

Calculation of Alkoxide and Hydroxide Ion Activity Ratios in the Water—Ethanol System

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The dissociation constants and ionic products of water and ethanol, equilibrium constants of the $\text{OH}^- + \text{ROH} \rightleftharpoons \text{H}_2\text{O} + \text{RO}^-$ reaction, and alkoxide and hydroxide ion activity ratios were determined in the water—ethanol system using various Gibbs energies of hydrogen ions transfer $\Delta G_{\text{tr}}^\circ(\text{H}^+)$. Validity of the Rochester equation is discussed on the basis of various literature data.

In the alkaline region in water—alcohol mixtures, equilibrium establishes between the alkoxide and hydroxide ions according to the equation



Equilibrium reaction (A) is characterized by the equilibrium constant

$$K = \frac{a_{\text{H}_2\text{O}} a_{\text{RO}^-}}{a_{\text{ROH}} a_{\text{OH}^-}} \quad (1)$$

where a_i are activities of particles. K can be expressed by dissociation constants of water and alcohol in mixtures S ($K_{\text{H}_2\text{O}}^S$, K_{ROH}^S) in this way

$$K = \frac{K_{\text{ROH}}^S}{K_{\text{H}_2\text{O}}^S} \quad (2)$$

In rich alcohol mixtures K can be determined by ^1H NMR spectroscopy [1] or by means of indicator colour changes [2]. In diluted alcohol mixtures K can be derived from the absorbance of the alkoxide ions [3]. An empirical equation suggested [4] for the water—methanol system is inapplicable in some other alcohols [5]. Murto [6] tried to derive K on the basis of kinetic measurement. K can also be determined by the method [7] based on the assumption of the linear dependence of Gibbs energies of lyate ions transfer and average Gibbs energies of halide ions transfer

$$\begin{aligned} \log \gamma_{\text{OH}^-} &= k_{\text{OH}^-} \log \gamma_{\text{h}} \\ \log \gamma_{\text{RO}^-} &= k_{\text{RO}^-} \log \gamma_{\text{h}} \end{aligned} \quad (3)$$

where k_{OH^-} , k_{RO^-} are the proportionality constants, γ_{OH^-} , γ_{RO^-} are activity coefficients of hydroxide and alkoxide ions transfer, γ_{h} is average activity coefficient of halide ions transfer, *i.e.* chloride, bromide, and iodide ions. On the basis of these assumptions Rochester [7] derived the equation

$$\begin{aligned} \log \frac{K_{\text{S}} \gamma_{\text{H}^+}}{a_{\text{H}_2\text{O}}^{\text{w}}} - \frac{K_{\text{ROH}}^{\text{w}} a_{\text{ROH}}^{\text{w}}}{a_{\text{H}_2\text{O}}^{\text{w}}} \gamma_{\text{h}}^{-k_{\text{RO}^-}} &= \\ &= -k_{\text{OH}^-} \log \gamma_{\text{h}} + \log K_{\text{H}_2\text{O}}^{\text{w}} \end{aligned} \quad (4)$$

where K_{S} is ionic product of a given mixture S , $K_{\text{ROH}}^{\text{w}}$ is the dissociation constant of alcohol in pure water, a_i^{w} are activities of particles related to water as the standard state, $K_{\text{H}_2\text{O}}^{\text{w}}$ is the dissociation constant of water in water, γ_{H^+} is the activity coefficient of hydrogen ions transfer from water to the certain mixture, γ_{h} is the average activity coefficient of the transfer of halide ions from water to the given mixture, for which it holds

$$\begin{aligned} \Delta G_{\text{tr}}^\circ(\text{H}^+) &= RT \ln \gamma_{\text{H}^+} \quad (5) \\ 1/3(\Delta G_{\text{tr}}^\circ(\text{Cl}^-) + \Delta G_{\text{tr}}^\circ(\text{Br}^-) + \Delta G_{\text{tr}}^\circ(\text{I}^-)) &= RT \ln \gamma_{\text{h}} \end{aligned}$$

Eqn (4) fits the experimental results for all alcohol concentration regions in the water—methanol system [7]. In other systems water—alcohol the applicability of eqn (4) is limited. It fits only up to a certain content of alcohol [5]. Nevertheless, the application of eqn (4) seems to be the most convenient to determine alkoxide and hydroxide ion activity ratios [5, 8, 9].

Pavelek [8] was interested in the influence of various $\Delta G_{\text{tr}}^\circ(\text{H}^+)$ on the calculation of K (eqn (1)) in the water—methanol system. This work pursues the same problem, but in the water—ethanol system. Solving of eqn (4) not only with γ_{h} , but also with γ_{Cl^-} , γ_{Br^-} , γ_{I^-} , or with $(\gamma_{\text{Cl}^-} + \gamma_{\text{Br}^-})/2$ also seemed to be interesting.

In the region where eqn (4) cannot be used, eqn (6) [9] can be used to calculate K

$$\Delta pK_{\text{HA}} = W(\Delta pK_{\text{HK}})^j \quad (6)$$

where $\Delta pK_{\text{HA}} = pK_{\text{HA}}^{\text{S}} - pK_{\text{HA}}^{\text{w}}$, $pK_{\text{HA}}^{\text{S}}$ and $pK_{\text{HA}}^{\text{w}}$ are pK of weak carboxylic acid in the mixture solvent S and in water, respectively. $\Delta pK_{\text{HK}} = pK_{\text{HK}}^{\text{S}} - pK_{\text{HK}}^{\text{w}}$, where $pK_{\text{HK}}^{\text{S}}$ and $pK_{\text{HK}}^{\text{w}}$ are pK of water in the mixture S and in water, respectively. W and j are the empirical constants.

METHOD

Constants k_{OH^-} , k_{EtO^-} from eqn (4) were determined by the way described earlier [10]. All quantities (ex-

cept γ_{H^+} , γ_h) needed to the calculation were also used like those in [10]. Gibbs energies of hydrogen and halide ions transfer were taken from [11–18]. $\Delta G_{tr}^\circ(H^+)$, $\Delta G_{tr}^\circ(Cl^-)$, $\Delta G_{tr}^\circ(Br^-)$, and $\Delta G_{tr}^\circ(I^-)$ were complete only in [11, 14]. γ_{H^+} and γ_{Cl^-} were given in [12, 13] and γ_{H^+} only in [15–18]. To calculate γ_{Cl^-} , γ_{Br^-} , γ_{I^-} corresponding to γ_{H^+} from [15–18] the following equation was used

$$\Delta G_{tr}^\circ(HX) = \Delta G_{tr}^\circ(H^+) + \Delta G_{tr}^\circ(X^-) \quad (7)$$

where HX is hydrogen halide. We took the average Gibbs energies of hydrogen halide ions transfer $\Delta G_{tr}^\circ(HX)$ from [11].

Rochester's equation (4) was used for the following combinations: γ_{H^+} with γ_h , γ_{Cl^-} , γ_{Br^-} , and γ_{I^-} , respectively, and γ_{H^+} with $(\gamma_{Cl^-} + \gamma_{Br^-})/2$. γ_{OH^-} , γ_{EtO^-} , K_{EtOH}^S , $K_{H_2O}^S$, K_{Eth}^S , K_w^S , K , alkoxide and hydroxide ion activity ratios $Q = a_{EtO^-}/a_{OH^-}$ were derived from k_{OH^-} and k_{EtO^-} by the way described earlier [10]. Ionic products of mixtures calculated by us were compared with those determined experimentally (ΔpK_S). On the basis of this comparison the best results were chosen and used to calculate $pK_{H_2O}^S$ according to eqn (6) in ethanol-rich mixtures. The dissociation constants of acetic acid were taken from the same literature as in [10].

RESULTS AND DISCUSSION

The proportionality constants k_{OH^-} , k_{EtO^-} from eqn (4), the dissociation constants of water and ethanol, ionic products of water and ethanol, the equilibrium constants K (eqn (2)), and alkoxide and hydroxide ion activity ratios in the system water–ethanol (10–90 mass % EtOH) were obtained as mentioned above and the results are given in Tables 1–3.

The proportionality constants k_{OH^-} and k_{EtO^-} obtained on the basis of different γ_{H^+} are listed in Table 1. The criterion of the use of Rochester's equation to solve the equilibrium (A) are always the differences between the calculated ionic products of the mixtures and those determined experimentally. These differences are listed in Table 2.

From Table 1 it is obvious that k_{OH^-} and k_{EtO^-} values obtained from *Jakuszewski's* literature data [17] differ most from the others. This is true both absolutely and relatively. The values of k_{EtO^-} are bigger than k_{OH^-} . This relation is opposite according to other literature data, k_{EtO^-} is smaller than k_{OH^-} .

From Tables 1 and 2 it is obvious where Rochester's equation was applicable with different literature values of $\Delta G_{tr}^\circ(H^+)$. *I.e.*, with $\Delta G_{tr}^\circ(H^+)$ determined by *Wells* [11] on the basis of measurement of the equilibrium constant of the reaction $H^+(H_2O)_{x+} + ROH \rightleftharpoons H^+(H_2O)_{x-1}(ROH) + H_2O$, which is considered constant over the whole con-

Table 1. The Proportionality Constants k_{EtO^-} , k_{OH^-} from Eqn (4) and Relative Errors e of These Constants

Parameter	k_{EtO^-}	k_{OH^-}	$e/\%$	Ref.
γ_h	0.96	1.30	28.0	[11]
	0.80	1.23	3.22	[14]
	1.00	1.24	–	[15]
	–0.29	2.10	64.6	[16]
	41.5	–71.8	66.0	[17]
γ_{Cl^-}	0.75	1.15	11.9	[11]
	–1.61	2.32	45.6	[12](TPTB)
	0.50	1.30	35.3	[12](TATB)
	0.45	1.32	30.2	[13]
	0.60	1.20	25.6	[14]
γ_{Br^-}	0.18	1.41	46.0	[16]
	0.86	1.23	8.3	[14]
	–0.48	2.35	68.1	[16]
γ_{I^-}	1.00	1.30	8.72	[14]
	–0.16	1.75	71.0	[16]
$(\gamma_{Cl^-} + \gamma_{Br^-})/2$	0.68	1.25	17.8	[11]

TPTB – tetraphenylphosphonium tetraphenylborate, TATB – tetraphenylarsonium tetraphenylborate.

Table 2. Differences between Calculated Ionic Products of the Mixtures and Those Determined Experimentally ΔpK_S

Parameter	ΔpK_S					Ref.
	$w(\text{EtOH})/\%$					
	10	20	30	40	50	
γ_h	0.03	–0.02	–0.09	–0.06	–0.03	[11]
	0.00	0.00	0.02	–0.10	–	[14]
	–0.01	–0.01	–	–	–	[15]
	0.00	–0.01	–0.02	–	–	[16]
	0.01	–0.04	–0.01	–	–	[17]
γ_{Br^-}	0.02	0.02	0.07	–0.01	0.09	[14]
	0.01	–0.02	0.04	–	–	[16]
γ_{Cl^-}	0.01	0.00	–0.03	0.01	0.03	[11]
	0.01	–0.04	0.18	–	–	[12]
	0.02	0.01	–0.05	0.02	0.10	[12]
	0.01	–0.01	0.10	0.04	0.10	[13]
	–0.05	–0.05	–0.09	–	–	[14]
γ_{I^-}	0.00	0.00	–0.01	–	–	[16]
	0.02	0.01	–0.05	–0.01	0.05	[14]
	0.00	0.00	0.02	–	–	[16]
$(\gamma_{Cl^-} + \gamma_{Br^-})/2$	0.02	0.01	–0.02	–0.04	–	[11]

centration region by the author, Rochester's equation was applicable: with γ_h and γ_{Cl^-} up to 50 mass % EtOH, with γ_{Br^-} and γ_{I^-} eqn (4) was not solvable, and with $(\gamma_{Cl^-} + \gamma_{Br^-})/2$ this equation was solvable up to 40 mass % EtOH.

The dissociation constants of water and ethanol in the mixture were also calculated from all k_{OH^-} and k_{EtO^-} . These dissociation constants did not differ too much (even the values obtained from *Jakuszewski's* values [17]). That is why we averaged the dissociation constants. These averaging values were further used for calculations according to eqn (6). The dependence of negative logarithms of these averaging dissociation constants of water and ethanol on reciprocal relative permittivity of the mixture is

Table 3. Dissociation Constants of Water $pK_{\text{H}_2\text{O}}^{\text{S}}$ and Ethanol $pK_{\text{EtOH}}^{\text{S}}$, Ionic Products of Water pK_{w}^{S} and Ethanol $pK_{\text{Eth}}^{\text{S}}$, the Equilibrium Constants K (eqn (2)), and Alkoxide and Hydroxide Ion Activity Ratios Q in the Water—Ethanol Mixture

$w(\text{EtOH})$ %	$pK_{\text{H}_2\text{O}}^{\text{S}}$	pK_{w}^{S}	$pK_{\text{EtOH}}^{\text{S}}$	$pK_{\text{Eth}}^{\text{S}}$	K	Q
10 ^a	15.94	14.21	15.88	15.56	1.15	0.02
20	16.16	14.46	15.84	15.25	2.09	0.20
30	16.39	14.70	15.74	15.00	4.46	0.62
40	16.57	14.89	15.80	14.97	5.88	0.82
50	16.75	15.10	15.86	14.99	7.75	1.14
60 ^b	16.96	15.32	16.14	15.23	6.62	1.24
70	17.21	15.60	16.47	15.52	5.49	1.19
80	17.49	15.94	16.60	15.60	7.75	2.16
90	17.84	16.44	17.88	16.82	0.91	0.41

a) Values obtained by averaging of values obtained from eqn (4) with various literature data [11—17]. b) Values obtained from eqn (6). For the calculation the dissociation constants of water (10—50 mass % EtOH) obtained from Rochester's equation (4), the dissociation constants of water in pure ethanol [10] and of acetic acid [10] in water—ethanol mixtures were used.

shown in Figs. 1 and 2. The dissociation constants with the different combination of halide ions do not differ very much. That is why these values were also averaged. These reaveraging values were used to the calculation of ionic products of water pK_{w}^{S} and ethanol $pK_{\text{Eth}}^{\text{S}}$, the equilibrium constants K , and alkoxide and hydroxide ion activity ratios, which are listed in Table 3. Eqn (4) with γ_{H^+} from [18] is not solvable.

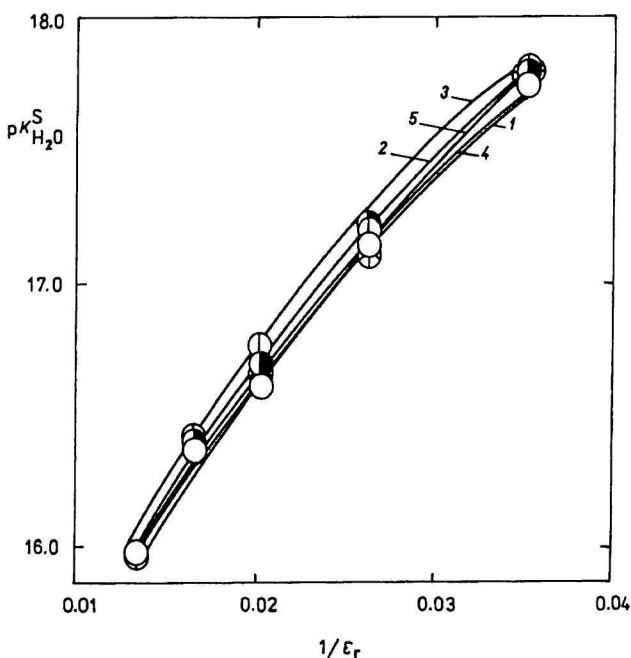


Fig. 1. Dependence of $pK_{\text{H}_2\text{O}}^{\text{S}}$ on $1/\epsilon_r$ in the water—ethanol system. Dissociation constants were calculated using $\circ \gamma_{\text{H}^+}$ (1), $\bullet \gamma_{\text{Cl}^-}$ (2), $\oplus \gamma_{\text{Br}^-}$ (3), $\otimes \gamma_{\text{I}^-}$ (4), $\ominus (\gamma_{\text{Cl}^-} + \gamma_{\text{Br}^-})/2$ (5).

Pavelek [8] obtained values for equilibrium constant K in the system water—methanol, which were dependent a little on the extrathermodynamic way of obtaining of $\Delta G_{\text{tr}}^{\circ}(\text{H}^+)$. Our results for the system water—ethanol are similar. It is probably so because there is lyates ions activity ratio in eqn (4), which is proportional to the difference of the corresponding Gibbs transfer energies. But this difference $\Delta G_{\text{tr}}^{\circ}(\text{RO}^-) - \Delta G_{\text{tr}}^{\circ}(\text{OH}^-)$ is independent of $\Delta G_{\text{tr}}^{\circ}(\text{H}^+)$.

We were also interested which halide ions were the best for the calculation. Eqn (4) was solvable with activity coefficients of chloride ions transfer and with the average activity coefficients of halide ions transfer for the most data.

The total Gibbs transfer energy can be divided into a contribution determined by electrostatic forces and a contribution determined by chemical forces, i.e. [19]

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

The electrostatic contribution can be calculated from Born's equation [20] according to which it differs only in the radii for different ions. According to conclusions of paper [10], $\Delta G_{\text{tr}}^{\circ}(i)$ is determined mostly by electrostatic forces in the medium with sufficiently high relative permittivity. Consequently, it results in the proportion of Gibbs energies of different ions transfer up to the certain content of alcohol and also Rochester's equation validity [10].

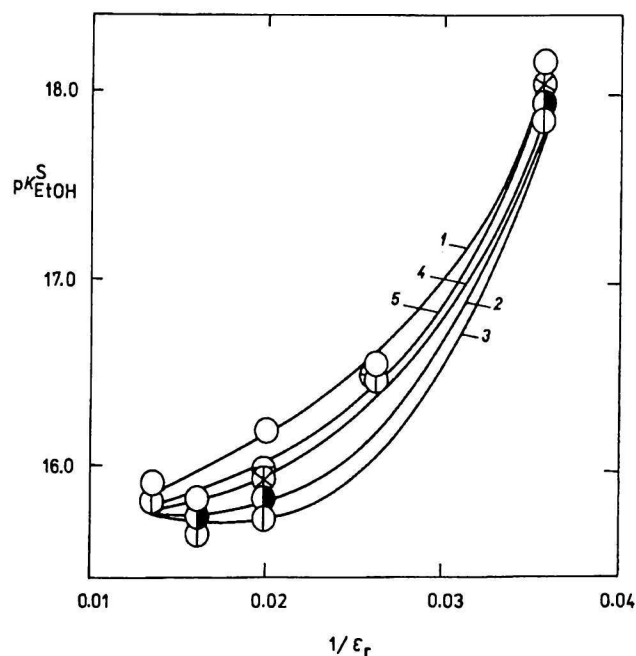


Fig. 2. Dependence of $pK_{\text{EtOH}}^{\text{S}}$ on $1/\epsilon_r$ in the water—ethanol system. Dissociation constants were calculated using $\circ \gamma_{\text{H}^+}$ (1), $\bullet \gamma_{\text{Cl}^-}$ (2), $\oplus \gamma_{\text{Br}^-}$ (3), $\otimes \gamma_{\text{I}^-}$ (4), $\ominus (\gamma_{\text{Cl}^-} + \gamma_{\text{Br}^-})/2$ (5).

Our work confirms conclusions of papers [8] and [10] and is a contribution to the knowledge about the equilibrium (A).

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