

Conductivity Studies on Some Alkali Metal Iodides in Aqueous N,N-Dimethylformamide Solutions at 298.15 K

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Summary. Conductance measurements for NaI, KI, RbI, and CsI in water/N,N-dimethylformamide mixtures over the whole composition range at 298.15 K are reported. The data were analyzed employing the *Fuoss-Justice* equation in terms of limiting molar conductances (Λ_0), *Walden* products ($\Lambda_0\eta$), and association constants (K_A). The results indicate that the salts are weakly associated in the above solvent mixture. Variation in the *Walden* products with solvent composition are briefly discussed. The results were also compared with values reported previously for some alkali metal chlorides and bromides.

Keywords. Conductances; NaI; KI; Rb; CsI; Water N,N-dimethylformamide mixtures; *Walden* products.

Untersuchungen zur elektrischen Leitfähigkeit einiger Alkalimetalliodide in wäßrigen N,N-Dimethylformamidlösungen bei 298.15 K

Zusammenfassung. Die elektrische Leitfähigkeit von NaI, KI, RbI und CsI wurde in N,N-Dimethylformamid-Wasser-Mischungen verschiedener Zusammensetzung bei 298.15 K gemessen. Die erhaltenen Daten wurden analysiert und bezüglich der Grenzäquivalenzleitfähigkeiten (Λ_0), der *Walden*-Produkte ($\Lambda_0\eta$) und der Assoziationskonstanten (K_A) ausgewertet. Die Ergebnisse zeigen, daß diese Salze in den verwendeten Lösungsmittelgemischen nur schwach assoziiert sind. Die Änderungen der *Walden*-Produkte in Abhängigkeit der Lösungsmittelzusammensetzung werden kurz diskutiert. Abschließend werden die Resultate mit Ergebnissen früherer Messungen, in denen das Verhalten von Alkalimetallchloriden und Alkalimetallbromiden untersucht wurde, verglichen.

Introduction

Conductometric properties of electrolyte solutions in water-DMF have been a subject of interest for many years. *Singh et al.* [1] have published conductance data for sodium nitrite, chloride, and acetate in water-DMF mixtures at 308.15 K. *Bahadur et al.* [2] have reported on conductivities of sodium, potassium, and ammonium nitrates in DMF-water mixtures at 298.15 K. Some transfer number data for potassium as well as the conductances of CsCl, KBr, KCl, and KSCN in the same solvent system at 298.15 K are also known from the literature [3]. A few

years ago we have published our results on the conductivity properties of some alkali metal chlorides in water-DMF mixtures at 298.15 K [4]. Very recently, we have reported on the results of conductivity measurements on some alkali metal bromides in water-DMF system at 298.15 K. Based on the above mentioned results, we have decided to extend our investigations to some alkali metal iodides. In our opinion, the new results can provide more detailed information on differences in conductometric properties of ions.

Results and Discussion

As in previously published papers [9–26], the conductance data were analyzed using the *Fuoss–Justice* equation [27–29] in the form

$$\Lambda = \alpha(\Lambda_0 - S(\alpha c)^{1/2} + E(\alpha c)\ln(\alpha c) + J(\alpha c) + J_{3/2}(\alpha c)^{3/2}) \quad (1)$$

together with

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

and

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

In these equations Λ_0 is the limiting molar conductance, α is the dissociation degree of the electrolyte, K_A is the ion association constant, R is the distance parameter of ions, and y_{\pm} is the mean activity coefficient of ions on the molar scale; the activity coefficient of the ion pairs is assumed to be equal to unity as usual for diluted solutions. A and B are the *Debye-Huckel* equation coefficients. The analytical forms of the parameters S , E , J , and $J_{3/2}$, are given in Refs. [27–30]. The values of Λ_0 , K_A , and R were obtained using the procedure given by *Fuoss* [31]. In this method, optimized values of Λ_0 and K_A for which the function $\sigma_{\Lambda} = f(R)$ has a sharp minimum are considered to be acceptable (σ_{Λ} : standard deviation of the experimental results). The error of the R value, *i.e.* ΔR , was estimated as $0.1 (\sigma_{\Lambda})_{\min}$. This means that the values of R lie within an interval of $\sigma_{\Lambda} \leq 1.1 (\sigma_{\Lambda})_{\min}$. The values of Λ_0 , K_A , and R thus obtained together with their standard deviations as well as the values of the *Walden* products of the investigated iodides and their viscosities are presented in Tables 1–4. The dependence of the limiting molar conductances (Λ_0) and viscosities (η) on the solvent composition is presented in Fig 1. The corresponding dependencies of the *Walden* products and association constants are illustrated in Figs. 2 and 3, respectively.

As can be seen from Fig. 1, the viscosity of the solvent mixtures increases rapidly with increasing content of *DMF*, reaching a maximum of nearly 3 times the viscosity of water at about 25 mole% of *DMF*. After passing the viscosity maximum, the values decrease with increasing *DMF* content in the mixture to 7.95 mP for pure *DMF* [8]. The limiting molar conductance for all four investigated iodides decreases with increasing *DMF* content reaching a minimum at *ca.* 35 mol% *DMF*. Subsequently, the values of the limiting molar conductance increase up to 100 mol% *DMF*. If one assumes, according to the model of *Stokes*, that the limiting molar conductances depend on the reciprocal of the macroscopic viscosity, the described dependencies $\Lambda_0 = f(\text{mol\% DMF})$ explain the changes of

Table 1. Limiting molar conductances (Λ_o), association constants (K_A), their standard deviations ($\sigma\Lambda_o$, σK_A), parameters R and their estimated errors (ΔR), viscosities of the mixed solvent (η), and Walden products ($\Lambda_o\eta$) for NaI in water-DMF mixtures at 298.15 K in all cases, $\Delta R = 0.5 \times 10^{-8}$ cm

DMF (mol%)	Λ_o (S · cm ² · mol ⁻¹)	$\sigma\Lambda_o$ (S · cm ² · mol ⁻¹)	K_A (dm ³ · mol ⁻¹)	σK_A (dm ³ · mol ⁻¹)	R (10 ⁻⁸ cm)	η (10 ² p)	$\Lambda_o\eta$ (S · cm ² · mol ⁻¹ · P)
0.00	126.96	0.03			4.0	0.890	1.130
2.50	101.67	0.02			4.0	1.100	1.118
5.00	84.60	0.03			4.0	1.325	1.121
10.00	63.65	0.02			4.0	1.737	1.106
15.00	51.96	0.01			4.5	2.110	1.100
20.00	45.38	0.03			4.5	2.358	1.070
25.00	41.71	0.01			5.0	2.485	1.037
35.00	39.37	0.03	0.9	0.3	5.0	2.405	0.947
50.00	44.09	0.01	1.1	0.5	5.0	1.865	0.822
70.00	57.50	0.01	1.9	0.5	5.5	1.245	0.719
80.00	65.41	0.03	2.2	0.7	5.5	1.040	0.680
90.00	73.75	0.04	3.7	0.9	6.0	0.900	0.664
100.00	82.48	0.02	5.9	1.1	7.0	0.795	0.656

Table 2. Limiting molar conductances (Λ_o), association constants (K_A), their standard deviations ($\sigma\Lambda_o$, σK_A), parameters R and their estimated errors (ΔR), viscosities of the mixed solvent (η), and Walden products ($\Lambda_o\eta$) for KI in water-DMF mixtures at 298.15 K; in all cases, $\Delta R = 0.5 \times 10^{-8}$ cm except for 66.39 mol% DMF and 100.00 mol% DMF where $\Delta R = 10^{-8}$ cm

DMF (mol%)	Λ_o (S · cm ² · mol ⁻¹)	$\sigma\Lambda_o$ (S · cm ² · mol ⁻¹)	K_A (dm ³ · mol ⁻¹)	σK_A (dm ³ · mol ⁻¹)	R (10 ⁻⁸ cm)	η (10 ² P)	$\Lambda_o\eta$ (S · cm ² · mol ⁻¹ · P)
0.00	150.33	0.01			4.0	0.890	1.338
2.65	118.71	0.02			4.0	1.100	1.306
6.14	92.05	0.01			4.0	1.410	1.298
10.56	71.97	0.02			4.0	1.785	1.285
20.32	51.25	0.01			4.5	2.370	1.215
26.98	45.84	0.01			4.5	2.502	1.147
34.74	43.93	0.01			4.5	2.410	1.059
37.47	43.97	0.01			4.5	2.330	1.025
49.86	47.65	0.01	0.6	0.3	5.0	1.868	0.890
66.39	57.60	0.02	1.1	0.5	5.0	1.337	0.770
83.68	71.03	0.02	2.4	0.8	5.5	0.983	0.698
89.45	75.59	0.03	2.8	1.1	5.5	0.904	0.683
100.00	83.47	0.5	3.6	1.3	6.0	0.795	0.664

the macroscopic viscosity of the solvent mixture. Simultaneously, one can understand the stability of the Walden products ($\Lambda_o\eta$), assuming that the effective radii of ions do not depend on the solvent composition. The effective ion radii are evidently connected to the ion-solvent interaction. For this reason, the

Table 3. Limiting molar conductances (Λ_o), association constants (K_A), their standard deviations ($\sigma\Lambda_o$, σK_A), parameters R and their estimated errors (ΔR), viscosities of the mixed solvent (η), and Walden products ($\Lambda_o\eta$) for RbI in water-DMF mixtures at 298.15 K; in all cases, $\Delta R = 0.5 \times 10^{-8}$ cm except for 10.00 mol% DMF, 80.00 mol% DMF, and 100.00 mol% DMF where $\Delta R = 10^{-8}$ cm; a_i interpolated value

DMF (mol%)	Λ_o ($S \cdot cm^2 \cdot mol^{-1}$)	$\sigma\Lambda_o$ ($S \cdot cm^2 \cdot mol^{-1}$)	K_A ($dm^3 \cdot mol^{-1}$)	σK_A ($dm^3 \cdot mol^{-1}$)	R (10^{-8} cm)	η (10^2 P)	$\Lambda_o\eta$ ($S \cdot cm^2 \cdot mol^{-1} \cdot P$)
0.00	154.72	0.01			3.5	0.890	1.378
2.50	123.24	0.02			4.0	1.100	1.356
5.00	101.95	0.04			4.0	1.325	1.351
10.00	75.24	0.02			4.0	1.737	1.306
15.00	60.49	0.04			4.5	2.110	1.276
20.00	51.22 ^a					2.358	1.208
25.00	46.86	0.02			4.5	2.485	1.164
35.00	44.29	0.02			5.0	2.405	1.065
50.00	48.63	0.03	1.1	0.4	5.0	1.865	0.907
70.00	61.69	0.04	2.9	0.6	5.5	1.245	0.768
80.00	70.11	0.04	3.7	1.2	5.5	1.040	0.729
90.00	77.28	0.04	4.0	1.5	5.5	0.900	0.696
100.00	84.86	0.04	6.1	1.8	6.0	0.795	0.675

Table 4. Limiting molar conductances (Λ_o), association constants (K_A), their standard deviations ($\sigma\Lambda_o$, σK_A), parameters R and their estimated errors (ΔR), viscosities of the mixed solvent (η), and Walden products ($\Lambda_o\eta$) for CsI in water-DMF mixtures at 298.15 K; in all cases, $\Delta R = 0.5 \times 10^{-8}$ cm except for 0.00 mol% DMF, 2.51 mol% DMF, and 81.83 mol% DMF where $\Delta R = 10^{-8}$ cm

DMF mol%	Λ_o ($S \cdot cm^2 \cdot mol^{-1}$)	$\sigma\Lambda_o$ ($S \cdot cm^2 \cdot mol^{-1}$)	K_A ($dm^3 \cdot mol^{-1}$)	σK_A ($dm^3 \cdot mol^{-1}$)	R (10^{-8} cm)	η (10^2 P)	$\Lambda_o\eta$ ($S \cdot cm^2 \cdot mol^{-1} \cdot P$)
0.00	154.30	0.05			4.0	0.890	1.374
2.51	122.78	0.05			4.0	1.106	1.358
7.47	86.24	0.01			4.0	1.518	1.309
10.69	72.21	0.03			4.0	1.797	1.298
19.44	52.15	0.01			4.0	2.340	1.220
27.35	45.37	0.01			4.5	2.501	1.135
36.79	44.01	0.02			4.5	2.350	1.034
49.99	48.82	0.01	1.5	0.5	5.0	1.862	0.909
68.33	61.61	0.01	3.5	0.9	5.5	1.285	0.792
81.83	72.58	0.04	5.1	1.2	6.0	1.013	0.735
87.68	77.37	0.03	5.5	1.0	6.0	0.929	0.719
100.00	87.13	0.05	5.8	1.8	6.0	0.795	0.693

dependencies $\Lambda_o\eta = f(\text{solvent composition})$ seem to be of some interest. In fact, as can be seen from Fig. 2, the values of the Walden products ($\Lambda_o\eta$) for all four iodides investigated in this paper decrease monotonically with increasing DMF content over in the whole range of solvent composition. In the region from *ca.*

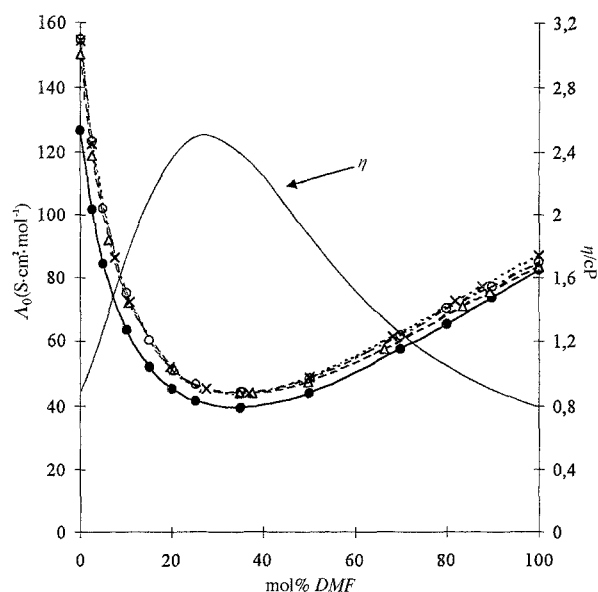


Fig. 1. Viscosity (η) of water-DMF mixtures and limiting molar conductances (Λ) at 298.15 K for NaI(—●—), KI(—△—), RbI(—○—), and CsI(—*—)

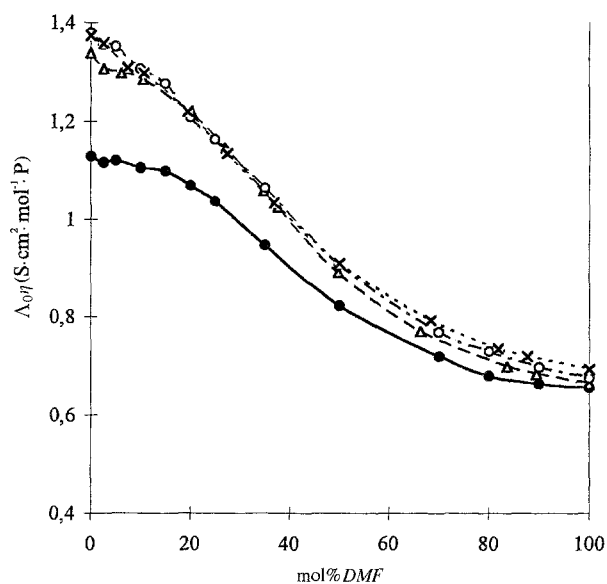


Fig. 2. Walden product ($\Lambda_0\eta$) in water-DMF mixtures at 298.15 K for NaI(—●—), KI(—△—), RbI(—○—), and CsI(—*—)

10 mol% up to 80 mol% DMF, the effect appears to be most pronounced. In mixtures containing small (up to *ca.* 10 mol%) or great (above 80 mol%) amounts of DMF, the dependencies differ substantially from those observed for alkali metal chlorides and bromides [4, 5]. In the case of chlorides [4], the addition of DMF to water causes no decrease of the Walden products. Above 80 mol% DMF, the values of $\Lambda_0\eta$ increase for chlorides [4], whereas they decrease for iodides. The increase of the value of the Walden product for alkali metal chlorides in mixtures containing small amounts of DMF [4] can be explained as follows: if DMF is added to water,

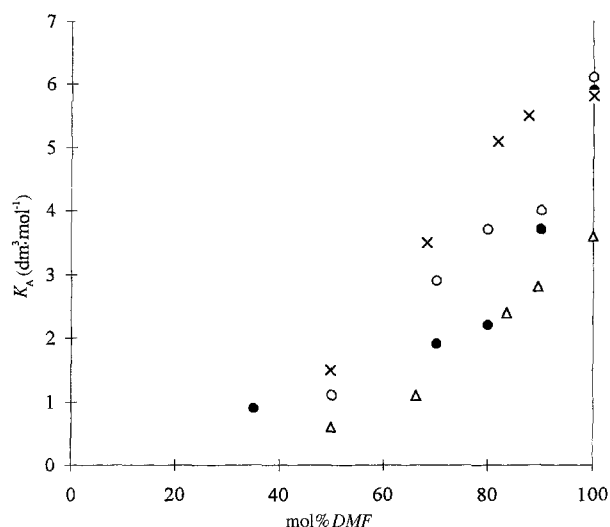


Fig. 3. Values of K_A as a function of the *DMF* content in water-*DMF* mixtures at 298.15 K for NaI(●), KI(Δ), RbI(○), and CsI(×)

the microscopic viscosity increases more slowly than the macroscopic viscosity. This can contribute to a greater mobility of ions as can be deduced from *Stokes'* law. If one assumes that the "sorting effect" hypothesis [32–35] is reasonable in the case of the cations of Li, Na, K, Rb, and Cs, then the differences in the dependencies $\Lambda_o\eta = f$ (composition) for iodides, chlorides, and bromides result from differences in the conductivity properties of chloride bromide and iodide anions. It is well known that these anions are weakly solvated by disubstituted amides [36–39]. According to the opinion mentioned above, the addition of *DMF* to water should not cause any changes in the solvation shell of the anions. Therefore, microscopic viscosities around anions are greater than the macroscopic viscosity, and for this reason one can assume an excess anion mobility and therefore a positive contribution to the values of the *Walden* products. This fact, however, leads us to the conclusion that differences in the solvation of anions by *DMF* occur, *i.e.* that probably iodide ions interact with the dipoles of *DMF* to a greater extent than Cl^- and Br^- . This might be due to the considerable polarizability of iodide ions and the notable dipole moment of the *DMF* molecule [36]. Obviously, for the analysis presented above it is better to use the *Walden* product values for single ions. However, in the present state we can conclude that the differences in the interactions of anions with the *DMF* dipoles are nevertheless present. This can be also confirmed by the conductivity properties of the investigated alkali metal chlorides [4], bromides [5] and iodides in the *DMF*-rich region, *i.e.* above 80 mol%. As mentioned earlier, the anions are weakly solvated by *DMF* [36–39]. For this reason one can assume that the chloride and bromide anions are rather desolvated when the composition of the mixed solvent changes from the *DMF*-rich region to the pure amide. The desolvation of these ions can contribute to the decrease in their effective radii, the increase of the anion mobility, and to the observed increase of the values of the *Walden* product in the range above 80 mol% *DMF*. In order to give more details on this subject, the values of the differences in the *Walden* products as defined by $\Lambda_o\eta(\text{MCl}) - \Lambda_o\eta(\text{MBr})$ and $\Lambda_o\eta(\text{MCl}) - \Lambda_o\eta(\text{MI})$ (*M*: any common cation) as a function of the solvent

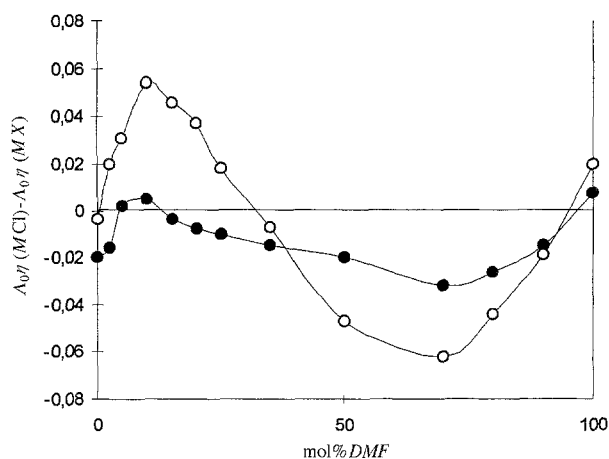


Fig. 4. Values of the differences in the Walden product, $\Lambda_0\eta(MCl) - \Lambda_0\eta(MX)$, as a function of the solvent composition (—●— for $X = Br$; —○— for $X = I$)

composition are presented in Fig. 4. As can be seen from Fig. 4, the differences in the mobilities of the chloride and bromide anions are rather small in the water-rich region of the solvent mixture. In contrast, the iodide ions show a considerably smaller ionic mobility. However, in the DMF-rich region of the solvent mixture, the mobility of chloride ions increases to a greater extent than that of bromide anions. In our opinion, the character of the changes of the values of the association constant (K_A) vs. solvent composition can also confirm the above conclusion. From the values of K_A (Table 1, Fig. 3) we can consider the investigated alkali metal iodides to be practically completely dissociated. In contrary, the values of the association constants for alkali metal bromides and particularly for alkali metal chlorides [4, 5] reach considerably greater values in pure DMF. This can result from the fact that the chloride and particularly bromide ions are weakly solvated by DMF, thus achieving a greater ability to contact ion pair formation. From the consideration presented above results that further investigation of the conductivity properties of electrolytes should be performed. This could perhaps allow to split the limiting molar conductance into its ionic contributions making possible a more accurate description of the interaction of ions with dipoles of the mixed solvent water-DMF.

Experimental

For details of experimental procedures, see Ref. [4]. Solutions and mixed solvent compositions were prepared by weight. The compositions were accurate to within $\pm 0.01\%$ (w/w). Conductance measurements were performed by an E-315 A type bridge produced by Mera-Tronic (Poland) with an accuracy better than 0.05%. The measurements were performed in the range of 0.0002 – $0.01 \text{ mol} \cdot \text{dm}^{-3}$, usually for 16 or more concentrations. All data were corrected with the specific conductance of the solvent at 298.15 K. The alkali metal iodides used in this investigation were of spectral grade (Merck); they were dried under reduced pressure for a long time immediately prior to use and used without further purification. Constant temperature was maintained using an oil bath ($298.15 \pm 0.005 \text{ K}$). Water and DMF (Apolda, Germany) were purified as given in Ref. [4]; their specific conductances were less than 10^{-6} and $10^{-7} \text{ S} \cdot \text{cm}^{-1}$, respectively. These values are in good agreement with literature data [1–3]. The values of relative permittivity and viscosity were taken from Refs. [6–8] and were interpolated numerically whenever necessary. We estimate the accuracy of the measured values of conductivity to be better than 0.05%.

References

- [1] Singh D, Bahadur L, Ramanamurti MV (1977) *J Solution Chem* **6**: 703
- [2] Bahadur L, Ramanamurti MV (1984) *Can J Chem* **62**: 1051
- [3] Chittleborough G, James C, Stell B (1988) *J Solution Chem* **17**: 1043
- [4] Kozłowski Z, Bald A, Szejgis A, Gregorowicz J (1989) *Polish J Chem* **63**: 547
- [5] Szejgis A, Bald A, Gregorowicz J, Kinart CM (1997) *Phys Chem Liq* **34**: 189
- [6] Douheret G, Morenas M (1967) *Comptes Rendus Acad Sci Paris Serie C* **264**: 729
- [7] Reynaud R (1967) *Comptes Rendus Acad Sci Paris Serie C* **266**: 489
- [8] Taniewska-Osińska S, Piekarska A, Kacperska A (1983) *J Solution Chem* **12**: 717
- [9] Taniewska-Osińska S, Piekarska A, Bald A, Szejgis A (1989) *J Chem Soc Faraday Trans I* **85**: 3709
- [10] Kacperska A, Taniewska-Osińska S, Bald A, Szejgis A (1989) *J Chem Soc Faraday Trans I* **85**: 4147
- [11] Kacperska A, Taniewska-Osińska S, Bald A, Szejgis A (1990) *J Chem Soc Faraday Trans I* **86**: 2225
- [12] Taniewska-Osińska S, Piekarska A, Bald A, Szejgis A (1990) *Phys Chem Liq* **21**: 217
- [13] Taniewska-Osińska S, Kozłowski Z, Nowicka B, Bald A, Szejgis A (1989) *J Chem Soc Faraday Trans I* **85**: 479
- [14] Bald A, Gregorowicz J, Szejgis A, Piekarski H (1992) *Thermochimica Acta* **205**: 51
- [15] Bald A, Gregorowicz J, Szejgis A (1992) *J Electroanal Chem* **340**: 153
- [16] Bald A, Szejgis A, Woźnicka J, Józwiak M (1992) *J Chem Research (S)* 117; (M) 0923
- [17] Bald A, Szejgis A, Woźnicka J, Józwiak M (1992) *J Chem Research (S)* 249; (M) 2201
- [18] Barczyńska J, Bald A, Szejgis A (1992) *J Chem Soc Faraday Trans* **88**: 2887
- [19] Bald A (1993) *Pol J Chem* **67**: 923
- [20] Bald A (1993) *J Chem Research (S)* 142; (M) 1001
- [21] Bald A, Gregorowicz J, Szejgis A (1993) *Phys Chem Liq* **26**: 121
- [22] Bald A (1993) *J Electroanal Chem* **352**: 29
- [23] Gregorowicz J, Szejgis A, Bald A (1995) *Pol J Chem* **69**: 131
- [24] Gregorowicz J, Szejgis A, Bald A (1996) *Phys Chem Liq* **32**: 133
- [25] Taniewska-Osińska S, Bald A, Nowicka B, Kacperska A (1993) *Phys Chem Liq* **25**: 113
- [26] Bald A, Barczyńska J (1993) *Thermochimica Acta* **22**: 33
- [27] Justice JC (1971) *Electrochim Acta* **16**: 701
- [28] Renard E, Justice JC (1974) *J Solution Chem* **3**: 633
- [29] Barthel J, Justice JC, Wachter R (1973) *Z Phys Chem N F* **84**: 100
- [30] Fuoss RM, Accascina L (1959) *Electrolytic Conductance*. Interscience, New York, p 195
- [31] Fuoss RM (1978) *J Phys Chem* **82**: 2427
- [32] Kay RL, Broadwater TL (1971) *Electrochim Acta* **16**: 667
- [33] Broadwater TL, Kay RL (1976) *J Solution Chem* **5**: 57
- [34] Broadwater TL, Kay RL (1970) *J Phys Chem* **74**: 3802
- [35] Singh D, MacLeod D, Parker AJ (1984) *J Solution Chem* **13**: 103
- [36] Cox BG, Hedwig RG, Parker AJ, Wats DW (1974) *Austr J Chem* **27**: 477
- [37] Parker AJ (1962) *Quart Rev* **16**: 163
- [38] Scholl H (1992) *Solvation and Electrochemical Processes in Nonaqueous Solvents*. Edition University Łódź
- [39] Spiro M (1971) In: Covington AK, Dickinson T (eds) *Physical Chemistry of Organic Solvent Systems*. Plenum Press, London