

## ACTIVITY RATIOS OF LYATE IONS IN THE WATER-ALCOHOL MIXTURES

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Received January 14, 1991

Accepted April 29, 1991

A new method for calculating the activity ratio of lyate ions in the water-alcohol mixtures is proposed on the basis of utilizing the linear relations between the Gibbs energies of ion transfer. The results for the water-methanol, -ethanol, and -2-propanol systems are compared with literature data. At the same time, the individual ionic products of water and alcohol in their mixtures were calculated. The accuracy of the method depends on the accuracy of experimental determination of the Gibbs energies of electrolyte transfer and of ionic products in mixed solvents.

In the binary mixtures of water (W) and alcohol (ROH), the ionic product,  $K_S$ , can be expressed by the relation<sup>1,2</sup>

$$K_S = a_{H^+}(a_{OH^-} + a_{RO^-}) = K_W + K_{ROH} = K_W(1 + Q_1), \quad (1)$$

where  $a_{H^+}$  is the proton activity,  $a_{OH^-}$ ,  $a_{RO^-}$  are the activities of hydroxide and alkoxide ions in the given mixture S,  $K_W$  and  $K_{ROH}$  are the individual ionic products of water and alcohol in the mixture,  $Q_1$  is the ratio of activities of alkoxide and hydroxide ions. Unfortunately, the individual ionic products  $K_W$ ,  $K_{ROH}$ , and/or ratio  $Q_1$  are not direct experimentally measurable quantities. For some special cases of binary mixtures (in pure solvents), constants  $K_1$  were determined for the equilibrium of lyate ions<sup>2-10</sup>. They are defined by the relation

$$K_1 = (a_{RO^-} - a_{H_2O}) / (a_{OH^-} - a_{ROH}) = Q_1 a_{H_2O} / a_{ROH} \quad (2)$$

but these constants were hitherto not determined experimentally and are along with  $K_W$ ,  $K_{ROH}$ , and ratio  $Q_1$  accessible only by calculating.

Gaboriaud and co-workers<sup>11</sup> suggested a solution of this problem for the water-methanol mixtures by introducing an empirical equation for the dependence of ionic product on the mixture composition from which it is possible to calculate the ratio of activities of lyate ions  $Q_1$ . By extending this method to the water-ethanol, -1-propanol, and -2-propanol mixtures has not been so successful<sup>9</sup> because the

analogous empirical equations have described the dependence of ionic product on the mixture composition at most up to 50 mass % of organic component.

Another procedure for the same system of mixed solvents was proposed by Rochester<sup>2</sup>. The ionic product of water and ionic product of methanol change with increasing methanol concentration. To express the dependence of ionic products of both the components on the mixture composition, he proposed two methods. The first one assumes that the activity coefficients of methoxide and hydroxide ions are a linear function of methanol mole fraction. The second one is based on the assumption that the Gibbs energies of transfer of methoxide and hydroxide ions are a linear function of the average Gibbs energy of transfer of halide ions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ). The results of both the methods are comparable and are as well comparable with those reported by Gaboriaud and co-workers<sup>11</sup>. A deficiency, however, consists in the applicability of both the methods only to 80 mass % methanol and a considerable dependence on the way of determining  $\Delta G_t^0(\text{ion})$  for halide ions<sup>12</sup>. On extending the Rochester methods to the mixtures of water with ethanol and 2-propanol, the results obtained were of limited validity<sup>9</sup> only.

Considering that the calculation of activity ratio of lyate ions and/or individual ionic products has hitherto been carried out only for the water-methanol mixture, it is therefore probable that the considered assumptions for this calculation are not of a general validity. This contribution shows the possibility of a new method for calculating the activity ratio of lyate ions,  $Q_1$ , in binary mixtures of water and alcohol.

### *Principle of the Method*

For the experimentally obtained Gibbs energies of transfer from a standard solvent (conventionally is chosen water<sup>13</sup>) into the given solvent S,  $\Delta G_t^0(\text{electrolyte})$ , it is assumed that they are additive<sup>14</sup>, i.e., equal to the sum of  $\Delta G_t^0(\text{anion}) + \Delta G_t^0(\text{cation})$ . This assumption follows from the requirement of choice of standard state as an infinitely diluted solution of the given electrolyte in an arbitrary solvent S where no interactions between cations and anions are considered any more.

Let, in the given solvent S, the Gibbs energies of transfer be known for electrolytes containing all combinations of  $A_1, A_2, \dots, A_n$  anions and  $K_1, K_2, \dots, K_m$  cations, that means altogether  $(n \times m)$  values of  $\Delta G_t^0(\text{electrolyte})$  which can be arranged in the matrix form.

$$\begin{bmatrix} \Delta G_t^0(K_1) + \Delta G_t^0(A_1) & \Delta G_t^0(K_1) + \Delta G_t^0(A_2) & \dots & \Delta G_t^0(K_1) + \Delta G_t^0(A_n) \\ \Delta G_t^0(K_2) + \Delta G_t^0(A_1) & \Delta G_t^0(K_2) + \Delta G_t^0(A_2) & \dots & \Delta G_t^0(K_2) + \Delta G_t^0(A_n) \\ \vdots & \vdots & & \vdots \\ \Delta G_t^0(K_m) + \Delta G_t^0(A_1) & \Delta G_t^0(K_m) + \Delta G_t^0(A_2) & \dots & \Delta G_t^0(K_m) + \Delta G_t^0(A_n) \end{bmatrix}_S \quad (3)$$

Matrix (3) describes the experimentally accessible values of Gibbs energies of

transfer of electrolyte in the given solvent S but at the same time it is evident that not all values in it are independent. The number of independent quantities (i.e., the base of the given system) is equal to the rank of matrix (3) which can be determined in the following way:

- the first column is subtracted from the other ( $n - 1$ ) columns,
- the first row is subtracted from the other ( $m - 1$ ) rows.

Matrix (4) of rank 2

$$\begin{bmatrix} \Delta G_i^0(K_1) + \Delta G_i^0(A_1) & \Delta G_i^0(A_2) - \Delta G_i^0(A_1) & \dots & \Delta G_i^0(A_n) - \Delta G_i^0(A_1) \\ \Delta G_i^0(K_2) - \Delta G_i^0(K_1) & 0 & \dots & 0 \\ \vdots & \vdots & & \vdots \\ \Delta G_i^0(K_m) - \Delta G_i^0(K_1) & 0 & \dots & 0 \end{bmatrix}_s \quad (4)$$

results from these rearrangements, which means that also the initial matrix (3) has therefore rank 2 and therefore, in given solvent S, the arbitrary Gibbs energy of transfer of electrolyte,  $\Delta G_i^0(\text{electrolyte})$ , is a linear function of two others. It is evident from matrix (4) as well that there exist linear relations between columns or rows which can be written in the general form

$$\Delta G_i^0(A_i) - \Delta G_i^0(A_j) = \alpha(ijk)_s [\Delta G_i^0(A_k) - \Delta G_i^0(A_j)], \quad (5)$$

$$\Delta G_i^0(K_i) - \Delta G_i^0(K_j) = \beta(ijk)_s [\Delta G_i^0(K_k) - \Delta G_i^0(K_j)], \quad (6)$$

where  $\alpha(ijk)_s$ ,  $\beta(ijk)_s$  are proportionality factors. Both the relations satisfy as well the first requirement of linear dependence between the Gibbs energies of electrolyte transfer on the assumption that the electrolytes have a common cation (Eq. (5)) or anion (Eq. (6)).

All the procedure was carried out for the case of univalent anions and cations. The extension for polyvalent ions, however, does not make substantial difficulties. The most important problem of applicability of these equations is the behaviour of coefficients  $\alpha(ijk)_s$  and  $\beta(ijk)_s$  in dependence on a change of solvent S which cannot be explained on the basis of thermodynamics. However, on the assumption that there exist linear relations between solvation energies or there exist some extra-thermodynamic relations describing the dependence of  $\Delta G_i^0(\text{ion})$  on solvent (an extensive discussion was carried out by Kamlet and co-workers<sup>14</sup>),  $\alpha(ijk)_s$  and  $\beta(ijk)_s$  will be constant in all solvents S, which means that Eqs (5) and (6) have the same form for the given anions  $A_i$ ,  $A_j$ ,  $A_k$  or for the given cations  $K_i$ ,  $K_j$ ,  $K_k$  in all solvents. The advantage of relations defined in this way is their independence of the estimate of ionic contribution  $\Delta G_i^0(\text{ion})$  because their differences are experimentally measurable, and the independence of the choice of definition (molar, molal, or rational).

In such a way defined relations can be used for estimating the activity ratio of

lyate ions  $Q_1$ . Let the Gibbs energies of transfer of electrolytes or ions be known in a mixture of water with non-protogenic organic solvent where  $\text{OH}^-$  is the only lyate ion (e.g., the water-dioxan mixture). For such systems, Eq. (5) is rewritten into the form

$$\Delta G_t^0(\text{OH}^-) - \Delta G_t^0(\text{BPh}_4^-) = \alpha_s [\Delta G_t^0(\text{Cl}^-) - \Delta G_t^0(\text{BPh}_4^-)], \quad (7)$$

where  $\alpha_s$  is the simplified record of coefficient  $\alpha(\text{OH}, \text{Cl}, \text{BPh}_4)_s$ . Values  $\Delta G_t^0(\text{OH}^-)$  in such systems are calculated from ionic products of water in mixture ( $K_s$ ) and in water ( $K_w$ ) by means of the relation

$$\Delta G_t^0(\text{OH}^-) = 2.303RT(\text{p}K_s - \text{p}K_w) - \Delta G_t^0(\text{H}^+). \quad (8)$$

By inserting Eq. (8) into Eq. (7) we get Eq. (9).

$$2.303RT(\text{p}K_s - \text{p}K_w) - \Delta G_t^0(\text{HCl}) = (\alpha_s - 1) [\Delta G_t^0(\text{Cl}^-) - \Delta G_t^0(\text{BPh}_4^-)] \quad (9)$$

from which it is possible to calculate coefficient  $\alpha_s$  for the mixtures of water with non-protogenic solvent.

In mixtures of water with protogenic solvent, however, Eq. (7) with the same value of  $\alpha_s$  will hold according to the above-mentioned assumption as well but Eq. (8) will take here form (10) with regard to the equilibrium of lyate ions:

$$\Delta G_t^0(\text{OH}^-) = 2.303RT(\text{p}K_s - \text{p}K_w) - \Delta G_t^0(\text{H}^+) + RT \ln(1 + Q_1). \quad (10)$$

By inserting Eq. (10) into Eq. (7) we get Eq. (11)

$$\begin{aligned} 2.303RT(\text{p}K_s - \text{p}K_w) - \Delta G_t^0(\text{HCl}) + RT \ln(1 + Q_1) = \\ = (\alpha_s - 1) [\Delta G_t^0(\text{Cl}^-) - \Delta G_t^0(\text{BPh}_4^-)]. \end{aligned} \quad (11)$$

On comparing Eqs (9) and (11) it is evident that the deviations from linearity defined by Eq. (9) in mixtures of water with protogenic solvent (ROH) are conditioned by term  $RT \ln(1 + Q_1)$  in Eq. (11) from which the activity ratio of lyate ions in the given mixture can be calculated.

## RESULTS AND DISCUSSION

The proposed method of calculating the activity ratio of lyate ions  $Q_1$  is based on the assumption that there exists the same linear relation between the differences of Gibbs energies of ions (Eq. (5) or (6)) for all solvents or their mixtures. To illustrate this assumption, the dependence can serve of difference of Gibbs energies of transfer  $[\Delta G_t^0(\text{Br}^-) - \Delta G_t^0(\text{BPh}_4^-)]$  on the difference of  $[\Delta G_t^0(\text{Cl}^-) - \Delta G_t^0(\text{BPh}_4^-)]$ . The values of Gibbs energies of transfer for this dependence were taken from literature

(Marcus<sup>15</sup> and Glikberg and Marcus<sup>16</sup> for pure solvents, Abraham and co-workers<sup>17</sup> for the water-methanol mixture, Wells<sup>18</sup> and Bax and co-workers<sup>19</sup> for water with ethanol, Basu, Kundu<sup>20</sup> and Juillard, Tissier<sup>21</sup> for water with tert-butanol, Wells<sup>22</sup> for water and dioxan, Wells<sup>23</sup> for water and dimethyl sulfoxide, Cox and co-workers<sup>24</sup> for the water-acetonitrile mixture, and Marcus<sup>25</sup> for mixtures of water with alcohols). The dependence mentioned is illustrated in Fig. 1 for 83 pure and mixed solvents (some points in the figure overlap). The validity of Eq. (5) in the considered systems with constant value of  $\alpha(\text{Br}, \text{Cl}, \text{BPh}_4)_S = 0.873$  and correlation coefficient  $r = 0.9949$  is evident from Fig. 1.

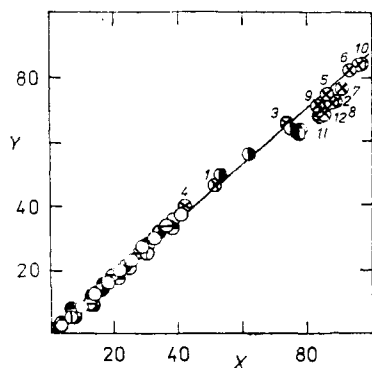


FIG. 1

The dependence of difference in Gibbs energies of ion transfer [ $\Delta G_i^0(\text{Br}^-) - \Delta G_i^0(\text{BPh}_4^-)$ ] on the difference [ $\Delta G_i^0(\text{Cl}^-) - \Delta G_i^0(\text{BPh}_4^-)$ ] in pure solvents [1-propanol (1), acetone (2), propylene carbonate (3), formamide (4), dimethylformamide (5), dimethylacetamide (6), N-methylpyrrolidone (7), nitrobenzene (8), trimethylsulfone (9), hexamethylphosphoric acid triamide (10), 1,1-dichloroethane (11), 1,2-dichloroethane (12)] and in mixtures of water and organic solvent [methanol-water  $\circ$ , ethanol-water  $\ominus$ , 2-propanol-water  $\ominus$ , 2-methoxyethanol-water  $\ominus$ , dioxan-water  $\bullet$ , ethylene glycol-water  $\ominus$ , acetonitrile-water  $\bullet$ , t-butanol-water  $\ominus$ , dimethylsulfoxide-water  $\bullet$ ] at 25°C.  $X = \Delta G_i^0(\text{Cl}^-) - \Delta G_i^0(\text{BPh}_4^-)$ ,  $Y = \Delta G_i^0(\text{Br}^-) - \Delta G_i^0(\text{BPh}_4^-)$

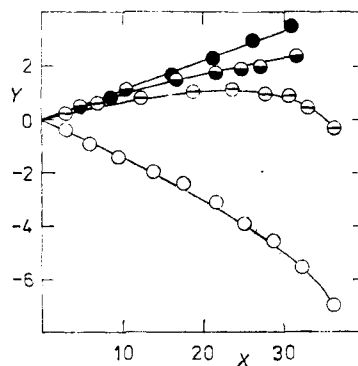


FIG. 2

The dependence of difference  $[2.303RT \cdot (pK_s - pK_w) - \Delta G_i^0(\text{HCl})]$  on difference in Gibbs energies of ion transfer [ $\Delta G_i^0(\text{Cl}^-) - \Delta G_i^0(\text{BPh}_4^-)$ ] for the binary mixtures water-dioxan  $\bullet$ , water-methanol  $\circ$ , water-ethanol  $\ominus$ , water-2-propanol  $\ominus$  at 25°C.  $X = \Delta G_i^0(\text{Cl}^-) - \Delta G_i^0(\text{BPh}_4^-)$ ,  $Y = 2.303 \cdot RT(pK_s - pK_w) - \Delta G_i^0(\text{HCl})$

Equations (9) and (11) were solved in a similar way. The literature values for the water-dioxan mixture (ionic products<sup>26</sup>, Gibbs energies of transfer<sup>22,27-31</sup>) were

TABLE I  
The calculated and literature values of the activity ratio of lyate ions  $Q_1$ , individual ionic products of water  $pK_W$  and alcohol  $pK_{ROH}$  in the mixtures water and alcohol at 25°C

Alcohol contents (wt. %)	Literature values of $Q_1$		$Q_1$	$pK_W$	$pK_{ROH}$	
	Gaboriaud	Rochester				
Water-methanol						
10.00	·09 <sup>a</sup>	·11 <sup>b</sup>	·11 <sup>c</sup>	·36	14.17	14.62
20.00	·30 <sup>a</sup>	·26 <sup>b</sup>	·26 <sup>c</sup>	·90	14.33	14.38
30.00	·58 <sup>a</sup>			1.70	14.50	14.27
40.00	1.20 <sup>a</sup>			3.02	14.68	14.20
50.00	1.95 <sup>a</sup>	1.06 <sup>b</sup>	1.16 <sup>c</sup>	4.94	14.87	14.18
60.00	2.80 <sup>a</sup>	1.59 <sup>b</sup>	1.82 <sup>c</sup>	8.32	15.10	14.18
70.00	3.90 <sup>a</sup>	2.51 <sup>b</sup>	2.97 <sup>c</sup>	13.64	15.38	14.25
80.00	6.50 <sup>a</sup>	4.54 <sup>b</sup>	5.69 <sup>c</sup>	22.26	15.79	14.44
90.00	14.50 <sup>a</sup>	12.75 <sup>b</sup>	13.26 <sup>c</sup>	40.27	16.10	14.50
Water-ethanol						
10.00	·18 <sup>d</sup>	·23 <sup>d</sup>		·04	14.21	15.74
20.00	·46 <sup>d</sup>	·52 <sup>d</sup>		·10	14.37	15.73
30.00	1.87 <sup>d</sup>	·89 <sup>d</sup>		·27	14.60	15.18
40.00				·51	14.82	15.11
50.00		1.91 <sup>d</sup>		·78	15.07	15.18
60.00				1.21	15.34	15.26
70.00				1.69	15.72	15.49
80.00				2.66	16.21	15.79
90.00				4.75	16.96	16.28
Water-2-propanol						
10.00	·18 <sup>d</sup>	·40 <sup>d</sup>		·02	14.28	15.94
20.00	·65 <sup>d</sup>	·89 <sup>d</sup>		·06	14.55	15.75
30.00	2.53 <sup>d</sup>	1.34 <sup>d</sup>		·13	14.76	15.64
40.00				·30	15.02	15.55
50.00	12.78 <sup>d</sup>	1.68 <sup>d</sup>		·39	15.29	15.70
60.00				·50	15.61	15.91
70.00				·53	16.12	16.39

<sup>a</sup> Ref.<sup>11</sup>, <sup>b</sup> ref.<sup>2</sup>, <sup>c</sup> ref.<sup>12</sup>, <sup>d</sup> ref.<sup>9</sup>.

used for calculating coefficient  $\alpha(\text{OH}, \text{Cl}, \text{BPh}_4)_S = 1.1$ . To calculate the ratio of lyate ions  $Q_1$ , the literature values of quantities needed were used as well, their values reported by more authors being averaged or interpolated (for the mixture of water with methanol<sup>1,17,28,32-39</sup>, with ethanol<sup>1,9,18,19,26,28,40-43</sup>, with 2-propanol<sup>1,9,20,26,28,40,44-47</sup>). The dependence of the left-hand side of Eq. (9) on the difference of Gibbs energies of transfer  $[\Delta G_t^0(\text{Cl}^-) - \Delta G_t^0(\text{BPh}_4^-)]$  is shown in Fig. 2. The deviations from linear dependence are caused by term  $RT \ln(1 + Q_1)$  which appears in Eq. (11) for protogenic mixtures. The values of  $Q_1$  given in Table I along with the literature ones<sup>2,9,11,12</sup> were calculated from these deviations. For the sake of completeness, the calculated individual ionic products of water  $pK_w$  and alcohol  $pK_{\text{ROH}}$  in the systems studied are given in Table I.

For the water-methanol system, the differences between the literature values<sup>2,11,12</sup> and calculated  $Q_1$  are evident from Table I. However, the given results are linearly dependent each other so that experiment should decide their rightness. In the systems of water with ethanol and 2-propanol, the literature values<sup>9</sup> are not mutually comparable and with regard to the results of kinetic studies<sup>3,4</sup>, they seem to be too high in comparison with the water-methanol system. On the contrary, the values calculated here comply with the qualitative anticipation that the ratio of activities of lyate ions in mixture will decrease, too, with decreasing polarity of organic component.

The proposed method makes it possible to calculate  $Q_1$  in the media where the hitherto used methods<sup>2,9,11,12</sup> have not been successful, and it is also less demanding as to the input information. In comparison with the method by Rochester<sup>2</sup>, it does not require the knowledge of activities of both components of solvent which are not always available. Its accuracy is connected with the accuracy of experimental determination of differences in the Gibbs energies of ion transfer and ionic products  $pK_s$ . The calculation will be subject to a great error for small values of  $Q_1$  so that the calculation will be difficult for the mixture of water with slightly polar organic solvent. For more polar organic solvents, the method may provide satisfactory results.

## REFERENCES

1. Rondinini S., Longhi S., Mussini P. R., Mussini T.: *Pure Appl. Chem.* **59**, 1693 (1987).
2. Rochester C. H.: *J. Chem. Soc., Dalton Trans.* **1972**, 5.
3. Murto J., Tomila E.: *Acta Chem. Scand.* **16**, 63 (1962).
4. Murto J.: *Acta Chem. Scand.* **18**, 1043 (1964).
5. Ballinger P., Long P. A.: *J. Am. Chem. Soc.* **82**, 795 (1960).
6. Unmack A.: *Z. Phys. Chem.* **133**, 45 (1928).
7. Wooley E. M., Tomkins J., Hepler L. G.: *J. Solution Chem.* **1**, 341 (1972).
8. Slonim I. Ya., Lyubomilov V. I.: *Zh. Fiz. Khim.* **48**, 842 (1974).
9. Mollin J., Pavelek Z., Schneiderová A., Vičar J., Šimánek V., Lasovský J.: *Collect. Czech. Chem. Commun.* **48**, 2156 (1983).

10. Hine J., Hine M.: *J. Am. Chem. Soc.* **74**, 5266 (1952).
11. Gaboriaud R., Lelièvre J., Schaal R.: *C. R. Acad. Sci., C* **266**, 746 (1968).
12. Pavelek Z.: *Chem. Papers* **42**, 299 (1988).
13. King E. J. in: *Physical Chemistry of Organic Solvent Systems* (A. K. Covington and T. Dickinson, Eds), Chapter 3. Plenum Press, London 1973.
14. Kamlet M. J., Abboud J. L. M., Taft R. W.: *Prog. Phys. Org. Chem.* **13**, 485 (1981).
15. Marcus Y.: *Pure Appl. Chem.* **55**, 977 (1983).
16. Glikberg S., Marcus Y.: *J. Solution Chem.* **12**, 255 (1983).
17. Abraham M. H., Hill T., Ling H. Ch., Schulz R. A., Watt R. A. C.: *J. Chem. Soc., Faraday Trans. 1* **80**, 489 (1984).
18. Wells C. F.: *J. Chem. Soc., Faraday Trans. 1* **80**, 2445 (1984).
19. Bax D., de Ligny C. L., Remijnse A. G.: *Rec. Trav. Chim. Pays-Bas* **91**, 965 (1972).
20. Basu M., Kundu K. K.: *Indian J. Chem. A* **23**, 812 (1984).
21. Juillard J., Tissier C.: *Electrochim. Acta* **27**, 123 (1982).
22. Wells C. F.: *J. Chem. Soc., Faraday Trans. 1* **74**, 1569 (1978).
23. Wells C. F.: *J. Chem. Soc., Faraday Trans. 1* **77**, 1515 (1981).
24. Cox B. G., Natarajan R., Waghorne W. E.: *J. Chem. Soc., Faraday Trans. 1* **75**, 86 (1979).
25. Marcus Y.: *Pure Appl. Chem.* **62**, 899 (1990).
26. Wooley E. M., Hurkot D. G., Hepler L. G.: *J. Phys. Chem.* **74**, 3908 (1970).
27. Elsemongy M. M., Fouda A. S., Amira M. F.: *J. Chem. Soc., Faraday Trans. 1* **77**, 1157 (1981).
28. Janz G. J. in: *Reference Electrodes. Theory and Practice* (D. J. G. Ives and G. J. Janz, Eds), Chapter 4. Academic Press, New York 1961.
29. Data J., Kundu K. K.: *Can. J. Chem.* **59**, 3149 (1981).
30. Bax D., Alfenaar M., de Ligny C. L.: *Rec. Trav. Chim. Pays-Bas* **90**, 1002 (1971).
31. Bax D., de Ligny C. L., Alfenaar M., Mohr N. J.: *Rec. Trav. Chim. Pays-Bas* **91**, 601 (1972).
32. Koskikallio J.: *Suom. Kemistilehti B* **30**, 111 (1957).
33. Wooley E. M., Tomkins J., Hepler L. G.: *J. Solution Chem.* **1**, 341 (1972).
34. Elsemongy M. M.: *J. Electroanal. Chem.* **90**, 67 (1978).
35. Oiwa I. T.: *J. Phys. Chem.* **60**, 754 (1956).
36. Paabo M., Bates R. G., Robinson A.: *J. Anal. Chem.* **37**, 462 (1965).
37. Paabo M., Robinson R. A., Bates R. G.: *J. Chem. Eng. Data* **9**, 374 (1964).
38. Bates R. G., Rosenthal D.: *J. Phys. Chem.* **67**, 1088 (1963).
39. Wells C. F.: *J. Chem. Soc., Faraday Trans. 1* **69**, 984 (1973).
40. Bose K., Das K., Das A. K., Kundu K. K.: *J. Chem. Soc., Faraday Trans. 1* **74**, 1051 (1978).
41. Popovych O., Dill A. J.: *Anal. Chem.* **41**, 456 (1969).
42. Popovych O., Gibofsky A., Berne D. J.: *Anal. Chem.* **44**, 811 (1972).
43. Sieckman E. F., Grunwald E.: *J. Am. Chem. Soc.* **76**, 3855 (1954).
44. Elsemongy M. M., Fouda A. S.: *J. Electroanal. Chem.* **114**, 25 (1980).
45. Morel J. P., Morin J.: *J. Chim. Phys.* **67**, 2018 (1970).
46. Robinson R. A., Stokes R. H.: *Electrolyte Solutions*, p. 471. Butterworths, London 1970.
47. Roy R. N., Bothwell A.: *J. Chem. Eng. Data* **15**, 548 (1970).

Translated by J. Linek.