EFFECT OF MEDIUM ON DISSOCIATION OF CARBOXYLIC ACIDS

Jiří MOLLIN[a], Zdeněk PAVELEK[b], Jitka NAVRÁTILOVÁ[a] and Alena RECMANOVÁ[a]

[a] *Department of Inorganic and Physical Chemistry,*
Palacký University, 771 46 Olomouc and
[b] *Research and Development Basis, Galena, 747 70 Opava*

pK Values of carboxylic acids have been measured in mixtures water–organic solvent and confronted with the Born equation. Solubilities of benzoic acid have been measured. From the pK and solubilities found the $\Delta G_t^0(C_6H_5COO^-)$ values have been calculated for various two-component solvents. The results agree with the idea that the ion transfer into another medium is affected not only by electrostatic, but also by non-electrostatic forces.

A number of papers (see refs[1,2]) deal with solvation of ions and its effect on dissociation of weak acids, nevertheless, this problem still attracts attention[3-5]. At present the most fruitful approach is based on the Gibbs energy of transfer of particles. The dissociation constants K^w and K^s apply to the dissociation equilibrium (A) (where M means the solvent) in water and in solvent S, respectively. The difference between their negative logarithms is given[6] by Eq. (1) which can be transcribed to the form (2), where $\Delta G_t^0(i)$ are the Gibbs energies of the particles transfer defined[7] by Eq. (3).

$$HA + M \rightleftharpoons MH^+ + A^- \tag{A}$$
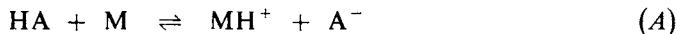
$$pK^s - pK^w = \log \gamma(H^+) + \log \gamma(A^-) - \log \gamma(HA) \tag{1}$$

$$2{\cdot}303RT(pK^s - pK^w) = \Delta G_t^0(H^+) + \Delta G_t^0(A^-) - \Delta G_t^0(HA) \tag{2}$$

$$\Delta G_t^0(i) = RT \ln \gamma(i) \tag{3}$$

For little soluble substances the Gibbs energy of transfer of neutral molecules is expressed[8] by Eq. (4). The Gibbs energy of transfer of ions can be divided into the electrical part given by the Born equation and the non-electrical part given[8] by Eq. (5). Finally the Eq. (2) can be transformed into Eq. (6) (ref.[9]).

$$\Delta G_t^0(HA) = RT \ln c_{sat}(H_2O) - RT \ln c_{sat}(S) \tag{4}$$

$$\Delta G_t^0(ion) = \Delta G_t^0(el) + \Delta G_t^0(non\text{-}el) \tag{5}$$

$$\Delta P = \Delta G_t^0(HA) - \Delta G_t^0(A^-) = 2\cdot303RT(pK^w - pK^s) + \Delta G_t^0(H^+) \qquad (6)$$

The dependence of ΔP on the solvent composition was followed in the water––methanol system for a number of compounds, but the dependence of ΔP or $\Delta G_t^0(i)$ of the individual particles in other binary solvent systems are not available. From Eqs (4) and (6) it is obvious that a solution of the problem will necessitate estimation of solubility and measurement of dissociation constants. In this work carboxylic acids have been chosen as the model group of compounds, their pK values being easily accessible and − in a number of cases − known with sufficient accuracy[10]. Changes in the size of the molecules in the group mentioned make it possible to estimate the applicability of the Born equation and, hence, operation of electrostatic effects accompanying a change of solvent.

EXPERIMENTAL

The pK values were measured titrimetrically at $25 \pm 0\cdot1°C$ using a glass and a silver chloride electrodes and a PHM-64 pH-meter (Radiometer, Copenhagen). The silver chloride electrode was filled with $0\cdot1$ mol dm^{-3} or saturated NaCl solution in the same solvent as that used for the titration. The electrodes system was immersed in the given solvent for 20 h before the measurement and then calibrated with buffers recommended in literature[11−17]. The electrode system with separated reference electrode gives results with the accuracy of $\pm0\cdot02$ pH (ref.[18]). The effect of temperature variations on pK is much lower than the error connected with the pH measurement in the given temperature interval[12,19,20]. Solutions of HCOONa, CH$_3$COONa, C$_2$H$_5$COOLi, C$_7$H$_7$COOLi, C$_6$H$_5$COOLi, and C$_{11}$H$_9$COOLi with concentrations of $0\cdot02$, $0\cdot01$, $0\cdot005$, $0\cdot0025$, $0\cdot00125$, and $0\cdot00062$ mol dm^{-3} were used for the titrations. The salts used were prepared by neutralization of formic, acetic, propionic, benzoic, phenylacetic, and 1-naphthylacetic acids with LiOH or NaOH solution, and their purity was checked analytically after recrystallization. Each titration was carried out twice, solution of HCl in the same solvent being used as the titration reagent. The pK values found were extrapolated to zero ionic strength using the expression $\sqrt{I}/(1 + \sqrt{I})$. The data obtained (in mol dm^{-3} scale) were converted to the scale defined by molar fractions using the known relations[9] and the known densities[21−25]. Concentration of saturated solutions of benzoic acid was measured titrimetrically at the temperature of $25 \pm 0\cdot1°C$.

RESULTS AND DISCUSSION

Enough accurate data are available on pK in water–methanol systems[10,26−29]. Therefore, only the pK values of phenylacetic and 1-naphthylacetic acid had to be measured. The literature data about pK of carboxylic acids are considerably incomplete for the water–ethanol, water–2-propanol, water–dioxane, water–dimethyl sulphoxide (DMSO), and water–dimethylformamide (DMFA) systems. To obtain the necessary uniformity, the pK values of carboxylic acids were remeasured in these media. The results are given in Table I. The solvent effects on dissociation constants are usually expressed by the dependence of pK vs $1/\varepsilon_r$, where ε_r means relative

TABLE I

Dissociation constants and ion radii of carboxylic acids at 25°C at zero ionic strength

Medium	% H$_2$O (by wt.)	formic	acetic	propionic	benzoic	phenyl-acetic	1-naphthyl-acetic	r_{HCOO^-} . 10^9 m
Water–methanol	80	—	—	—	—	4·70	4·70	
	60	—	—	—	—	5·26	5·25	1·3
	40	—	—	—	—	5·90	5·65	
	20	—	—	—	—	6·64	6·44	
	0	—	—	—	—	9·51^a	—	
Water–ethanol	100	3·75	4·75	4·88	4·20	4·31	4·23	
	90	3·90	4·92	5·21	4·59	4·74	4·55	
	70	4·12	5·25	5·49	5·21	5·19	5·37	
	50	4·64	5·89	6·22	5·83	5·91	5·78	1·6
	30	5·27	6·60	6·90	6·50	6·50	6·49	
	10	6·5	7·76	8·05	7·67	7·55	7·54	
	0	—	10·41^a	—	10·13^a	10·20^a	—	
Water–2-propanol	80	4·15	5·24	5·44	4·89	5·22	5·17	
	50	4·64	5·97	6·28	6·00	6·10	6·05	
	30	5·73	7·05	7·30	6·92	6·92	6·97	2·5
	10	6·92	8·25	8·86	8·26	8·12	8·00	
	0	—	—	—	10·20^b	—	—	
Water–dioxane	80	4·16	5·18	5·35	4·80	4·90	4·93	
	50	5·29	6·50	6·81	6·46	6·42	6·36	1·7
	30	7·13	8·30	8·66	8·30	8·44	8·21	
	18	8·67	9·59	10·17	9·67	9·73	9·69	
Water–dimethyl sulphoxide	80	4·13	—	—	4·49	—	—	
	60	4·31	—	—	4·94	—	—	
	40	5·11	—	—	5·72	—	—	0·14
	20	6·51	—	—	7·34	—	—	
	0	—	—	—	11·1^a	—	—	
Water–dimethyl-formamide^d	70	4·18	—	—	4·97	—	—	
	50	5·00	—	—	5·57	—	—	
	30	5·95	—	—	6·64	—	—	
	0	11·6^c	—	—	12·6^c	—	—	
r_{RCOO^-} . 10^9 m in 50% (by wt.) ethanol		1·6	1·2	1·0	0·8	0·8	0·8	

^{a} Ref.[10]; ^{b} Smolova[28]; ^{c} Petrov[29]; ^{d} the dimethylformamide concentration is given in % by vol..

permittivity of the medium. The necessary relative permittivities of the two-components solvents were taken from refs[30-33]. In this way the curves were obtained which are given in Figs 1 and 2 for formic and benzoic acids, respectively. From Fig. 2 it is clear that, in the water–alcohol and water–dioxane systems with low content of the organic component, pK of benzoic acid depends on $1/\varepsilon_r$ equally in all the mixtures. Only at higher content of the organic component the pK vs $1/\varepsilon_r$ dependence is different for different mixtures. In the region of high concentration of the organic component a high increase of pK with $1/\varepsilon_r$ was observed in all the solvents. This is due to the basicity change of the medium caused by decreasing water concentration: as water represents the more basic component of the system[34-39], its decreasing concentration shifts the equilibrium (A) to the left. The pK vs $1/\varepsilon_r$ dependences have entirely different course in the systems of water–dimethyl sulphoxide and water–dimethylformamide. Similar effects were observed with all the acids except formic acid and, partially, acetic acid, where the pK vs $1/\varepsilon_r$ dependences found were specific for each two-component solvent. Also the pK changes $(\Delta pK = pK^s - pK^w$, where the pK^i data are those of Table I) in a given system water–organic solvent are specific for each acid. The ΔpK values of formic, propionic, benzoic, and phenylacetic acids are plotted against $\Delta pK_{CH_3CO_2H}$ (for the water–ethanol system) in Fig. 3. Obviously, deviations of these dependences from linearity exceed
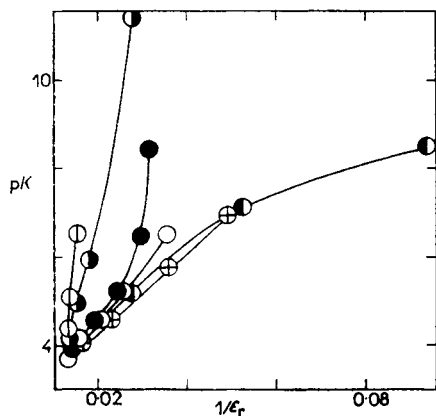

Fig. 1

Dependence of pK of formic acid on $1/\varepsilon_r$ of solvent at 25°C at zero ionic strength; ⊙ H_2O–DMSO, ◑ H_2O–DMFA, ● H_2O–CH_3OH, ○ H_2O–C_2H_5OH, ◐ H_2O–dioxane, ⊕ H_2O–$(CH_3)_2CHOH$
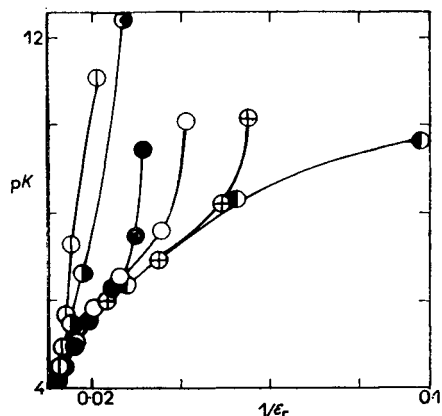
Fig. 2

Dependence of pK of benzoic acid on $1/\varepsilon_r$ of solvent at 25°C at zero ionic strength; ⊙H_2O–DMSO, ◑ H_2O–DMFA, ● H_2O–CH_3OH, ○ H_2O–C_2H_5OH, ⊕ H_2O–$(CH_3)_2CHOH$, ◐ H_2O–dioxane

the experimental error especially in the region of low concentrations of the organic cosolvent. Similar dependences were found for the other solvents.

Using the Born equation (7) derived from electrostatic model it is possible to calculate the ion radius. In Eq. (7) δ means the correction which transforms the molar scale into the molar fraction scale[9], ε_i are permittivities of the media, and the other symbols have their usual meaning. When introducing pK^i from Table I, we can calculate the ion radii

$$\Delta G_t^0(i) = \delta + 2.303RT(pK^s - pK^w) = \frac{Ne^2}{2r}\left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w}\right) \qquad (7)$$

which are given in Table I, too. For the calculation used were the pK obtained in the solvent containing $30-50\%$ (by wt.) of the organic component. Obviously, these radii agree only in order of magnitude (or the agreement is even worse) with those calculated from the bond lengths and angles. So, e.g. the diffraction methods[40,41] allow us to expect the radius of formiate ion equal to $0.14 \cdot 10^{-9}$ m, but the radii of formiate ion given in Table I are often greater. Moreover, it is not quite easy to explain the ten fold change of ionic radius when transferring the ion from the water--dimethyl sulphoxide system to water–alcohol. Finally, Eq. (7) necessitates a uniform pK^s vs $1/\varepsilon_s$ dependence which, however, was not observed. Thus the data of Table I
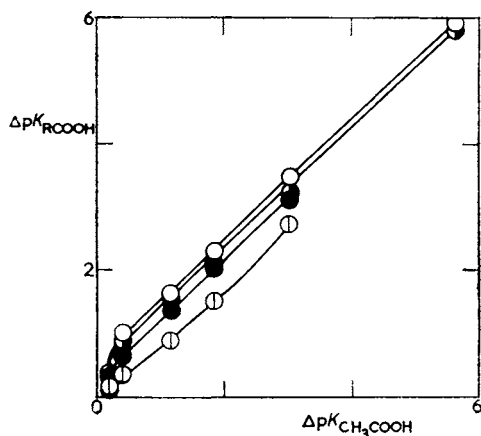

FIG. 3

Dependence of ΔpK of the acids on ΔpK of acetic acid in water–ethanol system. $\Delta pK = (pK^s - pK^w)$ calculated from Table I for ⊕ formic acid, ● propionic acid, ○ benzoic acid, ◐ phenylacetic acid
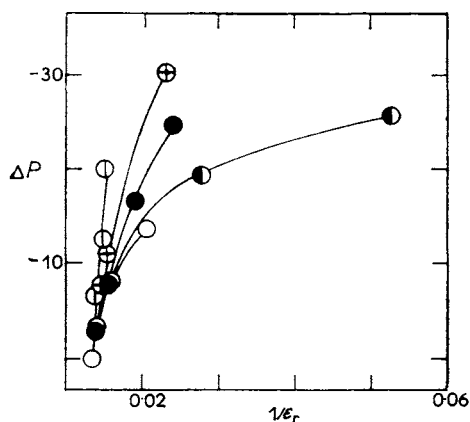
FIG. 4

Dependence of ΔP of benzoic acid on $1/\varepsilon_r$ of solvent at 25°C in the system: ⊕ H_2O--DMSO, ● H_2O–CH_3OH, ○ H_2O–C_2H_5.OH, ◖ H_2O–dioxane, ⊝ H_2O–$(CH_3)_2$.CHOH

confirm the view published earlier[8,26,42] that the pure electrostatic approach represents an only very rough model of the solvation processes.

A more detailed understanding of effects of solvent and solvation of the particles on pK is enabled by Eq. (6). For calculation of ΔP we took the pK's of Table I and transformed them into the data defined by means of molar fractions[9]. The Gibbs energy of the hydrogen ion transfer was taken from literature[43−46]. Figure 4 gives the dependence of the ΔP obtained for benzoic acid on $1/\varepsilon_r$ of the medium. The diversity of the curves obtained, as compared with the pK vs $1/\varepsilon_r$ dependence given in Fig. 2, consists in that the right-hand side of Eq. (6) also involves the Gibbs energy of the proton transfer which depends not only on electric properties of the solvent but also on the non-electric ones. Furthermore, it is obvious that the dependences found are linear in the region of low concentrations of the organic cosolvent, but they are curved above 50% concentration of the organic cosolvent. This effect is most distinct in the water–dioxane system and is due, to a considerable extent, to the dependence of $\Delta G_t^0(H^+)$ on composition of the mixture. Similar dependences were also found for the other acids.

From Eq. (6) we can also estimate $\Delta G_t^0(A^-)$. The necessary $\Delta G_t^0(HA)$ data can be

TABLE II

Solubility of benzoic acid, the Gibbs energies of transfer and radii of benzoate ion at 25°C

Medium	% H_2O by wt.	c_{sat} mol/dm^3	ΔP kJ/mol	$\Delta G_t^0(C_6H_5COO^-)$ kJ/mol	$r_{C_6H_5COO^-} \cdot 10^9$ m
Water–	100	0·0278	0	0	
–methanol	83·53	0·0516	— 3·0	1·47	
	65·53	0·206	— 7·7	2·7	1·1
	45·8	1·22	−16·8	7·4	
	24·06	—	−24·8	—	
Water–ethanol	90	—	— 3·3	2·1	
	70	—	— 8·2	0	0·73
	50	—	−13·2	3·2	
Water–	80	—	−11·1	6·4	0·45
–2-propanol	50	—	−30·6	18·9	
Water–dioxane	80	0·136	— 8·2	4·3	
	50	1·71	−19·8	9·6	0·71
	30	2·97	−25·6	14·0	
Water–dimethyl	80	0·0725	— 6·6	4·2	
sulphoxide	60	0·263	−12·9	7·4	0·047
	40	—	−20·3	—	

obtained from solubility according to Eq. (4). Table II gives the concentrations of the saturated solutions (necessary for the calculation) found at 25°C. The solubilities for the water–ethanol and water–2-propanol systems were taken from ref.[47] and ref.[48], resp.. The data of Table II agree well with literature[49,50]. Using Eq. (4) and these values, we calculated the Gibbs energy of the benzoic acid transfer $\Delta G_t^0(HA)$ which, introduced into Eq. (6), enables calculations of $\Delta G_t^0(A^-)$, i.e. the Gibbs energy of transfer of benzoate anion. These values are also given in Table II. The calculation of $\Delta G_t^0(HA)$ must respect the condition given in Eq. (4), i.e. low solubility of the compound. For sufficiently soluble compounds it is impossible to replace activity for concentration, and, hence, the $\Delta G_t^0(HA)$ values and the $\Delta G_t^0(A^-)$ values calculated therefrom (Table II) can be considered sufficiently accurate only for the solvents containing less than 50% (by wt.) of the organic component, because in such solvents concentration of saturated solution of benzoic acid is less than 1 mol dm^{-3}.

In the calculation of $\Delta G_t^0(A^-)$ the Gibbs energy of the proton transfer was respected. Therefore, it is interesting to verify the measure to which the $\Delta G_t^0(A^-)$ is affected by purely electrostatic forces, or, in other words, to which extent it is possible to neglect the $\Delta G_t^0(non\text{-}el)$ of benzoate ion in Eq. (5). This can be found easily by calculating the ion radius from Eq. (7). The ion radii calculated from the pK changes due to a solvent change from water to a mixed solvent water–organic solvent (with 20 to 30% by wt. of the latter) are also given in Table II. The benzoate anion radius found for the water–methanol system is greater than that given in ref.[9], but, except for the water–dimethyl sulphoxide system, these data agree in order of magnitude with the value $0 \cdot 5 \cdot 10^{-9}$ m which was calculated by means of bond lengths and bond angles. The obvious deviation of the radius of benzoate anion from the expected value (in water–dimethyl sulphoxide) again supports validity of Eq. (5) and distinct share of the non-electrostatic forces participating in the transfer of benzoate anion. Another criterion of significance of the terms at the right-hand side of Eq. (5) is the dependence of $\Delta G_t^0(C_6H_5CO_2^-)$ on $1/\varepsilon_r$ which should be linear according to the Born equation. The data of the present paper indicate its curvature at higher concentration of the organic cosolvent. Similar effects were observed also with other ions[51] and represent evidence in favour of non-zero value of $\Delta G_t^0(non\text{-}el)$ in Eq. (5).

The facts given show clearly that Eq. (2) describes, with sufficient accuracy, the solvation and the equilibrium processes connected therewith in solutions. The $\Delta G_t^0(H^+)$ values taken from literature[52] probably are sufficiently accurate, but a broader application of Eq. (2) is hindered by the present knowledge of the Gibbs energies of transfer of compounds in an only limited region of organic cosolvents[7], and, moreover, only few pieces of information are available on solubility and activity coefficients of compounds in two-component solvents. This restriction, however, does not decrease the importance of Eq. (2) and $\Delta G_t^0(i)$ values with respect to their mutual dependences on solubility and partial pressure of saturated vapours[8].

REFERENCES

1. Dyumaev K. M., Korolev B. A.: Usp. Khim. *49*, 2065 (1980).
2. King E. J. in the book: *Physical Chemistry of Organic Solvent Systems* (A. K. Covington and T. Dickinson, Eds). Plenum Press, London 1973.
3. Finkelshtein B. L., Istomin B. I.: Dokl. Akad. Nauk SSSR *256*, 1178 (1981).
4. Buleishvili M. I., Fialkov Yu. Ya., Chumak V. K.: Ukr. Khim. Zh. *49*, 599 (1983).
5. Nummert V. M.: Reakts. Sposobnost. Org. Soedin *20*, 275 (1983).
6. Alfenaar M., De Ligny C. L.: Rec. Trav. Chim. Pays-Bas *86*, 952 (1967).
7. Wells C. F.: Aust. J. Chem. *36*, 1739 (1983).
8. Alfenaar M., De Ligny C. L.:.Rec. Trav. Chim. Pays-Bas *86*, 929 (1967).
9. Wells C. F.: J. Chem. Soc., Faraday Trans. 1, *74*, 636 (1978).
10. Palm V. A., Ed.: *Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions*, Vol. 1. Viniti, Moscow 1975.
11. Bates R. G.: *Determination* of pH (russ.), p. 400. Chimiya, Leningrad 1972.
12. Bates R. G., Bennetto H. P., Sankar M.: Anal. Chem. *52*, 1598 (1980).
13. Gorina M. Yu., Seregina L. N.: Elektrokhimiya *8*, 829 (1980).
14. Levtchenko Yu. N., Malkova E. M., Shevalie V. I., Carapkina L. A.: Tr. Metrolog. Inst it. SSSR *161*, 19 (1975).
15. Bucharovitch A. A., Aleksandrov V. V.: Vest. Charkovskogo Univ. *46*, 14 (1970).
16. Aleksandrov V. V., Spirina S. V.: Zh. Fiz. Khim. *48*, 201 (1974).
17. Aleksandrov V. V.: *Kislotnost Nevodnykh Rastvorov*. Vysshaia Shkola, Charkov 1981.
18. Bacarella A. L., Grunwald E., Marshall H. P., Purlee L. E.: J. Phys. Chem. *62*, 856 (1958).
19. Strong L. E., Blubangh D. J., Cavalli C. R.: J. Solution Chem. *10*, 811 (1981).
20. Read A. J.: J. Solution Chem. *10*, 437 (1981).
21. Griffiths V. S.: J. Chem. Soc. *1952*, 1326.
22. Koglin W.: *Kurzes Handbuch der Chemie* (R. Vandenhoeck and V. Ruprecht, Eds), p. 243. Göttingen 1951.
23. Olsen A. L., Washburn E. R.: J. Phys. Chem. *42*, 275 (1938).
24. Shkodin A. M., Lovitskaya N. K., Lozhnikov V. A.: Zh. Obshch. Khim. *38*, 1006 (1968).
25. Morel J. P.: Bull. Soc. Chim. Fr. *1967*, 1405.
26. Bates R. G., Robinson R. A. in the book: *Chemical Physics of Ionic Solutions* (B. E. Conway, R. G. Barradas, Eds), p. 230. Wiley, New York 1966.
27. Shedlovsky T., Kay R. L.: J. Phys. Chem. *60*, 151 (1956).
28. Smolova N. T., Burmistrova T. I.: Zh. Fiz. Khim. *50*, 989 (1976).
29. Petrov S. M., Umanskii Yu. I.: Zh. Fiz. Khim. *42*, 3052 (1968).
30. Akerlof G.: J. Amer. Chem. Soc. *54*, 4125 (1932).
31. Critchfield F. E., Gibson J. A., Hall J. L.: J. Amer. Chem. Soc. *75*, 6044 (1953).
32. Lindeberg J. J., Kenttamaa J.: Suomen Kemistilehti *33B*, 104 (1960).
33. Douheret G., Morenas M.: C. R. Acad. Sci. *264C*, 729 (1967).
34. De Lisi R., Goffredi M., Liveri V. T.: J. Chem. Soc., Faraday Trans. 1, *74*, 1096 (1978).
35. Lilley T. H., De Perez M. M.: Electrochim. Acta *22*, 219 (1977).
36. Izmailov N. A., Aleksandrov V. V.: Zh. Fiz. Khim. *31*, 2619 (1957).
37. Perdoncin G., Scorano G.: J. Amer. Chem. Soc. *99*, 6983 (1977).
38. De Lisi R., Goffredi M., Liveri V. T.: J. Chem. Soc., Faraday Trans. 1, *72*, 436 (1976).
39. Contreras O. C., Figueroa S. N.: Bol. Soc. Chil. Quim. *27*, 28 (1982).
40. Schomaker V., O'Gorman J. M.: J. Amer. Chem. Soc. *69*, 2638 (1947).
41. Van Zandt W.: J. Chem. Phys. *15*, 232 (1947).
42. Feakins D., Watson P.: J. Chem. Soc. *1963*, 4686.

43. Wells C. F.: J. Chem. Soc., Faraday Trans. 1, *69*, 984 (1973).
44. Bhattacharyya A. K., Sengupta D., Lahiri S. C.: Z. Phys. Chem. (Leipzig) *265*, 372 (1984).
45. Wells C. F.: J. Chem. Soc., Faraday Trans. 1, *74*, 1569 (1978).
46. Wells C. F.: J. Chem. Soc., Faraday Trans. 1, *77*, 1515 (1981).
47. Gregg-Wilson N., Wright R.: J. Chem. Soc. *1928*, 3111.
48. Datta J., Kundu K. K.: J. Phys. Chem. 86, *4055* (1982).
49. Randall M., Failey C. F.: J. Amer. Chem. Soc. *49*, 2678 (1927).
50. Herz W., Lorentz E.: Z. Phys. Chem. (Leipzig) *140A*, 406 (1929).
51. Feakins D., Watson P.: J. Chem. Soc. *1963*, 4734.
52. Kundu K. K., Parker A. J.: J. Solution Chem. *10*, 847 (1981).

Translated by J. Panchartek.