

ALKOXIDE-TO-HYDROXIDE ION ACTIVITY RATIOS IN WATER-ETHYLENE GLYCOL AND WATER-1-PROPANOL SYSTEMS

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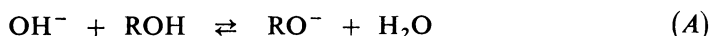
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The dissociation constants of water and alcohol, their ionic products as well the ionic product of the mixture, equilibrium constants of the $\text{OH}^- + \text{ROH} \rightleftharpoons \text{RO}^- + \text{H}_2\text{O}$ equilibrium, and the alkoxide-to-hydroxide ion activity ratios were determined in water-ethylene glycol and water-1-propanol systems. The conditions of validity of Rochester's equation are discussed.

In the alkaline region in water-alcohol mixtures, equilibrium establishes between the alkoxide and hydroxide ions according to Eq. (A),



characterized by the equilibrium constant

$$K = a(\text{H}_2\text{O}) a(\text{RO}^-) / [a(\text{ROH}) a(\text{OH}^-)]. \quad (1)$$

The values of this constant in highly concentrated (virtually neat) alcohols are usually determined by ^1H NMR spectroscopy¹ or by means of indicator colour changes². For systems of dilute alcohols, use is made of the absorbance of the alkoxide ions³. An empirical equation⁴ has been suggested for the calculation of the constant in water-methanol systems; to other water-alcohol systems, however, this equation is inapplicable⁵. For water-methanol, water-ethanol and water-2-propanol systems over wide alcohol concentration regions, Murto⁶ attempted to calculate the equilibrium constants via concentrations of reaction products of parallel reactions. The problem can also be tackled by employing Gibbs transfer energies⁷. In this case, Eq. (2) (Rochester's equation) can be derived:

$$\log \left[\frac{K_S \gamma_{\text{H}^+}}{a_{\text{H}_2\text{O}}^w} - \left(\frac{K_{\text{ROH}}^w a_{\text{ROH}}^w}{a_{\text{H}_2\text{O}}^w} \right) \gamma_{\text{h}}^{-k_{\text{RO}^-}} \right] = -k_{\text{OH}^-} \cdot \log \gamma_{\text{h}} + \log K_{\text{H}_2\text{O}}^w. \quad (2)$$

In the water-methanol system, Eq. (2) is applicable over a wide alcohol concentra-

tion region⁷, whereas in other water–alcohol systems its applicability is limited to narrower concentration ranges⁵. Nevertheless, this is the sole reliable method for calculating the alkoxide-to-hydroxide ion activity ratio^{5,8}. It was therefore also employed in the present work to calculate the equilibrium constant (I) and the alkoxide-to-hydroxide ion activity ratio in water–ethylene glycol and water–1-propanol systems on the molarity scale. For a comparison, the equilibrium constants and alkoxide-to-hydroxide ion activity ratios on the molarity scale were also newly calculated for the water–ethanol system; the reason for this lay in the fact that the dissociation constant of water on extrapolation to $w = 100\%$ ethanol, obtained previously⁸, seems to be too high.

CALCULATIONS

The dissociation constants of water and alcohols in water are known^{9–11}. For the water–ethylene glycol system, the value of $(pK_{EG})_{H_2O} = 14.59$ was used as the average of published values^{9,10}; for the water–1-propanol system, the published value⁹ of $(pK_{PrOH})_{H_2O} = 15.1$ was adopted; and for the water–ethanol system, the value used, $(pK_{EtOH}) = 15.915$, was again average of data from the literature^{10,11}. The pK value of 1-propanol seems somewhat too low in comparison with the pK value of water and alcohols in 2-propanol¹² and also with respect to the relative acidity of alcohols¹³; we failed, however, to find any other data in the literature. As to the value of $(pK_{PrOH})_{H_2O} = 16.1$ in ref.¹¹, the author states that it was obtained by estimation; preference was therefore given to the experimental value⁹.

The Gibbs energies of hydrogen and halide ion transfer in the water–ethylene glycol system were taken from refs^{14,15}. Data in ref.¹⁴ were given preference in view of the fact that in ref.¹⁵, the separation of $\Delta G_{tr}^0(HX)$ into contributions from the individual ions was based on extrapolation to infinitely large radii, which now is not considered reliable enough. The Gibbs energies of hydrogen and halide ion transfer in the water–1-propanol system¹⁶ and water–ethanol system¹⁷ were taken from the literature. The activities of water and alcohol with respect to water as the standard state were calculated from published data for the water–ethylene glycol¹⁸, water–1-propanol¹⁹ and water–ethanol²⁰ systems by using well-known equations²¹. Data for different scales were converted by employing conventional equations⁷ or relations derived from them on the molarity scale. Ionic products of water–ethylene glycol^{22,23} (the data from the two sources are in a good agreement), water–1-propanol^{5,24} and water–ethanol^{5,24} systems were taken from the literature, as were the densities of the water–alcohol systems^{25,26}.

At higher alcohol concentrations, Eq. (2) does not give good results, which is due to the limited validity of the empirical equations (3) and (4) on which it is based⁷:

$$\log \gamma_{OH^-} = k_{OH^-} \cdot \log \gamma_h \quad (3)$$

$$\log \gamma_{\text{RO}^-} = k_{\text{RO}^-} \cdot \log \gamma_{\text{h}} \quad (4)$$

Therefore, the constants (I) for $w = 50$ to 90% ethanol were calculated by using the dissociation constant of water in this system. As in ref.⁸, the $\text{p}K$ value of acetic acid was calculated by using the equation

$$(\Delta \text{p}K_{\text{H}_2\text{O}}) = W(\Delta \text{p}K_{\text{HAc}})^j, \quad (5)$$

where $\Delta \text{p}K_{\text{HAc}}$ is the difference between the $\text{p}K$ values of the acid in solvent S and in water and, similarly, $\Delta \text{p}K_{\text{H}_2\text{O}}$ is the difference of $\text{p}K$ of water in solvent S and in water; W and j are empirical constants. The requisite dissociation constants of acetic acid were taken from ref.²⁷ for the water–ethylene glycol system and from ref.²⁸ for the water–ethanol system. The ionic product of water in the mixture was calculated by multiplying the dissociation constant of water by its activity, the ionic product of alcohol in the mixture was calculated based on the experimental ionic product of the mixture and ionic product of water in it, by using the equation

$$K_{\text{S}} = a_{\text{H}^+} a_{\text{OH}^-} + a_{\text{H}^+} a_{\text{RO}^-} \quad (6)$$

The ionic product of alcohol divided by the activity of alcohol afforded the dissociation constants of the alcohol in the mixture, and the dissociation constant of alcohol divided by that of water gave constant K in Eq. (1).

For the water–1-propanol system, the dissociation constants of acetic acid at various solvent compositions are unavailable, and so the assumption expressed by Eq. (7) was adopted:

$$\log (\Delta \text{p}K'_{\text{H}_2\text{O}}) = \log W' + j' \log (\Delta \text{p}K''_{\text{H}_2\text{O}}), \quad (7)$$

where $(\Delta \text{p}K'_{\text{H}_2\text{O}})$ is the change in the dissociation constant of water brought about by change in the composition of the water–1-propanol system, $(\Delta \text{p}K''_{\text{H}_2\text{O}})$ is the analogous quantity for the water–ethanol system (at the same water mole fraction), and W' and j' are empirical constants. The applicability of Eq. (7) is conditional on the validity of the well-known dependence of the rate of recombination of the characteristic ions of the solvent on the alcohol mole fraction in the water–alcohol system²⁹. Over the experimentally accessible region, Eq. (7) complies well with the data in Tables II and III.

By inserting known data in Eq. (2), n equations could be obtained; from these, k_{OH^-} was expressed and the right-hand sides were put mutually equal. This gave $n!/2 [(n-2)!]$ equations in one unknown, k_{RO^-} . The equations were solved by seeking for the minimum of function $\Delta = f(k_{\text{OH}^-}) = L - R$, where L are the left-hand sides and R are the right-hand sides of the equations.

RESULTS AND DISCUSSION

The above procedures were applied to obtain the dissociation constants of water and alcohols in their mixtures, ionic products of the mixtures, constants (I) and the alkoxide-to-hydroxide ion activity ratios. The results, on the molarity scale for the water-ethylene glycol, water-1-propanol and water-ethanol systems at 25°C, are given in Tables I–III, respectively. The data in Table III are somewhat different from those reported previously⁸; this is due – for the region of $w > 50\%$ ethanol – to inaccuracy in the calculation of the dissociation constant of water extrapolated to $w = 100\%$ ethanol in ref.⁸. For the dilute alcohol region, the differences between the data in the two papers illustrate how different data handling procedures and differences in input data affect the final result. Still, more attention will have to be paid to the individual factors on the result of calculation.

At present, the establishment of the equilibrium according to Eq. (A) seems to be synthetically proved with a sufficient likelihood^{6,11,30–35}, and so it need not be discussed any more. A considerably lower degree of certainty can be attached to the calculation of constant K in Eq. (I) for the liquid phase, particularly for concentrated alcohols, in view of the fact that no alternative method exists for its calculation or determination over a wide alcohol concentration region, or at least for a direct and sufficiently accurate determination of the OH^- or RO^- ion concentration. In the gas phase, a value of $K = 0.75$ has been found³⁶ for the water-methanol

TABLE I

Negative common logarithms of dissociation constants of water and ethylene glycol in mixture, ionic product of water and alcohol in mixture, ionic product of mixture, its deviation from observed value, alkoxide-to-hydroxide ion activity ratio in mixture, and constant of Eq. (I) for the water-ethylene glycol system at 25°C on the molarity scale

w_{EG} %	$\text{p}K_{\text{H}_2\text{O}}$	$\text{p}K_{\text{EG}}$	$\text{p}K_{\text{w}}$	$\text{p}K_{\text{alc}}$	$\text{p}K_{\text{S}}$	$\delta(\text{p}K_{\text{S}})$	$\frac{a_{\text{RO}^-}}{a_{\text{OH}^-}}$	K
10	15.70	14.74	13.97	14.50	13.86	0.01	0.29	9.09
20	15.64	14.91	13.92	14.33	13.78	0.01	0.38	5.38
30	15.53	15.05	13.84	14.25	13.70	0.02	0.38	3.02
40	15.42	15.23	13.75	14.26	13.64	-0.01	0.29	1.55
50	15.34	15.45	13.72	14.32	13.62	0.00	0.26	0.78
60	15.35	15.58	13.77	14.32	13.66	-0.02	0.29	0.59
70	15.41	15.78	13.89	14.39	13.77	0.04	0.32	0.43
80	15.54 ^a	16.10 ^a	14.15	14.58	—	—	0.38	0.28
90	15.62 ^a	16.40 ^a	14.46	14.74	—	—	0.51	0.17

^a Calculated by using the dissociation constant of acetic acid (the remaining data calculated by means of Eq. (2)).

TABLE II

Negative common logarithms of dissociation constants of water and propanol in mixture, ionic product of water and alcohol in mixture, ionic product of mixture, its deviation from the observed value, alkoxide-to-hydroxide ion activity ratio in mixture, and constant of Eq. (1) for the water-1-propanol system at 25°C on the molarity scale

w_{PrOH} %	$pK_{\text{H}_2\text{O}}$	pK_{PrOH}	pK_{w}	pK_{alc}	pK_{S}	$\delta(pK_{\text{S}})$	$a_{\text{RO}^-}/a_{\text{OH}^-}$	K
10	16.04	15.17	14.31	15.05	14.24	-0.01	0.17	7.41
20	16.38	15.16	14.66	14.85	14.44	0.02	0.66	16.67
30	16.60	15.26	14.89	14.87	14.58	0.00	1.04	21.74
40	16.86	15.44	15.15	15.01	14.77	-0.01	1.40	26.32
50	17.11 ^a	15.65 ^a	15.41	15.21	—	—	1.57	28.57
60	17.42 ^a	15.82 ^a	15.72	15.37	—	—	2.24	40.00
70	17.66 ^a	16.13 ^a	15.96	15.67	—	—	1.95	34.48
80 ^b	17.96 ^a	16.61 ^a	16.29	16.13	—	—	1.45	20.41

^a Calculated by means of Eq. (7) (the remaining data, by means of Eq. (2)); ^b measurements at higher alcohol concentrations did not give satisfactory results.

TABLE III

Negative common logarithms of dissociation constants of water and ethanol in mixture, ionic product of water and alcohol in mixture, ionic product of mixture, its deviation from the observed value, alkoxide-to-hydroxide ion activity ratio in mixture, and constant of Eq. (1) for the water-ethanol system at 25°C on the molarity scale

w_{EtOH} %	$pK_{\text{H}_2\text{O}}$	pK_{EtOH}	pK_{w}	pK_{alc}	pK_{S}	$\delta(pK_{\text{S}})$	$a_{\text{RO}^-}/a_{\text{OH}^-}$	K
10	15.96	15.85	14.24	15.54	14.22	0.00	0.05	1.29
20	16.18	15.82	14.48	15.24	14.41	0.00	0.17	2.29
30	16.45	15.66	14.79	14.95	14.56	0.02	0.70	6.17
40	16.68	15.58	15.05	14.79	14.60	-0.10	1.82	12.66
50	17.04 ^a	15.82 ^a	15.43	15.00	—	—	2.72	16.67
60	17.27 ^a	16.07 ^a	15.68	15.21	—	—	2.98	15.87
70	17.55 ^a	16.40 ^a	16.00	15.51	—	—	3.07	14.08
80	17.86 ^a	16.60 ^a	16.39	15.68	—	—	5.17	18.18
90	18.22 ^a	17.64 ^a	16.92	16.68	—	—	1.75	3.80

^a Calculated by using the dissociation constant of acetic acid and Eq. (5) (the remaining data calculated by means of Eq. (2)).

system at 300 K; this value is fairly consistent with the liquid phase data, viz. $K = 0.58$ to 0.38 according to the concentration of alcohol³⁷. For other water-alcohol systems, however, gas phase data are unavailable.

Rochester's equation (2) fits the experimental results for $w \leq 40\%$ alcohol in the water-ethanol and water-1-propanol systems (Tables II and III) as well as in the water-2-propanol system⁵. While in the water-2-methyl-2-propanol system the applicability of Eq. (2) is even more limited⁵, in the water-ethylene glycol system it suits up to $w = 70\%$ alcohol (Table I). Limitation in this system rests in reliable $\Delta G_{tr}^{\circ}(i)$ values, requisite for the calculation, being unavailable at higher ethylene glycol concentrations. The validity of Eq. (2) is conditional on that of the assumptions expressed by Eqs (3) and (4), requiring simple interdependences between the activity coefficients of transfer of the individual anions. Actually, however, these relations hold true with a sufficient accuracy over the entire alcohol concentration region only for the water-methanol system⁷ and, as the results of the present work document, for the water-ethylene glycol system. In the remaining systems treated, the relations lose validity with increasing concentration of the organic co-solvent³⁸. This can be accounted for by the dependence of the Gibbs ion transfer energy on the solvent composition. The total Gibbs transfer energy can be divided into a contribution determined by electrostatic forces and a contribution determined by chemical forces (e.g., ref.¹⁴):

$$\Delta G_{tr}^{\circ}(i) = \Delta G_{tr}^{\circ}(i)_{elst} + \Delta G_{tr}^{\circ}(i)_{chem} \quad (8)$$

The former contribution can be calculated from Born's equation³⁹

$$\Delta G_{tr}^{\circ}(i)_{elst} = [(Nz^2e^2)/(2r)] (1/\epsilon_s - 1/\epsilon_w), \quad (9)$$

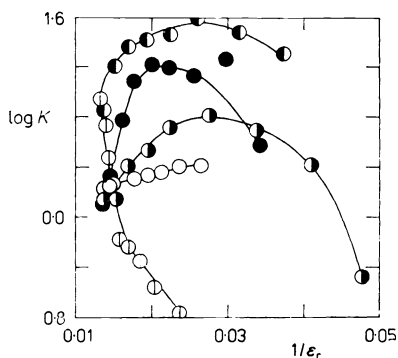


FIG. 1
Dependence of $\log K$ (Eq. (1)) on $1/\epsilon_r$ at 25°C for the following systems: \circ water-methanol, \bullet water-ethanol, \bullet water-1-propanol, \odot water-2-propanol, \odot water-ethylene glycol

where r is ionic radius, N is Avogadro's constant, z is the number of elementary charges of the ion, e is the electron charge, and ϵ_s and ϵ_w are the relative permittivities of solvent S and water, respectively.

For making it possible to assess the extent to which electrostatic forces solely participate in the transfer, logarithms of the equilibrium constants (I) were plotted in dependence on $1/\epsilon_r$ (Fig. 1). The relative permittivities were taken from ref.⁴⁰. Figure 1 demonstrates that in the water-ethanol, water-1-propanol and water-2-propanol⁸ systems, the dependences are bent at high alcohol concentrations. This indicates that the $\Delta G_{tr}^{\circ}(i)_{chem}$ contribution cannot be neglected with increasing alcohol contents of the systems. For the water-methanol³⁷ and water-ethylene glycol systems, on the other hand, the dependences are linear, although in the latter case a break is observed on the straight line. This suggests that in these cases, $\Delta G_{tr}^{\circ}(i)$ is primarily determined by the electrostatic term. It is clear from a comparison with Eq. (9) that $\Delta G_{tr}^{\circ}(i)$ of the halide and alkoxide ions must be mutually proportional, because they only differ in the radii. This implies the validity of Eq. (2) over a very wide alcohol concentration region and the possibility of calculating the dissociation constants and ionic products of water and alcohol. Comparison of the regions over which Eq. (2) is valid with the relative permittivities of the alcohols suggests^{5,7,8,37,40} that this equation will only be applicable in solvents possessing a sufficiently high relative permittivity. From this it follows that, regrettably, although representing a partial advance in the calculation of the equilibrium according to Eq. (A), Rochester's equation (2) is no general solution to the problem of the equilibrium between the hydroxide and alkoxide ions.

In conclusion, the outcome of the present work is, on the one hand, extension of the calculation of equilibrium (A) to the water-ethylene glycol and water-1-propanol systems, and, on the other hand, a deeper insight into the validity of Eqs (3) and (4), which is a prerequisite for the validity of Eq. (2) and thus, for the possibility of calculating the equilibrium constant of equilibrium (A).

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