N(I)$
Bz–MeOH	0.02	0.1	8.2
BN–MeOH	0.13	11.9	15.5
ACN–MeOH	0.14	14.1	18.9
AC–MeOH	0.17	17.0	12.5
DMF–MeOH	0.46	26.6	16.0
DMSO–MeOH	0.50	29.8	19.3
HMPT–MeOH	0.64	38.8	10.6
H_2O–MeOH	0.57	33.0	54.8
MeOH		25.7	41.3

points (Table II) and one may assume, therefore, that the donicities of DMF and DMSO are very close to that of MeOH. This result is completely inconsistent with the donor number of 19 originally assumed for methanol[1] but agrees well with the donicity of 25.7 obtained from $^{23}Na^+$ NMR measurements[20]. Similarly the relative molar fraction at the isosolvation point for water–MeOH mixtures is consistent with the donicity of 33 for the former[20]. Then, smooth dependences between A_N and χ_{MeOH} reflect the properties of the system in which both solvents are really characterized by very similar donicities.

The non-linear behaviour of A_N as a function of the solvent molar fraction has been observed for all remaining systems under study. In the case of curve *1* in Fig. 2 methanol appears to be preferentially solvating $Fe(CN)_2(phen)_2$ rather than benzene. Curves with distinct convexities were also found for MeOH–BN, MeOH–ACN, and MeOH–AC mixtures. All co-solvents belonging to this group have much lower acceptor numbers than MeOH and, therefore, preferential solvation of the probe molecule by methanol is not astounding. Note, moreover, that Bz, BN, ACN and AC have much lower donicities than MeOH, and this is a possible reason for which the strength of the solvent–solvent interaction is relatively small.

Next, HMPT is also a poor Lewis acid and its acceptor number of 10.6 is comparable with those for benzene (8.2) and acetone (12.3). Notwithstanding of this property, the A_N values for MeOH–HMPT mixtures occupy curve *3* in Fig. 2. As it can be seen this curve is depressed and, consequently, HMPT appears to solvate preferentially to MeOH. Recall, however, that the former is much more basic than the alcohol and, therefore, strong solvent–solvent interaction should be taken into account. We assume that the addition of HMPT to methanol destroys to a great extent the intermolecular structure of the latter. Moreover, the added molecules interact partially with the acidic centers of the MeOH molecules, which causes negative deviation from regular behaviour of the mixture. One may also suggest that other solvents being better electron-pair donors than MeOH should behave similarly. And this means that at least two factors contribute to the observed deviations of A_N from linearity in the studied systems: these are changes of liquid structure from that of the pure solvents and preferential solvation of the probe molecule.

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