

AUTOPROTOLYSIS CONSTANTS AND ACTIVITY RATIOS OF THE LYATE IONS IN WATER-ALCOHOL MIXTURES

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The autoprotolysis constants were determined potentiometrically for water-ethanol, water-1-propanol, water-2-propanol, and water-2-methyl-2-propanol mixtures containing alcohol in concentrations of 60% (m/m) and more. Three methods were employed for the calculation of the activity ratios of the lyate ions in the systems: an empirical method based on the autoprotolysis constant and the activities of the solvent constituents, a method based on thermodynamic data, particularly the Gibbs energies of ion transfer from water to the mixed solvent, and a method based on ¹H NMR data. The results of the three methods are mutually compared and discussed. The known heats of ionization for the water-ethanol system and the ionization constants of the components enabled the entropy of ionization of a mixture of water with ethanol to be calculated.

One of the significant constants of a solvent is the autoprotolysis constant, defined as

$$K_s = a_{H^+} a_{L^-}, \quad (1)$$

where a_{H^+} is the activity of protons and a_{L^-} is the activity of the lyate ions in the solvent in question. In a solvent containing two protogenic components, water and alcohol for instance, the reaction



takes place; as a result, hydroxyl and alkoxy ions coexist in the solution. Eq. (1) can be thus modified to

$$K_s = a_{H^+}(a_{OH^-} + a_{RO^-}) = K_w + K_{alc}, \quad (2)$$

where K_w and K_{alc} are the products of the activity of protons and that of the hydroxyl and alkoxy ions, respectively, in the solvent concerned. Eq. (2) then can be rearranged to give

$$K_s = K_w(1 + a_{RO^-}/a_{OH^-}) = K_w(1 + Q) \quad (3)$$

from which the activity ratio of the lyate ions $a_{RO^-}/a_{OH^-} = Q$ can be calculated if the K_s and K_w values are known.

The autoprotolysis constant is determined, most frequently, based on measurements of the electromotive voltage of a cell consisting of an indicating (usually hydrogen) electrode submerged in an acid or base solution in the solvent of interest, and a reference electrode, usually a silver

chloride electrode in the solvent concerned^{1,2} or a saturated calomel electrode in water connected with the solution measured *via* a salt bridge³. The constant thus obtained, involving an error of about ± 0.02 pK_s units due primarily to the liquid junction potentials (± 0.5 mV, refs^{4,5}), agrees well with the values obtained by other methods⁶.

Reaction (A) proceeds to an equilibrium characterized by the equilibrium constant

$$K = (a_{\text{OH}^-} a_{\text{ROH}}) / (a_{\text{RO}^-} a_{\text{H}_2\text{O}}) \quad (4)$$

Knowing the K value and the activities of water and alcohol in the mixture, the activity ratio of the lyate ions can be calculated, or *vice versa*, the value of the constant K is obtainable from the known Q ratio value and, again, the activities of water and alcohol in the mixture.

Three different methods have been suggested for the calculation of the activity ratio of the lyate ions.

In one of them⁷, use is made of the empirical equation

$$\text{p}K_s = \text{p}K_w - j \log a_{\text{H}_2\text{O}} + \log(1 + Q) \quad (5)$$

$$Q = k(a_{\text{ROH}})^p / (a_{\text{H}_2\text{O}})^q; \quad (6)$$

the k , j , p , q parameters are sought to fit well the experiment.

In the second method⁸, the Gibbs energies of hydrogen ion transfer from water to the solvent in question are used, assuming that the Gibbs energy of transfer of the lyate ions from water to the solvent is directly proportional to the mole fraction of alcohol, or to the Gibbs energy of transfer of halide ions from water to the solvent. Then the equation

$$\log [(K_s \gamma_{\text{H}^+} / a_{\text{H}_2\text{O}}^w) - (K_{\text{ROH}}^w a_{\text{ROH}}^w Y_1 / a_{\text{H}_2\text{O}}^w)] = -Y_2 + \log K_{\text{H}_2\text{O}}^w \quad (7)$$

can be derived; the superscript w refers to pure water as the standard state. If the Gibbs energies of transfer of the lyate ions from water to the water-alcohol mixture are directly proportional to the mole fraction of alcohol (x_{ROH}), then⁸

$$Y_1 = \exp(-k_{\text{RO}^-} x_{\text{ROH}} / RT); \quad Y_2 = 2.303 k_{\text{OH}^-} x_{\text{ROH}} / RT \quad (8a,b)$$

$$\gamma_{\text{OH}^-} = \exp(k_{\text{OH}^-} x_{\text{ROH}} / RT); \quad \gamma_{\text{RO}^-} = \exp(k_{\text{RO}^-} x_{\text{ROH}} / RT) \quad (9a,b)$$

If the Gibbs energies of transfer of the lyate ions from water to the solvent system are directly proportional to those of transfer of halide ions from water to the solvent system, then

$$Y_1 = \gamma_{\text{h}}^{-k_1}; \quad Y_2 = k_2 \log \gamma_{\text{h}} \quad (10a,b)$$

$$RT \ln \gamma_{\text{h}} = (\Delta\mu_{\text{Cl}^-}^0 + \Delta\mu_{\text{Br}^-}^0 + \Delta\mu_{\text{I}^-}^0) / 3 \quad (11)$$

$$\log \gamma_{\text{OH}^-} = k_2 \log \gamma_{\text{h}}; \quad \log \gamma_{\text{RO}^-} = k_1 \log \gamma_{\text{h}} \quad (12a,b)$$

In Eq. (7), γ_{H^+} is the activity coefficient of hydrogen ions with respect to pure water as the standard state.

The third method⁹ is based on ¹H NMR spectral measurements, the K value in Eq. (3) being calculated as

$$K = c_{\text{ROH}} (\Delta_{\text{H}_2\text{O}} - \alpha) / [c_{\text{RO}^-} (\Delta_{\text{RO}^-} - \Delta_{\text{OH}^-} + \alpha)], \quad (13)$$

where c_{ROH} and c_{RO^-} are the initial concentrations of alcohol and alkoxide, respectively, Δ are the differences of the O—H signal shifts extrapolated to zero concentration, and α is the ratio of the frequency difference of the O—H signal of the alkoxide-alcohol-water system to the water concentration difference,

$$\alpha = (d\delta/dc_{\text{H}_2\text{O}})_{c_{\text{H}_2\text{O}}=0} \quad (14)$$

EXPERIMENTAL

Methanol, ethanol, 2-propanol, and 2-methyl-2-propanol *p.a.* (Lachema) and 1-propanol (Reakhim, Erevan) were dried conventionally¹⁰ and distilled preventing access of atmospheric humidity. Acid and alkaline solutions were made up using HClO_4 and NaOH , respectively, both of *p.a.* purity (Lachema). NaClO_4 *p.a.* (Lachema) was employed for adjusting the ionic strength to 0.005–0.1 mol dm^{-3} .

The electromotive voltage of the hydrogen — saturated calomel electrode cell was measured on an OP-205 pH-meter (Radelkis, Budapest). All measurements were performed at $25 \pm 0.1^\circ\text{C}$.

For the ^1H NMR measurements, solutions of sodium alkoxide or water in alcohol were prepared in concentrations up to 15% mol (up to 5% mol. for 2-propoxide in 2-propanol). Solutions of water in alcohol-alkoxide mixtures contained water in concentrations up to 14.2% mol; alkoxide was present in a constant concentration of 10% mol (for 2-propoxide, 2.5% mol). The spectra were measured on a Varian T60 instrument using tetramethylsilane as the external standard. The chemical shifts were read by means of a Varian T 6024-3 frequency counter with a precision of ± 1 Hz.

RESULTS AND DISCUSSION

Autoprotolysis constants. The autoprotolysis constants for the water-alcohol mixtures were obtained by extrapolating the potentiometric data to zero ionic strength; the values are given in Table I. The error did not exceed ± 0.02 $\text{p}K_s$ units except for 90% (m/m) 2-methyl-2-propanol, where the well-known difficulties arising when working with concentrated solutions at low temperatures resulted in an error of ± 0.5 $\text{p}K_s$ units. In Fig. 1 the values are compared with published data. The autoprotolysis constants found in this work depend on the solution composition similarly as those for the water-methanol system¹¹, for the water-ethanol system they approach the published values¹², and for the other water-alcohol systems they are consistent with the data^{1,13-18}. In alcohol-rich regions the $\text{p}K_s$ values increase markedly with increasing alcohol content. This effect can be well explained in terms of basicity of the components: in water-alcohol systems, water is the more basic constituent¹⁸, and thus a decrease in its content necessarily leads to a decrease in the dissociation of acids and thus to an increase in the $\text{p}K_s$ values. In the range of twenty and more per cent alcohol there is an inflexion on the $\text{p}K_s$ vs alcohol concentration curve (Fig. 1); in this range the occurrence of alcohol hexahydrate has been suggested¹⁹. Other measurements also point to structure changes in the concentration region in question²⁰, particularly for the water-2-methyl-2-propanol system²¹.

Activity ratios of the lyate ions. Water-methanol system. This system has been studied^{6,8} and the ratios of activities of the lyate ions determined based on Eqs (5)–(12). The two methods used afford results in a mutual agreement to within 30% over the entire alcohol concentration region. In order to assess to what extent the spectral method⁹ gives results consistent with the preceding ones, the ¹H NMR spectra were measured for solutions of sodium methoxide in methanol, water in methanol, and water in methanol-methoxide system. The dependences were similar as in⁹; the value obtained are $\Delta_{\text{H}_2\text{O}} = -0.88 \text{ Hz}/\% \text{ mol}$, $\Delta_{\text{CH}_3\text{O}^-} = 14 \text{ Hz}/\% \text{ mol}$, and $\alpha = -1.28 \text{ Hz}/\text{mol}$ (Eq. (14)). By substituting in Eq. (13), the K values were calculated to be 0.34 or 0.43 for the values of $\Delta_{\text{OH}^-} = 3$ or $5 \text{ Hz}/\% \text{ mol}$ suggested in ref.⁹. Based on the published values of the lyate ion activity ratio for 90% (m/m methanol)^{6,8} and the activities of water and methanol⁸, the K values were calculated from Eq. (4) to be 0.40 (ref.⁸) or 0.35 (ref.⁶). The three methods are seen to afford mutually consistent results.

TABLE I
p*K*_s Values for water-alcohol mixtures at 25°C and zero ionic strength

Alcohol	p <i>K</i> _s for the alcohol content, % (m/m)					
	95	90	85	80	70	60
Ethanol	16.85	16.29	15.66	15.44	15.26	14.97
1-Propanol	17.50	16.78	16.01	15.75	15.35	15.10
2-Propanol	—	17.97	—	16.81	16.07	15.54
2-Methyl-2-propanol	—	19.4	—	17.03	16.32	15.66

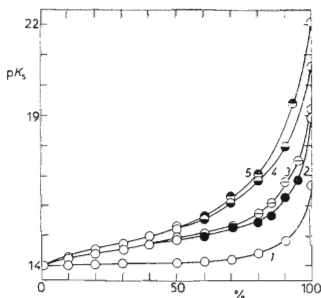


FIG. 1

Dependence of the autoprotolysis constant pK_s on the composition of the mixture (% (m/m) alcohol). System: 1 water-methanol, 2 water-ethanol, 3 water-1-propanol, 4 water-2-propanol, 5 water-2-methyl-2-propanol. The open circles represent published values^{1,11,13,18}

Water-ethanol system. For this system, the activity coefficients of the constituents^{22,23} as well as the Gibbs energies of transfer of hydrogen ions from water to 10, 20, 30, or 50% (m/m) ethanol²⁴ have been published, but no reasonable data could be derived when introducing these values in Eqs (7)–(9). Obviously, the starting assumption⁸ that the Gibbs energy of transfer of the lyate ions from water to the mixed solvent is directly proportional to the mole fraction of alcohol in the mixture is inapplicable to this system. Therefore, Eqs (7), (10)–(12) were employed; the Gibbs energies of transfer of halide ions from water to the mixed solvent were taken from ref.²⁴. The autoprotolysis constants of water and ethanol in mixture and the overall autoprotolysis constant were calculated from Eq. (2). The results are summarized in Table II along with the values obtained by interpolation of experimental data¹; the ratios of activities of the lyate ions calculated from Eq. (3) are given as well. The values calculated for 50% (m/m) ethanol disagree with the experiment. Since the activity coefficients of water and ethanol^{22,23} are in a good agreement, the cause of the difference is to be sought in a limited validity either of the extrathermodynamic assumption used in the calculation of the Gibbs energies of transfer of the ions²⁴, or of Eq. (11). Insufficient information is available for a detailed discussion. The calculation was therefore refined formally so that a γ_{H^+} value was chosen in Eq. (7) such that the left side complied with the linear character of the right side. The refined data are given in Table II too.

The known pK_s values of the water-ethanol system (ref.¹ and this work, Table I) and the activities of water and ethanol, calculated by means of concentrations and the activity coefficients^{22,23}, afforded the numerical values of the constants in Eqs (5) and (6), $p = 5.3$, $q = 0.98$, $k = 1.2$, $j = -10.4$. By using these values and Eq. (6), the activity ratios of the lyate ions were calculated; the data are also included in Table II. The results differ from those derived from Eq. (3); for 95% (m/m) ethanol, with the Q value calculated from Eq. (6) to be 1 175, Eq. (4) gives $K = 3 \cdot 10^{-3}$.

Equilibrium (A) was subjected also to spectral investigation. The experimentally obtained data were inserted in Eq. (13) ($\Delta_{NaOH} = 4 \text{ Hz/\% mol}$) to give $K = 3.55$. This is a value three orders of magnitude different from that derived from Eq. (4) using Q values obtained from Eqs (5), (6). This fact, together with the different Q value given in Table II, indicates that Eq. (5) is only applicable to low alcohol concentrations, for which the results agree with those of Eqs (7), (10)–(12) within an order of magnitude.

From the values of Table II inserted in equation²⁵ (15), defining the ΔG^0 quantity, and from the heats of ionization²⁷, the entropies of ionization of the mixed solvent at 25°C were calculated based on the relation $\Delta G^0 = \Delta H^0 - T\Delta S^0$. The results are also given in Table II.

$$\Delta G^0 = -RT(\beta_{OH^-} - \ln K_w + \beta_{C_2H_5OH}) \quad (15)$$

$$\beta_{\text{OH}^-} = n_{\text{OH}^-} / (n_{\text{OH}^-} + n_{\text{C}_2\text{H}_5\text{O}^-}); \quad \beta_{\text{C}_2\text{H}_5\text{O}^-} = 1 - \beta_{\text{OH}^-} \quad (16a,b)$$

n is the number of moles.

Water-1-propanol system. There are no data available concerning the Gibbs energies of ion transfer from water to this solvent; Eqs (7)–(12) were therefore inapplicable, and only Eqs (4)–(6) could be evaluated. By using the experimental autoprotolysis constants¹ and activities of water and 1-propanol calculated from the concentrations and activity coefficients²⁶, the constants of Eqs (5), (6) were calculated to be $p = 9.3$, $q = 0.96$, $k = 0.64$, $j = -18$. In this manner data were obtained

TABLE II

Autoprotolysis constants pK of water and alcohol in mixtures at 25°C, overall autoprotolysis constants calculated from Eq. (2), fractions of the lyate ion activities Q , and the Gibbs energies (kJ mol⁻¹), enthalpies (kJ mol⁻¹), and entropies (J mol⁻¹ K⁻¹), of ionization

Alcohol content (% m/m)	pK_w	pK_{alc}	pK_s		Q		ΔG^0	ΔH^{0b}	ΔS^0
			Eq. (2)	exp. ^a	Eq. (3)	Eq. (6)			
Water-ethanol system									
10	14.29	15.06	14.22	14.22	0.18	0.23	82.1	57.1	83.9
20	14.57	14.84	14.39	14.41	0.46	0.52	83.6	57.1	88.9
30	15.00	14.73	14.54	14.54	1.87	0.89	84.5	55.8	96.3
50	15.60	14.61	14.57	14.86	—	1.91	—	47.8	—
^c	—	14.95	14.86	—	4.52	—	85.7	—	127.2
Water-1-propanol system									
10	—	—	—	—	—	0.3	—	—	—
20	—	—	—	—	—	0.64	—	—	—
30	—	—	—	—	—	0.85	—	—	—
50	—	—	—	—	—	1.14	—	—	—
Water-2-propanol system									
10	14.36	15.11	14.29	14.28	0.18	0.40	—	—	—
20	14.73	14.93	14.52	14.56	0.65	0.89	—	—	—
30	15.31	14.90	14.76	14.76	2.53	1.34	—	—	—
50	16.11	15.01	14.97	15.23	12.78	1.68	—	—	—
^c	—	15.51	15.41	—	4.00	—	—	—	—

^a Interpolation of published data; ^b ref.²⁶; ^c calculated from the γ_{H^+} value satisfying the linear nature of Eq. (7).

requisite for the calculation of the activities of the lyate ions (Table II). For 95% (m/m) 1-propanol, $Q = 468$, whence the constant in Eq. (4) is $K = 4 \cdot 10^{-3}$, The NMR spectrometric investigation of the equilibrium afforded dependences from which the constant, for $\Delta_{\text{NaOH}} = 4 \text{ Hz/\% mol}$, is $K = 4.9$. Although being in accordance with the above-mentioned values for water-methanol, water-ethanol, and water-1-butanol⁹ ($K = 13$) systems, this value differs by three orders of magnitude from that obtained from Eqs (5), (6).

Water-2-propanol system. For this system both the activity coefficients of water and alcohol in their mixture²⁸ and the Gibbs energies of ion transfer from water to the solvent²⁴ are known. Similarly as for the water-ethanol system, the water and alcohol autoprotolysis constants cannot be calculated based on the assumption that the Gibbs energies of transfer of the lyate ions from water to the mixture are directly proportional to the mole fraction of alcohol. Eqs (8), (9) did not afford reasonable results either. Obviously the cause lies again in a departure of the water-2-propanol mixture from ideality¹⁹. The use of Eq. (11) resulted in satisfactory values only for highly dilute solutions of 2-propanol. Very likely, responsible for this effect is the well-known fact that the Gibbs energies of transfer of the ions from water to the solvent, and thus their activity coefficients in the solvent (aqueous solution represents the standard state), are dependent upon the ionic radii and upon the solvation²⁹. If the ions are approximately of the same size, the ionic radius is not relevant in the calculation of the Gibbs energy of ion transfer from water to the solvent and the average Gibbs energy of halide ion transfer can be employed. If, however, the ionic radii are different, as is the case with the OH^- and $(\text{CH}_3)_2\text{CHO}^-$ ions, the ion size has to be respected. Therefore, the original method⁸ was modified for this system so that the activity coefficients of OH^- ions were calculated from the Gibbs energies of transfer of Br^- ions, whereas those of the $(\text{CH}_3)_2\text{CHO}^-$ ions were calculated from the Gibbs energies of transfer of I^- ions according to the equations

$$\log \gamma_{\text{OH}^-} = k_{\text{OH}^-} \log \gamma_{\text{Br}^-} ; \quad \log \gamma_{\text{RO}^-} = k_{\text{RO}^-} \log \gamma_{\text{I}^-} ; \quad (17a, b)$$

the γ_{Br^-} and γ_{I^-} values thus replace the γ_{h} values in Eq. (12). These values were calculated from the relation

$$\Delta\mu_{\text{x}^-}^0 = RT \ln \gamma_{\text{x}^-} \quad (\text{X} = \text{Br}, \text{I}) . \quad (18)$$

The $\text{p}K_{\text{w}}$ and $\text{p}K_{\text{alc}}$ values so obtained are given in Table II. The autoprotolysis constant for 50% (m/m) 2-propanol evaluated by substituting in Eq. (2) and that found experimentally¹ are different. Therefore, similarly as for the water-ethanol system, the γ_{H^+} coefficient in Eq. (7) was chosen so that the left side complied with the linear character of the right side. The data thus obtained are given in Table II too.

The last method of measuring the activity ratio of the lyate ions is the spectral method. The ^1H NMR spectra were evaluated and the values of $\Delta_{\text{alkoxy}} = 10 \text{ Hz/\% mol}$, $\Delta_{\text{H}_2\text{O}} = -0.31 \text{ Hz/\% mol}$, $\alpha = -Y.67 \text{ Hz/\% mol}$ were obtained. For Δ_{NaOH} the mean value⁹ of 4 Hz/\% mol was chosen. By inserting in Eq. (13), $K = 13$ was obtained, agreeing with the K value for the water-1-butanol system⁹.

Water-2-methyl-2-propanol system. The Gibbs energies of transfer of hydrogen and halide ions water to this system^{24,30} as well as the activities of water and alcohol in the mixture³¹ are known, but their substitution in Eqs (7)–(12), (17), (18) did not give satisfactory results. This is probably due to the thermodynamic properties of the system being rather intricate¹⁹. Therefore, the likelihood of the results derived from Eqs (5), (6) could not be verified either. Unfortunately, the spectral method based in Eq. (13) was inapplicable because of the difficulties arising in the preparation of homogeneous solutions of 2-methyl-2-propoxide in 2-methyl-2-propanol at 25°C . Thus, there is so far no reliable method available for gaining information on the activity ratio of the lyate ions in the system under study.

It can be concluded that for a calculation of the equilibrium constant of reaction (A) the theoretically best founded results are obtained by means of the method based on Eq. (7). A weak point of the method is the necessity to know the Gibbs energies of transfer of the ions from water to the solvent under investigation, which can only be calculated under extrathermodynamic assumptions the choice of which is not always strictly objective. This shortcoming is to a degree offset by the fact that the validity of the assumption is manifested by the agreement of the experimental K_s values with those calculated from Eq. (2). The spectral method⁹ based on Eq. (13) provides information on the equilibrium only for solutions with low contents of water, and moreover, the Δ_{OH^-} value is only estimated. The last, and least founded, method relies on Eqs (5), (6). Its major shortcoming stems from the fact that the equations have no theoretical background, and thus the limits of their applicability cannot be theoretically estimated. As it appears, most adequate for the study of reaction (A) are Eqs (7)–(13), while Eqs (5), (6) have only a supplementary role.

The constants of autoprotolysis of water, as found in Table II and in ref.⁸, indicate that the ionization of water decreases with increasing content of alcohol in the solvent system. To a degree this is due to the loss of water as the basic component. For equal mass per cent contents of water, K_w decreases in order of systems water-methanol, water-ethanol, water-2-propanol. This decrease can be understood qualitatively taking into account the decrease in the relative permittivity of medium. The ionization of alcohol varies with the changing composition of the system in another manner, K_{alc} being maximum in the range where anomalies have been found in a thermodynamic study¹⁹. Unfortunately, our insight into the problem is not deep enough for a detailed discussion.

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