Empirical Parameters of Lewis Basicity of Binary Solvent Mixtures, Part II
Mixtures with Water

Piotr K. Wrona, Tadeusz M. Krygowski*, and Urszula Zielkowska

University of Warsaw, Department of Chemistry, Pasteura 1, 02093 Warsaw, Poland

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Empirical Parameters, Lewis Basicity, Binary Solvent Mixtures

The Kamlet and Taft basicity parameters β_{KT} for twelve mixtures of organic solvents with water are reported. Also the data for water-butanols (*n*-BuOH, *i*-BuOH, and *s*-BuOH) and alcohols (MeOH, EtOH, *n*-PrOH, and *i*-PrOH)-*n*-hexane mixtures are given. It was found that in the case of mixtures of 1,4-dioxane, acetone, tetrahydrofuran, dimethylsulfoxide, and acetonitrile with water, the basicity parameters of the mixture are higher than that of pure solvents in a region of smaller concentrations of water.

These results, together with earlier reported results for THF and Et_2O mixtures with MeOH are discussed in terms of breaking off the structure of the more structurized solvent (water and MeOH). All these mixtures, except the W–THF mixture, show the excess thermodynamic functions (ΔH^E and ΔS^E) analogous to MeOH–CCl_4 mixtures, where depolymerization of MeOH clusters was postulated.

Relativity of different basicity scales in respect to the acidic probe molecule is also shortly discussed.

Introduction

Recently we have reported [1] the Kamlet–Taft (KT) parameters [2] of Lewis basicity, β_{KT}, for fourteen mixtures of solvents with methanol.

It was shown that, basing on the β_{KT} *vs* mol fraction plot, these mixtures may be divided into two groups:

1. Excess mixtures (MeOH–THF and MeOH–Et_2O (for abbreviations see Table I)), where the basicity parameter goes through a maximum and
2. Regular mixtures, where the basicity parameter changes monotonically.

This dual behaviour was ascribed to changes of the solvent structure. Particularly interesting was the first case, *i.e.* the formation of a maximum. Similar behaviour has been observed by Kamlet *et al.* for β_{KT} values determined for DMSO–CCl_4 mixtures [3], as well as for $E_T(30)$-values by Reichardt *et al.* [4] in the case of mixtures of DMSO, dimethyl ketones and esters of phosphoric acids with chloroform, and by Langhals [5] in the case of 1-butanol-nitromethan mixture.

A relation between $E_T(30)$ and the concentration of one solvent for binary mixtures has recently been analyzed by Langhals [5, 6].

To investigate this phenomenon more deeply, we carried out additional measurements of the Lewis basicity of mixtures with water, since water molecules should be more strongly associated than the molecules of methanol.

The procedure of β_{KT} determination was similar to that proposed by Kamlet and Taft [2, 7].

Results and Discussion

The Kamlet–Taft parameters were measured for twelve mixtures of solvents with water. In the case of butanols (*n*-BuOH, *i*-BuOH, and *s*-BuOH) the β_{KT}-values for their mixtures with water were measured up to maximum miscibility. The results are presented in Table I. As it follows from the results presented in this Table, the water-organic solvent mixtures may be divided into two groups:

1. Excess mixtures (W–AC, W–Diox, W–THF, W–AN and W–DMSO).
2. Regular mixtures with positive deviations (all other mixtures).

The main problem which we would like to discuss in this paper is the occurrence of the excess mixtures. Summing up the results presented earlier and obtained in this paper we may state that the excess mixtures have been observed for the following pairs of solvents: MeOH–THF, MeOH–Et_2O, W–Diox, W–AC, W–THF, W–DMSO and W–AN.

Except of W–THF mixtures, for all other mixtures one observes values of β_{KT} higher than that for

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* Reprint requests to Prof. Dr. T. M. Krygowski.

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Table I. Empirical Lewis basicity parameters β_{KT} for mixtures of water with organic solvents.

Mol.% of W	MeOH	EtOH	*n*PrOH	*i*PrOH	*t*BuOH	AN	DMF	AC	Diox	DMSO	THF	FA
0	0.62	0.77	0.86	0.88	0.94	0.37	0.72	0.54	0.39	0.76	0.54	0.55
10	0.60	0.76	0.78	0.84	0.88	0.40	0.70	0.54	0.45	0.79	0.49	0.51
20	0.54	0.71	0.77	0.83	0.84	0.43	0.69	0.54	0.50	0.77	0.45	0.47
30	0.55	0.68	0.74	0.79	0.80	0.44	0.69	0.55	0.55	0.70	0.43	0.46
40	0.54	0.66	0.71	0.75	0.77	0.42	0.68	0.56	0.54	0.66	0.43	0.45
50	0.53	0.63	0.68	0.73	0.74	0.40	0.64	0.57	0.51	0.62	0.41	0.44
60	0.50	0.60	0.66	0.69	0.72	0.40	0.61	0.55	0.50	0.56	0.43	0.43
70	0.43	0.57	0.64	0.65	0.69	0.41	0.58	0.51	0.48	0.50	0.47	0.41
80	0.36	0.51	0.60	0.60	0.68	0.39	0.50	0.47	0.45	0.45	0.52	0.35
90	0.27	0.31	0.53	0.49	0.64	0.34	0.41	0.42	0.36	0.35	0.55	0.29
100	0.19	0.10	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19
$\Delta\beta_{KT}$	0.12	0.18	0.24	0.23	0.30	0.16	0.20	0.21	0.26	0.12	0.32	0.09

Mol.% of W	*n*BuOH	Mol.% of W	*i*BuOH	Mol.% of W	*s*BuOH
0	0.84	0	0.90	0	0.94
10	0.77	5	0.83	10	0.88
15	0.75	10	0.81	20	0.84
20	0.71	15	0.79	30	0.79
25	0.70	20	0.77	40	0.76
30	0.70	25	0.75	50	0.74
35	0.70	30	0.73	55	0.73
40	0.70	35	0.72	60	0.72
49	0.70	43	0.70	66	0.68
99	0.19	98	0.29	96	0.43
100	0.19	100	0.19	100	0.19

Abbreviations: MeOH, methanol; EtOH, ethanol; *n*PrOH, *n*-propanol; *i*PrOH, *i*-propanol; *t*BuOH, *t*-butanol; AN, acetonitrile; DMF, dimethylformamide; AC, acetone; Diox, 1,4-dioxan; DMSO, dimethylsulfoxide; THF, tetrahydrofuran; FA, formamide; *n*BuOH, *n*-butanol; *i*BuOH, *i*-butanol; *s*BuOH, *s*-butanol; W, water; Et_2O, diethylether; Bz, benzene; MeAc, methyl acetate; EtAc, ethyl acetate; TriMe Phos, trimethyl phosphate; TriEt Phos, triethyl phosphate; DMA, dimethylacetamide; TMU, tetramethylurea; HMPA, hexamethylphosphortriamide; NMePyrrolidon, N-methylpyrrolid-2-one; PN, propionitrile; BzN, benzonitrile; Py, pyridine; NM, nitromethane; $\Delta\beta_{KT}$, maximal deviation from an ideal behaviour.

pure solvents in the region of higher concentration of organic solvent. This result differs from that observed in water-alcohol mixtures (Fig. 1). As it follows from the results presented in this Figure, with an increase of the number of carbon atoms in alcohols one observes an increase of basicity in the series MeOH<EtOH<*n*-PrOH≃*i*-PrOH<*t*-BuOH. Results presented in this Figure are in very good agreement with those presented by Gordon [8], and by Langhals [5, 9]. Our interpretation of these results is in line with that given by Gordon, which follows from the Frank and Wen paper [10]. We assume that addition of alcohols to water results in strengthening of water structure. This conclusion may be further supported by a closer inspection of the thermodynamic excess functions $T\Delta S^E$, ΔH^E, and ΔG^E for these mixtures and also by other results [11]. In

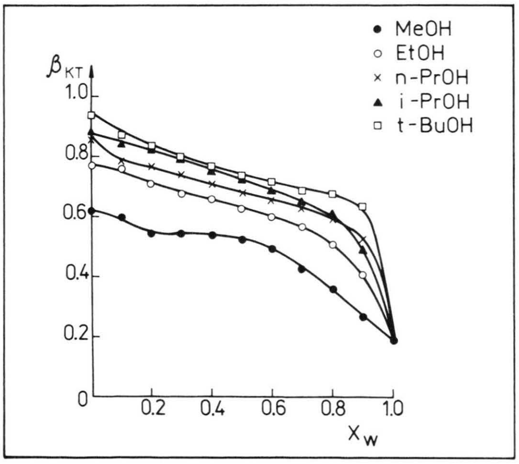

Fig. 1. The Kamlet–Taft basicity parameter β_{KT} of water-alcohols mixtures. X_w is the mol fr. of water.

all these cases one observes negative values of $T\Delta S^E$ and also negative values of ΔH^E. The minima of the latter excess function are observed approximately in the same region where maximal β_{KT}-values are observed, *i.e.* at lower concentrations of alcohols. However, in all these cases the β_{KT}-values of the mixtures are lower than those observed for pure solvents.

On the other hand, opposite results are obtained for the excess mixtures where the β_{KT}-values for the mixture are higher than those for pure solvents. In our opinion, the formation of a maximum follows from the fact that in the mixture occur molecules of water or alcohols which are less associated than those in the pure solvent. An increase of hydroxylic solvent concentration should lead to their more pronounced association (formation of clusters).

One may assume that in water or methanol there is an equilibrium, which approximately may be presented as

$$n,k\,H_2O = n(H_2O)_k = (H_2O)_{n+k} \qquad (1)$$

Introduction of a pure alcohol or water to a neutral solvent, *i.e.* to a solvent which does not show any basic or acidic properties, for example to *n*-hexane, should shift this equilibrium towards less associated molecules. To check this hypothesis we measured the basicity parameters of mixtures of MeOH, EtOH, *n*-PrOH and *i*-PrOH with *n*-hexane. The results obtained are presented in Figure 2 (Table II) in the form of β_{KT} *vs* mol percent of *n*-hexane. As it follows from the results presented in this Figure, the EtOH-*n*-Hex mixtures show higher β_{KT}-values than pure EtOH (equal to 0.77) in a wide range of EtOH content. The shape of this dependence is such as it should be expected if the above hypothesis would operate. At smaller concentrations of EtOH one observes a maximal β_{KT}-values which probably correspond to the mixture in which less associated EtOH molecules dominate over more associated ones. With an increase of EtOH content one observes lowering of basicity, which should correspond to the formation of a more associated structure. Our interpretation is in line with that given [12] by Badger and Bauer for MeOH$-$CCl$_4$ mixtures.

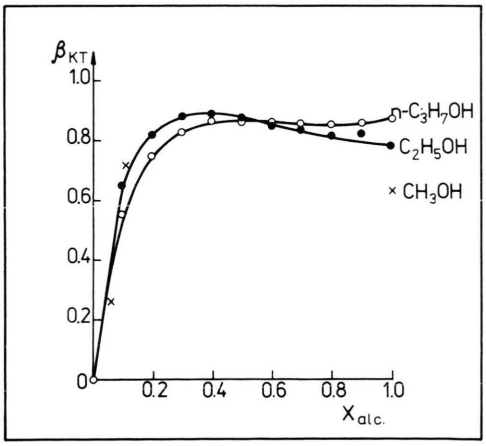

Fig. 2. The Kamlet–Taft basicity parameters β_{KT} of *n*-hexane-alcohols mixtures. X_{alc} = mol fr. of alcohols.

Table II. Empirical Lewis basicity parameters β_{KT} for mixtures of alcohols with *n*-hexane.

Hex Mol.%	EtOH	*n*PrOH	*i*PrOH	Hex Mol.%	MeOH
0	0.77	0.86	0.92	0	0.62
10	0.81	0.85	0.90	88	0.71
20	0.80	0.84	0.89	94	0.25
30	0.83	0.85	0.88	100	0.00
40	0.84	0.85	0.88		
50	0.87	0.85	0.89		
60	0.88	0.86	0.87		
70	0.87	0.82	0.82		
80	0.81	0.74	0.73		
90	0.64	0.54	0.69		
100	0.00	0.00	0.00		

In the case of *n*-PrOH and *i*-PrOH one does not observe a maximum, which is probably connected to the fact that these alcohols do not show marked association.

Our interpretation of the above mentioned facts follows from an analysis of the thermodynamic excess functions observed for this group of solvents. In the case of MeOH$-$CCl$_4$ mixture at lower MeOH concentrations one observes [11] a depolymerization (see ref. [5, 9]) of methanol with heat absorption ($\Delta H^E > 0$) and negative entropy, which suggests that the structure of this mixture is stronger than that of both solvents. In practice the same picture (*i.e.* $\Delta H^E > 0$) is observed for MeOH$-$Et$_2$O [13], MeOH$-$THF [14], W$-$Diox [15] and W$-$AN [16] mixtures. Data for W$-$DMSO [17] are analogous. In the case of W$-$THF mixtures one observes a behaviour similar to that observed for alcohols-water mixtures, *i.e.* higher basicities for higher water concentrations.

Our interpretation differs from that given by Kamlet *et al.* [3] who investigated DMSO$-$CCl$_4$ mixtures and also observed higher basicities of mixtures than those of both solvents. Kamlet *et al.* propose three explanations of this fact:

1. Complexes of *p*-nitroaniline (**1**) with DMSO are "tighter" (*i. e.* stronger) in the less polar solvent mixture;
2. Molecules of **1** are more completely hydrogen bonded in the 10% DMSO$-$CCl$_4$ solution than in the neat DMSO solvent;
3. Specific solvation of **1** by DMSO is greater than that of N,N-dimethyl-*p*-nitroaniline (**2**).

It is not easy to say which interpretation is more probable. Data on the entropy of solvation of **1** and **2** would be of a great help. If Kamlet's *et al.* interpretation were correct, these entropies should be markedly different. On the other hand we would rather expect that differences between the cybotactic regions of **1** and **2** should not be great since **1** is a very weak Lewis acid.

Recently it was shown [18$-$20] by several authors that the basicity of water hydroxylic solvent dimers is higher than that of monomers. On the other hand Gordon has shown that the basicity of water in W-*t*-BuOH mixture near 6 mol% of *t*-BuOH. This result is in line with our findings (Fig. 1).

Two main problems arise when one tries to look at the water structure from the point of view of various basicity parameters. Following the Kamlet and Taft suggestion [2] the basicity parameters (BP) may be normalized as follows:

$$B^N = \frac{B(\text{solvent}) - B(n\text{-Hex})}{B(\text{HMPA}) - B(n\text{-Hex})}$$

Then it appears that: (i) The B^N parameters of water depend markedly on the method of determination. Namely, the B^N is equal to 0.47, 0.46, 0.33 and 0.19 for DN [21], B_K [22], B_{KP} [23], and β_{KT}, respectively.

On the other hand, in the normalized acidity E^N (0$-$1) scale, water for all scales shows the highest acidity.

(ii) The β_{KT}-value for water is smaller than that for alcohols (Fig. 4).

(i) Basicity of water in different basicity scales.

We would like to analyze shortly the two most important basicity parameters, namely DN and β_{KT}. Intercorrelation of other basicity scales will be given in a separate paper [24].

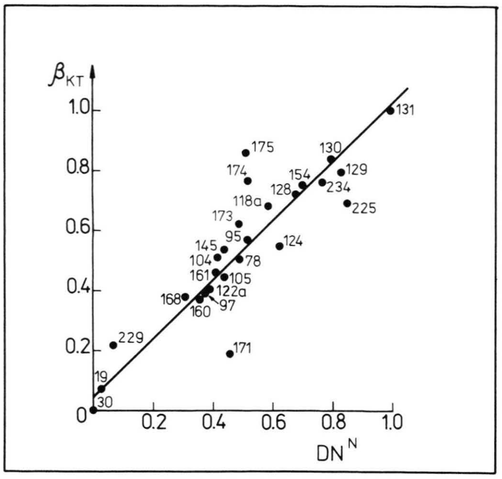

Fig. 3. Dependence of the Kamlet$-$Taft basicity parameter β_{KT} on the normalized Gutmann's DN for pure solvents. Solvents are numbered according to assignements in Table II of the Koppel and Palm review (I. A. Koppel and V. A. Palm, in N. B. Chapman and J. Shorter (eds.): Advances in Linear Free Energy Relationship, Plenum Press, London (1972). 19-Bz, 30-CCl$_4$, 78-Et$_2$O, 95-THF, 97-Diox, 104-MeAc, 105-EtAc, 118a-TriMe Phos, 122a-TriEt Phos, 124-FA, 128-DMF, 129-DMA, 130-TMU, 131-HMPA, 145-AC, 154-NMePyrrolidon, 160-AN, 161-PN, 168-BzN, 171-W, 173-MeOH, 174-EtOH, 175-*n*-PrOH, 225-Py, 229-NM, 234-DMSO.

One should expect that in the case of highly structured solvents their basicity parameters should depend on the type of the probe molecule. In Fig. 3 there is given a dependence of the primary DN on β_{KT} for 25 solvents. As it follows from the results presented in this Figure, for 19 solvents there is a good linear correlation between both basicity parameters ($\beta_{KT} = 0.046 + 0.972\ DN^N$, $R = 0.989$). Fig. 3 in our paper and Fig. 3 in ref. [25] show similarity. In both cases the point for pyridine deviates from other solvents. However, as it follows from the results presented in Fig. 3 in our paper, points for hydroxylic solvents (171-W, 172-MeOH, 174-EtOH, 175-*n*-PrOH) show a behaviour different from that observed by Kamlet *et al.* [26] for FD (family dependent) parameters. Kamlet *et al.* observed that in this case one should observe nearly parallel lines for different families, whereas the points for hydroxylic solvents constitute a line which differs in slope significantly. One should expect that there should be rather good correlation between DN and β_{KT} as far as the solvent is not strongly structured. This expectation is in line with the observation that the largest deviations are found for water, alcohols, FA, and Py, *i. e.* chiefly those solvents which have a strong structure. Basing on the results presented in this Figure one may expect that the β_{KT}-values for water measured under the same conditions as is DN (the same concentration of H_2O in $ClCH_2CH_2Cl$) should be of the order of 0.5, whereas the measured β_{KT} value for pure water is much lower (0.19).

On the other hand, the secondary DN value (the bulk donicities [21]) obtained from the regression of DN *vs* $\delta^{23}Na^+$ data uncorrected for magnetic susceptibility is for water close to 33. The value corrected for magnetic susceptibility [27] is still higher, about 38, whereas correlations with other basicity scales [28] give DN close to 43. In our opinion these results clearly show that Na^+ behaves as a strong acid capable to destroy the structure of water and to form its own structure.

Recently [29] Schmid has proposed a new set of DN's estimated from the DN dependence on B (Koppel, Palm, Shorter). In this new set the DN value for water is lower than the secondary DN and is equal to 17. In our opinion all these values are correct since in both cases the acidic probe molecules show different strength.

(ii) In Fig. 4 there is shown the dependence of β_{KT}-values on the number of carbon atoms in the chain of normal alcohols (for water $n = 0$). It follows from these results that for alcohols with $n = >3$ the β_{KT}-values are in practice constant and equal to $\simeq 0.85$. For branched alcohols the β_{KT}-values are a bit higher, for example for *i*-PrOH and *i*-BuOH they are equal to 0.92 and 0.90, respectively. In our opinion this constancy of the β_{KT}-values is mostly due to the fact that the structure of these solvents is similar. Since water, MeOH, and EtOH are most probably more structured than higher alcohols [9, 30] we would conclude that the observed lowering of basicity parameters for these three solvents is a result of a different type of the solvent structure (see *e. g.* ref. [30]). Keeping in mind earlier literature information [18, 31, 32] about higher basicity of linear dimers over monomers we would postulate that reduced basicity is a result of formation of three-dimensional clusters. In such clusters part of the basicity centers might be hidden inside the cluster, and the number of basicity centers interacting with the probe molecule should be lower than in higher alcohols.

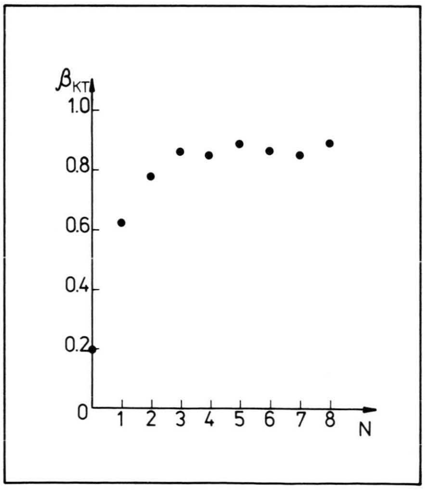

Fig. 4. The Kamlet–Taft basicity parameters β_{KT} for normal alcohols. N-stands for number of carbon atoms in alcohols; for water N = 0.

Coming back to the equilibrium (1) one should expect that with an increase of water concentration in a neutral solvent one might at first observe an increase (formation of linear multimers) and next lowering the basicity parameters (formation of three-dimentional clusters).

On the other hand, Kollman and Allen [18] have carried out CNDO calculations for the water pentamer. From their results it follows that also in the pentamers there should be an increase of negative charge at the oxygen atom, *i. e.* an increase of basicity. If for larger polymers an analogous increase of the negative charge at oxygen should be observed, it would be rather difficult to explain the fact that water has a smaller basicity than the probable basicity of molecules of water. One may suspect that this may be due to steric hindrances and such an interpretation is similar to that given by Kamlet *et al.* [3].

Conclusions

1. The Kamlet and Taft Lewis basicity scale of solvents was used to analyze the structural changes of mixtures of organic solvents with water and methanol. It was found that introduction of an organic solvent to water may lead to excess mixtures where the basicity parameter of the mixture is higher than that of the pure solvents. This phenomenon was ascribed to depolimerization of water structure.

2. Analysis of different basicity scales leads to the conclusion that the basicity of highly structured solvents may depend considerably on the nature of probe molecule which are Lewis acids of different strength. Similar phenomena were up to now not observed in the case of acidity parameters.

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[7] To define the reference line we measured the absorption spectra of N,N-diethyl-*p*-nitroaniline (**2**) and *p*-nitroaniline (**1**) in the following solvents; *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, cyclopentane, cyclohexane, decaline, CCl_4 and CH_2Cl_2. The equation reads: $\nu_{\max}(1) = 1.003 \cdot \nu_{\max}(2) + 3.528$, $R = 0.999$, $n = 9$. We have chosen this group of solvents for two reasons: (i) the regression coefficient (slope) was closest to 1.0. In our opinion there are no reasons for the reference line to have a slope other than 1.0, *i. e.* identity for solute-solvent interactions for both compounds in NHB solvents. (ii) the best correlation coefficient was obtained.

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