CORRELATIONS BETWEEN EMPIRICAL LEWIS ACID–BASE SOLVENT PARAMETERS AND THE THERMODYNAMIC PARAMETERS OF ION SOLVATION. PART II. ACIDITY PARAMETERS OF CATIONS AND BASICITY PARAMETERS OF ANIONS

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The parameters α, β and γ of the equation ${}^W\Delta^S G_t(MX) = \alpha B_{KT} + \beta E_T + \gamma$ were calculated and analysed for different salts (MX) in pure solvents and in non-aqueous solvent–water mixtures (S). Among 109 different equations, only 64 were taken for the final analysis since in the case of 38 equations the parameters B_{KT} and E_T were highly correlated. After a statistical analysis and normalization, on the basis of the coefficients α and β obtained, it was found that the ions analysed may be divided into three classes characterized by the different dependences of α on β: class I, H^+, Li^+, Na^+, Rb^+, Cs^+, Me_4N^+, Cl^-, Br^- and I^-, where $\alpha^N = 1 \cdot 074 \beta^N + 1 \cdot 639$; class II, Ag^+, Cl^-, Br^-, I^-, OAc^-, SCN^- and N_3^- where $\alpha^N = 2 \cdot 057 \beta^N + 2 \cdot 147$; and class III, Ph_4As^+, BPh_4^-, Ph_4C and Ph_4Ge, where α^N is variable and β^N is almost constant. Two main conclusions can be drawn out from the results obtained: the behaviour of ions considered as Lewis acids and bases reflects different hard–soft properties of the ions, and the behaviour of the Ph_4As^+ ion is different from that of BPh_4^-.

INTRODUCTION

The influence of solvents on the thermodynamic parameters of ion solvation is one of the most important problems in chemistry. Since the accurate determination of the standard chemical potential μ_i^S of a single ion (i) in a given solvent (S) is in principle impossible,[1] this parameter has been estimated approximately in different ways.[2] One of the most interesting methods is the use of so-called empirical Lewis acid–base parameters of the solvents.[3] In a previous paper,[4] two thermodynamic parameters of ion solvation which were available from an experiment, namely the free real energy of the ion solvation (α_i^S) and the free energy of transfer of the salt MX from water (W) to the organic solvent (S), ${}^W\Delta^S G_t(MX)$, were found to be correlated with empirical Lewis acid–base parameters of the solvents.

The aim of this paper is to analyse the coefficients α, β and γ of the equation

$$ {}^W\Delta^S G_t(MX) = \alpha BP + \beta AP + \gamma \qquad (1) $$

where BP is a Lewis basicity, and AP a Lewis acidity parameter of a solvent. Different applications of this equation were described by Krygowski and Fawcett[5] and later by other workers.[6,7] Analysis of equation (1) using a large number of experimental data may allow for more general conclusions and should be free from the ambiguity related to the use of the empirical Lewis parameters in the case of small numbers of data. Since we analyse the free energies of transfer of salts, we shall not use the data for the free energies of transfer of ions,[8] since they are based on the thermodynamic assumption $\Delta_t G(Ph_4As^+) = \Delta_t G(BPh_4^-)$, which, as we show later, is probably not true.

CALCULATIONS

As Lewis basicity (BP) and Lewis acidity (AP) solvent parameters, the Kamlet and Taft,[9] B_{KT}, and the Dimroth and Reichardt,[2a] E_T, parameters were used. Many of these parameters, especially for binary mixtures, have been determined in our laboratory. Most of

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Table 1. Parameters of the equation $^W\Delta^SG_t = \beta B_{KT} + \alpha E_t^N + \gamma$

No.	Salt[a]	$\alpha \pm$ S.D.	$\beta \pm$ S.D.	R	ψ	$\pm$S.D.	N
1	AgCl	-103 ± 11	-132 ± 15	0·972	0·270	6·0	9
2	AgBr	-102 ± 14	-111 ± 14	0·951	0·356	7·7	9
3	AgI	-104 ± 15	-80 ± 17	0·954	0·354	7·1	8
4	AgOAc	-112 ± 22	-168 ± 29	0·960	0·362	10·2	6
5	AgSCN	-102 ± 13	-78 ± 17	0·957	0·335	7·2	9
6	AgN$_3$	-99 ± 14	-110 ± 19	0·947	0·370	7·9	9
7	AgBPh$_4$	-83 ± 14	24 ± 19	0·970	0·283	7·9	9
8	LiCl	-149 ± 12	-178 ± 13	0·991	0·168	5·5	7
9	NaCl	-48 ± 13	-113 ± 18	0·904	0·473	11·0	12
10	KCl*	-94 ± 42	-159 ± 30	0·972	0·301	10·5	6
11	KBr	-29 ± 17	-68 ± 21	0·871	0·601	7·6	7
12	KClO$_4$	-96 ± 24	-73 ± 21	0·946	0·460	6·9	5
13	CsCl	-50 ± 94	-154 ± 60	0·866	0·612	24·3	7
14	Me$_4$NI	-33 ± 12	-56 ± 11	0·962	0·387	6·0	5
15	Me$_4$NClO$_4$	-44 ± 15	-41 ± 14	0·930	0·521	7·3	5
16	Ph$_4$AsI*	2 ± 7	29 ± 7	0·941	0·413	2·7	11
17	Ph$_4$AsBPh$_4$*	-14 ± 9	102 ± 14	0·958	0·322	7·2	11
18	LiCl	-126 ± 7	-178 ± 3	0·999	0·039	1·1	6
19	NaCl	-81 ± 6	-135 ± 3	0·999	0·045	0·9	6
20	KCl	-72 ± 8	-121 ± 4	0·999	0·068	1·3	6
21	RbCl	-74 ± 8	-121 ± 4	0·999	0·065	1·2	6
22	CsCl	-72 ± 8	-118 ± 4	0·999	0·070	1·3	6
23	KBr	-56 ± 9	-93 ± 4	0·997	0·098	1·4	6
24	KI	-48 ± 7	-68 ± 3	0·997	0·099	1·0	6
25	Ph$_4$AsPic*	-106 ± 31	35 ± 15	0·963	0·346	4·9	6
26	KPic	-48 ± 3	-25 ± 2	0·995	0·135	0·5	6
27	KBPh$_4$*	-121 ± 14	-184 ± 7	0·994	0·118	2·5	12
28	LiCl	-83 ± 22	-147 ± 11	0·979	0·226	4·0	12
29	NaCl	-83 ± 22	-147 ± 10	0·979	0·226	4·0	12
30	NaBr	-134 ± 7	-178 ± 10	0·998	0·061	1·2	12
31	KCl	-72 ± 19	-131 ± 10	0·980	0·220	3·5	12
32	KBr	-53 ± 21	-103 ± 10	0·964	0·295	3·8	12
33	KI	-45 ± 9	-71 ± 5	0·984	0·199	1·7	12
34	CsCl	-78 ± 20	-130 ± 10	0·977	0·237	3·7	12
35	AgBr	-96 ± 6	-56 ± 3	0·986	0·182	1·2	12
36	AgI	-66 ± 5	-11 ± 3	0·976	0·242	1·0	12
37	KBPh$_4$	-94 ± 20	27 ± 10	0·944	0·366	3·7	12
38	Ph$_4$AsI*	-97 ± 7	-3 ± 4	0·982	0·206	1·4	12
39	LiCl*	-9 ± 8	-46 ± 8	0·996	0·110	0·9	6
40	NaCl	-34 ± 11	-87 ± 10	0·997	0·100	1·2	6
41	KCl	-30 ± 10	-85 ± 9	0·998	0·082	1·0	6
42	RbCl	-27 ± 6	-83 ± 5	0·999	0·050	0·6	6
43	CsCl	-44 ± 11	-102 ± 10	0·998	0·090	1·2	6
44	KBr	4 ± 7	-30 ± 6	0·997	0·099	0·7	6
45	KI*	8 ± 13	-7 ± 12	0·954	0·426	1·4	6
46	KPic	37 ± 5	67 ± 5	0·999	0·059	0·2	5
47	Ph$_4$AsPic*	17 ± 1	100 ± 1	0·999	0·004	0·05	5
48	KBPh$_4$*	-41 ± 51	40 ± 57	0·990	0·200	2·7	5
49	Ph$_4$AsBPh$_4$	-177 ± 41	89 ± 17	0·932	0·388	7·6	16
50	Ph$_4$C	-60 ± 15	38 ± 6	0·939	0·369	2·8	16
51	Ph$_4$Ge	-69 ± 17	38 ± 7	0·936	0·379	3·1	16
52	AgBPh$_4$	-172 ± 31	64 ± 14	0·967	0·284	5·0	11
53	Ph$_4$AsBPh$_4$	-58 ± 17	90 ± 14	0·994	0·121	2·7	15
54	Ph$_4$C	-15 ± 6	41 ± 5	0·995	0·104	0·9	15
55	Ph$_4$Ge	-20 ± 5	40 ± 4	0·996	0·095	0·8	15
56	Ph$_4$AsBPh$_4$*	-9 ± 17	109 ± 20	0·974	0·267	7·2	8

Table 1. (*Continued*)

No.	Salt[a]	$\alpha \pm$ S.D.	$\beta \pm$ S.D.	R	ψ	$\pm$ S.D.	N
57	Ph₄C*	3 ± 4	51 ± 5	0·988	0·176	0·4	9
58	Ph₄Ge	4 ± 4	55 ± 4	0·991	0·155	0·4	9
59	HCl	− 82 ± 19	− 118 ± 17	0·951	0·329	1·9	18
60	HCl	− 112 ± 15	− 144 ± 12	0·967	0·273	1·5	18
61	HCl	− 48 ± 5	− 71 ± 6	0·981	0·205	0·6	18
62	HCl	− 145 ± 43	− 159 ± 33	0·955	0·314	2·2	18
63	RbCl	− 97 ± 18	− 157 ± 16	0·979	0·271	1·8	18
64	RbCl	− 108 ± 22	− 151 ± 20	0·949	0·337	1·9	17
65	RbCl	− 47 ± 8	− 108 ± 9	0·993	0·125	0·9	18
66	RbCl	− 149 ± 45	− 175 ± 35	0·972	0·249	0·9	18
67	HCl	− 168 ± 15	− 212 ± 16	0·982	0·199	1·0	18
68	RbCl	− 213 ± 19	− 283 ± 20	0·989	0·158	1·3	18
69	HCl*	15 ± 17	− 8 ± 33	0·912	0·437	1·2	17
70	RbCl*	51 ± 27	8 ± 53	0·961	0·295	1·9	18
71	HCl*	4 ± 11	− 21 ± 20	0·869	0·628	1·7	18
72	RbCl*	13 ± 21	− 46 ± 38	0·913	0·434	3·3	18
73	HCl*	− 3 ± 43	− 54 ± 64	0·881	0·505	3·2	17
74	RbCl*	− 3 ± 24	− 29 ± 37	0·860	0·545	1·8	17
75	HCl	68 ± 11	80 ± 18	0·957	0·307	1·3	18
76	RbCl	104 ± 17	108 ± 27	0·972	0·251	1·8	17
77	NaCl	250 ± 79	204 ± 76	0·996	0·114	0·5	6
78	LiCl	255 ± 64	185 ± 64	0·996	0·110	0·4	6
79	HCl	0 ± 0	− 45 ± 1	0·992	0·131	0·8	18
80	HCl	51 ± 35	31 ± 36	0·992	0·136	0·4	18
81	NaCl*	68 ± 42	32 ± 43	0·996	0·091	0·5	18
82	KCl*	90 ± 54	48 ± 55	0·995	0·101	0·6	8
83	RbCl*	2 ± 80	40 ± 83	0·992	0·134	0·8	18
84	CsCl*	81 ± 59	43 ± 61	0·993	0·124	0·7	18
85	NaCl*	75 ± 27	48 ± 53	0·977	0·236	1·9	12
86	NaBr*	73 ± 31	56 ± 62	0·973	0·258	1·8	11
87	NaI*	69 ± 23	67 ± 46	0·964	0·292	1·5	13
88	HCl*	44 ± 121	36 ± 125	0·878	0·617	1·0	6
89	HBr*	− 24 ± 78	17 ± 80	0·906	0·517	0·7	7
90	HI*	− 88 ± 62	− 60 ± 63	0·994	0·151	0·5	5
91	LiCl*	− 510 ± 260	− 557 ± 266	0·944	0·367	2·5	11
92	NaCl*	− 274 ± 161	− 326 ± 164	0·986	0·185	1·6	11
93	KCl*	− 121 ± 105	− 172 ± 108	0·994	0·118	1·0	11
94	RbCl	− 229 ± 118	− 284 ± 121	0·994	0·126	1·2	11
95	CsCl*	− 233 ± 133	− 283 ± 135	0·990	0·157	1·3	11
96	NaBr*	58 ± 28	38 ± 28	0·998	0·069	0·3	11
97	NaI	− 4 ± 1	− 3 ± 1	0·997	0·082	0·0	11
98	KBr	109 ± 36	86 ± 37	0·998	0·076	0·4	11
99	KI	11 ± 4	9 ± 4	0·997	0·082	0·0	11
100	AgCl*	− 196 ± 106	− 208 ± 108	0·852	0·586	1·0	11
101	AgBr*	67 ± 60	82 ± 61	0·978	0·231	0·6	11
102	AgI*	71 ± 92	110 ± 94	0·993	0·134	0·9	11
103	Bu₄NI	159 ± 103	159 ± 103	0·947	0·372	0·8	11
104	KBPh₄	504 ± 227	504 ± 22	0·993	0·135	2·2	11
105	Ph₄AsI	− 126 ± 23	− 126 ± 23	0·9997	0·029	0·2	11
106	HCl	− 145 ± 35	− 145 ± 35	0·956	0·312	3·3	19
107	HBr	− 172 ± 35	− 172 ± 35	0·952	0·323	3·3	19
108	HCl	75 ± 12	75 ± 12	0·963	0·285	1·4	19
109	HBr	68 ± 18	68 ± 18	0·894	0·475	2·1	19

[a] For the compounds marked with asterisks, $F_{imp} < F_i$ and the data were not considered in the statistical analysis (see Appendix).

these data have been published.[10] The E_T parameters were used in their normalized form:[11]

$$E_T^N = \frac{E_T - E_T(n - \text{hexane})}{E_T(\text{water}) - E_T(n - \text{hexane})} \quad (2)$$

Several workers have reported values of the free energy of transfer of certain salts [$^W\Delta^S G_t(\text{MX}) = \Delta G_t$] from water to organic solvents or their mixtures with water.[12-23] Since we are using the molar scale, appropriate recalculations of the data was carried out when necessary.

In the case of the silver salts (Nos 1–7 in Table 1), in order to obtain the recalculated ΔG_t values equal to the experimental values within the limits of the 0.95 confidence level, it was necessary to reject the data for alcohols, formamide and acetonitrile. For these solvents, the differences between the experimental ΔG_t values and those calculated with the use of the equation (1) obtained for all solvents were the highest. In the case of other salts in pure solvents (Nos 8–17), the data for alcohols and formamide exhibited the highest deviations. As a consequence, data for these solvents were also not taken into account.

A large number of data (Nos 59–84) were obtained with the use of ion-selective electrodes (ISEs) by Smits

et al.[19] According to Das et al.,[13] the data obtained with the use of ISEs were less reliable from the thermodynamic point of view than those found with the application of amalgam electrodes. Nonetheless, there is good agreement between the data of Das et al.[13] and of Cox et al.[12] although the latter workers used an ISE. Since a similar conclusion was also reached by Feakins and Voice,[20] we decided to analyse all the data of Smits et al.

The smallest number of data used for analysis was five (seven equations). Results of these calculations for 109 equations are given in Table 1.

Of the total of 109 equations, after the statistical analysis, we finally obtained 71 equations for which it was found that additions of the second explaining parameter was statistically justified (see Appendix). From the point of view of the so-called 'goodness of fit' (GOF) functions,[24] (ψ–Exner function), these equations may be divided into the following groups:

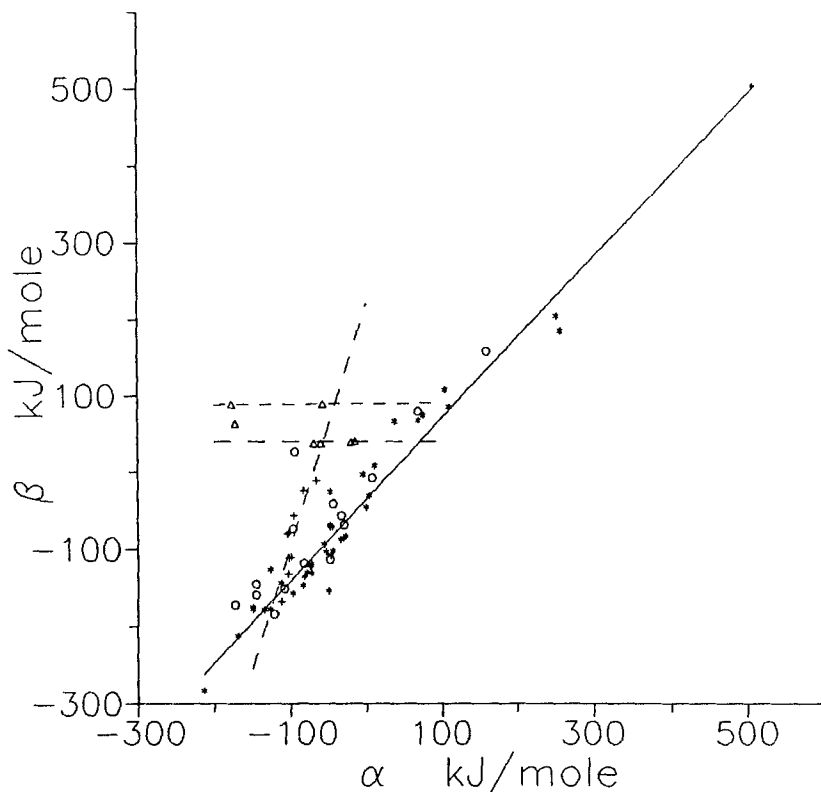| GOF (ψ)	No. of equations
0–0.1	19
0.1–0.2	15
0.2–0.3	14
0.3–0.4	16
>0.4	7

Figure 1. Dependence of β on α. Points belong to (*) group I ($\psi < 0.3$), (○) group I, (+) group II and (△) group III

For a final analysis, only the equations with $\psi < 0.4$ were taken (64 equations), and for the final calculations only the equations with $\psi < 0.3$ (48 equations) were considered. Thus we are confident (0.95 confidence level) that the final results are statistically significant.

As follows from the results presented in Figure 1, exhibiting the dependence of α on β, all salts and molecules can be divided into three groups as follows.

(a) H^+, Li^+, Na^+, Rb^+, Cs^+, Me_4N^+, Cl^-, Br^- and I^-, where a distinct dependence of α on β occurs described by the equation

$$\alpha = 32.09 + 0.915\beta; \quad R = 0.980, \ N = 36 \quad (3)$$

(b) Ag^+, Cl^-, Br^-, I^-, OAc, SCN^- and N_3^-. For this group the slope of the dependence of α on β is almost five times lower than that for the first group:

$$\alpha = -81.0 + 0.192\beta; \quad R = 0.830, \ N = 9 \quad (4)$$

(c) Large ions (Ph_4As^+, GPh_4^-) and molecules (Ph_4C and Ph_4Ge), for which in practice a constant value of β is observed. The parameter α for Ph_4C and Ph_4Ge is approximately half that for Ph_4AsBPh_4.

The position of Pic ions is not certain. Points for mixed salts ($AgBPh_4$, $KBPh_4$) are located close to lines formed by the main groups.

DISCUSSION

Analysis of equation (1)

For $\Delta G_t = 0$, equation (1) can be written as $0 = 0.19\alpha + \beta + \gamma$, since for water $B_{KT} = 0.19$ and $E_T = 1$. Hence the values of $\gamma = -0.19\alpha - \beta$ are not given in Table 1, since they can be easily calculated from the α and β values.

The second problem is the physical meaning of the parameters α and β. Since we have considered in the analysis only those equations in which E_T and B_{KT} are not uncorrelated, the interpretation

$$\alpha = \frac{\partial \Delta G_t}{\partial B_{KT}}, \quad \beta = \frac{\partial \Delta G_t}{\partial E_T} \quad (5)$$

is probable at the 0.05 confidence level. As the parameters E_T and B_{KT} describe at least intentionally) Lewis acidity and basicity, respectively, one may assume that the parameters α and β describe properties of cations and anions, respectively. We call them empirical basicity parameters of anions (β) and empirical acidity parameters of cations (α).

The third problem is related to the fact that the α and β coefficients of various salts in the same water–organic solvent mixture have different values. For example, for the first group of ions in water–acetonitrile mixtures (Nos 18–24), the α and β values change from -178 and -126 to -68 and -48 for LiCl (No. 18) and KI (No. 24), respectively. If, however, the α and β coefficients were divided by the maximum (experimental) ΔG_t value

for a given salt, the normalized α^N and β^N coefficients for all salts reach almost the same values. In the case analysed, the average values of α^N and β^N parameters are ca -1.5 and -2.4 respectively.

The results obtained after normalization are presented in Figure 2. The dependences of α^N on B^N are as follows:

Group I:
$$\alpha^N = 1.638 + 1.074\beta^N; \quad R = 0.995, \ N = 25 \quad (6)$$

Group II:
$$\alpha^N = 2.147 + 2.057\beta^N; \quad R = 0.988, \ N = 5 \quad (7)$$

The latter equation is less justified since the Exner functions for five equations are in the range $0.3 < \psi < 0.4$.

As follows from the results presented in Figure 2, the grouping of ions remained the same as before. Almost identical values of α^N and β^N, in the same water–non-aqueous solvent mixtures even for different salts, suggest that the free energies of transfer contain a common term describing the properties of cations and anions.

Analysis of results presented in Table 2 reveals also that the α^N and β^N coefficients for the same salt vary over wide ranges. For examples, α^N and β^N for RbCl are 4.46 and 4.30 [water–isopropanol (i-PrOH)], 4.56 and -1.98 [water–dimethylformamide (DMF)], -5.65 and -3.49 [water–acetone (AC)], -5.70 and 4.69 [water–dioxane (DIOX)], -8.16 and -5.84 [water–acetonitrile (AN)] and -10.07 and -7.58 [water–tetrahydrofuran (THF)]. On the basis of the data of Smits *et al.*,[19] one observes the following sequence of increase in α^N and β^N parameters for RbCl: THF < AN < DIOX < AC < DMF < W < i-PrOH. This sequence, with one exception (DIOX), coincides with the sequence of so-called ionizing power parameter, *IPP*, defined as $IPP = E_T + B_{KT}$.[11] The *IPP* values for these solvents are 0.76, 0.85, 0.55, 0.87, 1.12, 1.19 and 1.42, respectively.

Origins of dependence of α on β

Before discussing the nature of the dependence of α on β, we return to properties of equation (1). This equation can be written in the following form:

$$\Delta G_t = \alpha(B_{KT} - 0.19) + \beta(E_T^N - 1) \quad (8)$$

Inspection of the experimental data reveals that all values of $E_T - 1$ change from 0 (water) to more negative values. Hence the sign of β is always opposite to that determined, i.e. it is positive for most solvents. In terms of LFER or similarity models, this means that anions interacting with solvent molecules behave similarly to the betaine (30) (Figure 3), or more precisely to the oxygen atom of this compound.

On the other hand, all values of $B_{KT} - 0.19$ change

Table 2. Normalized parameters α^N and β^N of equation (1) and statistical analysis of the experimental data

| No. | Salt | α^N | β^N | $E_T = a + bB_{KT}$ | | | R $(\Delta G_t - E_T^N)$ | R $(\Delta G_t - B_{KT})$ | F_{imp} | F_i (0.05) |
				a	b	R				
1	AgCl	−1·58	−2·02	0·771	−0·510	−0·697	−0·319	−0·435	95·8	4·7
2	AgBr	−1·90	−2·07	0·771	−0·510	−0·697	−0·132	−0·582	41·4	4·7
3	AgI	−2·80	−2·15	0·794	−0·565	−0·669	0·025	−0·716	26·5	5·1
4	AgOAc	−1·37	−2·05	0·857	−0·581	−0·761	−0·489	−0·163	35	6·9
5	AgSCN	−2·57	−1·97	0·771	−0·510	−0·697	0·174	−0·795	23·6	4·7
6	AgN₃	−1·94	−2·15	0·771	−0·510	−0·697	−0·159	−0·556	39·9	4·7
7	AgBPh₄	1·14	−0·33	0·771	−0·510	−0·697	0·755	−0·910	13·4	4·7
8	LiCl	−1·66	−1·98	0·769	−0·550	−0·580	−0·155	−0·350	189	4·1
9	NaCl	−0·57	−1·35	0·587	−0·320	−0·435	−0·738	−0·146	14·9	6·9
10	KCl*	−1·02	−1·73	−1·046	−1·246	−0·794	−0·915	0·558	6·5	5·8
11	KBr	−0·76	−1·79	0·867	−0·636	−0·766	−0·915	0·323	13·6	9·6
12	KClO₄	−4·93	−3·75	0·980	−0·867	−0·780	−0·915	−0·516	18·0	5·8
13	CsCl	−0·47	−1·46	1·005	−1·201	−0·775	−0·915	0·598	7·9	9·6
14	Me₄NI	−0·82	−1·39	0·647	−0·360	−0·339	−0·798	−0·240	11·7	9·6
15	Me₄NClO₄	−1·35	−1·26	0·647	−0·360	−0·339	−0·798	−0·560	12·2	4·3
16	Ph₄AsI*	−0·10	−1·51	0·880	−0·717	−0·733	0·940	−0·655	0·1	4·3
17	Ph₄AsBPh₄*	0·18	−1·28	0·620	−0·314	−0·464	0·947	−0·574	2·3	6·9
18	LiCl	−1·75	−2·47	1·204	−1·183	−0·567	−0·945	0·269	210	6·9
19	NaCl	−1·44	−2·41	1·204	−1·183	−0·567	−0·961	0·32	149	6·9
20	KCl	−1·43	−2·41	1·204	−1·183	−0·567	−0·961	0·325	145	6·9
21	RbCl	−1·49	−2·43	1·204	−1·183	−0·567	−0·959	0·315	157	6·9
22	CsCl	−1·48	−2·43	1·204	−1·183	−0·567	−0·959	0·317	157	6·9
23	KBr	−1·45	−2·42	1·204	−1·183	−0·567	−0·959	0·320	50	6·9
24	KI	−1·79	−2·54	1·204	−1·183	−0·567	−0·942	0·264	71	6·9
25	Ph₄AsPic*	3·03	−1·00	1·204	−1·183	−0·567	0·804	−0·893	7·2	6·9
26	KPic	−9·98	−5·20	1·204	−1·183	−0·567	−0·545	−0·376	278	6·9
27	KBPh₄*	4·01	−0·67	1·204	−1·183	−0·567	0·719	−0·946	3·6	4·1
28	LiCl	−1·68	−2·56	1·232	−1·215	−0·615	−0·944	0·335	81	4·1
29	NaCl	11·48	−2·62	1·232	−1·215	−0·615	−0·943	0·375	17	4·1
30	NaBr	−1·89	−2·50	1·232	−1·215	−0·615	−0·929	0·283	32·3	4·1
31	KCl	−1·43	−2·61	1·232	−1·215	−0·615	−0·947	0·384	16	4·1
32	KBr	−1·38	−2·68	1·232	−1·215	−0·615	−0·936	0·396	7·5	4·1
33	KI	−1·68	−2·65	1·232	−1·215	−0·615	−0·934	0·347	39	4·1
34	CsCl	−1·61	−2·68	1·232	−1·215	−0·615	−0·936	0·357	17	4·1
35	AgBr	−9·98	−5·02	1·232	−1·215	−0·615	−0·551	−0·557	240	4·1
36	AgI	8·30	1·38	1·232	−1·215	−0·615	0·323	−0·506	20·8	4·1
37	KBPh₄	3·75	−1·08	1·232	−1·215	−0·615	0·323	−0·897	8·0	4·1
38	Ph₄AsI*	7·02	0·22	1·232	−1·215	−0·615	0·323	−0·981	0·6	6·9
39	LiCl*	−0·38	−1·93	1·246	−1·063	−0·968	−0·995	−0·950	1·0	6·9
40	NaCl	−0·96	−2·45	1·246	−1·063	−0·968	−0·988	0·924	11·9	6·9
41	KCl	−0·83	−2·36	1·246	−1·063	−0·968	−0·991	0·931	13·9	6·9
42	RbCl	−0·75	−2·31	1·246	−1·063	−0·968	−0·994	0·937	19·9	6·9
43	CsCl	−1·13	−2·62	1·246	−1·063	−0·968	−0·985	0·915	25·8	6·9
44	KBr	0·19	−1·44	1·246	−1·063	−0·968	0·833	0·971	34·2	6·9
45	KI*	0·87	−0·76	1·246	−1·063	−0·968	−0·945	0·946	0·8	9·6
46	KPic	−3·45	−6·26	1·181	−0·879	−0·988	−0·971	−0·923	43·7	9·6
47	Ph₄AsPic*	−0·52	−3·04	1·181	−0·879	−0·988	0·999	−0·982	0	9·6
48	KBPh₄*	1·27	−1·24	1·181	−0·879	−0·988	0·987	−0·987	0·9	3·7
49	Ph₄AsBPh₄	10·75	−5·41	1·197	−1·152	−0·476	−0·828	−0·772	19·5	3·7
50	Ph₄C	9·10	−5·77	1·197	−1·152	−0·476	−0·860	−0·742	16·8	3·7
51	Ph₄Ge	9·91	−5·46	1·197	−1·152	−0·476	−0·842	−0·759	18·9	4·3
52	AgBPh₄	2·98	−1·11	1·220	−1·241	−0·564	0·825	−0·879	22·5	3·8
53	Ph₄AsBPh₄	3·08	−4·78	1·310	−1·152	−0·947	−0·987	−0·971	15·1	3·8
54	Ph₄C	2·05	−5·61	1·310	−1·152	−0·947	−0·992	−0·964	7·8	3·8
55	Ph₄Ge	2·55	−5·11	1·310	−1·152	−0·947	−0·992	−0·969	12·9	5·1
56	Ph₄AsBPh₄*	0·11	−1·35	0·859	−0·639	−0·765	0·966	−0·739	2·1	4·7

Table 2. (Continued)

No.	Salt	α^N	β^N	$E_T = a + bB_{KT}$			R $(\Delta G_t - E_T^N)$	R $(\Delta G_t - B_{KT})$	F_{imp}	F_t (0.05)
				a	b	R				
57	Ph₄C*	−0·09	−1·56	0·859	−0·639	−0·765	0·990	−0·728	0	5·6
58	Ph₄Ge*	−0·12	−1·60	0·859	−0·639	−0·765	0·990	−0·733	0·8	4·5
59	HCl	−4·21	−6·05	1·255	−1·059	−0·971	−0·887	0·777	19·7	4·5
60	HCl	−5·77	−7·42	1·207	−1·116	−0·930	−0·829	0·597	61	4·5
61	HCl	−5·15	−7·59	1·180	−0·880	−0·981	−0·860	0·751	95	4·5
62	HCl	−6·20	−6·79	1·272	−1·272	−0·993	−0·919	0·883	12·3	4·5
63	RbCl	−3·49	−5·65	1·255	−1·059	−0·971	−0·936	0·840	31·7	4·5
64	RbCl	−5·84	−8·16	1·207	−1·116	−0·930	−0·856	0·689	25·2	4·5
65	RbCl	−1·98	−4·56	1·180	−0·880	−0·981	−0·978	0·925	33·9	4·5
66	RbCl	−4·69	−5·70	1·272	−1·269	−0·993	−0·953	0·925	10·6	4·5
67	HCl	−9·33	−11·78	1·202	−0·920	−0·993	−0·825	0·758	127	4·5
68	RbCl	−7·58	−10·07	1·202	−0·920	−0·993	−0·888	0·832	139	4·5
69	HCl*			1·077	−0·505	−0·992		0·911	0·2	4·5
70	RbCl*			1·077	−0·505	−0·992		0·961	0	4·5
71	HCl*			1·053	−0·545	−0·978		0·858	1·2	4·5
72	RbCl*			1·053	−0·545	−0·978		0·904	1·6	4·5
73	HCl*			1·097	−0·658	−0·994		0·854	3·1	4·5
74	RbCl*			1·097	−0·658	−0·994		0·875	0	4·5
75	HCl	4·82	5·67	1·070	−0·608	−0·989	−0·837	0·896	21·5	4·5
76	RbCl	4·30	4·46	1·070	−0·608	−0·989	−0·892	0·939	17·1	7·7
77	NaCl	22·99	18·74	1·196	−0·608	−0·999		0·987	8·9	7·7
78	LiCl	24·73	20·40	1·196	−0·608	−0·999		0·985	10·9	3·6
79	HCl	0	−8·65	1·179	−0·971	−0·999	−0·785	0·786	367	3·6
80	LiCl*			1·179	−0·971	−0·999		0·991	2·0	3·6
81	NaCl*			1·179	−0·971	−0·999		0·996	0	3·6
82	KCl*			1·179	−0·971	−0·999		0·995	0	3·6
83	RbCl*			1·179	−0·971	−0·999		0·993	0	3·6
84	CsCl*			1·179	−0·971	−0·999	−0·992	0·981	2·3	4·1
85	NaCl*	3·44	2·19	1·074	−0·500	−0·990	−0·957	−0·975	0·0	4·3
86	NaBr*	3·79	2·92	1·074	−0·500	−0·990		−0·970	1·0	4·0
87	NaI*	4·43	4·30	1·074	−0·500	−0·990		0·956	2·4	6·9
88	HCl*			1·181	−0·977	−0·999		0·875	0·1	5·8
89	HBr*			1·181	−0·977	−0·999		−0·905	0·1	9·6
90	HI*			1·181	−0·977	−0·999		−0·992	1·0	4·3
91	LiCl*	−21·77	−23·75	1·187	−0·978	0·999	−0·916	0·912	4·3	4·3
92	NaCl*	−10·06	−11·98	1·187	−0·978	0·999	−0·981	0·979	3·2	4·3
93	KCl*	−4·59	−6·62	1·187	−0·978	0·999	−0·994	0·993	0	4·3
94	RbCl	−8·31	−10·30	1·187	−0·978	0·999	−0·991	0·989	4·5	4·3
95	CsCl*	−8·99	−10·92	1·187	−0·978	0·999	−0·986	0·989	3·6	4·3
96	NaBr*	4·96	3·22	1·187	−0·978	0·999	−0·997	0·998	0	4·3
97	NaI	8·81	7·17	1·187	−0·978	0·999	0·994	−0·995	6·0	4·3
98	KBr	8·16	6·42	1·187	−0·978	0·999	−0·995	0·996	9·0	4·3
99	KI	8·59	6·96	1·187	−0·978	0·999	−0·994	0·995	6·0	4·3
100	AgCl*	−33·41	−35·45	1·187	−0·978	0·999	−0·780	0·774	3·9	4·3
101	AgBr*	−9·99	−12·26	1·187	−0·978	0·999	0·975	0·974	1·2	4·3
102	AgI*	−3·71	−5·70	1·187	−0·978	0·999	0·992	0·992	4·3	4·7
103	Bu₄NI	−23·80	−26·86	1·187	−0·978	0·999	0·925	0·921	2·8	4·3
104	KBPh₄	−10·31	−12·37	1·187	−0·978	0·999	0·988	0·986	6·4	4·3
105	PH₄AsI	5·39	3·71	1·187	−0·978	0·999	0·998	0·999	18·0	3·6
106	HCl	−4·11	−4·75	1·323	−1·405	−0·979	−0·906	0·824	18·4	3·6
107	HBr	−4·97	−5·34	1·323	−1·405	−0·979	−0·874	0·761	25·8	3·6
108	HCl	4·58	5·18	1·323	−1·405	−0·979	−0·869	−0·919	19·4	3·6
109	HBr	4·47	5·30	1·323	−1·405	−0·979	−0·869	−0·919	19·4	3·6

ᵃ For the compounds marked with asterisks, $F_{imp} < F_t$ and the data were not considered in the statistical analysis (see Appendix).
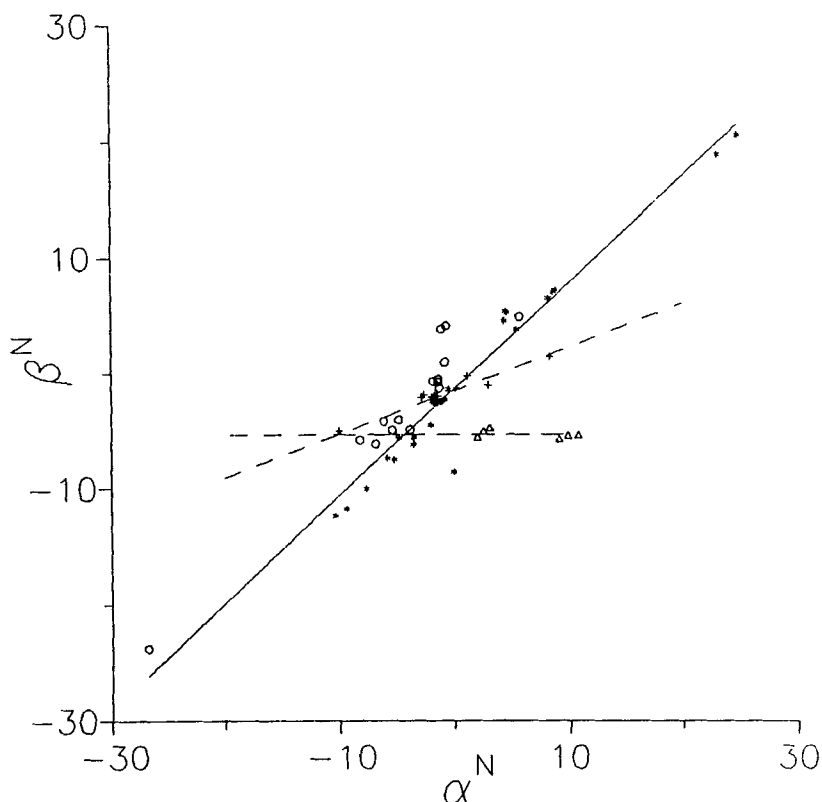
Figure 2. Dependence of normalized β^N and α^N. Symbols as in Figure 1

from 0 to more positive values. In this case the sign of α is the same as that determined, i.e. it is negative for most solvents. This is unexpected. In terms of similarity models, it means that cations and substances used for the B_{KT} determinations, i.e. of a hydrogen atom covalently bonded to nitrogen atoms in p-nitroaniline, exhibit opposite but proportional behaviour.

On the basis of the two dependences of α on β, one for the first group of ions and the other for the silver group, it is possible to draw the following conclusions. In the first group, anions show a similar and proportional response to Lewis acidity as defined by the E_T parameter, and cations show an opposite but proportional response to Lewis basicity in terms of the B_{KT} parameter. The regression coefficient of the dependence of a^N on β^N is close to unity (1·074), which means that the responses of anions and cations to changes in E_T and B_{KT} are almost identical. Thus, a relationship $\alpha^N + \beta^N = $ constant is probable. On the other hand, the regression coefficient for the silver group is 2·057. This means that the response to B_{KT} of the silver group is different from that of cations from the first group and also different from that of anions to E_T.

Large anions and molecules show a totally different behaviour, which is mostly manifested by almost constant values of β. As follows from the results presented in Figure 2, if one goes from W–AN to W–DMF mixtures, one observes that β^N for Ph_4AsBPh_4 is almost constant and α^N changes almost fourfold. Hence one could expect the behaviour of Ph_4As^+ to be similar to that of the first group of ions where both α^N and β^N are variable, whereas that of BPh_4 is not. One could finally conclude that behaviour of $PhAs_4^+$ ions is makedly different from that of BPh_4^-, a result which is clearly at variance with the widely used assumption[8] $\Delta G_t(Ph_4As^+) = \Delta G_t(BPh_4^-)$.

The analysis given above also allows the origin of the parameters E_T and B_{KT} to be discussed briefly. An interpretation of the negative sign of α^N and the positive sign β^N is not simple. A possible explanation is that E_T is of enthalpic and B_{KT} of entropic nature, which would, however, imply colinearity of the enthalpic and the entropic terms.

An analogy between the results presented in this paper and Pearson's[26] HSAB principle seems probable, but at present it is too early to draw any final conclusions.
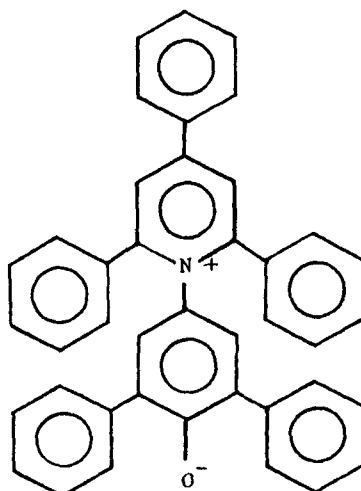
Figure 3. Formula of the betaine (30)

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APPENDIX

Statistical analysis of the results in Table 1

Statistical analysis of the results presented in Table 1 was performed from two points of view, namely (a) the analysis of the mutual dependence of E_T on B_{KT} and (b) from calculations of the improvement functions, which makes it possible to decide if an introduction of the second explaining parameter is statistically justified.

(a) The $E_T = a + bB_{KT}$ dependences were calculated for all pure solvents and water–non-aqueous solvent mixtures. Correlation coefficients R of these dependences are given in Table 2. It was found that in the case of water–alcohol and water–DMSO mixtures the acidity and the basicity parameters are highly correlated ($R > 0.99$). As a consequence, the improvement functions were smaller than the statistically justified ones.

(b) In the first step the $\Delta G_t = a_1 + b_1 B_{KT}$ and $\Delta G_t = a_2 + b_2 E_T$ dependences were calculated. Correlation coefficients of these dependences are given in Table 2. The improvement functions[11,25] (F_{imp}) were calculated according to the equation

$$F_{imp} = \frac{(R_{21}^2 - R_{11}^2)(N - 2)}{(1 - R_{21}^2)} \qquad (A1)$$

where R_{11} and R_{21} are the correlation coefficients for one- and two-parameter equations, respectively, and N is the number of points. Table 2 also gives values of the F_t functions taken from statistical tables. In all cases the 0.05 significance level was assumed. Data for which $F_{imp} < F_t$ were not considered in further analysis. These data are marked with asterisks.