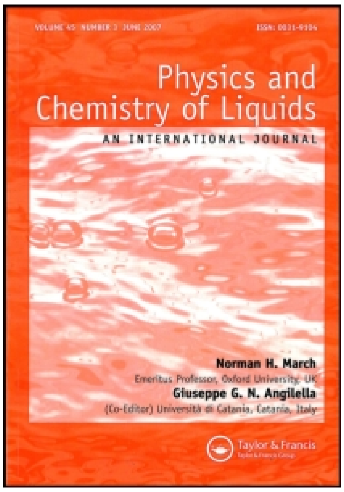

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Effect of Ionic Association On the B Coefficient for Cacl$_2$ in Ethanol-Water Mixtures at 298.15 K

Adam Bald[a]; Adam Szejgis[a]; Jolanta Barczyńska[b]; Henryk Piekarski[b]
[a] Department of Chemical Didactics, University of Lodz, Poland [b] Department of Physical Chemistry, University of Lodz, Lodz, Poland

To cite this Article Bald, Adam , Szejgis, Adam , Barczyńska, Jolanta and Piekarski, Henryk(1999) 'Effect of Ionic Association On the B Coefficient for Cacl$_2$ in Ethanol-Water Mixtures at 298.15 K', Physics and Chemistry of Liquids, 37: 2, 125 — 135

To link to this Article: DOI: 10.1080/00319109908045121

URL: http://dx.doi.org/10.1080/00319109908045121

Phys. Chem. Liq., 1999, Vol. 37, pp. 125–135
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

EFFECT OF IONIC ASSOCIATION ON THE *B* COEFFICIENT FOR $CaCl_2$ IN ETHANOL-WATER MIXTURES AT 298.15 K

ADAM BALD[a], ADAM SZEJGIS[a],
JOLANTA BARCZYŃSKA[b,*] and HENRYK PIEKARSKI[b]

[a] *Department of Chemical Didactics, University of Lodz, Pomorska 163, 90-236, Poland;*
[b] *Department of Physical Chemistry, University of Lodz, Pomorska 165, 90-236 Lodz, Poland*

(Received 8 October 1997)

The viscosity and density of $CaCl_2$ solutions in the water-ethanol systems have been measured up to 90 mol% alcohol at 298.15 K. The conductance measurements made it possible to obtain the association constants and the degrees of dissociation in these systems and they revealed that ionic association is appreciable in $CaCl_2$ solution in mixtures containing above 15 mol% of ethanol. For that reason an extended form of the Jones-Dole equation was used introducing the following coefficients: $B_1 = B_{CaCl^+} + B_{Cl}$ and $B_2 = B_{Ca^{2+}} + 2B_{Cl}$ that were calculated by the last squares method. The A coefficients of the above equation were theoretically calculated using the limiting conductivities of Cl^- from another investigation. The ion-solvent interactions, as results from the extended Jones-Dole equation analysis, increase in $CaCl_2$ solutions as the permittivity of the medium decrease and are much higher than it results from B without correction.

Keywords: Viscosity; density; conductance; water-alcohol mixtures; $CaCl_2$

INTRODUCTION

The present work is part of a continuing efforts from our laboratories to examine the influence of ionic association on the B coefficient of the

---

*Corresponding author.

Jones-Dole equation:

$$\eta_r = 1 + Ac^{1/2} + Bc \qquad (1)$$

as a quantitative formulation of the ion-ion and ion-solvent interactions. In the above equation η_r is the relative viscosity of solution and c is the molar concentration of electrolyte and A and B are the coefficients depending on the solute, the solvent and the temperature. As a rule, these coefficients are obtained by fitting η_r to eqn. (1). The A term which depends on the interactions forces can be evaluated theoretically: Falkenhagen equation [1]. For its calculation some data which can be determined from the conductivity measurements are necessary. These in turn give us the limiting conductances of the ions and they are very useful in studying ionic association. If the A coefficient is know, eqn. (1) can be rearranged to give;

$$(\eta_r - 1A - c^{1/2})\,/c = B \qquad (2)$$

which made it possible to determine the B coefficient by the least squares method.

For several years our attention have been focused on the asymmetric electrolyte solutions, where ionic association is appreciable and the presence of species other the dissociated ions becomes important. $CaCl_2$ was chosen as a representative of this important and large group of electrolytes. So far, the water-alcohol mixtures in which ionic association is significant and which can dissolved a lot of inorganic salts have been investigated in detail. Water-ethanol mixture is a solvent system having scientific and practical interests and therefore it was chosen to examine the influence of ionic association on viscosity. In the solution where the electrolyte is incomplete dissociated the classical Jones-Dole equation should be extended, introducing the degree of dissociation, according to Davies and Malpass suggestion [2]. In the previous paper we proposed [3] and recently [4] have examined such extended form of the equation for the asymmetrical electrolytes. In the water-propanol mixtures we have also showed that the values of B for $CaCl_2$ calculated from eqn. (2) and those found, when the modified equation is used are the same only in these mixtures (to 10 mol% of propanol), where ionic association in the investigated system practically does not occur. In the remaining region with a large propanol content the differences in the B values can even reach 100%.

In the present paper, the measurements of densities and viscosities and electric conductivity of dilute solutions of $CaCl_2$ in the mixtures of water with ethanol up to 90 mol% of alcohol at 298.15 K are described. The results of conductance measurements made it possible calculation of the A coefficients as well as the determination the association constants and the degrees of dissociation in these systems. Having at disposal the mentioned above values we are able to calculate the B coefficients for different species present in the solution.

EXPERIMENTAL

Viscosity measurements were made by means of Ubbelohde-type viscometers with flow times of 200–500 s for various solutions. The liquids used as standards were water and *n*-butanol. The temperature stability was *ca*: $2 \cdot 10^{-4}$ K. Conductivity measurements were carried out using a bridge type E 315A (Mera-Tronik, Poland), and a cell with capacity of *ca*. 350 cm^3. The temperature was kept constant within $\pm 5 \cdot 10^{-3}$ K. More details on the purification of the salt and experimental procedure have been described previously [4, 5]. Analytical-grade ethanol (POCH-Gliwice, Poland) was purified by distillation and analysed for its water content. The final product had a specific conductivity of $1 \cdot 10^{-8}\ \Omega^{-1}\ cm^{-1}$. The specific conductivities of purified double-distilled water were better than $1 \cdot 10^{-6}\ \Omega^{-1}cm^{-1}$ at 298.15 K. All the mixtures and solutions of electrolytes were prepared by weight in a dry box.

RESULTS AND DISCUSSION

For the ternary electrolyte under consideration, i.e., $CaCl_2$, the following association equilibria can take place:

$$CaCl^+ + Cl^- \overset{K_{a1}}{\rightleftarrows} CaCl_2 \tag{3a}$$

$$Ca^{2+} + Cl^- \overset{K_{a2}}{\rightleftarrows} CaCl^+ \tag{3b}$$

The association constants K_a, connected with the above equilibria can be described by the following:

$$\begin{aligned} K_{a1} &= \frac{1-\alpha_1}{c\alpha_1^2(1-\alpha_2^2)y_\pm^2} \\ K_{a2} &= \frac{1-\alpha_2}{c\alpha_1\alpha_2(1+\alpha_2)y_{Ca^{2+}}} \end{aligned} \tag{4}$$

were: c is the total concentration of the electrolyte, while α_1 and α_2 denote the degree of dissociation connected with the primary and secondary steps of dissociation.

Assuming:

$$y_{CaCl_2} = 1 \text{ and } y_{Cl^-} = y_{CaCl^+} = y_\pm$$

the activity coefficients of individual species in the solution can be calculated from the Debye-Huckel equation:

$$\ln y_i = -\frac{|z_i|^2 A_{DH} I^{1/2}}{1 + RB_{DH} I^{1/2}} \tag{5}$$

The ionic strength is: $I = c\alpha_1(1+2\alpha_2)$ and ion distance parameter R is assumed to be equal Bjerrum's distance according to Justice's [6, 7] suggestion.

The determination of association constants from conductivity measurements is a well established procedure but only for symmetrical electrolytes [5, 8]. The unsatisfactory state of the theory concerning unsymmetrical electrolytes makes the interpretation of the obtained results for the $CaCl_2$ solutions rather difficult. Nevertheless, it seems both interesting and reasonable to make such attempts based on existing theories.

For the analysis of the $CaCl_2$ conductivity measurements in water-ethanol mixtures we used the Fuoss-Edelson method [9] and verified its usability over a wide range of the mixed solvent composition (0–90 mol% of ethanol). The values of limiting conductivity Λ_0 ($1/2CaCl_2$) and association constant K_{a2} (assuming $K_{a1} = 0$) were calculated from eqn. (6):

$$\Lambda^* = \Lambda_0 - \frac{K_{a2}}{\Lambda_0} x \tag{6}$$

where Λ^* and x are described by the following equations:

$$\Lambda^* = \Lambda \left[\frac{1}{1 + \frac{\lambda_0 \left(1/2\,\mathrm{Ca}^{2+}\right)}{2\Lambda_o}} \right] \left[\frac{1}{1 - \frac{S_{2:1}}{\Lambda_o} c^{1/2}} - \frac{\lambda_0 \left(1/2\,\mathrm{Ca}^{2+}\right)}{2\Lambda} \right] \tag{6a}$$

$$x = 2cy_{\mathrm{Ca}^{2+}} \Lambda^* \left(\Lambda^* - \frac{\Lambda_0}{2} \right) \tag{6b}$$

In this equation: $\lambda_0(1/2\ \mathrm{Ca}^{2+}) = \Lambda_0 - \lambda_0\ (\mathrm{Cl}^-)$ and $S_{2:1}$ is the limiting slope for 2:1 electrolytes according to the Debye-Huckel-Onsager (DHO) theory.

Table I contains the calculated values of molar conductivity Λ(1/2 CaCl$_2$), in the water-ethanol mixtures necessary for to calculation of Λ^* in all investigated solutions. Table II gives the limiting molar conductivities of electrolyte, Λ_0 (1/2CaCl$_2$), and ions λ_0 (1/2Ca^{2+}), in water-ethanol mixtures containing up to 90 mol% of alcohol. In the water-rich region up to 15 mol% of ethanol the values of Λ_0 were calculated using the limiting DHO equation. For the mixtures containing more than 15 mol% of ethanol the values of Λ_0 were analysed by the use of equations (6)–(6b), similarly as showed in our previous paper [4]. The calculated values of the K_{a2} and its standard deviation at the investigated solvent composition range are summarised in Table II. It can be assumed from the K_{a2} data, that CaCl$_2$ is complete dissociated electrolyte in pure water and in the mixtures containing up to 15 mol% of ethanol. For the mixtures containing more than 15 mol% of ethanol the K_{a2} values increase considerably with increasing ethanol content while the relative premittivity of the solvent decreases [10]. So, the possible formation of various ionic species favoured by the low value of the relative permittivity of the medium should be taken into account. In fact the CaCl$_2$ formation in the undissociated form can be neglected ($\alpha_1 = 1$) and only the presence of free ions and the CaCl$^+$ species considered, according to equilibrium (3b). In this case we can modify the classical Jones-Dole

TABLE I Molar conductivities, Λ, of (1/2$CaCl_2$) in water ethanol mixtures at 298.15 K

$c/10^{-4}$ $mol\ dm^{-3}$	$\Lambda/cm^2\Omega^{-1}$ mol^{-1}	$c/10^{-4}$ $mol\ dm^{-3}$	$\Lambda/cm^2\Omega^{-1}$ mol^{-1}
$x_2{}^a = 0.0$		$x_2{}^a = 5.0$	
1.347	133.05	1.954	92.86
2.335	132.10	2.833	92.20
3.199	131.44	4.139	91.54
5.126	130.22	6.441	90.72
6.148	129.76	8.182	90.13
7.806	129.07	10.108	89.63
9.594	128.41	11.976	89.15
11.264	127.83	14.056	88.64
12.840	127.36	17.526	87.98
16.499	126.31	21.398	87.25
19.677	125.56	24.800	86.74
22.777	124.84	28.247	86.24
26.188	124.20	34.051	85.41
30.444	123.45		
$x_2{}^a = 10.0$		$x_2{}^a = 30.0$	
1.242	71.63	0.677	47.72
2.243	70.93	1.211	47.13
2.938	70.39	1.883	46.66
4.209	69.82	2.586	46.18
4.933	69.53	3.280	45.83
5.895	69.20	4.098	45.44
7.715	68.71	5.067	45.03
9.615	68.37	6.747	44.42
23.009	65.98	7.828	44.10
26.173	65.53	9.245	43.65
30.583	65.26	10.412	43.35
		12.236	42.93
$x_2{}^a = 50.0$		14.455	42.44
		16.877	41.97
0.672	43.60	19.356	41.55
1.357	42.47	21.473	41.23
2.752	40.93	24.069	40.85
3.494	40.27		
4.000	39.89	$x_2{}^a = 70.0$	
5.412	38.92		
6.559	38.24	1.017	42.26
8.034	37.47	1.539	40.99
9.305	36.88	2.068	39.99
11.858	35.91	2.554	39.18
14.399	35.08	2.928	38.63
16.726	34.40	3.910	37.36
19.038	33.81	4.786	36.43
22.558	33.05	5.737	35.48
		6.582	34.80
$x_2{}^a = 90.0$		8.372	33.56
		9.996	32.64
0.720	36.94	11.781	31.77
1.219	34.49		

TABLE I (Continued)

$c/10^{-4}$ $mol\ dm^{-3}$	$\Lambda/cm^2\Omega^{-1}$ mol^{-1}	$c/10^{-4}$ $mol\ dm^{-3}$	$\Lambda/cm^2\Omega^{-1}$ mol^{-1}
1.915	32.06	13.310	31.10
2.599	30.37	15.750	30.15
3.317	28.95		
3.873	28.10		
5.157	26.46		
6.421	25.26		
7.651	24.33		
8.835	23.57		
11.268	22.34		
13.623	21.41		
16.027	20.68		
18.281	20.06		
21.837	19.25		

x_2[a], mol% of ethanol.

TABLE II Limiting molar conductivities, Λ_0, of $CaCl_2$ and the association constants, K_{a2}, in water-ethanol mixtures at 298.15 K

x_2[a]	$\Lambda_0/cm^2\ \Omega^{-1}$ mol^{-1}	$\sigma\Lambda_0$	K_{a2}/dm^3 mol^{-1}	σK_{a2}	$\lambda_0(Cl^-)$[d]	$\lambda_0(1/2\ Ca^{2+})$
0	135.95[b]	0.06	–	–	76.4	59.6
5	95.33	0.06	–	–	51.2	44.1
10	72.87	0.07	–	–	38.1	34.8
15	60.89[c]	–	–	–	32.0	28.9
20	54.94[c]	–	12.0	–	28.7	26.2
30	48.92	0.03	24.9	1.5	25.4	23.5
33	47.85[c]	–	30	–	24.7	23.2
50	45.69	0.04	144	5	22.9	22.8
60	45.92[c]	–	220	–	22.6	23.3
70	46.66	0.06	409	10	22.5	24.2
80	46.40[c]	–	1040	–	22.3	24.1
90	44.3	0.10	2100	30	22.0	22.3

[a] x_2 mol% of ethanol; K_{a2}, association constants described eqn. (3b), σK_{a2}, standard deviations of K_{a2}.

[b] from ref. [4].

[c] values calculated by the method of interpolation of ours date.

[d] from ref. [11].

equation to the form given below:

$$\eta_r = 1 + A\,(c\,\alpha_2)^{1/2} + B_1\,c\,(1-\alpha_2) + B_2\,c\,\alpha_2 \tag{7}$$

where α_2 is the degree of dissociation of the $CaCl^+$ species and:

$$B_1 = B_{CaCl^+} + B_{Cl^-}$$
$$B_2 = B_{Ca^{2+}} + 2B_{Cl^-}$$

In order to find the values of coefficients B_1 and B_2 the eqn. (7) was converted as follows [3]:

$$\frac{\eta_r - 1 - A(c\alpha_2)^{1/2}}{c\,\alpha_2} = B_2 + B_1\,\frac{1-\alpha_2}{\alpha_2} \tag{8}$$

which made it possible to calculate B_1 and B_2 by the least squares method. The K_{a2} values determined from conductivity measurements were used to calculate of the degree of dissociation, α_2. The values of A coefficients were calculated theoretically, applying the ionic limiting conductivities for Cl^- obtained by Kay and co-workers [11] and $\lambda_0(1/2\ Ca^{2+})$ obtained by us in this paper (Tab. II). All the relative viscosities result and densities of $CaCl_2$-water-ethanol systems at 298.15 K are given in Table III. Table IV gives information on B_1 and B_2 obtained from eqn. (8) in $CaCl_2$-water-ethanol systems. For comparison, the B-coefficients values, calculated from eqn. (2) without correction for the ionic association, are also given in the same table.

The conductivity measurements suggested that below 15 mol% of ethanol, the K_{a2} values can be neglected. In this case the presence of free ions is only considered. Thus, in this water-rich region the effect of an electrolyte on the solvent structure may be, to some extent, analysed with the sign of the temperature coefficient of the relative viscosity ($\Delta\eta_r/\Delta T$) (like ($\Delta B/\Delta T$)) [12]. It was shown from our earlier research [13] that this coefficient for $CaCl_2$ changes the sign twice in water-rich region. Within the 293–303 K temperature range the coefficient retains a negative sign characteristic of aqueous solutions of electrolyte up to 5 mol% of ethanol and then changes the sign to positive, which it preserves up to *ca.* 30 mol% of ethanol. It may suggest that $CaCl_2$ is a structure-ordering salt in water but destroys the structure of mixtures. However, it must be interpreted with some caution as the analysis is based on η_r values only. The observed effect was considerably smaller than in the case of other investigated electrolytes in this highly aqueous region [13]. Above 30 mol% of

TABLE III Density, ρ and relative viscosity, η_r, for $CaCl_2$ in water-ethanol mixtures at 298.15 K in various molar concentrations of electrolyte, c

$c/10^{-3}$ $mol\ dm^{-3}$	$\rho/$ $g\ cm^{-3}$	η_r	$c\ 10^{-3}$ $mol\ dm^{-3}$	$\rho/$ $g\ cm^{-3}$	η_r
	$x_2^a = 0.0$			$x_2^a = 5.0$	
17.4	0.9991	1.0068	16.6	0.9792	1.0056
23.0	0.9999	1.0090	28.0	0.9803	1.0097
28.5	1.0002	1.0111	43.7	0.9818	1.0156
37.0	1.0009	1.0135	44.1	0.9820	1.0143
41.1	1.0017	1.0157	46.7	0.9822	1.0144
53.8	1.0022	1.0193	48.8	0.9826	1.0182
53.9	1.0022	1.0201	53.6	0.9827	1.0171
60.0	1.0036	1.0218	66.4	0.9843	1.0237
65.4	1.0037	1.0240	70.4	0.9841	1.0228
71.3	1.0039	1.0249	75.2	0.9848	1.0231
76.9	1.0044	1.0269	90.2	0.9861	1.0288
77.4	1.0046	1.0281			
80.5	1.0047	1.0288		$x_2^a = 15.0$	
108.0	1.0070	1.0369			
144.2	1.0100	1.0478	24.8	0.9514	1.0102
149.2	1.0110	1.0496	43.8	0.9531	1.0167
			51.0	0.9535	1.0197
	$x_2^a = 10.0$		51.8	0.9536	1.0190
			57.3	0.9541	1.0212
28.83	0.9661	1.0103	61.7	0.9546	1.0230
31.00	0.9624	1.0110	74.7	0.9558	1.0276
34.06	0.9641	1.0120	93.9	0.9574	1.0335
34.12	0.9664	1.0113			
37.58	0.9670	1.0132		$x_2^a = 20.0$	
48.13	0.9680	1.0178			
48.15	0.9684	1.0177	36.15	0.9370	1.0166
54.57	0.9685	1.0189	46.64	0.9378	1.0204
59.74	0.9689	1.0240	50.90	0.9382	1.0218
90.16	0.9861	1.0288	62.54	0.9393	1.0262
			66.70	0.9395	1.0272
	$x_2^a = 33.0$		72.25	0.9404	1.0303
			77.21	0.9407	1.0322
42.52	0.9006	1.0257	81.96	0.9409	1.0332
50.37	0.9012	1.0296			
56.56	0.9018	1.0321		$x_2^a = 60.0$	
57.24	0.9019	1.0324			
67.80	0.9028	1.0389	21.94	0.8433	1.0267
71.98	0.9031	1.0408	29.63	0.8435	1.0318
91.56	0.9046	1.0505	33.21	0.8438	1.0393
			35.29	0.8440	1.0405
			39.26	0.8446	1.0418
	$x_2^a = 70.0$		42.08	0.8449	1.0459
			46.01	0.8453	1.0499
26.24	0.8273	1.0353	75.99	0.8480	1.0695
28.16	0.8278	1.0372	87.11	0.8493	1.0785

TABLE III (Continued)

$c/10^{-3}$ mol dm^{-3}	$\rho/$ g cm^{-3}	η_r	c 10^{-3} mol dm^{-3}	$\rho/$ g cm^{-3}	η_r
35.36	0.8286	1.0501			
52.41	0.8296	1.0720		$x_2^a = 80.0$	
57.37	0.8302	1.0690			
70.1b3	0.8316	1.0839	25.97	0.8136	1.0411
70.79	0.8318	1.0924	32.87	0.8142	1.0496
72.92	0.8324	1.0998	34.70	0.8143	1.0515
80.86	0.8328	1.0952	44.40	0.8155	1.0645
			45.90	0.8156	1.0675
	$x_2^a = 90.0$		50.09	0.8160	1.0726
			52.20	0.8161	1.0743
17.95	0.7993	1.0332	64.63	0.8174	1.0937
21.82	0.7998	1.0403	83.20	0.8187	1.1157
25.84	0.8003	1.0406	85.15	0.8189	1.1173
38.07	0.8015	1.0709	85.63	0.8198	1.1194
44.76	0.8022	1.0682			
52.02	0.8031	1.0867			
52.95	0.8032	1.1068			
67.12	0.8042	1.1070			
77.43	0.8058	1.1241			

[a] x_2^a mol% of ethanol.

TABLE IV Coefficients of the Jones-Dole equation: $A(dm^{3/2}\ mol^{-1/2})$ and B, B_1 and B_2 $(dm^3\ mol^{-1})$ for $CaCl_2$ in water-ethanol mixtures at 298.15 K

X_2^a	A^b	B^c	σB	B_1^d	σB_1	B_2^d	σB_2
0	0.0156	0.291	0.012	–		–	
5	0.0147	0.265	0.025	–		–	
10	0.0148	0.289	0.020	–		–	
15	0.0156	0.308	0.005	–		–	
20	0.0171	0.355	0.004	0.195	0.153	0.400	0.004
33	0.0219	0.487	0.003	0.356	0.078	0.563	0.004
60	0.0348	0.918	0.028	0.845	0.080	1.150	0.071
70	0.0401	1.119	0.025	1.037	0.101	1.540	0.103
80	0.0469	1.242	0.007	1.297	0.030	1.921	0.037
90	0.0577	1.422	0.051	1.533	0.059	2.433	0.050

[a] x_2 mol% of ethanol.

[b] A, values of A coefficients calculated theoretically.

[c] B, values of B coefficients, considering no association; σB, standard deviation of B.

[d] B_1, B_2, values of coefficients B_1 and B_2 calculated from eqn. (8) and described following: $B_1 = B_{CaCl^+} + B_{Cl^-}$ and $B_2 = B_{Ca^{2+}} + 2B_{Cl^-}$; σB_1, σB_2, standard deviation of B_1 and B_2.

ethanol the coefficient $\Delta\eta_r/\Delta T$ is negative, as for most electrolyte solution in water-alcohol mixtures.

Beyond the water-rich region we found considerable influence of ionic association on the values of B coefficient and when eqn. (9) was used and the coefficients B_1 and B_2 values could be found (Tab. IV).

Both coefficients increase with ethanol content to presence of species other than dissociated ions and their different type interactions with mixed solvent.

The influence of alcohol on the value of ionic constants and a deeper analysis of changes in values of B_1 and B_2 as functions of quantity and kind of the alcohol added will be analysed soon after investigating methanol-water-$CaCl_2$ system.

References

[1] Falkenhagen, H. and Dole, M. (1929). *Phys. Z.*, **30**, 611; *Z. Phys. Chem. Teil B*, **6**, 159.
[2] Davies, C. W. and Malpass, V. E. (1964). *Trans. Faraday Soc.*, **60**, 2075.
[3] Bald, A. (1991). *Acta Univ. Lodz. Folia Chimica*, **9**, 33; **9**, 45.
[4] Barczyńska, J., Bald, A. and Szejgis, A. (1992). *J. Chem. Soc. Faraday Trans. I*, **88**, 2887.
[5] Kacperska, A., Taniewska-Osińska, S., Bald, A. and Szejgis, A. (1989). *J. Chem. Soc. Faraday Trans. I*, **85**, 4147.
[6] Justice, J. C. (1968). *J. Chim. Phys.*, **65**, 353.
[7] Justice, J. C. (1977). *Electrochim. Acta*, **18**, 701.
[8] Kacperska, A., Taniewska-Osińska, S., Bald, A. and Szejgis, A. (1990). *J. Chem. Soc. Faraday Trans. I*, **86**, 2225.
[9] Fuoss, R. M. and Edelson, D. (1951). *J. Am. Chem. Soc.*, **73**, 269.
[10] Akhadov, Y. Y., *Dielectric Properties of Binary Solutions* (Pergamon Press, Oxford, 1981).
[11] Kay, R. L. and Broadwater, T. L. (1976). *J. Solution Chem.*, **5**, 57.
[12] Kaminsky, M. (1957). *Discuss. Faraday Soc.*, **24**, 171.
[13] Nowicka, B., Kacperska, A., Barczyńska, J., Bald, A. and Taniewska-Osińska, S. (1988). *J. Chem. Soc. Faraday Trans. I*, **84**, 3877.