Comparison of the methods used for studying the equilibrium of the lyate ions in water—methanol mixture

Z. PAVELEK

Galena, n.e., CS-747 70 Opava

The methods of calculation of the equilibrium constant corresponding to the equilibrium of the methoxide and hydroxide ions in water—methanol mixture were confronted. On the basis of comparison of the calculated and experimental values of the equilibrium constants, the most appropriate method of calculation was selected.

Проведено сравнение методов расчета констант равновесия между метоксид- и гидроксид-ионами в водно—метанольной смеси. На основании сравнения рассчитанных и экспериментально найденных величин этих констант равновесия был выбран наиболее подходящий метод расчета.

In a mixture of protŏgenic water—methanol solvents an equilibrium of the lyate ions is established according to the equation

$$OH^- + MeOH \; \rightleftharpoons \; MeO^- + H_2O \qquad (A)$$
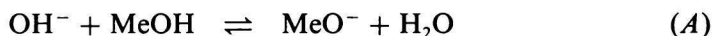
The following equation is valid for the pertinent equilibrium constant $K(S)$

$$K(S) = \frac{a(MeO^-)\, a(H_2O)}{a(OH^-)\, a(MeOH)} = \frac{c(MeO^-)\, c(H_2O)}{c(OH^-)\, c(MeOH)} \cdot \frac{f(MeO^-)f(H_2O)}{f(OH^-)f(MeOH)} \qquad (1)$$

where $a(i)$, $c(i)$, and $f(i)$ are activity, concentration, and activity coefficient of particles i, respectively. As the activities of the lyate ions are not directly measurable in contrast to the activities of water and methanol, the value of $K(S)$ is to be calculated only if the dissociation constants of water $K(H_2O)$ and methanol $K(MeOH)$ in the given solvent are known

$$K(H_2O) = \frac{a(H^+)\, a(OH^-)}{a(H_2O)} \qquad K(MeOH) = \frac{a(H^+)\, a(MeO^-)}{a(MeOH)} \qquad (2)$$

By dividing $K(MeOH)$ by $K(H_2O)$ we obtain

$$K(S) = \frac{K(MeOH)}{K(H_2O)} \qquad (3)$$

Eqns (*1—3*) have been solved in literature by different methods. *Murto* [1] has used the kinetic method which is however, theoretically not clear. The *Slonim* method [2] enables us to determine $K(S)$ on the basis of spectral data in pure alcohol. *Gaboriaud* [3] has calculated the ratio of activities of the lyate ions Q by means of the empirical equation

$$Q = \frac{a(\text{MeO}^-)}{a(\text{OH}^-)} = \text{const} \frac{[a(\text{MeOH})]^p}{[a(\text{H}_2\text{O})]^q} \qquad (4)$$

which may be inserted into eqn (*1*) for calculating $K(S)$. The *Rochester* methods [4] are also based on empirical equations. The first of them is built on the assumption that the Gibbs energy of the transfer of ion i from water to water —methanol mixture $\Delta G_{tr}^o(\text{i})$ is proportional to the mole fraction of methanol x and gives the relations

$$\gamma(\text{OH}^-) = \exp\left[\frac{k(\text{OH}^-)\,x}{RT}\right] \text{ and } \gamma(\text{MeO}^-) = \exp\left[\frac{k(\text{MeO}^-)\,x}{RT}\right] \qquad (5)$$

where $\gamma(\text{i})$ stands for the activity coefficient of the transfer of ion i from water to water—methanol mixture and $k(\text{i})$ is the constant of proportionality. In the second method [4], it is assumed that the Gibbs energy of transfer of the lyate ions depends linearly on the average Gibbs energy of transfer of the halide ions $(\Delta G_{tr}^o(\text{X}^-) = 1/3(\Delta G_{tr}^o(\text{Cl}^-) + \Delta G_{tr}^o(\text{Br}^-) + \Delta G_{tr}^o(\text{I}^-)))$ which leads to the expressions

$$\gamma(\text{OH}^-) = \exp\left[\frac{k'(\text{OH}^-)\,\Delta G_{tr}^o(\text{X}^-)}{RT}\right] \text{ and}$$

$$\gamma(\text{MeO}^-) = \exp\left[\frac{k'(\text{MeO}^-)\,\Delta G_{tr}^o(\text{X}^-)}{RT}\right] \qquad (6)$$

Though eqn (*6*) seems to be the most convenient for calculating $K(S)$ from eqn (*1*) [5, 6], it involves a certain unclearness owing to which it deserves attention. The basic problem of eqn (*6*) consists in determination of the Gibbs energies of ion transfer which are to be obtained by splitting the measured Gibbs energies of electrolyte transfer into contributions of individual ions on the basis of nonthermodynamical presumptions [7]. According to literature, the skeptical view on the obtained values of $\Delta G_{tr}^o(\text{i})$ is not widely accepted [8]. Nevertheless, the individual methods give different results [9—15]. It ensues from this fact that different values in eqn (*6*) give different values of $\gamma(\text{OH}^-)$ and $\gamma(\text{MeO}^-)$ and thus different values of $K(S)$. The influence of inaccurate experimental values on $K(S)$ has not yet been mentioned in literature and thus it seems convenient to

pay attention to this problem, at least for the water—methanol system because the literature data concerning this system are the most numerous.

Experimental

The equilibrium constant $K(S)$ was calculated from the equation

$$K(S) = K(W) \cdot \frac{\gamma(OH^-)\,\gamma(MeOH)}{\gamma(MeO^-)\,\gamma(H_2O)} \tag{7}$$

where $K(W)$ is the equilibrium constant for water. This constant as well as the activity coefficients of water and methanol was taken from literature [4]. The activity coefficients of the lyate ions were calculated from eqn (6) and the average Gibbs energies of transfer of the halide ion were obtained from the equation

$$\Delta G_{tr}^{\circ}(X^-) = \frac{1}{3}\,[\Delta G_{tr}^{\circ}(HCl) + \Delta G_{tr}^{\circ}(HBr) + \Delta G_{tr}^{\circ}(HI)] - \Delta G_{tr}^{\circ}(H^+) \tag{8}$$

The calculated Gibbs energies of proton transfer from water to water—methanol mixture were taken from literature [9—15]. The measured Gibbs energies of hydrohalide transfer were also borrowed from literature [16—21]. The proportionality constants $k'(OH^-)$ and $k'(MeO^-)$ necessary for calculating the activity coefficients of the lyate ions were calculated by the simplex method from the following equation

$$K = K(H_2O) \cdot \frac{a(H_2O)}{\gamma(H^+)\,\gamma(OH^-)} + K(MeOH) \cdot \frac{a(MeOH)}{\gamma(H^+)\,\gamma(MeO^-)} \tag{9}$$

where K was the constant of autoprotolysis in water—methanol mixture. The minimization of the sum of squares $[(K(\text{calc.}) - K(\text{exp.}))/K(\text{exp.})]^2$ was used as a criterion of calculation.

Results and discussion

The proportionality constants $k'(OH^-)$ and $k'(MeO^-)$ calculated on the basis of different literature values of the Gibbs energies of proton transfer from water to water—methanol mixture [9—15] are listed in Table 1. The values of *Alfenaar* [9] and *Wells* [12] could not be employed for calculation because no minimum sum of squares of relative errors existed. As a mean relative error of 5 % corresponds approximately to an error of 0.02 pH units for the constant of autoprotolysis, all other calculated proportionality constants may be used for calculation of the equilibrium constants $K(S)$. These constants as well as the pertinent literature references are given in Table 2.

Table 1

The proportionality constants $k'(OH^-)$ and $k'(MeO^-)$ calculated from different values of $\Delta G_{tr}^{o}(H^+)$ at 25 °C

Ref.	[10]	[11]	[13]	[14]	[15]
$k'(OH^-)$	0.9995	0.9815	0.9575	0.6475	0.8690
$k'(MeO^-)$	0.8855	0.7075	0.6915	0.5855	0.4420
$\bar{\Delta}/\%^a$	3.05	2.11	1.03	1.04	7.78

a) Mean relative error of calculation Δ.

Table 2

The calculated and literature equilibrium constants $K(S)$, mean constants $K(S)$, and activity ratios of the lyate ions in water—methanol mixture at 25 °C

w(methanol)/%	$K(S)$									Q^e
	[10]	[11]	[13]	[14]	[15]	a	b	c	d	
10	1.78	1.81	1.76	1.59	1.54	1.36	1.71	1.70	1.72	0.11
20	1.91	2.00	1.94	1.54	1.47	2.13	1.83	1.84	1.83	0.26
28.5	2.10	2.10	2.00	1.50	1.56	—	1.88	1.94	1.94	0.43
50	2.37	2.17	2.03	1.23	1.71	3.47	1.88	1.99	2.07	1.16
60	2.46	2.22	2.06	1.11	1.76	3.32	1.89	2.00	2.16	1.82
70	2.61	2.33	—	1.00	1.84	2.97	1.91	2.04	2.26	2.97
80	2.75	2.61	—	0.94	2.22	2.89	2.02	2.09	2.53	5.69
90	3.08	2.82	—	0.90	1.97	2.87	2.24	2.18	2.62	13.26

a) $K(S)$ calculated from Q according to *Gaboriaud* [3]; b) *Rochester* values of $K(S)$ [4] calculated from eqn (5); c) *Rochester* values of $K(S)$ [4] calculated from eqn (6); d) mean $\dot{K}(S)$ calculated from mean values of $\Delta G_{tr}^{o}(H^+)$ [10, 11, 13, 15]; e) mean Q calculated in the same way as mean $K(S)$ in column d.

It results from Table 2 that solely the $K(S)$ values calculated from the *Abrham* [14] values of $\Delta G_{tr}^{o}(H^+)$ differ in dependence on the composition of solvent. The equilibrium constants $K(S)$ calculated from different $\Delta G_{tr}^{o}(H^+)$ values according to *Andrews* [10], *Bax* [11], *Chakraboty* [13], and *Popovych* [15] are in plausible agreement as regards the dependence on the composition of solvent as well as their magnitude. The $K(S)$ values obtained by the empirical method [3] also differ in dependence on the composition of solvent. On the other hand, both methods according to *Rochester* [4] give comparable results.

The experimental values ought to be a criterion of correctness of the calculated in this study and literature values of $K(S)$. Unfortunately, these values were determined only in pure water at 25 °C (4.48 [1], 3.48 [22], 1.74 [23], and 1.55 [4]) or in pure methanol (in the interval 2.33—2.94 according to [5] and in

the interval 0.56—2.36 at 18 °C according to [24]). If we compare these values with the values in Table 2, we can see that the values of $K(S)$ calculated from the values of $\Delta G_{tr}^{o}(H^+)$ presented by *Abrham* [14] are likely erroneous. Other calculated $K(S)$ values are consistent with experimental data.

Additionally, the first *Rochester* method [4] based on eqns (5) was also examined. Unfortunately, the results obtained by this method using different literature values of $\Delta G_{tr}^{o}(H^+)$ [9—15] are not comparable and do not agree with experimental values of $K(S)$ as well. Only the values of *Alfenaar* [9], as stated by *Rochester* [4], give good results, but this fact may be incidental.

The equilibrium constants $K(S)$ calculated on the basis of the linear relationship between the Gibbs energies of transfer of the lyate and halide ions (eqn (6)) seem to be rather independent of the $\Delta G_{tr}^{o}(H^+)$ values which have been obtained on the basis of different nonthermodynamical assumptions [10, 11, 13, 15]. As they are in agreement with available experimental values of $K(S)$ for water and methanol, the presented method seems to be quite appropriate for calculating the constants $K(S)$ in water—methanol mixture. The mean values of $K(S)$ calculated from $\Delta G_{tr}^{o}(H^+)$ [10, 11, 13, 15] and the corresponding ratios of the lyate ions Q are also given in Table 2. The values thus obtained may be the most reliable for describing equilibrium (A) in the water—methanol system.

The equilibrium solvation of proton in two-component solvents is known [25]. It results from the data in Table 2 that the Rochester equation (6) is able to solve plausibly the equilibrium in alkaline region of the water—methanol system. After completing with further assumptions it might be used for other water—alcohol systems as well [6]. That enables us to extend our knowledge of acid—base equilibria taking place in those regions where they have not been hitherto known or are known with great uncertainty.

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