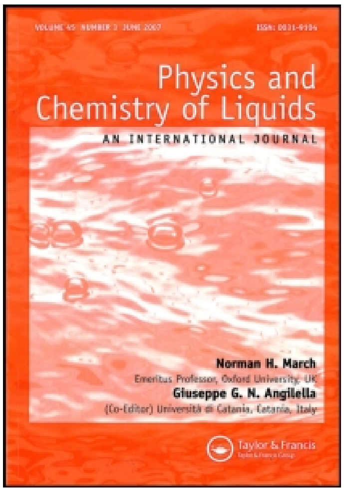

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Gibbs Energy and Conductivity Properties of NaCl Solutions in Water ISO-Propanol Mixtures at 298.15 K

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GIBBS ENERGY AND CONDUCTIVITY PROPERTIES OF NaCl SOLUTIONS IN WATER + ISO-PROPANOL MIXTURES AT 298.15 K

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The electrical conductivity of NaCl solutions and the emf of the cell: glass electrode (Na)|NaCl|AgCl|Ag in water + iso-propanol mixtures have been measured at 298.15 K. The values of limiting molar conductances (Λ_o), Walden products ($\Lambda_o\eta$), association constants (K_A), parameters of distance of ions (R) and the Gibbs energies of transfer of NaCl ($\Delta_t G^\circ$), taking into account the ionic association of electrolyte, were calculated. From literature data and those obtained in this paper the values of entropy of transfer ($\Delta_t S^\circ$) were calculated.

KEY WORDS: Conductivity, mixed solvent properties, water + iso-propanol mixture properties.

INTRODUCTION

This work is continuation of our study on thermodynamic properties of 1:1 electrolytes in water + alcohol mixtures[1–7]. In these investigations mainly sodium iodide was selected as electrolyte in the mixtures of water with three isomeric butanols[1–3], *n*-propanol[4], iso-propanol[5] and butanediols[6].

Recently we have reported on thermodynamic properties of NaCl solutions in water + *n*-propanol mixtures[7]. The pertinent literature shows, that the data on thermodynamic properties of 1:1 electrolyte in water + iso-propanol mixtures are only fragmentary. In the paper of Wells[8] are given, derived from literature, the values of Gibbs energies of transfer from water into water + iso-propanol mixtures for hydrogen and chloridium ions. In the review papers of Marcus[9,10] standard molar Gibbs energies of transfer of ions from water into water + iso-propanol mixtures were calculated on the basis of literature data. However in those papers[9,10] no data are given for sodium ions. Other data on $\Delta_t G^\circ$ for NaCl in water + iso-propanol system were not found. For this reason, conductometric and potentiometric studies on NaCl solution in the mixtures water + iso-propanol were performed. Potentiometric studies were made with the use of the cell containing glass sodium electrode. The

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usefullness of the glass electrodes in water-organic mixtures was presented elsewhere[11]. The system NaCl + water + iso-propanol has already been examined calorimetrically, in the range 0–35 wt% of iso-propanol[12]. Our investigations were restricted to the mixtures containing up to 80 wt% (53.43 mol%) of iso-propanol (i-PrOH), because the solubility of NaCl becomes too low.

EXPERIMENTAL

The procedures used in this work are similar to those described earlier[1-6]. The solutions were prepared by weight and compositions were accurate to within ± 0.01 wt%. As it was suggested in paper of Covington *et al.*[13] two different types of electrodes were used, in order to obtain the reliable values of Gibbs energy of transfer of electrolyte. As previously[1-6], a glass electrode reversible to sodium ions type ESL-051G-05 and additionally an OP-Na-711P electrode (Radelkis, Hungary)[7,11], both of ca 50 MΩ of nominal impedance at 298.15 K, were used. The emf measurements were carried out with a precise pH/mV meter, type LPH 430T (made by Solea Tacussel, France) with an inner impedance greater than 10^{12} Ω, the resolution of which was ± 0.1 mV. The range of electrolyte molality for emf measurements (always 12 molalities) was 0.01–0.1 mol kg^{-1}. The range of the corresponding concentrations for conductivity measurements are given in Table 1.

The temperature was kept constant within 0.01 K. The viscosities, densities and electric permittivities necessary for calculations were taken from the literature[14-17].

Table 1 Molar conductances (Λ) and corresponding concentrations (c) for NaCl in water + iso-propanol mixtures at 298.15 K.

$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ
5 wt% i-PrOH		10 wt% i-PrOH		20 wt% i-PrOH	
2.7756	104.39	0.8831	87.58	4.0163	63.16
4.6442	104.04	3.5757	87.27	5.0253	63.04
5.8080	103.86	6.4644	86.73	6.7116	62.88
7.6392	103.56	8.1940	86.56	8.2134	62.76
9.5121	123.38	13.428	86.10	10.394	62.60
13.257	102.97	15.218	85.93	12.938	62.42
17.395	102.67	17.064	85.83	18.253	62.14
20.405	102.39	21.120	85.62	21.050	61.99
24.405	102.12	24.453	85.38	26.604	61.75
28.660	101.82	28.277	85.19	31.859	61.53
33.672	101.59	33.958	84.89	37.750	61.35
38.995	101.30	38.346	84.73	42.381	61.18
43.581	101.05	42.953	84.53	47.559	61.05
50.610	100.78	55.861	84.04	52.539	60.91
56.595	100.49	63.137	83.83	62.544	60.67
64.747	100.20	71.014	83.55	71.553	60.46
73.887	99.90	80.046	83.36	80.786	60.26
81.694	99.50	88.187	83.17	89.807	60.09
90.026	99.40				

Table 1 *(Contd.)*

30 wt% i-PrOH		40 wt% i-PrOH		50 wt% i-PrOH	
5.7929	49.99	5.2249	41.73	6.9479	35.055
7.9331	49.78	6.5039	41.62	8.6131	34.896
9.4658	49.67	8.0779	41.50	10.744	34.727
11.556	49.54	10.082	41.34	12.317	34.613
14.991	49.38	12.710	41.16	14.605	34.450
17.207	49.24	17.010	40.92	19.237	34.160
20.852	49.07	19.695	40.77	23.942	33.911
26.133	48.86	24.413	40.56	27.900	33.720
30.808	48.67	29.095	40.38	33.621	33.492
35.920	48.51	33.612	40.22	37.535	33.320
40.569	48.36	37.254	40.06	42.942	33.134
45.594	48.22	43.262	39.89	48.805	32.498
52.379	48.04	49.624	39.71	54.948	32.763
58.984	47.86	55.035	39.68	63.167	32.526
67.733	47.68	63.046	39.35	70.670	32.323
76.580	47.49	71.146	39.16	79.491	32.101
85.360	47.29	79.217	38.99	86.941	31.933
93.589	47.15	87.430	38.83		

60 wt% i-PrOH		70 wt% i-PrOH		80 wt% i-PrOH	
4.2358	30.153	2.9729	26.817	3.4298	24.124
5.9271	29.913	3.8555	26.614	3.9635	23.963
7.2305	29.759	5.1058	26.348	4.8727	23.705
8.8205	29.587	6.3428	26.159	5.9535	23.420
10.555	29.406	7.9957	25.899	6.7405	23.228
11.914	29.290	10.020	25.609	7.3359	23.090
16.108	28.940	11.727	25.308	9.7038	22.618
23.627	28.430	13.643	25.173	11.313	22.326
28.430	28.147	17.668	24.745	12.352	22.143
32.004	27.971	21.417	24.425	14.259	21.858
37.012	27.732	25.405	24.116	15.484	21.545
47.643	27.287	29.609	23.815	21.739	20.886
53.585	27.062	33.006	23.602	24.645	20.573
61.567	26.814	37.439	23.333	27.600	20.376
69.077	26.591	48.320	22.775	31.722	19.934
77.110	26.354	55.517	22.436	35.432	19.533
84.339	26.148	62.610	22.141	39.593	19.324
		70.032	21.875		
		77.157	21.836		

Units: c/mol dm^{-3}, Λ/S cm^2 mol^{-1}

RESULTS AND DISCUSSION

Measurements of the Conductivity

The molar conductances of NaCl solutions in water + i-PrOH systems at 298.15 K for various electrolyte concentrations are given in Table 1. The conductometric data were analysed using the Fuoss-Justice equation[18,19] in the following form:

$$\Lambda = \alpha[\Lambda_o - S\alpha^{1/2}c^{1/2} + E(\alpha c)\ln(\alpha c) + J(\alpha c) + J_{3/2}\alpha^{3/2}c^{3/2}] \tag{1}$$

where: Λ_o – is a limiting molar conductance.

Table 2 Limiting molar conductance, Λ_o, ionic association constant K_A, standard deviations $\sigma\Lambda_o$ and σK_A, parameter R and estimated error ΔR, and Walden product, $\Lambda_o\eta$, for NaCl in water + iso-propanol mixtures at 298.15 K.

i–PrOH wt%	*i–PrOH mol%*	Λ_o	K_A	σK_A	R	ΔR	$\Lambda_o\eta$
0*	0*	126.49	0.4	0.1	4.5	0.5	1.126
5	1.55	105.62			4.0	1.0	1.184
10	3.22	88.33			4.5	1.0	1.254
20	6.97	64.10			4.5	1.0	1.339
30	11.40	51.01	1.2	1.0	5.0	2.5	1.347
40	16.66	42.72	2.8	1.0	5.0	1.0	1.256
50	23.06	36.29	6.3	1.5	5.5	1.0	1.105
60	31.02	31.24	14.4	2.2	6.0	1.0	0.942
70	41.16	27.98	35.2	2.8	6.5	1.0	0.792
80	54.53	26.04	98.2	4.8	8.0	1.0	0.658

* – value from ref. (7) in all cases $\sigma\Lambda_o = 0.01$ S cm^{2}mol^{-1}.
Units: Λ_o/S cm^2 mol^{-1}; $\sigma\Lambda/S$ cm^2 mol^{-1}; K_A/dm^3 mol^{-1}; σK_A/dm^3 mol^{-1}; $R/10^{-8}$cm; $\Delta R/10^{-8}$cm; $\Lambda_o\eta/S$ cm^2 mol^{-1}P

The degree of dissociation of electrolyte (α) was calculated from the relationship:

$$(1-\alpha)/\alpha^2 c\gamma_\pm^2 = K_A \tag{2}$$

where $\gamma_\pm$ is the activity coefficient, K_A is the ionic association constant and

$$\ln\gamma_\pm = -(A\alpha^{1/2}c^{1/2})/(1 + BR\alpha^{1/2}c^{1/2}) \tag{3}$$

A and B are the coefficients of the Debye-Hückel equation and R is the parameter of distance of ions. The analytical forms of the remaining parameters i.e. S, E, J and $J_{3/2}$ have been presented elsewhere[18–21].

The values of Λ_o, K_A and R (collected in Tab. 2) were obtained with the use of the well-known procedure (see for example paper of Fuoss[22]). In this method the optimized values of Λ_o and K_A were acceptable, for which the function $\sigma_\Lambda = f(R)$ did have a sharp minimum (σ_Λ is the standard deviation of the experimental results), as it was explained in paper[7].

The obtained in this manner values of Λ_o, K_A and R together with their standard deviations are collected in Table 2.

The dependencies of Λ_o, $\Lambda_o\eta$, K_A and R vs. mixed solvent composition are presented in Figures 1–4, respectively.

As it is shown in Table 2 and Figure 1, the values of Λ_o for NaCl decrease gradually with increasing of the i-PrOH content in the mixture, particularly in the range of the small amounts of the alcohol content in the system. This behaviour can be attributed mainly to the increase of the viscosity of the solvent with increasing of the iso-propanol content. For this reason, it is better to discuss the results in terms of the Walden product ($\Lambda_o\eta$). As results from our earlier studies[1–7] and from

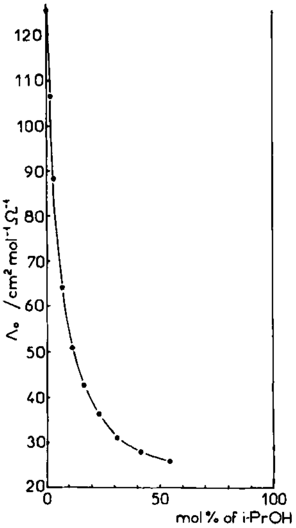

Figure 1 Limiting molar conductances, Λ_o, for NaCl in water + iso-propanol mixtures at 298.15 K.

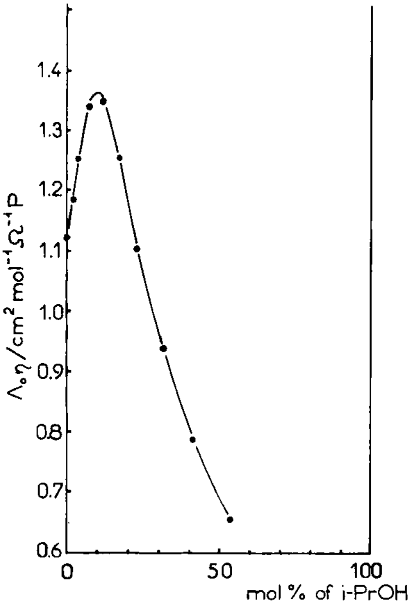

Figure 2 Walden products, $\Lambda_o\eta$, for NaCl in water + iso-propanol mixtures at 298.15 K.

literature data[29,24], the non-monotonic course of relationship $(\Lambda_o\eta) = f$(content) can be connected with selective solvation of ions by water dipoles, in the water-rich region.

The above conclusion can be also confirmed by the dependencies presented in Figures 3 and 4.

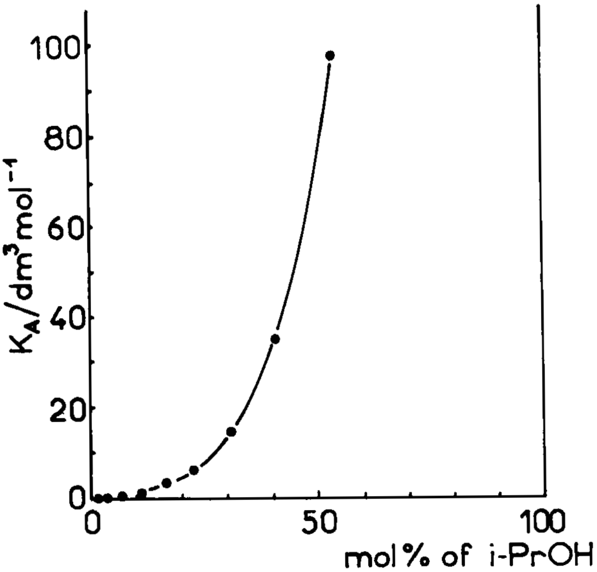

Figure 3 Values of K_A as a function of the iso-propanol content for NaCl in water + iso-propanol mixtures at 298.15 K.

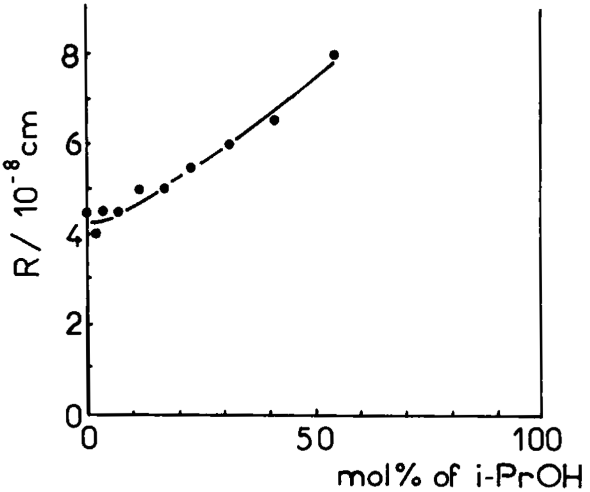

Figure 4 Values of R as a function of the iso-propanol contents for NaCl in water + iso-propanol mixtures at 298.15 K.

As it is seen, any considerable changes in the R and K_A values are observed, when small amounts of iso-propanol are added to water. At higher alcohol contents (above 10 mol%) an increasing displacement of water dipoles by iso-propanol dipoles occurs. The increase in the effective ionic radius results in a decrease of the

Walden product. Simultaneously, the values of R and K_A increase with the increasing of alcohol content in the mixture. This may be connected with the main role of the relative electric permittivity in the ion pair formation process.

The Emf Measurements

The values of the standard emf ($E^{\circ\prime}$) of the cell: Glass electrode (Na)|NaCl|AgCl|Ag in water + i-PrOH mixtures at 298.15 K was determined by extrapolation to $m\alpha = 0$ the function:

$$f(m\alpha) = E + \frac{2R_gT}{F}\ln m\alpha - \frac{2R_gT}{F}\frac{A\sqrt{\rho_0 m\alpha}}{1 + BR\sqrt{\rho_0}\alpha} - \frac{2R_gT}{F}\ln(1 + 0.002\, m\alpha M_1) \quad (4)$$

The meaning of all symbols used in (4) is described in[1-5]. The degree of the electrolyte dissociation, α, was calculated from the ionic association constant, K_A, obtained in this work. The standard emf, $E^{\circ\prime}$, and their standard errors are listed in Table 3. The association constants for NaCl in the investigated mixtures are relatively small. However, even in this case, the correction for ionic association should be taken account during the calculations of the standard emfs of the cells.

For example, in the mixture containing 31.02 mol% iso-PrOH, the value of K_A for NaCl is equal 14.4 and the electrolyte may be considered as completely dissociated.

However, the difference between the values of $E^{\circ\prime}$ obtained with and without taking into consideration ionic association are -0.2530 V and -0.2489 respectively, which corresponds with the change in the Δ_tG° value of 395 J mol^{-1}.

The Gibbs energies of NaCl transfer from water to the mixed solvents can be calculated by using

$$\Delta_tG^\circ = -F(E^{\circ\prime\text{mix}} - E^{\circ\prime\text{w}}) \quad (5)$$

where $E^{\circ\prime\text{mix}}$ and $E^{\circ\prime\text{w}}$ are the standard electromotive forces of the cell, determined from (4), in the mixed solvents and in water, respectively. The reason for which the values of the asymmetry potential of glass electrode can be neglected in the water-alcohol mixtures, was given previously[4-6].

Taking into account the statistical error of the $E^{\circ\prime}$ values and the errors of K_A values (ΔK_A), we estimated the error of $E^{\circ\prime}$ on ca. 0.3–0.4 mV and the error of Δ_tG° values on ca. 80 J mol^{-1}. The values of Δ_tG° (calculated from (5)) are collected in Table 3. In the same Table are also collected, derived from the literature[12], the values of the enthalpy of transfer of NaCl (Δ_tH°) together with the standard entropies of transfer (Δ_tS°) determined from

$$\Delta_tS^\circ = (\Delta_tH^\circ - \Delta_tG^\circ)/T \quad (6)$$

As is seen from the data given in Table 3, the values of $E^{\circ\prime}$ obtained from two types of electrodes i.e. ESL-51G-05 and OP-Na-711P are quite different. However, the values of Δ_tG° obtained with two types of electrodes are almost the same (Tab. 3). This fact confirms additionally our earlier opinion[7,11,25] that the Δ_tG° values

Table 3 The values of standard emf $E^{\circ\prime}$ and thermodynamic functions of transfer of NaCl from water to water + iso-propanol mixtures at 298.15 K.

n-PrOH/ wt%	*n-PrOH/ mol%*	E°	$\Delta_t G^\circ$	$\Delta_t H^\circ$	$\Delta_t S^\circ$
0.00	0.00	−0.1063[a]	0	0	0
		−0.1929[b]	0	0	0
5.00	1.55	−0.1178[a]	1109	1500	1.31
		−0.2042[b]	1090		
10.00	3.22	−0.1278[a]	2074	3005	3.12
		−0.2147[b]	2103		
15.00	5.02	−0.1400[a]	3251	4495	4.17
		−0.2269[b]	3280		
20.00	6.97	−0.1517[a]	4380	5915	5.14
		−0.2383[b]	4380		
25.00	9.15	−0.1646[a]	5625	7105	4.96
		−0.2512[b]	5625		
30.00	11.40	−0.1730[a]	6435	7025	1.98
		−0.2596[b]	6435		
35.00	13.90[c]	−0.1841[a]	7506	6545	−3.22
		−0.2709[b]	7525		
40.00	16.66	−0.1956[a]	8616		
		−0.2822[b]	8616		
50.00	23.06	−0.2209[a]	11057		
		−0.3079[b]	11096		
60.00	31.02	−0.2530[a]	14156		
		−0.4787[b]	14144		
80.00	54.53	−0.3532	23822		
		−0.4401	23851		

[a] - ESL-51G-05 electrode.

[b] - OP-Na electrode.

[c] - value of K_A interpolated from the data obtained in this work in all cases σE° did not exceed 0.0002 V for both types of the electrodes used.

Units: $E^{\circ\prime}$/V; $\Delta_t G^\circ$/J mol^{-1}; $\Delta_t H^\circ$/J mol^{-1}; $\Delta_t S^\circ$/J mol^{-1}K^{-1}.

obtained with different glass electrodes (including those used in the present study) do not depend substantially on the type of the electrode used. A similar conclusion are given by Covington *et al.*[13]. The dependencies of $\Delta_t G^\circ$, $\Delta_t H^\circ$ and $\Delta_t S^\circ$ on the mixed solvent composition are presented in Figure 5.

As it is seen in Figure 5, the values of $\Delta_t G^\circ$ increase monotonically with increasing iso-propanol content within the investigated range of the mixed solvent composition. The increase of the $\Delta_t G^\circ$ value with increasing iso-propanol content suggest, that the spontaneous solvation of NaCl decreases along with increasing iso-propanol content. The monotonic course of $\Delta_t G^\circ$ is probably due to the commonly observed compensation of the entropic and enthalpic effect. In fact, as it follows from Table 3 and Figure 5, both the enthalpies and entropies of transfer of NaCl from water to water + iso-propanol mixtures have their maxima in the water-rich region, which is typical for the water + alcohol mixtures. These maxima are extensively explained and discussed in paper[12].

As it was mentioned earlier, the symmetrical 1:1 electrolytes in water + iso-propanol mixtures has not been well studied[9,10]. This suggest, that further studies are necessary in order to obtain values of $\Delta_t G^\circ$ for single ions.

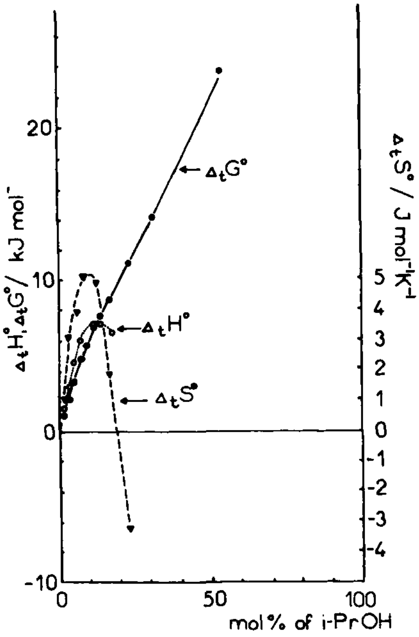

Figure 5 Gibbs energy Δ_tG°, enthalpy Δ_tH° and entropy $T\Delta_tS^\circ$ of transfer of NaCl from water to water + iso-propanol mixtures at 298.15 K.

The appropriate studies are in way and their results will be given in subsequent paper.

This work is dedicated to Professor Heinz Schmidkunz (University Dortmund, Faculty of Chemistry, Germany) on the occasion of his 65th birthday.

References

1. A. Bald, J. Gregorowicz, A. Szejgis and H. Piekarski, *Thermochim. Acta*, **205**, 1143 (1992).
2. A. Bald, J. Gregorowicz and A. Szejgis, *J. Electroanal. Chem.*, **340**, 153 (1992).
3. A. Bald, J. Gregorowicz and A. Szejgis, *Phys. Chem. Liq.*, **26**, 121 (1993).
4. A. Bald, *Pol. J. Chem.*, **67**, 923 (1993).
5. A. Bald, *J. Electroanal. Chem.*, **352**, 29 (1993).
6. A. Bald, *J. Chem. Research* **(S)**, **142** (1993); **(M)**, **1001** (1993).
7. J. Gregorowicz, A. Szejgis and A. Bald, *Pol. J. Chem.* (1995) in press.
8. C. F. Wells, *J. Chem. Soc. Fraday Trans.* I, **70**, 694 (1974).
9. Y. Marcus, *Pure Appl. Chem.*, **55(6)**, 977 (1983).
10. Y. Marcus, *Pure Appl. Chem.*, **62(5)**, 899 (1990).
11. J. Gregorowicz and A. Bald, *J. Electroanal. Chem.*, **374**, 109 (1994).
12. H. Piekarski, *Can. J. Chem.*, **64**, 2127 (1986).
13. A. K. Covington and J. M. Thain, *J. Chem. Soc. Faraday Trans.*, **I**, **71**, 78 (1975).
14. H. Piekarski, Ph. D. Thesis, University of *Łódź*, 1975.
15. J. Timmermans, "The Physico-Chemical Constant of Binary Systems in Concentrated Solutions", vol IV, Interscience Publishers Inc., New York, 1960, pp. 213, 217.
16. S. Taniewska-Osińska and A. Kacperska, *Acta Univ. Lodz. Folia Chimica*, **2**, 25 (1983).
17. S. Taniewska-Osińska and A. Kacperska, *Pol. J. Chem.*, **54**, 1351 (1979).
18. J. C. Justice, *Electrochim. Acta*, **16**, 701 (1971).

19. E. Renard and J. C. Justice, *J. Solution Chem.*, **3**, 633 (1974).
20. J. Barthel, J. C. Justice and R. Wachter, *Z. Phys. Chem.*, NF, **84**, 100 (1973).
21. R. M. Fuoss and L. Accascina, "Electrolytic Conductance", Interscience, New York, 1959, p.195.
22. R. M. Fuoss, *J. Phys. Chem.*, **82**, 2427 (1978).
23. T. Broadwater and R. L. Kay, *J. Phys. Chem.*, **74**, 3802 (1970).
24. G. Petrella and H. Petrella, *Electrochim. Acta*, **27**, 1733 (1982).
25. Z. Kozłowski, A. Bald and J. Gregorowicz, *J. Electroanal. Chem.*, **288**, 75 (1990).