LINEAR SOLVATION ENERGY RELATIONSHIPS BETWEEN ELECTROLYTE pK VALUES AND SOLVENT PROPERTIES FOR SEVERAL 2-METHYLPROPAN-2-OL–COSOLVENT MIXTURES

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The dissociation pK values of picric acid, tetrabutylammonium picrate, bromide and hydroxide and tetramethylammonium hydroxide in some 2-methylpropan-2-ol–cosolvent mixtures were determined and correlated with the Taft and Kamlet solvatochromic parameters π^*, δ, α and β. The results show the most important solvent properties that affect electrolyte dissociation are polarity, polarizability and hydrogen bond acidity. These results were confirmed by analysis of published literature data.

INTRODUCTION

The study of solute–solvent and solvent–solvent interactions in mixed solvents has been gaining significance in the recent years,[1] because of the increasing applications of these solvents. In previous work,[2–4] dissociation pK values of electrolytes were determined in binary solvents of low permittivity, with 2-methylpropan-2-ol or propan-2-ol as the main solvents. Equations which relate the pK values with the solvent composition were derived and tested. The equations[2,3] were restricted to a limited range of main solvent–cosolvent mixtures, but the inclusion of a preferential solvation term extended the range of applicability.[4] The parameter describing preferential solvation depends on the specific solute–main solvent and solute–cosolvent interactions, and therefore it is different for each electrolyte and cosolvent.

One attempt to generalize the proposed equations[3] was made relating the pK values with the $E_T(30)$ Dimroth–Reichardt solvatochromic parameter,[5] which is a measure of the polarity of the medium. However, the correlations were limited to a restricted range of cosolvent and they deviated from the theoretical predictions depending on the particular cosolvent added. Deviations were attributed to specific interactions between the cosolvent and E_T dye (which is sensitive to the solvent polarity and hydrogen bond acidity) or between the cosolvent and the electrolyte (which

depend on the polarity but also on the hydrogen bond capabilities of the electrolyte and cosolvent). A better result should be obtained if the pK values were correlated with all the independent parameters which measure the significant solute–solvent interactions. The purpose of this paper is the correlation of dissociation pK values of electrolytes in 2-methylpropan-2-ol–cosolvent mixtures with the most significant solvent properties (polarity and hydrogen bond properties) in order to determine the influence of each property on the dissociation process. The ΔpK values previously determined for picric acid, tetrabutylammonium bromide, picrate and hydroxide and tetramethylammonium hydroxide in mixtures of 2-methylpropan-2-ol with propan-2-ol, ethanol and methanol[4] have been used. However, addition of the previously studied cosolvents produces variation of pK values in the same way (decrease of pK) and the study was extended with the determination of the variation of pK values with addition of the aprotic cosolvents n-hexane and benzene, which increase the pK value. The inclusion of the two new cosolvents also produces a wider variation of the solvent properties.

Solvent properties have been measured by means of the π^*, α and β Taft and Kamlet solvatochromic parameters.[6–8] These parameters can be easily determined from the shift of the maximum of the absorption spectrum of indicator probes, and they have been successfully related with many solute properties. In this work, the ΔpK values of the electrolytes studied were correlated with variation of solvatochromic parameters. The good correlations obtained over the whole range of

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solvent composition studied allow an easy interpretation of the influence of any solvent property on the electrolyte dissociation.

DISSOCIATION CONSTANTS AND SOLVENT PROPERTIES

In an extensive series of papers, Taft, Kamlet and co-workers proposed the use of solvatochromic parameters in order to evaluate solute–solvent interactions for many Gibbs free energy-related properties through correlation analysis [linear solvation energy relationships (LSER)]. In 1985, the number of properties correlated exceeded 300,[9] including the formation constants of acid–base pairs in CCl_4, cyclohexane and o-dichlorobenzene[6,10] and dissociation constants of protonated bases in water.[11,12] However, application of the method to dissociation of the same electrolyte in different solvents or solvent mixtures was not investigated. Recently, Casassas and co-workers[13,14] used factor analysis for the correlation of solvatochromic parameters with dissociation constants of acids in 1,4-dioxane–water mixtures.

The number of terms in the equation used to correlate the studied property depends on the significance of the solute–solvent interactions. When the property studied refers to a single solute in multiple solvents, the general equation is usually expressed as[9]

$$XYZ = XYZ_0 + h\delta_H^2 + s(\pi^* + d\delta) + a\alpha + b\beta \quad (1)$$

where XYZ is the free energy-related property, δ_H is the Hildebrand solubility parameter, which accounts for the cavity term, π^* measures the solvent dipolarity/polarizability, δ is a polarizability correction term ($\delta = 1$ for aromatic, 0·5 for polychlorinated and 0 for other organic compounds), α measures the solvent hydrogen bond donor capability, β measures the solvent hydrogen bond acceptor capability and XYZ_0, h, s, d, a and b are the intercept and coefficients of the correlation.

When the property correlated does not involve significant changes in the cavity volumes, the term δ_H^2 drops out of equation (1).[9] This occurs for binary solvents when the structure of the main solvent is retained because the amount of cosolvent added is not very large, as in this work. Therefore, an appropriate form of equation (1) applied to dissociation pK values of electrolytes in binary solvents rich in one solvent component should be:

$$pK = pK_0 + s(\pi^* + d\delta) + a\alpha + b\beta \quad (2)$$

This equation was used by Casassas et al.[14] for 1,4-dioxane–water, although the final results led to statistically non-significant a and b coefficients.

In our previous work[4] we used ΔpK instead of pK when we related the change in pK with the addition of a cosolvent to a solution of the electrolyte in a pure

solvent. If this variation in pK (ΔpK) is related to the variation of solvent properties by the addition of a cosolvent ($\Delta\pi^*$, $\Delta\delta$, $\Delta\alpha$ and $\Delta\beta$), equation (2) becomes

$$\Delta pK = a_0 + s(\Delta\pi^* + d\Delta\delta) + a\Delta\alpha + b\Delta\beta \quad (3)$$

where ΔpK, $\Delta\pi^*$, $\Delta\delta$, $\Delta\alpha$ and $\Delta\beta$ use as reference one solvent (2-methylpropan-2-ol in our case), a_0 is the intercept of the correlation, which should equal zero, and the correlation coefficients s, d, a, and b measure the susceptibility of the change in pK to changing solvent polarity, polarizability, hydrogen bond acidity and hydrogen bond basicity, respectively.

EXPERIMENTAL

Apparatus. A Beckman DU-7 spectrophotometer, with 10 mm cells, connected to a microcomputer via a serial port was used for acquisition and numerical treatment of absorbance data. Density, viscosity and conductivity were measured with the apparatus described previously.[2–4]

Solvatochromic indicators. The dyes used for determination of solvatochromic parameters were 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinium)-1-phenolate (Dimroth– Reichardt betaine dye; >95%, Aldrich), 4-nitroanisole (Merck) purified with active carbon and recrystallized from acetone–water and 4-nitroaniline (RPE, >99%, Carlo Erba).

Solvents. The main solvent (2-methylpropan-2-ol) and the cosolvents (propan-2-ol, ethanol, methanol, n-hexane, benzene and triply distilled water) were the same as used in earlier work.[2–4]

Electrolytes. The electrolytes were the same as used previously.[4]

Procedure. For the spectrophotometric measurements, measured volumes of each cosolvent were added to 50 ml of 10^{-4} M (for Dimroth–Reichardt's betaine dye and 4-nitroanisole) or 5×10^{-5} M (for 4-nitroaniline) indicator dye solution in pure 2-methylpropan-2-ol. The spectrum of the indicator dye was recorded in the ranges 500–800 nm (Dimroth–Reichardt's dye), 275–325 nm (4-nitroanisole) and 340–400 nm (4-nitroaniline). The absorbance data was acquired using the DUMOD program.[15] For conductivity measurements the method described previously was used.[4] A closed vessel with exterior thermostating at 30 ± 0.2 °C with a water flow was used.

Calculation of solvatochromic parameters. The wavelengths of maximum absorption of the Dimroth–Reichardt betaine dye, 4-nitroanisole and 4-nitroaniline spectra in each solvent mixture were obtained after numerical smoothing of the absorbance data. The

Taft–Kamlet solvatochromic parameters (π^*, β and α) were calculated using the following equations:[8,16,17]

$$\pi^* = \frac{34\cdot12 - \bar{\nu}_1}{2\cdot343} \qquad (4)$$

$$\beta = \frac{31\cdot10 - 3\cdot14\pi^* - \bar{\nu}_2}{2\cdot79} \qquad (5)$$

$$\alpha = 0\cdot198\bar{\nu}_3 - 2\cdot091 - 0\cdot899(\pi^* - 0\cdot211\delta) - 0\cdot148\beta \qquad (6)$$

where $\bar{\nu}$ (in kK = $1000\,\text{cm}^{-1}$) is the wavenumber of the absorbance maximum; the subscripts 1, 2 and 3 refer to 4-nitroanisole, 4-nitroaniline and Dimroth–Reichardt betaine solvatochromic indicators, respectively. In fact, equations (4)–(6) were developed for pure solvents, but following Marcus and Migron's work in different solvent mixtures[16,18] we assume here that they can be applied to solvent mixtures.

Calculation of pK. The pK values of the electrolytes in 2-methylpropan-2-ol–hexane and 2-methylpropan-2-ol–benzene mixtures were calculated using the Shedlovsky equation according to the procedure described earlier.[4]

RESULTS AND DISCUSSION

The π^*, α and β values of the pure solvents used to prepare the binary solvents were determined and are presented in Table 1, together with the accepted literature values at 25 °C.[17] n-Hexane is a non-polar, non-hydrogen bond donor and non-hydrogen bond acceptor solvent. Benzene has also no hydrogen bonding properties, but its polarity is similar to that of 2-methylpropan-2-ol. Propan-2-ol has polarity and hydrogen bond acceptor capabilities very similar to those of 2-methylpropan-2-ol, but it is a stronger hydrogen bond donor. Ethanol and methanol are stronger hydrogen bond donors and weaker hydrogen bond acceptors than 2-methylpropan-2-ol. The polarities of ethanol and methanol are similar

to that of 2-methylpropan-2-ol. Therefore, addition of these cosolvents to 2-methylpropan-2-ol should change all the solvent properties.

The π^*, β and α values for the solvent mixtures studied were calculated using equations (4)–(6). However, in calculating α by means of equation (6), it is not clear which δ value should be used for the 2-methylpropan-2-ol–benzene mixtures. For this reason, in the first instance α values were calculated only for the other solvent mixtures, for which $\delta = 0$. The variations in π^*, β and α values ($\Delta\pi^*$, $\Delta\beta$ and $\Delta\alpha$, given in Table 2) with respect to the value in pure 2-methylpropan-2-ol were correlated with the ΔpK values given elsewhere[4] for methanol, ethanol and propan-2-ol cosolvents, and with the ΔpK values obtained here for n-hexane cosolvent (Table 3). The correlation obtained is presented in Table 4, and a graphical example is given in Figure 1 for picric acid. The hypothetical ΔpK values for picric acid which should be obtained for benzene mixtures if these mixtures were not susceptible to polarizability effects have also been included in Figure 1. These ΔpK values were calculated from the correlation obtained for the other mixtures and the $\Delta\pi^*$, $\Delta\beta$ and a hypothetical $\Delta\alpha$ value for benzene mixtures, the latter parameter calculated from equation (6) assuming $\delta = 0$. Figures similar to Figure 1 were obtained for the other electrolytes. In all these figures, the calculated ΔpK values for benzene mixtures deviate from the correlation line. Figure 2 presents the deviations obtained [ΔpK (experimental) $- \Delta pK$ (calculated)] as a function of the mole fraction of benzene in the mixture. For all the electrolytes studied the deviation is proportional to the mole fraction of benzene. Therefore, we conclude that for a non-polarizable main solvent polarizability effects can be considered to be proportional to the mole fraction of polarizable cosolvent:

$$\delta_{\text{mixture}} = x_{\text{main solvent}}\,\delta_{\text{main solvent}}$$
$$+ x_{\text{cosolvent}}\,\delta_{\text{cosolvent}} = x_{\text{cosolvent}}\,\delta_{\text{cosolvent}} \qquad (7)$$

The α values of 2-methylpropan-2-ol–benzene were calculated with equation (6) using these δ mixture values. The results are presented in Table 2.

Table 1. Solvatochromic parameters of pure solvents

Solvent	Literature values at 25 °C[17]				This work at 30 °C			
	π^*	α	β	δ	π^*	α	β	δ
Methanol	0·60	0·98	0·66	0·00	0·610	1·051	0·776	0·00
Ethanol	0·54	0·86	0·75	0·00	0·555	0·853	0·877	0·00
Propan-2-ol	0·48	0·76	0·84	0·00	0·495	0·633	1·050	0·00
2-Methylpropan-2-ol	0·41	0·42	0·93	0·00	0·504	0·303	1·064	0·00
Benzene	0·59	0·00	0·10	1·00	0·601	−0·069	0·081	1·00
n-Hexane	0·00	0·00	0·00	0·00	−0·064	0·095	0·011	0·00

Table 2. Variation in π^*, α and β solvatochromic parameters in 2-methylpropan-2-ol by addition of cosolvents

Cosolvent	v^a	x^a	$\Delta\pi^*$	$\Delta\alpha$	$\Delta\beta$	$\Delta\delta$
n-Hexane	0·00200	0·00146	0·000	−0·001	−0·003	0·000
	0·00398	0·00292	0·000	−0·001	−0·003	0·000
	0·00794	0·00581	−0·005	0·001	0·000	0·000
	0·01961	0·01441	−0·009	0·000	−0·002	0·000
	0·03846	0·02841	−0·014	−0·003	−0·007	0·000
	0·05660	0·04202	−0·023	−0·002	−0·007	0·000
	0·09091	0·06812	−0·037	−0·003	−0·012	0·000
	0·12281	0·09284	−0·051	−0·002	−0·014	0·000
	0·13793	0·10472	−0·060	0·000	−0·014	0·000
	0·16667	0·12755	−0·074	0·003	−0·019	0·000
Benzene	0·00200	0·00214	0·000	0·000	−0·003	0·002
	0·00398	0·00427	0·000	0·000	−0·005	0·004
	0·00794	0·00851	0·000	0·000	−0·010	0·009
	0·01961	0·02100	0·005	−0·004	−0·031	0·021
	0·03846	0·04113	0·005	−0·005	−0·051	0·041
	0·05660	0·06046	0·009	−0·009	−0·077	0·060
	0·09091	0·09686	0·009	−0·012	−0·110	0·097
	0·12281	0·13054	0·014	−0·018	−0·144	0·131
	0·13793	0·14646	0·019	−0·023	−0·162	0·146
	0·16667	0·17661	0·023	−0·030	−0·190	0·177
Propan-2-ol	0·00200	0·00249	0·000	0·002	0·000	0·000
	0·00398	0·00496	0·000	0·004	0·000	0·000
	0·00794	0·00987	0·000	0·007	0·000	0·000
	0·01961	0·02432	0·005	0·014	−0·003	0·000
	0·03846	0·04748	0·005	0·029	0·000	0·000
	0·05660	0·06957	0·005	0·042	0·002	0·000
	0·09091	0·11081	0·005	0·065	0·005	0·000
	0·12281	0·14854	0·009	0·080	0·002	0·000
	0·13793	0·16624	0·009	0·088	0·005	0·000
	0·16667	0·19950	0·009	0·103	0·007	0·000
Ethanol	0·00200	0·00326	0·000	0·007	−0·013	0·000
	0·00398	0·00649	0·000	0·012	−0·015	0·000
	0·00794	0·01290	0·000	0·023	−0·020	0·000
	0·01961	0·03164	0·000	0·050	−0·023	0·000
	0·03846	0·06133	0·005	0·084	−0·028	0·000
	0·05660	0·08926	0·005	0·115	−0·028	0·000
	0·09091	0·14041	0·005	0·163	−0·028	0·000
	0·12281	0·18612	0·005	0·200	−0·031	0·000
	0·13793	0·20720	0·009	0·211	−0·036	0·000
	0·16667	0·24625	0·009	0·236	−0·036	0·000
Methanol	0·00200	0·00469	0·000	0·020	0·000	0·000
	0·00398	0·00933	0·000	0·036	−0·003	0·000
	0·00794	0·01849	0·000	0·063	−0·003	0·000
	0·01961	0·04498	0·000	0·120	−0·008	0·000
	0·03846	0·08609	0·000	0·183	−0·015	0·000
	0·05660	0·12381	0·005	0·225	−0·028	0·000
	0·09091	0·19061	0·005	0·292	−0·041	0·000
	0·12281	0·24795	0·009	0·337	−0·059	0·000
	0·13793	0·27368	0·009	0·358	−0·064	0·000
	0·16667	0·32019	0·009	0·393	−0·074	0·000

[a] v = Volume fraction of cosolvent; x = mole fraction of cosolvent.

Table 3. Variation of pK values of electrolytes in 2-methylpropan-2-ol on addition of benzene and n-hexane

Cosolvent	v[a]	x[a]	η (P)[a]	d (g ml^{-1})[a]	ΔpK[b]				
					HPi	Bu$_4$NPi	Bu$_4$NBr	Bu$_4$NOH	Me$_4$NOH
Benzene	0·00200	0·00214	0·0330	0·7776	0·02	0·01	0·02	0·01	0·02
	0·00398	0·00427	0·0326	0·7778	0·04	0·03	0·03	0·03	0·04
	0·00794	0·00851	0·0318	0·7782	0·08	0·06	0·06	0·07	0·08
	0·01961	0·02100	0·0296	0·7794	0·21	0·16	0·16	0·18	0·19
	0·03846	0·04113	0·0265	0·7813	0·41	0·32	0·31	0·34	0·37
	0·05660	0·06046	0·0239	0·7831	0·61	0·49	0·46	0·49	0·55
	0·09091	0·09686	0·0200	0·7866	0·99	0·78	0·74	0·79	0·90
	0·12281	0·13054	0·0173	0·7898			1·01		1·23
	0·13793	0·14646	0·0162	0·7914			1·13		1·39
	0·16667	0·17661	0·0147	0·7943	1·83	1·44	1·36	1·46	1·70
n-Hexane	0·00200	0·00146	0·0330	0·7772	0·01	0·01	0·01	0·03	0·02
	0·00398	0·00292	0·0326	0·7769	0·03	0·03	0·03	0·05	0·04
	0·00794	0·00581	0·0319	0·7765	0·06	0·06	0·06	0·09	0·07
	0·01961	0·01441	0·0299	0·7751	0·15	0·16	0·15	0·19	0·18
	0·03846	0·02841	0·0270	0·7729	0·31	0·32	0·29	0·34	0·36
	0·05660	0·04202	0·0242	0·7708	0·47	0·47	0·44	0·50	0·54
	0·09091	0·06812	0·0204	0·7668	0·78	0·77	0·72	0·80	0·88
	0·12281	0·09284	0·0175	0·7630			0·98		1·22
	0·13793	0·10472	0·0163	0·7612			1·10		1·39
	0·16667	0·12755	0·0145	0·7579	1·54	1·45	1·34	1·51	1·71

[a] η = Viscosity; d = density; v and x as in Table 2.
[b] HPi = picric acid; Bu$_4$NPi = tetrabutylammonium picrate; Bu$_4$NBr = tetrabutylammonium bromide; Bu$_4$NOH = tetrabutylammonium hydroxide; Me$_4$NOH = tetramethylammonium hydroxide. pK values in pure 2-methylpropan-2-ol are 5·33 (HPi), 4·45 (Bu$_4$NPi), 5·07 (Bu$_4$NBr), 4·89 (Bu$_4$NOH) and 5·03 (Me$_4$NOH).

In a second correlation, the variation of pK was correlated with the variation of the α, β, π^* and δ parameters for all the electrolytes and mixtures studied (including benzene mixtures). The results obtained for this correlation are presented in Table 4.

The independent term is statistically not different from zero, which means that the properties of the solvent expressed by the solvatochromic parameters can describe well the variations in the dissociation of electrolytes to modifying the composition of the solvent. Therefore, as expected, equation (3) can be simplified to

$$\Delta pK = s(\Delta \pi^* + d\Delta \delta) + a\Delta \alpha + b\Delta \beta \qquad (8)$$

The s coefficients are negative in all instances, which means that an increase in the polarity of the mixed solvent decreases the pK value. Thus an increase in polarity increases the solvation of the ions, and therefore dissociation. The effect of polarity is similar in all the electrolytes studied, but slightly higher for picric acid and tetramethylammonium hydroxide, which have the smallest size and therefore the ions with the highest charge density.

The negative sign of the d coefficients means that the polarizability of the solvent has an opposite effect to the polarity, that is, an increase in the polarizability increases the pK value. This increase is attributed to

solvation of the non-dissociated ion pair of the electrolyte by the polarizable cosolvent. The π electrons of a benzene molecule surrounding an ion pair are repelled by the negative anion, but attracted by the positive cation. Hence a charge distribution is induced in the benzene molecule, which solvates specifically the ion pair. Therefore, solvation of the ion pair by polarizability of benzene is stronger than solvation of the dissociated ions and dissociation of the ion pair is disfavoured. This effect is similar in all the electrolytes studied since the d coefficients are very similar.

The a coefficients are negative for all the electrolytes because an increase in the hydrogen bond donor capability of the solvent increases the solvation of the anion by hydrogen bond donation from the solvent to the anion, and therefore it increases electrolyte dissociation and decreases pK. The absolute values of a are lower than those of s because solvation by hydrogen bond donation from the solvent affects only the anion, whereas solvation by polarity affects both anion and cation. The ratio s/a, included in Table 4, shows that solvation by polarity is about four times more important than solvation by hydrogen bond donation, except for picric acid, for which it is about seven times larger, probably because of the small size of the hydrogen ion.

The b coefficient is not significant in most cases. Application of Student's t-test shows that it is

Table 4. Correlations of variation of pK values of electrolytes in 2-methylpropan-2-ol–cosolvent mixtures with variation of solvent properties[a]

Electrolyte	Correlation No.	a_0	a	b	s	d	R	s/a	σ	N
Picric acid	1[b]	(-0.01 ± 0.01)	-2.97 ± 0.15	(-0.51 ± 0.81)	-21.04 ± 0.54		0.9971	7.08	0.041	32
	2	(-0.01 ± 0.01)	-2.99 ± 0.14	(-0.65 ± 0.75)	-20.90 ± 0.51	-0.56 ± 0.04	0.9980	6.99	0.040	40
	3	(-0.01 ± 0.01)	-2.89 ± 0.07		-21.06 ± 0.47	-0.59 ± 0.01	0.9980	7.29	0.040	40
Tetramethylammonium hydroxide	1[b]	(0.02 ± 0.01)	-6.34 ± 0.18	(1.30 ± 1.00)	-23.61 ± 0.55		0.9982	3.72	0.052	37
	2	(0.01 ± 0.01)	-6.32 ± 0.16	(1.11 ± 0.93)	-23.45 ± 0.52	-0.53 ± 0.04	0.9985	3.71	0.050	47
	3	(0.01 ± 0.01)	-6.46 ± 0.11		-23.18 ± 0.46	-0.48 ± 0.01	0.9985	3.59	0.050	47
Tetrabutylammonium hydroxide	1[b]	(0.02 ± 0.01)	-4.51 ± 0.11	-2.13 ± 0.62	-19.70 ± 0.41		0.9988	4.37	0.031	32
	2	(0.02 ± 0.01)	-4.46 ± 0.11	-2.09 ± 0.61	-19.69 ± 0.41	-0.38 ± 0.04	0.9989	4.41	0.032	40
	3	(0.02 ± 0.01)	-4.15 ± 0.68		-20.21 ± 0.44	-0.49 ± 0.01	0.9985	4.87	0.037	40
Tetrabutylammonium bromide	1[b]	(0.02 ± 0.01)	-4.26 ± 0.14	1.67 ± 0.76	-18.68 ± 0.45		0.9984	4.38	0.043	40
	2	(0.02 ± 0.01)	-4.26 ± 0.13	1.49 ± 0.70	-18.56 ± 0.42	-0.58 ± 0.04	0.9987	4.36	0.041	50
	3	(0.02 ± 0.01)	-4.51 ± 0.06		-18.14 ± 0.39	-0.50 ± 0.01	0.9985	4.02	0.043	50
Tetrabutylammonium picrate	1[b]	(0.04 ± 0.02)	-4.35 ± 0.27	(1.08 ± 1.58)	-19.59 ± 0.98		0.9921	4.50	0.074	31
	2	(0.03 ± 0.02)	-4.31 ± 0.24	(0.90 ± 1.42)	-19.58 ± 0.89	-0.54 ± 0.08	0.9939	4.54	0.069	39
	3	(0.03 ± 0.01)	-4.42 ± 0.16		-19.37 ± 0.82	-0.49 ± 0.01	0.9938	4.38	0.068	39

[a] Values in parentheses are not statistically significant at the 95% confidence level by Students' t-test. σ = standard deviation; N = number of points.
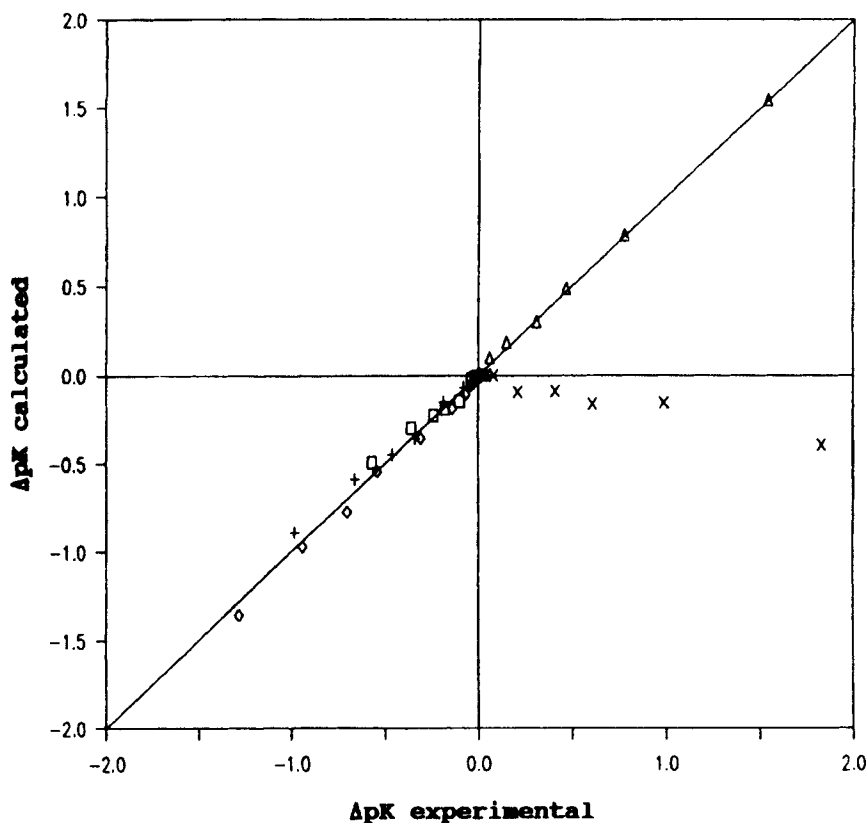[b] 1 = excluding benzene as cosolvent.

Figure 1. ΔpK (calculated) vs ΔpK (experimental) for picric acid in 2-methylpropan-2-ol–cosolvent mixtures according to the results of correlation 1 in Table 4. Cosolvents: □, 2-propanol; +, ethanol; ◇, methanol; △, n-hexane; ×, benzene

significantly different from zero at the 95% confidence level only for tetrabutylammonium bromide and hydroxide. For the latter, it is significant only at the 96% confidence level. Therefore, equation (8) probably can be simplified to

$$\Delta pK = s(\Delta \pi^* + d\Delta\delta) + a\Delta\alpha \qquad (9)$$

Application of Ehrenson's criterion[19] shows that there are no significant differences between the fits of equations (8) and (9) for picric acid, tetrabutylammonium picrate and tetramethylammonium hydroxide at the 90% confidence level. For tetrabutylammonium bromide the confidence level is 96% and for tetrabutylammonium hydroxide it is 99·9%. Anyway, the contribution of the $b\Delta\beta$ term is much smaller than those of the others, and since this contribution accounts for hydrogen bond donation from the solute to the solvent, which is not feasible for the tetraalkylammonium electrolytes and clearly not significant for picric acid, the preferred correlation equation for the studied electrolytes in the mixed solvents should be equation (9). The applicability of this equation was confirmed by the good fits obtained (Table 4 and Figure 3).

A similar equation was applied by Taft et al.[20] to Gibbs free energies of transfer (ΔG_t^0) of tetraalkylammonium halide pairs and dissociated ions between pure solvents.

$$\Delta G_t^\circ = (\Delta G_t^\circ)_0 + s\pi^* + a\alpha + h\delta_H^2 \qquad (10)$$

Their results showed that the main factors that affect the transfer are polarity/polarizability (π^*), hydrogen bond acidity (α) and the solubility parameter (δ_H^2). The last term is needed because of the large differences in the structures of the pure solvents involved. Inclusion of a $b\beta$ term produces no improvement in the statistical goodness of fit. The inclusion of a $d\delta$ term was not necessary because none of the correlated solvents was polarizable.

From the correlation of ΔG_t° of the ions and ion pairs studied,[20] the correlation of ΔpK values for ion-pair dissociation was calculated. The coefficients of the equation obtained:

$$\Delta pK = s\Delta\pi^* + a\Delta\alpha + h\Delta\delta_H^2 \qquad (11)$$

for each electrolyte are given in Table 5 and they are in good agreement with those in Table 4, confirming that
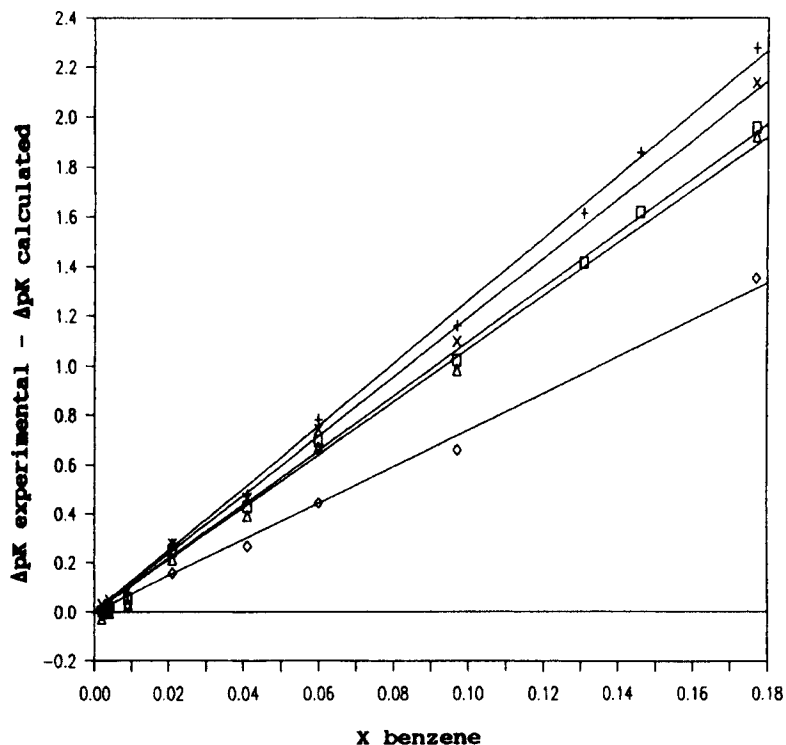
Figure 2. Differences between ΔpK (experimental) and ΔpK (calculated) vs mole fraction of benzene for different electrolytes. ×, Picric acid; ◇, tetrabutylammonium hydroxide; +, tetramethylammonium hydroxide; △, tetrabutylammonium picrate; □, tetrabutylammonium bromide
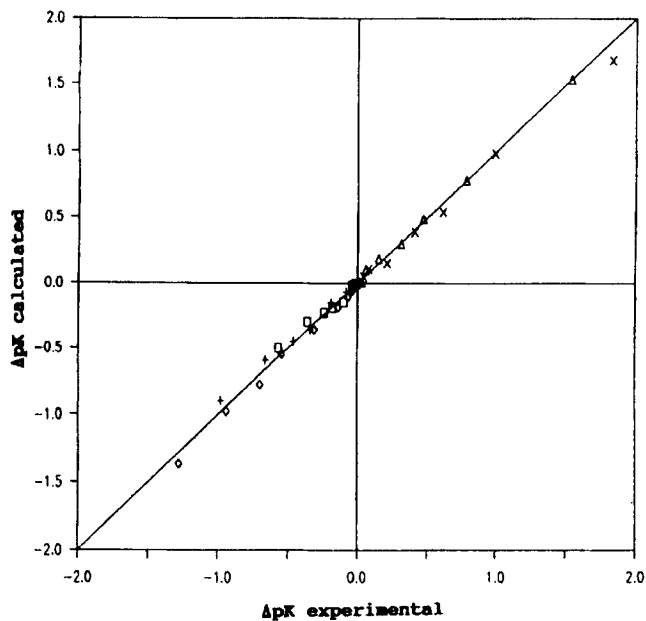

Figure 3. ΔpK (calculated) vs ΔpK (experimental) for picric acid in 2-methylpropan-2-ol–cosolvent mixtures according to the results of correlation 3 in Table 4. Symbols as in Figure 1

Table 5. Correlations of variation of pK values of tetraalkylammonium halides in pure solvents calculated from Ref. 20

Halide	a	s	$h \times 100$
Tetramethylammonium iodide	−7·5	−19·3	+3·0
Tetramethylammonium bromide	−7·5	−18·8	+2·9
Tetramethylammonium chloride	−7·8	−18·7	+2·9
Tetraethylammonium iodide	−7·0	−17·9	+2·9
Tetraethylammonium bromide	−6·7	−17·5	+2·6
Tetraethylammonium chloride	−7·0	−17·5	+2·7

the order of importance of the main solvent properties which affect dissociation of electrolytes is polarity ≫ polarizability > hydrogen bond acidity > structure of the medium ≫ hydrogen bond basicity.

The results obtained in this work demonstrate the applicability of the LSER approach to dissociation of electrolytes in binary solvents of low permittivity as an appropriate method for quantification of the main solute−solvent interactions which affect dissociation processes.

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