

RATIO OF LYATE IONS ACTIVITIES IN TWO-COMPONENTS PROTOGENIC SOLVENTS

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Kinetic method for the evaluation of lyate ions activities in two-component protogenic solvents has been discussed. Spectral methods for the measurement of equilibria between alkoxide and hydroxide ions have been compared. A correlation between dissociation constants of water and of weak organic acids in solvent mixtures has been found. By means of this correlation, ratios of lyate ions activities in water-ethanol and water-2-propanol mixtures have been calculated. These activity ratios, together with the known composition of reaction products, have been used to evaluate the selectivity of the neutral and alkaline solvolysis of phthalic anhydride and benzyl chloride in solvent mixtures quoted above.

Dissociation equilibria in solvents are for the most part experimentally accessible and well known. An exception is the equilibrium (A) between lyate ions of a two-components protogenic solvent in basic region



where HX and HY denote the two solvent components. The equilibrium (A) is characterized by equations

$$K_h = \frac{a(\text{X}^-) \cdot a(\text{HY})}{a(\text{HX}) \cdot a(\text{Y}^-)} = \frac{K(\text{HX}) \cdot a(\text{HY})}{a(\text{HX}) \cdot K(\text{HY})} = \frac{K^*(\text{HX})}{K^*(\text{HY})}, \quad (1)$$

where $a(\text{X}^-)$, $a(\text{HX})$, $a(\text{Y}^-)$ or $a(\text{HY})$ are the activities of reactants in Eq. (A), $K(\text{HX})$ or $K(\text{HY})$ are the equilibrium autoprotolysis constant in the solvent mixture defined as $K(\text{HX}) = a(\text{X}^-) \cdot a(\text{H}^+)$ or $K(\text{HY}) = a(\text{Y}^-) \cdot a(\text{H}^+)$, and $K^*(\text{HX})$ or $K^*(\text{HY})$ are the dissociation constants of the components in the mixture defined as $K^*(\text{HX}) = K(\text{HX})/a(\text{HX})$ or $K^*(\text{HY}) = K(\text{HY})/a(\text{HY})$, respectively. The values of the constants $K(\text{HX})$ and $K(\text{HY})$ are known for a limited number of the water-alcohol systems^{1,2}. Their evaluation is based on the assumption of a linear relationship between the Gibbs energies of transfer from water to a non-aqueous solvent

for hydroxide or alkoxide ions and that for halogenide ions (X^-)

$$\Delta G_{tr}^0(OH^-) = const \cdot \Delta G_{tr}^0(X^-); \quad \Delta G_{tr}^0(RO^-) = const' \cdot \Delta G_{tr}^0(X^-), \quad (2)$$

where the empirical constants *const* and *const'* are to be derived from the experimental data¹. In the water–dimethylsulphoxide³ and water–dioxane⁴ systems, Eq. (2) holds with a plausible accuracy only at low concentrations of the organic co-solvent. On the contrary, in the water–methanol system it gives reasonable results over the whole range of methanol concentrations. However, this case appears to be rather exceptional, because for other water–alcohol as well as the two-component solvents^{3,4} the applicability of Eq. (2) is limited, *e.g.* in the water–ethanol mixture the linear relationship between the Gibbs energies of anion transfer holds only for ethanol concentrations lower than 35 wt. % (ref.⁵). Thus, without introducing some additional assumptions, the comparison between the results based on Eq. (2) and those of the spectral method⁶ will remain to be restricted to the water–methanol system⁷. However, more extensive comparison would be obviously worthwhile.

The differences in pK^* values of carboxylic acids in a solvent *S* and in water $pK^*(HA)_S - pK^*(HA)_{H_2O} = \Delta pK^*(HA)$ are related to each other through⁸

$$\Delta pK^*(HA) = W \cdot (\Delta pK(HAc))^j, \quad (3)$$

where HAc denotes the standard and HA the correlated weak acid, and *W* or *j* are the empirical constants. If this equation were applicable also to a general acid such as water, it could be used to solve the problems inherent in the equilibrium expressed by Eq. (1).

An alternative approach to the solution of the problem consists in the use of kinetic data and the analysis of reaction products^{9,10}. In order to make the equations soluble, the medium effect on the rate constant was neglected. Moreover, the constant K_h was considered to be the true equilibrium constant, which is independent of medium^{9,10}. However, the latter assumption has not been confirmed^{1,2,7,11}. From the theoretical point of view, the former assumption is incorrect, but the experimental data, which would enable us to estimate the extent to which the error involved is significant, are absent. In this communication we intend to analyse the possibility of using Eq. (3) for the solution of the equilibrium (1), as well as to present the kinetic data suitable for the verification of the kinetic method.

EXPERIMENTAL

Chemicals

Solvents (Lachema, *p.a.*) were dried¹² and freshly distilled prior to the use. Methyl, ethyl and 2-propyl phthalate^{13,14}, diphenyl phenylphosphonate¹⁵, triphenyl phosphate¹⁶, diphenyl anilido-

phosphate, phenyl dianilidophosphate¹⁷, and benzylmethyl ether¹⁸ were prepared as described in literature. Other chemicals were commercially available (Lachema *p.a.*).

Procedures

The autoprotolysis constants $pK' \pm 0.02$ at $25 \pm 0.1^\circ\text{C}$ were measured using the standard procedure¹⁹ with help of a glass electrode (Radiometer G 202 B) and a saturated calomel electrode. In these measurements the solutions of acid or base having the concentrations of 0.02, 0.01, 0.005, 0.0025 or 0.00125 mol dm⁻³ were used. The measured values were extrapolated to the zero ionic strength by using the equation

$$pK = pK' + \sqrt{I}/(1 + \sqrt{I}). \quad (4)$$

In case that the presence of the electrolyte led to the formation of two phases, electrolyte concentration was chosen below that causing such an effect. For the water-dioxane system the following pK values were obtained: 15.80 (50), 16.68 (60), 17.84 (70), 19.07 (82) and 20.43 (90), while for the water-acetone system $pK = 16.95$ (70) or 17.63 (80), where the numbers in parentheses give the concentration of the organic co-solvent in wt. %.

The dissociation constants of acetic acid $pK^* = 11.27$ in 90 wt. % dioxane and $pK^* = 7.25$ or 8.48 in 70% or 80 wt. % acetone, respectively, were determined by titration. The concentrations of sodium acetate used in these experiments were the same as those of electrolytes in determination of autoprotolytic constants. As a titrant, the ten times more concentrated solution of perchloric acid in the same solvent was used. Extrapolation to the zero ionic strength was made according to the relationship analogous to Eq. (4). Prior to measurements, the electrode system was calibrated by means of the buffer solutions recommended in literature²⁰. Esters of anilidophosphoric and dianilidophosphoric acids undergo the dissociation in strongly basic medium. Their pK was evaluated from spectrophotometric measurements on VSU 2 P instrument (Zeiss, Jena) using the equation

$$A = [a(\text{H}^+)/K^*][A(\text{HA}) - A] + A(\text{A}^-), \quad (5)$$

where $a(\text{H}^+)$ is the proton activity, A is the measured absorbance of the solution and $A(\text{HA})$ or $A(\text{A}^-)$ are the absorbances of the solution containing only the undissociated or fully dissociated acid, respectively. The proton activities were measured in the hydrogen-silver-silver chloride cell filled with the same solvent at 25°C and at the ionic strength of 0.05 mol dm⁻³. The correct function of the electrode system was checked with the help of a set of the buffer solutions^{20,21}. Since the pK values of the phosphoric acid derivatives fall in the far basic region, their extrapolation to the zero ionic strength was not possible.

Solvolysis of the derivatives of phosphoric and phosphonic acids was followed at 25°C on VSU 2 P (Zeiss) and Pye-Unicam 8-100 instruments. Rate constants were evaluated from the equation

$$\ln(A_\infty - A_t) = -k_{\text{exp}} \cdot t + \text{const} \quad (6)$$

the maximum error being 5%. In Eq. (6), A_t or A_∞ are the solution absorbances at a time t or after the reaction studied was complete, respectively. The second term on the r.h.s. of Eq. (6) was usually equal to zero except for diphenyl anilidophosphate and phenyl dianilidophosphate, in which cases its non-zero value was due to a time delay at the beginning of reaction. The rate constant k_{exp} was measured in glycinate buffers at least at four values of the ionic strength in the range from 0.02 to 0.2 mol dm⁻³. The kinetic data thus obtained were extrapolated to the zero ionic strength according to the relationship²²: $\log k = \log k^0 + \text{const} \cdot I$.

Rate constants of solvolysis of phthalic anhydride were calculated from the equation

$$-dc_{\text{anh}}/dt = k \cdot c_{\text{anh}}, \quad (7)$$

where c_{anh} is the anhydride concentration. The constant k in Eq. (7) is given by

$$k = k(\text{H}_2\text{O}) c(\text{H}_2\text{O}) + k(\text{ROH}) c(\text{ROH}) \quad (8)$$

$$k = k(\text{OH}^-) c(\text{OH}^-) + k(\text{RO}^-) c(\text{RO}^-), \quad (9)$$

where $k(\text{H}_2\text{O})$, $k(\text{ROH})$, $k(\text{OH}^-)$ or $k(\text{RO}^-)$ are the constants of the hydrolytic or alcoholic reaction in the neutral or basic medium, $c(\text{H}_2\text{O})$ or $c(\text{ROH})$ are the concentrations of water or alcohol in the mixture and $c(\text{OH}^-)$ or $c(\text{RO}^-)$ are the concentrations of hydroxide or alkoxide ions, respectively. The hydrolytic and alcoholic reactions proceed in parallel and therefore

$$k(\text{ROH}) c(\text{ROH})/k(\text{H}_2\text{O}) c(\text{H}_2\text{O}) = c(\text{ester})/c(\text{acid}) \quad (10)$$

$$k(\text{RO}^-) c(\text{RO}^-)/k(\text{OH}^-) c(\text{OH}^-) = c(\text{ester})/c(\text{acid}), \quad (11)$$

where $c(\text{acid})$ or $c(\text{ester})$ are the concentrations of the acid formed or of its monoester, respectively. In order to determine the ratio of the product concentrations, the amount of phthalic anhydride weighed was dissolved in ether, which was free of peroxides, and 0.1 cm³ of this solution was added to 25 cm³ of the water-alcohol mixture. After the reaction was complete, the solution was analyzed by means of liquid chromatography on Spectra-Physics SP — 8 700 instrument with C₁₈-LiChrosorb column.

After several weeks of reaction between benzyl chloride and the two-component water-methanol solvent in neutral or basic region a solution was obtained, which contained benzyl alcohol, benzyl methyl ether and negligible amount of benzyl chloride. By means of chromatographic analysis the data were obtained, which upon their substitution into equations analogous to Eqs (10) and (11), made it possible to calculate the ratios of rate constants.

In dry ethanol, which contained 0.19 wt. % of water (as determined by Fischer titration), sodium was dissolved at a concentration of $2.352 \cdot 10^{-4}$ mol dm⁻³ (as determined by titration) and the solution was diluted by water distilled under nitrogen to give the molar fractions of water in the mixture $x_{\text{H}_2\text{O}} = 0.0241, 0.0426, 0.0607$ and 0.0784 . Spectra of these solutions against that of NaOH in water having approximately the same concentration were recorded on Pye-Unicam SP 8-100 instrument. The maximum was found at the wavelength of 208 nm. Absorbance measured against the aqueous solutions of NaOH at this wavelength conformed to the Lambert-Beer law and was used for the analysis of mixture. Molar absorption coefficients $\epsilon(\text{NaOH})$ and $\epsilon(\text{EtONa})$, which were obtained by direct measurement, were assumed to be independent of medium. In case of the water-ethanol mixture, the hydroxide concentration was calculated from the equation

$$A = \epsilon(\text{NaOH}) c(\text{NaOH}) + \epsilon(\text{EtONa}) \cdot [c(\text{T}) - c(\text{NaOH})],$$

where A is the absorbance measured, $c(\text{T})$ is the total concentration of sodium ions, $c(\text{NaOH})$ is the hydroxide concentration and $c(\text{EtONa}) = c(\text{T}) - c(\text{NaOH})$ is the concentration of sodium ethoxide in the mixture. An analogous procedure applied to the water-2-propanol system gave the spectra which did not fit in the Lambert-Beer law and which therefore were not considered further.

RESULTS AND DISCUSSION

In order to estimate errors of the kinetic method, which presumes no effect of medium on the rate constant, the solvolysis was followed of phthalic anhydride and phosphoric acid esters in neutral and basic water-alcohol mixtures, respectively. The net rate constants k of the solvolytic reaction of phthalic anhydride in the water-ethanol and water-2-propanol systems are summarized in Table I, together with the rate constants $k(\text{H}_2\text{O})$ or $k(\text{ROH})$ of hydrolysis or alcoholysis, respectively. The used experimental method made it possible to measure the rate constants in the water-ethanol system with the water content less than 70 wt. %. It is apparent that the rate constants vary considerably with the solution composition, namely they

TABLE I

Rate constants k from Eq. (7), $k(\text{H}_2\text{O})$ and $k(\text{ROH})$ from Eq. (10), their ratio and the ratio of concentrations $c(\text{acid})$ and $c(\text{ester})$ of products in solvolysis of phthalic anhydride in the water-alcohol mixtures

Alcohol conc., wt. %	$k \cdot 10^3$, s^{-1}	$\frac{c(\text{ester})}{c(\text{acid})}$	$k(\text{H}_2\text{O}) \cdot 10^4$, $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$k(\text{ROH}) \cdot 10^4$, $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$\frac{k(\text{H}_2\text{O})}{k(\text{ROH})}$
Water-ethanol					
10	—	0.085	—	—	0.511
20	—	0.204	—	—	0.479
30	9.32	0.348	1.78	3.87	0.481
40	7.20	0.498	1.53	3.02	0.523
50	5.30	0.650	1.26	2.14	0.589
60	4.11	0.82	1.16	1.64	0.707
70	2.49	1.02	0.84	0.974	0.873
80	1.38	1.33	0.612	0.555	1.10
90	0.915	1.97	0.648	0.391	1.66
Water-2-propanol					
10	10	0.011	1.98	5.3	0.351
20	8.55	0.027	1.71	3.7	0.462
30	5.88	0.041	1.28	2.43	0.527
40	3.94	0.054	0.93	1.72	0.54
50	2.73	0.071	0.76	1.10	0.69
60	2.06	0.081	0.71	0.68	1.04
70	1.44	0.109	0.63	0.54	1.17
80	0.95	0.165	0.58	0.37	1.57
90	0.41	0.28	0.47	0.16	2.94

decrease with the decreasing dielectric permittivity and the ratios $k(\text{H}_2\text{O})/k(\text{ROH})$ also change.

For basic hydrolysis enough data regarding the effect of medium on the rate constant can be found in modern literature, but mixtures of water with aprotic solvent are used in recent literature for the equilibrium expressed by the equation (A). In two-component solvents with only one protogenic component, the rate constant is usually a function of the inverse relative dielectric permittivity of the solvent. For a verification of this correlation in water-alcohol systems, the esters of phosphoric acid were chosen as substrates, the solvolytic mechanism of which is known²³⁻²⁵. It was shown by means of chromatographic analysis that these substances undergo the re-esterification with a conversion degree no more than 3% in 50 wt. % ethanol and even less in 50 wt. % 2-propanol. Therefore the re-esterification can be neglected, which makes the reacting system more transparent.

In the kinetic study of solvolysis, the dissociation constants of esters of anilido- and dianilidophosphoric acids were measured first, cf. Table II for the results. The dissociation has an effect on the experimental rate constant k_{exp} of hydrolysis of these acids, which was therefore corrected using

$$k = k_{\text{exp}}[K^* + a(\text{H}^+)]/a(\text{H}^+), \quad (12)$$

where k is the corrected rate constant and K^* is the dissociation constant given in Table II. For substances which do not dissociate, the constants k_{exp} and k equal to each other. The constants obtained in this way were extrapolated to the zero ionic strength to yield $\log k^0(\text{OH}^-)$ (Table III). From the known autoprotolysis

TABLE II

Dissociation constants of phenyl dianilidophosphate (I) and diphenyl anilidophosphate (II) in the water-alcohol system at 25°C and ionic strength 0.05 mol dm⁻³

Medium	Alcohol conc., wt. %	pK*	
		I	II
Water-ethanol	10	12.7	13.2
	20	12.75	—
	30	12.9	13.7
	40	13.2	—
	50	13.5	14.8
Water-2-propanol	20	13.2	13.8
	50	14.0	14.3

constants²⁶, ratio of activities of lyate ions² and the pH found, the activity of OH⁻ ions was calculated according to the equation

$$K = a(\text{H}^+) \cdot a(\text{OH}^-) [1 + (a(\text{RO}^-)/a(\text{OH}^-))]. \quad (13)$$

Upon dividing the rate constant $k^0(\text{OH}^-)$ by the activity of OH⁻ ions, the second-

TABLE III

First- and second-order rate constants $k^0(\text{OH}^-)$ and $k^0 = k^0(\text{OH}^-)/a(\text{OH}^-)$, respectively, for hydrolysis of phosphoric acids esters in various media at zero ionic strength and 25°C

Medium	pH/−log $k^0(\text{OH}^-)$					−log k^0
$(\text{C}_6\text{H}_5\text{O})_2\text{P}(\text{O})\text{C}_6\text{H}_5$						
10% EtOH	12.50/2.12	12.06/2.51	11.85/2.78	10.46/4.15		0.32
30% EtOH	12.69/2.89	12.58/3.04	12.10/3.54	12.02/3.60		0.47
50% EtOH	13.11/3.06	12.85/3.32	12.58/3.65	12.30/3.92		0.36
20% 2-PrOH	12.82/2.58	12.60/2.85	12.38/3.10	12.08/3.40		0.45
50% 2-PrOH	13.32/3.06	13.26/3.20	13.15/3.30	12.22/4.21		0.47
$(\text{C}_6\text{H}_5\text{O})_3\text{PO}$						
10% EtOH	12.35/3.17	12.32/3.22	12.25/3.26	12.16/3.37	11.90/3.64	1.17
30% EtOH	12.79/3.69	12.73/3.78	12.69/3.83	12.59/3.88	12.20/4.30	1.50
50% EtOH	13.25/3.74	13.11/3.86	13.00/4.00	12.88/4.15	12.68/4.40	0.99
20% 2-PrOH	12.90/3.33	12.74/3.50	12.48/3.73	12.24/3.90	11.20/4.85	1.70
50% 2-PrOH	13.48/3.80	13.38/3.90	13.08/4.19	12.75/4.50		1.45
$(\text{C}_6\text{H}_5\text{O})_2\text{P}(\text{O})\text{NHC}_6\text{H}_5$						
10% EtOH	12.42/4.02	12.33/4.15	12.18/4.25	12.16/4.29	11.95/4.49	2.23
20% EtOH	12.68/3.87	12.42/4.19	12.15/4.48	11.60/4.99		1.79
30% EtOH	12.76/3.92	12.68/4.01	12.58/4.15	12.53/4.14	12.05/4.66	1.62
50% EtOH	12.92/3.92	12.81/4.02	12.52/4.34			1.32
50% EtOH	13.22/4.15	13.15/4.22	13.07/4.29	13.02/4.34	12.66/4.73	1.65
20% 2-PrOH	12.92/3.75	12.80/3.99	12.55/4.25	12.13/4.68		1.72
50% 2-PrOH	13.46/4.09	13.34/4.17	13.10/4.39	12.90/4.61		1.76
$\text{C}_6\text{H}_5\text{OP}(\text{O})(\text{NHC}_6\text{H}_5)_2$						
10% EtOH	12.52/4.77	12.40/4.90	12.30/4.99	12.19/5.11	11.89/5.29	3.35
30% EtOH	12.82/5.01	12.77/5.03	12.72/5.11	12.60/5.23	12.50/5.37	2.49
50% EtOH	13.19/5.17	13.16/5.23	13.09/5.35	13.04/5.38	12.90/5.51	2.44
20% 2-PrOH	12.90/4.77	12.72/5.00	12.55/5.13	12.36/5.36	12.15/5.55	2.89
50% 2-PrOH	13.56/4.83	13.35/5.09	13.25/5.26	12.54/5.95		2.33

-order rate constant k^0 of the hydrolysis was obtained

$$v = k^0 \cdot a(\text{OH}^-) \cdot c(\text{ester}). \quad (14)$$

Logarithms of the rate constants k^0 evaluated by least square method are given in Table III. In general, it is assumed that the logarithm of the rate constant for the reaction between an ion and a dipole should be a linear function of the inverse relative permittivity ϵ_r of solvent²². The correlation of $\log k^0$ with the inverse ϵ_r taken from literature²⁷ is shown in Fig. 1. It is apparent that the experimental data on hydrolysis in water-ethanol and water-2-propanol systems fall on a single line. Unfortunately, the plots obtained for diphenyl anilidophosphate and phenyl di-anilidophosphate have a visible maximum, in contrast to theoretical predictions. Experimental results on hydrolysis of triphenyl phosphate suffer probably from an error caused by the subsequent hydrolysis of resulting diphenylester. Therefore, it seems that in the concentration range studied only diphenyl phosphonate fulfills the requirement of low or negligible effect of the solvent composition on k^0 .

The reaction centre of the model substrates used, *i.e.* phosphor atom, is sterically strongly hindered and only the hydrolytic reaction occurs here, thus making the reacting system simpler. The non-linear dependence of $\log k^0$ on the solvent composition, together with the results obtained in the study of solvolysis of phthalic

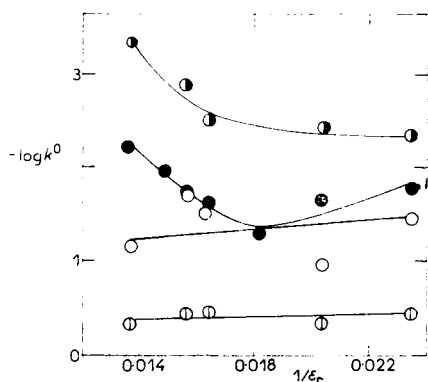


FIG. 1

Dependence of $\log k^0$ on $1/\epsilon_r$ for hydrolysis of phenyl esters of phosphoric acid in the water-ethanol and water-2-propanol systems at 25°C: $\text{C}_6\text{H}_5\text{O}-\text{P}(\text{O})(\text{NHC}_6\text{H}_5)_2$ ● $(\text{C}_6\text{H}_5\text{O})_2\text{P}(\text{O})\text{NHC}_6\text{H}_5$ ● $(\text{C}_6\text{H}_5\text{O})_3\text{PO}$ ○ $(\text{C}_6\text{H}_5\text{O})\text{P}(\text{O})\text{C}_6\text{H}_5$ ○

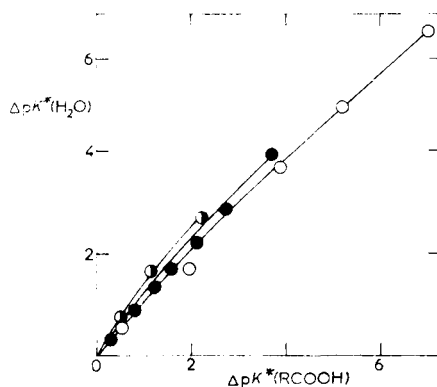


FIG. 2

Correlation between $\Delta pK^*(\text{H}_2\text{O})$ and $\Delta pK^*(\text{CH}_3\text{COOH})$ in the water-dioxane ○ and water-acetone ● systems or between $\Delta pK^*(\text{H}_2\text{O})$ and $\Delta pK^*(\text{HCOOH})$ in the water-dimethylsulphoxide ● system at 25°C and zero ionic strength

anhydride, indicate that neglecting the effect of medium on $\log k^0$ can in some cases lead to considerable errors. Though it may happen that some of reactions have the rate constant of hydrolysis independent of the solvent composition, existence of such a model reaction is not implied by kinetic experiments only.

The difficulties encountered in using the kinetic method for the evaluation of activities of lyate ions led us to attempts at the extension of Eq. (3) to cases when the general acid HA is water. Since this equation is empirical one, its validity in other cases must be verified experimentally. Such a verification is shown in Fig. 2 for the water-dioxane, water-acetone and water-dimethylsulphoxide systems. In the former two systems acetic acid was used as a standard, whose pK^* values were taken from the literature^{8,29} or derived from present measurements, as described in the experimental section. In case of the water-dimethylsulphoxide system few pK^* values for acetic acid are available over the sufficiently broad concentration range of the organic co-solvent. Therefore formic acid was used here as a standard, for which pK^* values were taken from the literature⁸. The constants of autoprotolysis of water were also taken from the literature^{26,29-32} and supplemented by data given in the experimental section. Upon dividing $K(H_2O)$ by the activity of water, its dissociation constants $K^*(H_2O)$ in the mixture were obtained. The values of activity coefficients were again taken from the literature^{30,33} or, eventually, calculated from the literature data³⁴. The activity coefficients are usually given in the molar fraction scale. The pK values from the literature, which refer to the molarity scale, were therefore re-calculated to give those in the mole fraction scale using the known equations³⁵ and the density data^{30,36-38}. From Fig. 2 the conclusion can be drawn that the experimental data fit in Eq. (3).

Eq. (3) was further applied to the water-ethanol and water-2-propanol systems. The values of $K(H_2O)$ were taken from the literature² or calculated according to Eq. (1) from the known values of K_b (ref.²), $K(ROH)$ and $a(ROH)$, where $K(ROH)$ is the constant of autoprotolysis of ethanol³⁹⁻⁴¹ or 2-propanol^{39,41-43} and $a(ROH)$ is the activity of alcohol. Activity coefficients of water or alcohol in a mixture^{44,45} and densities of the two-component solvents are known as well^{46,47}. The $pK^*(H_2O)$ values obtained in this way are summarized in Table IV. The corresponding differences $\Delta pK^*(H_2O)$ together with $\Delta pK^*(CH_3COOH)$, which were calculated from the literature data^{8,48}, represent a sufficiently large set of data for the evaluation of the constants W and j in Eq. (3) by least square technique. Once these parameters were known, the $\Delta pK^*(CH_3COOH)$ values for the individual mixtures were inserted into Eq. (3) to get $\Delta pK^*(H_2O)$, which along with $pK^*(H_2O) = 15.74$ for pure water, were used for the evaluation of $pK^*(H_2O)$ and inversely of $pK(H_2O)$ in mixtures quoted in Table IV. On the basis of the known constant of autoprotolysis^{2,26,29} the $pK(C_2H_5OH)$ values can be inferred, which are also given in Table IV. It is apparent that, except for 10 wt. % ethanol, the agreement between the ionization constants of ethanol calculated from the literature data² by means of Eqs (2) and (3)

is good. Autoprotolysis constants of water in mixtures^{2,26,29} were used for the evaluation of the ratio of lyate activities according to Eq. (13), with the results also given in Table IV.

In a similar way, the $pK^*(H_2O)$ values were obtained from the literature data² for the water–2-propanol system, cf. Table IV. Unfortunately, the $pK^*(CH_3COOH)$ values in pure 2-propanol which would be sufficiently reliable, were not found in the literature. Therefore, benzoic acid was used as the model acid, for which the

TABLE IV

Dissociation constants (in mole fraction scale) and constants of autoprotolysis (in molarity scale) of water and alcohol in mixtures, and the ratio of lyate ion activities at 25°C

Alcohol conc., wt. %	$pK^*(H_2O)^a$	$pK^*(ROH)^a$	$pK^*(H_2O)^b$	$pK^*(ROH)^b$	$pK(H_2O)$	$pK(ROH)$	$a(RO^-)$ $a(OH^-)$
Water–ethanol							
0	15.74	—	—	—	14.00	—	—
10	16.02	15.95	16.05	15.57	14.33	14.71	0.41
20	16.29	15.93	16.31	15.97	14.61	14.79	0.66
30	16.71	16.07	16.57	16.17	14.89	14.84	1.13
40	—	—	16.81	16.38	15.17	14.97	1.57
50	17.30	16.41	17.28	16.50	15.68	15.04	4.36
60	—	—	17.62	16.69	16.08	15.20	7.52
70	—	—	18.02	16.81	16.56	15.28	19.0
80	—	—	18.62	17.03	17.28	15.45	68.1
90	—	—	19.25	17.94	18.17	16.30	74.9
100	22.37 ^c	—	—	—	—	18.67	—
Water–2-propanol							
10	16.08	16.25	16.14	16.02	14.41	14.88	0.34
20	16.48	16.31	16.49	16.34	14.77	14.96	0.65
30	16.85	16.35	16.85	16.44	15.15	14.99	1.46
40	—	—	17.19	16.65	15.50	15.14	2.33
50	17.56	17.02	17.57	16.85	15.89	15.34	3.55
60	—	—	17.97	17.15	16.29	15.63	4.62
70	—	—	18.42	17.72	16.76	16.17	5.84
80	—	—	18.98	18.55	17.32	16.97	2.25
90	—	—	19.65	20.12	18.13	18.49	0.44
100	21.20 ^d	—	—	—	—	20.58	—

^a Calculated from constants of autoprotolysis² and activities of water and alcohol. ^b By using Eq. (3). ^{c,d} From the literature data (refs^{2,41} or refs^{2,42}, respectively).

ΔpK^* values were calculated from the literature data^{11,49}. The results obtained by using the same procedure as above are also given in Table IV.

A difficulty encountered here consists in that for the evaluation of K_h from the experimental data the proton shift in hydroxyl group $\Delta(\text{OH}^-)$ has to be estimated⁶, which may introduce a subjective error. In order to avoid this uncertainty, UV spectra were analysed. The values of K_h thus obtained can be compared with those derived by Slonim method⁶ only after their extrapolation to the zero water concentration. Unfortunately, the dependences of K_h on both $x(\text{H}_2\text{O})$ and $1/\epsilon_r$ are not linear and hence, their extrapolation is not safe. Moreover, the assumption involved, that the absorption coefficients are independent of medium, could not be verified and finally, the alcohol used was not quite dry. Apart from this uncertainty, K_h was estimated to be higher than 0.5. The data $K_h = 0.46, 0.5$ and 1.27 found in the literature⁵⁰ are based on the use of indicators, while the analysis of ^1H NMR spectra yields $K_h = 3.55$ (ref.²). Obviously, UV or visible spectroscopy give the estimates, which are somewhat lower but, nevertheless, not very different from the NMR value. Since then the former methods are based on unverified assumptions, the value derived from ^1H NMR spectra need not be necessarily revised.

In order to check the reliability of the $pK^*(\text{H}_2\text{O})$ values found, the data from Table IV were plotted *vs* $1/\epsilon_r$ (ref.²⁷). These plots are shown in Fig. 3 together with those for the water-methanol or water-acetone systems, the latter two being based on the values derived from the literature data or calculated in constructing plots for Fig. 2, respectively. While the water-methanol system exhibits a quite different behaviour, the $pK_{\text{H}_2\text{O}}^*$ *vs* $1/\epsilon_r$ plots for the water-ethanol and water-2-propanol systems coincide with that for the water-acetone system up to the alcohol concentration of 50 wt. %. For the water-ethanol and water-acetone systems this coincidence even extends towards higher alcohol concentrations. It seems therefore that the $pK^*(\text{H}_2\text{O})$ values in the water-ethanol system were determined with the sufficient accuracy. Less transparent is the situation in the water-2-propanol systems, for which

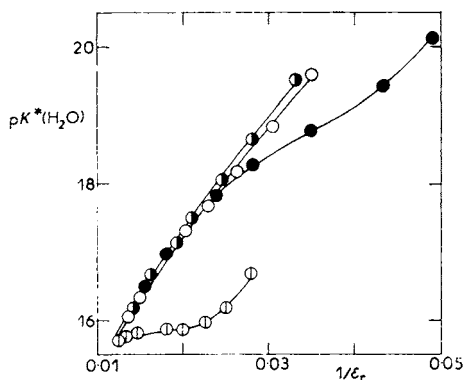


FIG. 3

Dependence of $pK^*(\text{H}_2\text{O})$ on $1/\epsilon_r$ at 25°C in the water-methanol \circ ; water-acetone \bullet , water-ethanol \circ , and water-2-propanol \bullet systems

TABLE V
Ratio of the product concentrations in solvolysis of phthalic anhydride and the ratio of the rate constants for solvolytic reactions in alcoholic solutions at 25°C

Alcohol conc., wt. %	System									
	water-methanol				water-ethanol				water-2-propanol	
	neutral		alkaline		alkaline		alkaline		alkaline	
$\frac{c(\text{ester})}{c(\text{acid})}$	$\frac{k(\text{H}_2\text{O})}{k(\text{MeOH})}$	$\frac{c(\text{ester})}{c(\text{salt})}$	$\frac{k(\text{OH}^-)}{k(\text{MeO}^-)}$	$\frac{c(\text{ester})}{c(\text{salt})}$	$\frac{k(\text{OH}^-)}{k(\text{EtO}^-)}$	$\frac{c(\text{ester})}{c(\text{salt})}$	$\frac{k(\text{OH}^-)}{k(\text{EtO}^-)}$	$\frac{c(\text{ester})}{c(\text{salt})}$	$\frac{k(\text{OH}^-)}{k(2\text{-PrO}^-)}$	
10	0.286	0.218	4.41	0.024	1.9	0.216	0.553	0.095	0.606	
20	0.647	0.217	5.78	0.044	2.7	0.244	0.771	0.161	0.800	
30	1.09	0.221	6.54	—	3.64	0.311	0.908	0.247	1.023	
40	1.613	0.232	6.93	—	4.44	0.353	0.987	0.369	0.464	
50	2.097	0.268	7.54	0.140	5.27	0.827	0.908	0.438	0.330	
60	2.538	0.332	8.07	0.197	5.59	1.345	0.987	0.476	0.464	
70	3.125	0.420	8.66	0.290	5.61	3.384	0.987	0.601	0.464	
80	3.806	0.590	8.79	0.516	6.00	11.34	0.987	0.772	0.464	
90	4.839	1.045	8.75	1.457	6.04	12.39	0.987	0.941	0.330	

the drop in $pK^*(H_2O)$ at higher concentration of alcohol need not be caused by a systematic error, because it is not clear which type of dependence is to be expected.

The data given in Table IV make it possible to compare the selectivity of the neutral and alkaline solvolysis in various types of reactions. These selectivities are defined by Eqs (15) and (16), which follow immediately from Eqs (10) and (11)

$$S_{\text{neutr.}} = \log [k(H_2O)/k(ROH)] = \\ = \log \{ [c(ROH)/c(H_2O)] [c(\text{acid})/c(\text{ester})] \} \quad (15)$$

$$S_{\text{alk.}} = \log [k(OH^-)/k(RO^-)] = \\ = \log \{ [c(RO^-)/c(OH^-)] [c(\text{salt})/c(\text{ester})] \} . \quad (16)$$

As the model reactions the solvolyses of phthalic anhydride and benzyl chloride were chosen, because the solvolytic reactions of anhydrides follow S_N2 mechanism^{51,52}, while in solvolysis of benzyl chloride both S_N1 and S_N2 mechanisms can be encountered⁵³. For the evaluation of selectivity of alkaline solvolysis, the concentration ratios of the reaction products of phthalic anhydride were followed, which upon their insertion into Eq. (16) along with the known ratios of nucleophiles, made it possible to calculate the ratio $k(OH^-)/k(RO^-)$ cf. Table V. In Fig. 4 $\log [k(OH^-)/$

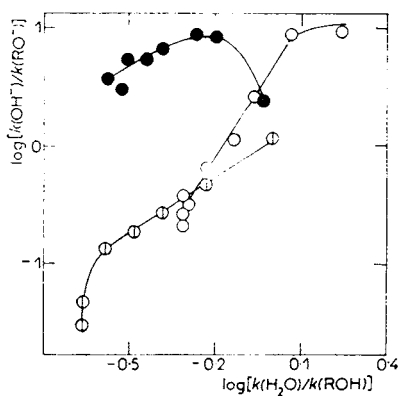


FIG. 4

Neutral and alkaline selectivity of solvolysis of phthalic anhydride at 25°C in various mixtures. Plots of $\{ \log [k(OH^-)/k(MeO^-)] - 1 \}$ vs $\log [k(H_2O)/k(MeOH)]$ ○; $\log [k(OH^-)/k(EtO^-)]$ vs $\log [k(H_2O)/k(EtOH)]$ ⊙; and $\log [k(OH^-)/k(2-PrO^-)]$ vs $\{ \log [k(H_2O)/k(2-PrOH)] - 1 \}$ ●

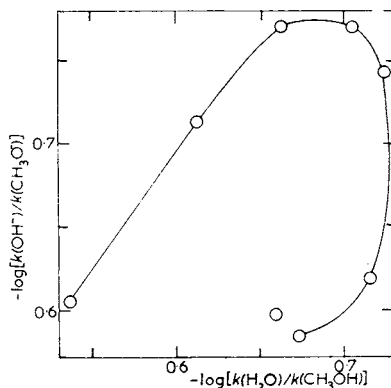


FIG. 5

Neutral and alkaline selectivity of solvolysis of benzyl chloride in the water-methanol system at 25°C. For alkaline selectivity the values of $\log [k(OH^-)/k(CH_3O^-)]$ at the base concentration of 0.01 mol dm^{-3} were used

$k/(\text{RO}^-)]$ is correlated with $\log [k(\text{H}_2\text{O})/k(\text{ROH})]$ found in the study of the neutral solvolysis. In the case of the water/methanol system the ratios of lyate activities were taken from the literature¹, for other systems the data in Table IV were confronted with the previous ones², which were preferred in the case of disagreement. Advantegously, by this procedure the effects are removed of the solvent structure and of the change in solvation of phthalic anhydride, which should be the same in both the neutral and alkaline regions. As it can be seen from Fig. 4, unlike the selectivity of the neutral solvolysis that of the alkaline one begins to vary from the very low methanol concentrations. This is true up to the methanol concentration of 50 wt. %, above which the selectivity of the neutral solvolysis also changes. Apparently, the water-ethanol system shows about the same behaviour, variation in the selectivity of neutral solvolysis being more pronounced for the ethanol concentrations close to 100%.

The correlation between selectivities in the water-2-propanol system is somewhat different, namely the selectivity of both the neutral and alkaline solvolysis starts to vary with the first portions of the organic co-solvent. At the concentrations of 2-propanol higher than 60 wt. %, only the selectivity of the neutral solvolysis varies and the system resembles the water-ethanol one with the high alcohol concentration. For 90 wt. % 2-propanol the selectivity of the alkaline solvolysis decreases, this point is not shown in Fig. 4. Since the correlation selectivity-selectivity results from the stabilization of the reactants, activated complex and intermediates (if any) by the

TABLE VI

Ratio of concentrations of benzyl methyl ether and benzyl alcohol produced in solvolysis of benzyl chloride in neutral and alkaline region in the water-methanol system at 25°C and various concentrations of NaOH in the solution

Methanol conc., wt. %	Neutral	Concentration ratio in alkaline medium (NaOH, mol dm ⁻³)			
		0.01	0.02	0.03	0.05
10	0.294	0.409	0.555	0.72	0.846
20	0.639	1.024	1.410	1.848	2.151
30	1.263	1.965	2.718	3.690	4.670
40	2.030	3.482	5.056	6.975	8.471
50	2.993	5.905	8.644	11.798	23.339
60	4.294	9.457	14.704	21.408	45.504
70	6.032	15.014	25.467	41.644	114.263
80	9.201	23.488	54.808	—	—
90	17.325	51.14	109.5	—	—

solvent both in the neutral and alkaline solvolysis, this decline is difficult to discuss. Owing to the lack of information about this effect, such a decline cannot be excluded in advance.

When another substrate is used, the correlation between selectivities can change considerably. To illustrate the point, Fig. 5 shows the correlation selectivity-selectivity for the alkaline and neutral solvolysis of benzyl chloride in the water-methanol system. In this case the substrate as well as the reaction mechanism and, undoubtedly, the substrate-solvent interactions, differ considerably from the previous ones, thus underlying the correlation quite dissimilar to those shown in Fig. 4. Experimental data, which are summarized in Table VI, indicate that the selectivity of the reaction depends strongly on the base concentration. The reason for this effect is not clear.

Obviously, for the different substrates the different correlations selectivity-selectivity are found, though the general validity of this conclusion need to be confirmed by additional experimental data. Nevertheless, one of applications suggested by the present work is the study of the selectivity of the alkaline solvolysis. For its evaluation, the ratio of lyate ion activities has to be known. When the results obtained by various methods⁷ are compared, the data reported¹ for the ratios of activities in the water-methanol system appears to be rather accurate. With the reference to Figs 3 and 4, their accuracy is satisfactory also for the water-ethanol system, whereas there is some uncertainty at higher alcohol concentrations in the water-2-propanol system, for which the plots shown in Figs 3 and 4 decline from those for all other water-organic co-solvent systems. Consequently, the latter system deserves some more attention.

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