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NMR-Spectroscopic Studies on Solvent Electrophilic Properties, Part II*: Binary Aqueous—Non Aqueous Solvent Systems

By

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With 6 Figures

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Acceptor numbers have been determined for binary mixtures of water with acetonitrile (*AN*), dioxane, acetone (*AC*), pyridine (*PY*), N,N-dimethylformamide (*DMF*), dimethyl sulfoxide (*DMSO*), hexamethylphosphoramide (*HMPA*), methanol, ethanol and *i*-propyl alcohol. The electrophilic properties of binary aqueous—non aqueous solvent mixtures are determined both by selective solvation and specific solvent—solvent interactions. The variation of the acceptor number as a function of solvent composition is interpreted in terms of the previously determined nucleophilic and electrophilic properties of the pure components and their specific solvent structure.

1. Introduction

In the first part of this series the so-called "acceptor number" (*AN*) has been introduced as a quantitative empirical measure of the acceptor (electrophilic) properties of solvents[1]. Its definition, equation (1), is based on the strong solvent dependence of the ^{31}P chemical shift of triethylphosphine oxide which serves as reference base. The electrophilic attack of a solvent at the basic oxygen atom induces a polarization of the P—O bond and thereby a decrease in electron density at the phosphorus atom which manifests in a downfield chemical shift.

$$AN \equiv \frac{\delta_{\mathrm{corr}}}{\delta_{\mathrm{corr}}\,(Et_3\mathrm{PO}\cdot\mathrm{SbCl_5})} \times 100 = \delta_{\mathrm{corr}} \times 2{,}348. \qquad (1)$$

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* In eq. (1), δ_{corr} means the ^{31}P chemical shift of Et_3PO at concentration zero in a solvent *S* referred to an infinitely dilute solution of Et_3PO in *n*-hexane and corrected for differences in volume susceptibilities between *S* and hexane, $\delta_{\mathrm{corr}}\,(Et_3\mathrm{PO}\cdot\mathrm{SbCl_5})$ denotes the corresponding chemical shift value for the adduct $Et_3\mathrm{PO}\cdot\mathrm{SbCl_5}$ at infinite dilution in 1,2-dichloroethane which is arbitrarily assigned an *AN* = 100.

In contrast to classical solvent parameters such as dielectric constant, dipole moment or polarizability, the acceptor number allows an interpretation of many solvent dependent NMR-, IR-, Raman-, UV-visible spectroscopic and kinetic data[1–3].

Together with the donor number[4, 5] (representing a measure of the nucleophilic properties of the solvents) the acceptor numbers are of fundamental importance for the interpretation of many solvent dependent processes[2, 5–11]. As the majority of chemical reactions is influenced both by nucleophilic and electrophilic interactions with solvent molecules the knowledge of their donor and acceptor numbers offers a possibility to predict the course of many reactions in a qualitative and sometimes even in a quantitative way[2, 6–11].

Acceptor properties of solvent mixtures are interesting both from a practical and theoretical point of view. First, many chemical and electrochemical processes might be carried out more advantageously in solvent mixtures. The proper choice of a mixed solvent system requires the knowledge of both the nucleophilic and electrophilic properties of the solvent mixtures. Secondly, solvent mixtures usually do not behave as expected from statistical considerations. The observed deviations from ideal behaviour are indicative of the extent of preferential solvation and the existence of specific solvent—solvent interactions and solvent structures.

The present study is concerned with the acceptor properties of binary mixtures of water with several protic and aprotic solvents.

2. Experimental Part

All measurements were carried out as described previously[1]. For each solvent mixture the chemical shift was measured at five different concentrations in the range 0.05–0.5 mole/litre and extrapolated to concentration zero. The variation of the chemical shift as a function of concentration was usually not negligible and may amount up to 1.3 ppm in the concentration range studied. Volume susceptibilities χ for the various mixtures were calculated from the volume susceptibilities χ_1 and χ_2 of the pure solvent components[12] according to *Wiedemann*'s additivity law, eq. (2), where v_1 and v_2 denote the volume fractions of the components.

$$\chi = v_1 \cdot \chi_1 + v_2 \cdot \chi_2 \qquad (2)$$

3. Results and Discussion

Acceptor numbers for mixtures of water with *AN*, dioxane (*DX*), *AC*, *DMF*, *PY*, *DMSO, HMPA,* methanol, ethanol, and *i*-propyl alcohol are listed in Table 1 and illustrated in Figs. 1—3. In no case the acceptor numbers vary linearly with the mole fraction as should be expected from purely statistical considerations. Positive deviations from the ideal straight line are most pronounced in the systems H_2O—*AN*, H_2O—*DX*, and H_2O—*AC* whereas predominantly negative deviations occur in H_2O—*DMSO*, H_2O—*HMPA*, and water—alcohol mixtures. Both types of non-ideal behaviour are found in H_2O—*DMF* and H_2O—*PY* mixtures.

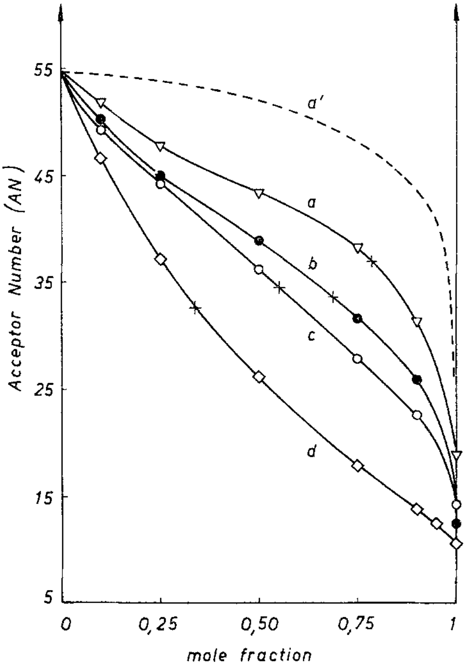

Fig. 1. Acceptor numbers (*AN*) for binary mixtures of water with acetonitrile (*a*), *AC* (*b*), *PY* (*c*), and *HMPA* (*d*) and the corresponding isosolvation points (+). Abscissa indicates mole fraction of nonaqueous solvent component. Curve *a'*: experimental curve for the system water—acetonitrile obtained by using the corrected mole fraction $\bar{x}_{H_2O}$ (see text)

3.1. *Mixtures of Water With Aprotic Solvents*

According to Table 2 water is a much stronger electrophilic agent than the aprotic solvents. Addition even of a small amount of water to the pure aprotic solvent should therefore cause a well-pronounced increase in acceptor number. This behaviour is observed for mixtures of water with *AN*, *DX*, and *AC* whereas in H_2O—*DMSO* and H_2O—*HMPA* addition of water produces only a comparatively small increase in acceptor number. In case of preferential solvation, the reference base Et_3PO should be more strongly hydrated in H_2O—*HMPA* mixtures than in H_2O—*AN* mixtures since *HMPA* is a weaker acceptor

Table 1. *Acceptor Numbers for Binary Mixtures of Water With Various Solvents S at Different Mole Fractions* x_S

x_S	Acceptor number (*AN*)									
	*AN**	*DX*	*AC*	*PY*	*DMF*	*DMSO*	*HMPA*	*Me*OH	*Et*OH	^{i}*Pr*OH
0.00	54.8	54.8	54.8	54.8	54.8	54.8	54.8	54.8	54.8	54.8
0.10	51.9	49.7	50.2	49.3	50.2	50.7	46.7	53.3	52.2	51.0
0.25	47.8	43.7	45.0	44.4	44.2	44.4	37.2	51.0	48.1	45.9
0.50	43.4	37.7	38.9	36.2	35.3	35.1	26.2	46.7	43.6	41.4
0.75	38.2	31.2	31.6	27.9	28.0	27.6	17.9	43.6	40.4	37.4
0.90	31.2	25.2	25.9	22.6	23.1	23.4	13.8	42.8	38.9	35.4
0.95		22.0					12.5	42.4	38.0	34.6
1.00	18.9	10.8	12.5	14.2	16.0	19.3	10.6	41.3	37.1	33.5

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* *AN* = abbreviation for acetonitrile.

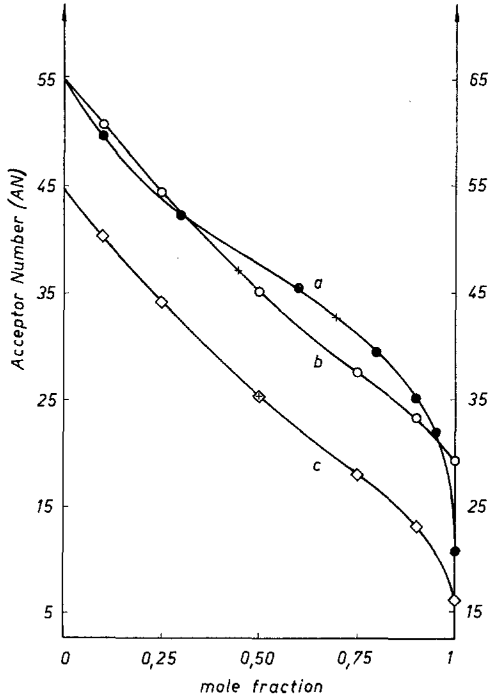

Fig. 2. Acceptor numbers (*AN*) for binary mixtures of water with dioxane (*a*) and *DMSO* (*b*) (left hand ordinate) and *DMF* (*c*) (right hand ordinate) and the corresponding isosolvation points (+). Abscissa indicates mole fraction of nonaqueous solvent component

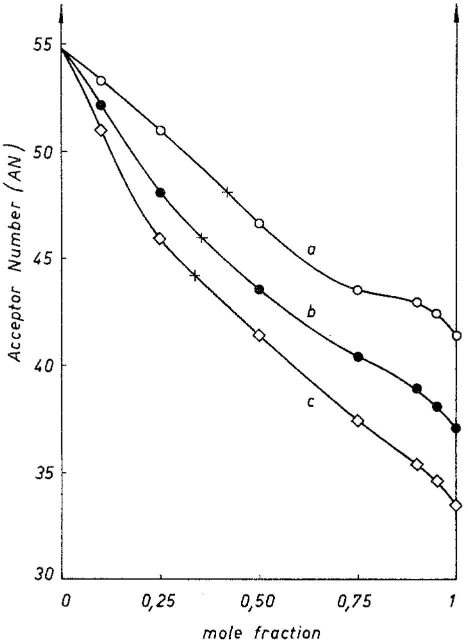

Fig. 3. Acceptor numbers (*AN*) for binary mixtures of water with methanol (*a*), ethanol (*b*) and *i*-propyl alcohol (*c*) and the corresponding isosolvation points (+). Abscissa indicates mole fraction of nonaqueous solvent component

Table 2. *Acceptor Numbers (AN) and Donor Numbers (DN) of Various Nonaqueous Solvents and Mole Fractions* $x^{iso}_{H_2O}$ *for the Isosolvation Points of Their Binary Mixtures With Water*

Solvent	*AN*	*DN*	$x^{iso}_{H_2O}$
*AN**	18.9	14.1	0.213
DX	10.8		0.300
AC	12.5	17.0	0.313
PY	14.2	33.1	0.449
DMF	16.0	26.6	0.500
DMSO	19.3	29.8	0.555
HMPA	10.6	38.8	0.660
*Me*OH	41.3	19.0	0.580
*Et*OH	37.1		0.647
^{i}*Pr*OH	33.5		0.660
H_2O	54.8	18.0	

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* Abbreviation for acetonitrile.

solvent than *AN*. Actually, the opposite behaviour is observed. This can be ascribed to water—solvent interactions of the donor—acceptor type which are expected to be stronger for the stronger donor solvent *HMPA*. Comparison of Figs. 1—3 shows that the slope of the curves near $x_{H_2O} = 0$ fairly regularly increases with decreasing donor number of the aprotic solvent being smallest for *HMPA* and largest for *AN*. Quantitatively this behaviour may be characterized by the mole fraction $x^{iso}_{H_2O}$ of the isosolvation point[13], i.e. the solvent composition at which the acceptor number of the mixture lies midway between those of the pure solvent components. Isosolvation points for the various solvent mixtures are listed in Table 2. According to Fig. 4 a relationship exists between $x^{iso}_{H_2O}$ and *DN* for mixtures of water with aprotic solvents. *PY* provides an exception, as it behaves as a weaker donor (effective *DN* ≈ 25) than expected from its donor number (towards $SbCl_5$, *DN* = 33,1). This is in agreement with the results of investigations on the solvation of Na^{+}[14, 15], ion-association of $Na^{+}AlBu_4^{-}$[16] and on the conductance behaviour of organotin halides[17] which also showed pyridine to behave as a weaker base than expected from its donor number.

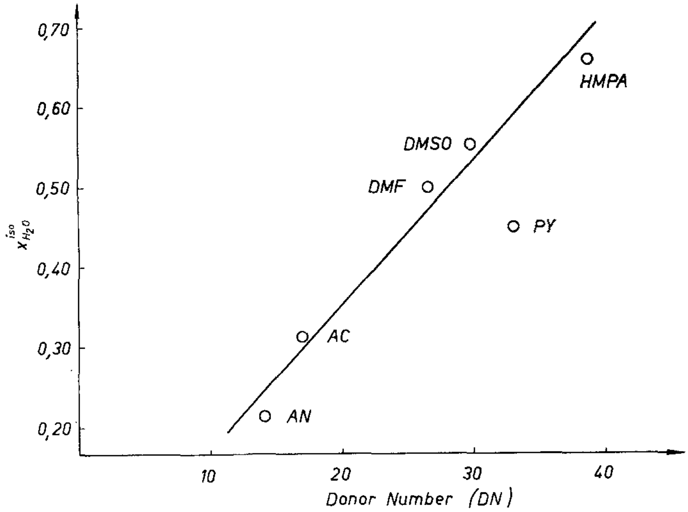

Fig. 4. Variation of the isosolvation point $x^{iso}_{H_2O}$ for binary mixtures of water with various aprotic solvents as a function of the donor number of the aprotic solvent component

The slopes of the curves in water-rich systems are unexpected. As water is a much stronger acceptor than aprotic solvents, its acceptor number should change but slightly on addition of small amounts of cosolvent, i.e. the curves should be nearly horizontal near $x_{H_2O} = 1$. The observed considerable decrease in acceptor number by addition even of weak donor solvents such as *AN*, *AC*, or *DX* may be due to the unique solvent structure of water. The mole fraction x_{H_2O} used in physical chemical studies is based on the molecular weight of monomeric water, while water in the pure liquid state is highly associated[18]. Acceptor sites are available only on the surface of the water clusters, i.e. the number of non-bonded acidic hydrogen atoms is considerably smaller than would be expected for monomeric water molecules. Hence even small amounts of added solvent acting as donor towards the water clusters may effectively reduce the number of acceptor sites. The resulting effect can be qualitatively demonstrated by replacing the conventional mole fraction x_{H_2O} by a "corrected" mole fraction $\bar{x}_{H_2O}$ which allows for the polymeric nature of water. Both quantities are related by eq. (3) where f denotes the average number of water molecules contained in a cluster.

$$\bar{x}_{H_2O} = \frac{x_{H_2O}}{x_{H_2O} + f\,(1 - x_{H_2O})} \tag{3}$$

The dotted line (a') in Fig. 1 represents the experimental curve obtained for the system H_2O—*AN* by substituting $\bar{x}_{H_2O}$ for x_{H_2O} and assuming arbitrarily $f = 10$. This curve corresponds qualitatively to the behaviour expected for a mixture of a strong and a weak acceptor solvent with comparatively weak donor—acceptor interactions between the solvent components. Curve (a') is qualitatively correct for small mole fractions x_S only, since addition of large amounts of co-solvent will necessarily break the original water structure. As expected the decrease in acceptor number in the water rich mixtures is closely related to the donor number of the co-solvent (Fig. 1) reflecting the increasing strength of the solvent—solvent interactions.

3.2. Water—Alcohol Mixtures

Alcohols are similar to water in that they act both as donors and strong acceptors (Table 2). In alcohol—water mixtures, *Et*$_3$PO is therefore less strongly hydrated than in mixtures of water with acetone, which has a similar donor strength as the alcohols but much weaker acceptor properties (Table 2). This can be also seen from the position of the isosolvation points which occur at higher mole fractions x_{H_2O} than would be expected from Fig. 4 for *DN*-values of ≈ 19—20. The observed mainly negative deviations from the ideal straight line (Fig. 3) must again be attributed to the presence of water clusters in the mixtures. The resulting effect is less pronounced than for mixtures of water with aprotic solvents (see section *3.1.*) since the alcohols themselves are associated to some extent.

As for mixtures of water with aprotic solvents, the mole fraction $x_{H_2O}^{iso}$ increases with increasing donor strength of the alcohols, i.e. in the sequence *Me*OH, *Et*OH, ^{i}*Pr*OH*. Just the oppositve behaviour would be expected on the basis of the acceptor numbers which decrease in the order *Me*OH > *Et*OH > ^{i}*Pr*OH. It appears that in water—alcohol mixtures the acceptor properties of the alcohols are levelled owing to the presence of alcohol associates. The latter are increasingly aggregated in the series *i*-propylalcohol, *Et*OH, *Me*OH, which leads to a corresponding decrease in the number of free acceptor sites or of their effective acceptor properties, respectively.

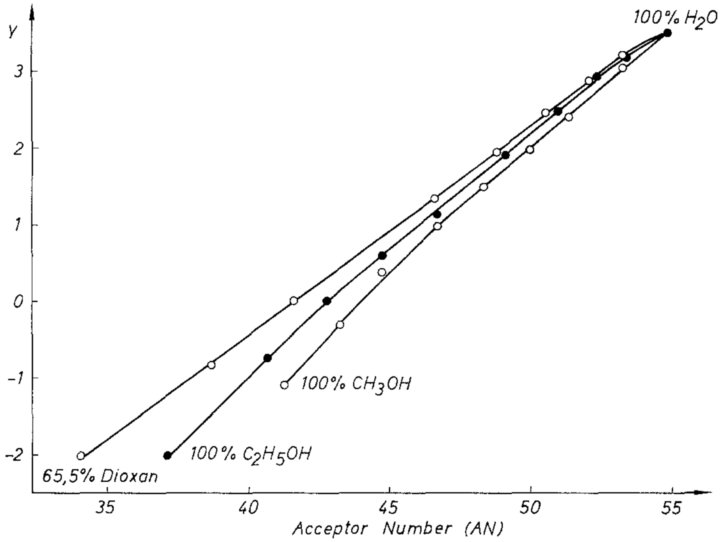

Fig. 5. Relationship between the acceptor numbers (*AN*) and *Winstein—Grunwald*'s *Y* values for binary mixtures of water with methanol, ethanol and dioxane

3.3. *Relationship Between Acceptor Numbers and Other Empirical Solvent Parameters*

Correlations to other empirical solvent parameters, as found for the pure solvents[1] are also observed for solvent mixtures. Fig. 5 shows the

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* Donor numbers for *Et*OH and ^{i}*Pr*OH are not available. Comparison of the donor numbers of water ($DN = 18$) and *Me*OH ($DN = 19$) (inductive effect of the methyl group!) suggests that the donor numbers of *Et*OH and ^{i}*Pr*OH are somewhat higher than that of *Me*OH.

nearly linear relationships between acceptor number and *Winstein—Grunwald*'s Y value for mixtures of water with methanol, ethanol and dioxane. Correlations to the *Dimroth—Reichardt*'s E_T values are given in Fig. 6. Similar, non-linear relationships also exist with *Kosower*'s Z- and *Brooker*'s χ-values[19].

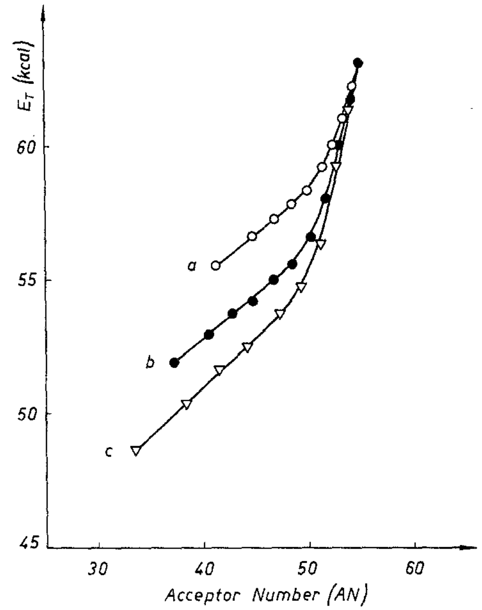

Fig. 6. Relationship between the acceptor numbers (AN) and *Dimroth—Reichardt*'s E_T values for binary mixtures of water with methanol (*a*), ethanol (*b*) and *i*-propyl alcohol (*c*)

4. Conclusions

The electrophilic properties of binary aqueous—nonaqueous solvent systems are strongly influenced by specific donor—acceptor interactions between water and the non-aqueous solvent. This implies that it is not possible to predict the acceptor properties of the mixtures from those of the pure components. The strength of the solvent—solvent interactions was found to increase with the donor number of the co-solvent as evidenced by the position of the isosolvation points, which are related to the donor number of the aprotic solvent component *and not* to its Acceptor Number as would be expected in the absence of specific donor—acceptor interactions between the solvent components. The acceptor properties of the water-rich mixtures reflect the influence of the specific water structure, with clusters being present over an appreciable range in solvent composition.

Work is in progress on the electrophilic properties of other binary systems and on the use of some other probe nuclei in anionic reference bases.

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