

## ADDITIVITY OF MOLAR METACHORS OF CHLORIDES IN AQUEOUS SOLUTIONS

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For the molar metachor, a quantity expressing the electrostatic contribution from free (non-associated and noncomplexed) ions to the surface tension of aqueous solutions of electrolytes, its additivity was verified for completely dissociating chlorides of univalent and divalent metals at concentrations up to  $5 \text{ mol dm}^{-3}$ . Owing to this property, the degree of dissociation could be estimated for associating components of solutions containing also completely dissociated electrolytes. Measurements revealed that NaCl, LiCl,  $\text{MgCl}_2$  and  $\text{CaCl}_2$  in mixed solutions are completely dissociated whereas  $\text{ZnCl}_2$ ,  $\text{CdCl}_2$  and  $\text{UO}_2\text{Cl}_2$  at molar ratios  $\text{NaCl} : \text{MeCl}_2 = 2 : 1$  and higher (at  $c_{\text{Cl}^-} = 5 \text{ mol dm}^{-3}$ ) are completely transformed into electroneutral and anionic chloro complexes, the latter forming ion pairs and triplets with  $\text{Na}^+$  ions.

Following up Sudgen's concept of the parachor  $P_i = V_i \sigma_i^{1/4}$ , a quantity introduced to make up for the temperature dependence of molar volumes  $V_i$  of individual substances in liquid state by combining them with surface tension  $\sigma_i$ , the concept of the molar metachor  $M_{e,i}$  has been introduced<sup>1-3</sup>. This is based on the model<sup>4</sup> from which it has been deduced theoretically that the Sudgen's exponent 1/4 (or values close to this) derive from the exponent in the dependence of the short-range intermolecular forces on distance. This suggested that long-range Coulomb forces, such as act between ions of electrolytes in aqueous solutions, should bring about additional effects into Sudgen's parachor, and owing to this it should be possible to determine the number of free charges causing them, by using surface tension measurements. This concept has been applied<sup>1-3</sup> to one-electrolyte solutions, where the function of the molar volume of the individual substances  $V_i$  is taken over by the apparent molar volume  $\Phi_i$  of solute in the solution. In analogy to this, the apparent molar parachor  $\Pi_i$  has been defined as that part of the parachor  $V\sigma^{1/4}$  of the whole solution that corresponds to a mole of solute after subtracting the contribution from the solvent present (regarded as a free liquid substance at the same temperature). This is expressed by the formulas

$$\Phi_i = (V - V_0)/n_i \quad (1)$$

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$$\Pi_i = (V\sigma^{1/4} - V_0\sigma_0^{1/4})/n_i, \quad (2)$$

where  $V$  is the total volume of the solution,  $\sigma$  is its surface tension,  $V_0$  is the total volume of water used for its preparation,  $\sigma_0$  is the surface tension of water and  $n_i$  is the number of moles of solute in volume  $V$ .

Theoretical considerations<sup>1</sup> showed that to an approximation, the effect of the apparent molar volume of solute can be eliminated from the apparent parachor by dividing the latter by the fourth root of the surface tension of the pure solvent. This difference is referred to by us as the molar metachor:

$$M_{\epsilon,i} = \Pi_i/\sigma_0^{1/4} - \Phi_i. \quad (3)$$

For a one-electrolyte solution, Eqs (1) and (2) give the relation

$$c_i M_{\epsilon,i} = (\sigma/\sigma_0)^{1/4} - 1. \quad (4)$$

Here the short-range effect of the electrolyte species on the volume of the adjacent water is eliminated, and what remains is the net effect of long-range Coulomb forces by which the free ions affect each other.

Based on the model mentioned<sup>1</sup>, the proportionality

$$M_{\epsilon,i} = k(\sum_j \nu_j |z_j|)_i \quad (5)$$

has been derived to an approximation; here  $\nu_j$ 's are the numbers of free ions per electrolyte formula unit and  $z_j$ 's are their charge numbers; the summation involves ions of one sign only. The proportionality factor  $k$  should be common to all the ions irrespective of their concentrations in the solution. In the case of more than one solute, all electrolytes should contribute to the (experimentally accessible) quantity  $(\sigma/\sigma_0)^{1/4} - 1$  in Eq. (4). If the contributions from the ions are additive according to Eq. (5) — the verification of which is the aim of the present work — then the above quantity will be equal to the sum of contributions from the individual electrolytes, i.e.

$$(\sigma/\sigma_0)^{1/4} - 1 = \sum_i c_i M_{\epsilon,i}, \quad (6)$$

where  $M_{\epsilon,i}$ 's are the molar metachors measured for each electrolyte ( $i$ ) in one-electrolyte solutions under conditions where its dissociation is the same as in the mixture. (It should be mentioned that for obtaining the left-hand side data with  $M_{\epsilon,i}$ 's in  $\text{cm}^3 \text{mol}^{-1}$  while inserting concentrations in  $\text{mol dm}^{-3}$ , the left-hand side must be multiplied by  $10^3$ .) For electrolytes that are subject to association or complexation, it should then be possible to determine their molar metachors in mixed

solutions containing completely dissociating electrolytes, viz. by subtracting the contribution from the latter, established in one-electrolyte solutions, from the experimental values of the left-hand side of Eq. (6). This in turn would enable conclusions to be drawn concerning association and complexation in the system under study.

## EXPERIMENTAL

Similarly as previously<sup>5</sup>, LiCl, NaCl, MgCl<sub>2</sub> and CaCl<sub>2</sub> were used as the completely dissociating salts, ZnCl<sub>2</sub>, CdCl<sub>2</sub> and UO<sub>2</sub>Cl<sub>2</sub> as complexing salts; the preparation procedures were as in refs<sup>2-5</sup>. Solutions in redistilled water contained the salts at  $c_{\text{Cl}^-} \leq 5 \text{ mol dm}^{-3}$ .

The Škramovský's modification of the bubble method was employed for the surface tension measurements (see refs<sup>1,2,5</sup>). For each group of solutions the apparatus was re-calibrated with pure water, and the one-electrolyte values obtained were compared with published data<sup>6</sup>. For data evaluation, use was made of the fact that over the temperature region of 10 to 30°C the difference between the surface tension of aqueous solution of electrolyte and that of pure water is virtually temperature independent<sup>6</sup>. Thus, the  $\sigma$  values measured within this temperature region (the surface tension of water  $\sigma_0$  being also measured at the some temperature and with the same capillary) can be related to a chosen (standard) temperature for which reliable published data are available. A temperature of 20°C, at which  $\sigma_0 = 72.75 \text{ mN m}^{-1}$ , was chosen in this work, and the majority of measurements were carried out at this temperature.

## RESULTS AND DISCUSSION

### *Molar Metachors of Completely Dissociated Chlorides, Measured in One-Electrolyte Solutions*

The molar metachors  $M_{e,i}$  for one-electrolyte solutions of the completely dissociating electrolytes were calculated from Eq. (4) using tabulated surface tension data<sup>6</sup>. The results are given in Table I. Up to a concentration of  $c_{\text{Cl}^-} = 3 \text{ mol dm}^{-3}$  the metachors of the completely dissociating salts are virtually constant; at higher concentrations the values increase largely, the increments, however, are on average one order of magnitude lower than the increments of the apparent volumes or of the parachors. Actually, it is possible to nearly eliminate the observed increase in the molar metachors by increasing the denominator in Sudgen's formula to above 4.0 (this is justified theoretically if, in the model of particle vibration in a triangle-potential well, the vertical wall on the "inner" side of the well is replaced by a continuous energy increase with decreasing distance between the particles, with a power corresponding to the dependence of the repulsive forces on distance; for details see ref.<sup>4</sup> and references in paper<sup>3</sup>). In the present work, however, this approach was abandoned because the property of additiveness of molar metachors is lost if the Sudgen's exponent is adjusted for each salt individually. Instead, the additivity tests were performed using  $M_{e,i}$  values (with the exponent of 1/4) averaged over the concentration region where the mixed solutions were to be measured. The data, denoted  $\langle M_{e,i} \rangle$ , are given in Table II.

However, allowance should be made for the fact that the experimental error in the surface tension measurements, which is basically concentration independent, is mirrored in the molar metachor roughly proportionally to  $1/c_i$ . Thus, provided that the differences between the  $M_{\epsilon,i}$  values for a salt at different concentrations are due to the error of measurement solely, the different effect of the differences on the result can be allowed for by including a weight factor which is directly proportional to the solute concentration. This corrected mean value of the molar metachor then can be calculated as

$$\langle M'_{\epsilon,i} \rangle = \frac{\sum_{j=1}^n (c_i)_j (M_{\epsilon,i})_j}{\sum_{j=1}^n (c_i)_j} \quad (7)$$

TABLE I

Molar metachors  $M_{\epsilon}$  ( $\text{cm}^3 \text{mol}^{-1}$ ) of NaCl,  $\text{MgCl}_2$  and  $\text{CaCl}_2$  in aqueous solutions at concentrations  $c$  ( $\text{mol dm}^{-3}$ ) and at  $20^\circ\text{C}$ , calculated from surface tension values  $\sigma$  ( $\text{mN m}^{-1}$ ) taken from ref.<sup>6</sup> and using density data from ref.<sup>7</sup> and the value of  $\sigma_0 = 72.75 \text{ mN m}^{-1}$

NaCl			$\text{MgCl}_2$			$\text{CaCl}_2$		
$c$	$\sigma$	$M_{\epsilon}$	$c$	$\sigma$	$M_{\epsilon}$	$c$	$\sigma$	$M_{\epsilon}$
—	—	—	0.10	73.07	10.98	0.10	73.05	10.29
0.25	73.17	5.76	0.25	73.53	10.68	0.25	73.53	10.68
0.49	73.57	5.73	0.495	74.45	10.47	0.49	74.27	10.58
0.96	74.39	5.82	0.985	75.79	10.44	0.985	75.95	10.98
1.91	76.03	5.80	1.90	79.10	11.13	1.91	79.65	11.99
2.82	77.65	5.83	2.78	82.98	12.03	2.77	83.75	12.93
3.68	79.29	5.91	3.33	85.70	12.55	3.59	87.70	12.32
4.51	80.98	5.98	—	—	—	4.33	91.15	13.39
5.33	82.55	6.02	—	—	—	—	—	—

TABLE II

Average unweighted molar metachors  $\langle M_{\epsilon} \rangle$  and weighted molar metachors  $\langle M'_{\epsilon} \rangle$  (Eqs (7) and (8)) ( $\text{cm}^3 \text{mol}^{-1}$ ) and the corresponding constants  $k$  and  $k'$  in Eq. (5) ( $\text{cm}^3 \text{mol}^{-1}$ ) for NaCl,  $\text{MgCl}_2$  and  $\text{CaCl}_2$

Salt	$\langle M_{\epsilon} \rangle$	$\langle M'_{\epsilon} \rangle$	$k$	$k'$
NaCl	$5.86 \pm 0.10$	$5.92 \pm 0.09$	$5.86 \pm 0.10$	$5.92 \pm 0.09$
$\text{MgCl}_2$	$11.18 \pm 0.81$	$11.75 \pm 0.84$	$5.59 \pm 0.41$	$5.87 \pm 0.42$
$\text{CaCl}_2$	$11.77 \pm 1.30$	$12.77 \pm 1.01$	$5.89 \pm 0.65$	$6.39 \pm 0.51$

with the mean square deviation

$$\Delta'_i = \left[ n \sum_{j=1}^n (c_i)_j (\Delta_i)_j^2 / (n-1) \sum_{j=1}^n (c_i)_j \right]^{1/2}, \quad (8)$$

where the subscripts  $i$  and  $j$  refer to the individual electrolyte and to the particular measurement, respectively; the total number of measurements is  $n$ . The  $\langle M'_{\epsilon,i} \rangle$  and  $\Delta'_i$  values are also included in Table II along with the corresponding  $k$  and  $k'$  values in Eq. (5).

Table I, however, demonstrates that the error of measurement plays a minor part in the differences between the  $M_{\epsilon,i}$  values in the various measurements. The systematic concentration dependence of  $M_{\epsilon,i}$  as mentioned above is considerably more substantial. So, for the additivity testing, the narrower concentration region of  $c_{\text{Cl}^-} = 3-5 \text{ mol dm}^{-3}$  was used for the averaging although the weight factors were included as well. Based on the  $M_{\epsilon,i}$  values in Table I, calculated based on published data<sup>6</sup>, and on our measurements for LiCl giving molar metachors of 6.30, 6.40 and 6.42  $\text{cm}^3 \text{ mol}^{-1}$  at  $c_{\text{Cl}^-} = 1, 3$  and  $5 \text{ mol dm}^{-3}$ , respectively, the values of  $M_{\epsilon,i} = 6.4, 6.0, 11.6$  and  $12.0 \text{ cm}^3 \text{ mol}^{-1}$  were adopted for LiCl, NaCl,  $\text{MgCl}_2$  and  $\text{CaCl}_2$ , respectively; these correspond to the weighted averages for chloride concentrations such as were used subsequently for measurements in mixed systems.

#### *Solutions of Pairs of Completely Dissociating Chlorides*

Pairs of salts of the same or different valence types were subject to measurement. The results of the additivity tests are given in Table III and demonstrate that the differences between the experimental sums of  $c_i M_{\epsilon,i}$  and those calculated from the molar metachors measured for each salt separately are tenths or, at most, a unit of  $\text{cm}^3 \text{ mol}^{-1}$ , hence, units per cent with respect to the sums themselves. And what is most important: even at chloride concentrations as high as  $5 \text{ mol dm}^{-3}$ , the differences are mere fractions of the differences between metachors of strong electrolytes of different valence types. This is of crucial importance if we wish to examine association of ions and their complexation in aqueous solutions.

#### *Mixed Electrolyte Solutions Containing Complexing Ions*

The fact that molar metachors of completely dissociating electrolytes exhibit the property of additivity enabled us, based on Eq. (6) to determine experimentally the  $M_{\epsilon,i}$  values of chlorides of complexing cations in mixtures with NaCl. The results are given in Table IV, along with the charge numbers for charges of one sign (Eq. (5)), calculated using the mean value of  $k = 6.0 \text{ cm}^3 \text{ mol}^{-1}$  obtained for chloride concentrations about  $5 \text{ mol dm}^{-3}$ .

While  $\text{CaCl}_2$  retains a  $z_i$  value close to 2.0 over the entire region of  $\text{Na}^+ : \text{Ca}^{2+}$

ratios used, for  $\text{CdCl}_2$ ,  $\text{UO}_2\text{Cl}_2$  and, in particular,  $\text{ZnCl}_2$  the  $z_i$  values are considerably lower even in the absence of  $\text{NaCl}$ , and as the  $\text{Na}^+ : \text{Me}^{2+}$  ratio is increased, the values decrease to zero (as would correspond to complete association) and further to negative values, corresponding to degrees of association higher than 100%. The course of this transition is shown in Fig. 1, depicting the plot of  $c_{\text{Na}^+}$  vs the degree of association

$$\beta = 1 - M_{\epsilon,i}/M_{\epsilon,i}^0, \quad (9)$$

calculated using the value of  $M_{\epsilon,i}^0 = 12.0 \text{ cm}^3 \text{ mol}^{-1}$  adopted for the completely dissociated state.

TABLE III

Testing the additivity of metachors  $M_\epsilon$  ( $\text{cm}^3 \text{ mol}^{-1}$ ) in aqueous solutions at  $20^\circ\text{C}$  for salts 1 and 2 at concentrations  $c_1$  and  $c_2$ , respectively ( $\text{mol dm}^{-3}$ );  $\sigma$  is surface tension measured,  $\Delta = 10^3[(\sigma/\sigma_0)^{1/4} - 1]_{\text{exp}} - (\sum_i c_i M_{\epsilon,i})_{\text{calc}}$ . The values of  $M_{\epsilon,i} = 6.0, 6.4, 12.0$  and  $11.6$  for  $\text{NaCl}$ ,  $\text{LiCl}$ ,  $\text{CaCl}_2$  and  $\text{MgCl}_2$ , respectively, and  $\sigma_0 = 72.75 \text{ mN m}^{-1}$  were employed

$c_1$	$c_2$	$\sigma$	$\Delta$	$c_1$	$c_2$	$\sigma$	$\Delta$
NaCl (1) + LiCl (2)				NaCl (1) + $\text{CaCl}_2$ (2)			
0.00	1.00	74.60	-0.1	0.00	0.500	74.54	+0.1
0.00	3.00	78.50	0.0	0.00	1.500	78.00	-0.4
0.00	5.00	82.54	+0.1	0.00	2.500	82.00	+0.4
0.25	0.75	74.64	+0.1	0.25	0.375	74.52	0.0
0.50	0.50	74.62	+0.2	0.50	0.250	74.50	0.0
0.50	2.50	78.43	0.0	0.50	1.250	77.91	-0.7
0.50	4.50	82.42	-0.1	0.50	2.250	82.10	+0.7
0.75	0.25	74.71	+0.5	0.75	0.125	74.59	+0.3
1.00	0.00	74.61	+0.3	1.00	0.000	74.44	-0.2
1.00	2.00	78.34	-0.1	1.00	1.000	78.00	-0.4
1.00	4.00	82.31	-0.3	1.00	2.000	82.16	+0.9
1.50	1.50	78.35	+0.1	1.50	0.750	78.15	+0.1
1.50	3.50	82.22	-0.3	1.50	1.750	82.10	+0.7
2.00	1.00	78.35	+0.3	2.00	0.500	78.08	-0.2
2.00	3.00	82.14	-0.4	2.00	1.500	82.01	+0.4
2.50	0.50	78.12	-0.2	2.50	0.250	78.12	0.0
2.50	2.50	82.20	0.0	2.50	1.250	82.10	+0.7
3.00	0.00	78.09	-0.1	3.00	0.000	78.23	+0.3
3.00	2.00	82.14	0.0	3.00	1.000	82.05	+0.5
3.50	1.50	81.97	-0.3	3.50	0.750	81.87	0.0
4.00	1.00	82.13	+0.4	4.00	0.500	81.93	+0.2
4.50	0.50	82.03	+0.3	4.50	0.250	81.77	-0.3
5.00	0.00	82.00	+0.4	5.00	0.000	82.17	+0.9

TABLE III  
(Continued)

$c_1$	$c_2$	$\sigma$	$\Delta$	$c_1$	$c_2$	$\sigma$	$\Delta$
LiCl (1) + MgCl <sub>2</sub> (2)				MgCl <sub>2</sub> (1) + CaCl <sub>2</sub> (2)			
0.00	0.500	74.44	0.0	0.000	0.500	74.60	+0.3
0.00	1.500	78.00	+0.2	0.000	1.500	78.16	+0.1
0.00	2.500	81.85	+0.9	0.000	2.500	82.15	+0.8
0.25	0.375	74.47	-0.05	0.125	0.375	74.58	+0.25
0.50	0.250	74.55	0.0	0.250	0.250	74.47	0.0
0.50	1.250	78.00	-0.1	0.250	1.250	78.16	+0.2
0.50	2.250	81.80	+0.4	0.250	2.250	82.20	+1.1
0.75	0.125	74.51	-0.25	0.375	0.125	74.50	+0.15
1.00	0.000	74.56	-0.3	0.500	0.000	74.48	+0.1
1.00	1.000	78.10	-0.1	0.500	1.000	78.05	-0.1
1.00	2.000	81.85	+0.3	0.500	2.000	81.91	+0.3
1.50	0.750	78.20	-0.1	0.750	0.750	78.01	-0.1
1.50	1.750	81.90	+0.1	0.750	1.750	82.05	+0.8
2.00	0.500	78.25	-0.2	1.000	0.500	77.99	-0.1
2.00	1.500	82.00	+0.2	1.000	1.500	81.95	+0.6
2.50	0.250	78.40	0.0	1.250	0.250	78.01	+0.1
2.50	1.250	82.10	+0.2	1.250	1.250	81.93	+0.6
3.00	0.000	78.46	-0.1	1.500	0.000	78.04	+0.2
3.00	1.000	82.15	0.0	1.500	1.000	81.98	+0.9
3.50	0.750	82.20	-0.1	1.750	0.750	81.86	+0.6
4.00	0.500	82.40	+0.2	2.000	0.500	81.80	+0.6
4.50	0.250	82.30	-0.4	2.250	0.250	81.90	+1.0
5.00	0.000	82.60	+0.3	2.500	0.000	81.79	+0.8

These results cannot be explained in terms of formation of the complex anions  $[\text{MeCl}_n]^{(n-2)-}$  solely if they remain free in the solution, because in this case the total number of free charges does not vary on the addition of the  $\text{Cl}^-$  ions to the electroneutral ion combination. The cause can be sought in the association of the bulky complex anions with  $\text{Na}^+$  cations.

Ion pair formation has been proved by molar metachor measurements<sup>2</sup> for solutions of  $\text{Na}_4[\text{Fe}(\text{CN})_6]$  and of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  at low concentrations (not exceeding  $0.1 \text{ mol dm}^{-3}$ ), where it could be confirmed by conductivity data. For  $\text{ZnCl}_2$  in solutions in the presence of  $\text{HCl}$ ,  $\text{LiCl}$  and  $\text{NaCl}$  at  $c_{\text{Cl}^-} = 1$  to  $3 \text{ mol dm}^{-3}$ , densimetric measurements<sup>8</sup> revealed a sharp transition from the aqua complexes  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$  to anionic complexes with a total coordination number 4, without any plateau in the

TABLE IV

Molar metachors  $M_{\text{e}}$  ( $\text{cm}^3 \text{mol}^{-1}$ ) of divalent metal chlorides ( $\text{MeCl}_2$ ) in mixed solutions with NaCl at  $20^\circ\text{C}$ , calculated from measured surface tension  $\sigma$  ( $\text{mN m}^{-1}$ ) according to Eq. (6), and charge numbers  $z_i$  of species with central  $\text{Me}^{\text{II}}$  cations in these solutions, calculated according to Eq. (5); the values of  $M_{\text{e,NaCl}} = 6.0 \text{ cm}^3 \text{mol}^{-1}$  and  $k = 6.0 \text{ cm}^3 \text{mol}^{-1}$  (in Eq. (5)) were employed

$c(\text{MeCl}_2)$ $\text{mol dm}^{-3}$	$c(\text{NaCl})$ $\text{mol dm}^{-3}$	$\text{CaCl}_2$			$\text{CdCl}_2$			$\text{UO}_2\text{Cl}_2$			$\text{ZnCl}_2$		
		$\sigma$	$M_{\text{e}}$	$z_i$	$\sigma$	$M_{\text{e}}$	$z_i$	$\sigma$	$M_{\text{e}}$	$z_i$	$\sigma$	$M_{\text{e}}$	$z_i$
2.50	0.00	82.00	12.15	2.03	75.30	3.46	0.58	76.12	4.55	0.76	74.01	1.72	0.29
2.25	0.50	82.30	12.58	2.10	75.76	3.19	0.53	—	—	—	—	—	—
2.00	1.00	82.16	12.44	2.07	76.02	2.52	0.42	75.73	2.04	0.34	74.35	-0.27	-0.04
1.75	1.50	82.10	12.39	2.06	76.40	1.89	0.32	—	—	—	—	—	—
1.50	2.00	82.01	12.27	2.05	76.64	0.74	0.12	76.23	-0.17	-0.03	74.72	-3.53	-0.59
1.25	2.50	82.10	12.55	2.09	77.29	0.20	0.03	—	—	—	—	—	—
1.00	3.00	82.05	12.53	2.09	78.07	-0.20	-0.03	76.81	-4.33	-0.72	75.73	-7.91	-1.32
0.75	3.50	81.87	11.97	2.00	78.37	-2.96	-0.49	—	—	—	—	—	—
0.50	4.00	81.93	12.31	2.05	79.28	-4.56	-0.76	78.54	-9.32	-1.55	77.14	-18.49	-3.08
0.25	4.50	81.97	13.12	2.19	80.33	-7.59	-1.27	81.99 <sup>a</sup>	—	—	82.22 <sup>a</sup>	—	—

<sup>a</sup>  $c(\text{MeCl}_2) = 0.00 \text{ mol dm}^{-3}$ ,  $c(\text{NaCl}) = 5.00 \text{ mol dm}^{-3}$ .



$n = 2$  range that would indicate the occurrence of significant fractions of the electro-neutral complex. A continuous transition from cationic to anionic chloro complexes has also been found ionophoretically<sup>9</sup> for  $\text{UO}_2^{2+}$  ions in solutions of  $\text{LiCl}$ , but only at chloride concentrations of about  $7 \text{ mol dm}^{-3}$ . This is not surprising, because the balance of the zero ionophoretic spot displacement comprises, in addition to the electroneutral complex, also the  $\text{Li}^+ \cdot [\text{UO}_2\text{Cl}_3(\text{H}_2\text{O})_x]^-$  ion pairs and  $2 \text{Li}^+ \cdot [\text{UO}_2\text{Cl}_4(\text{H}_2\text{O})_y]^{2-}$  triplets whose formation (shifted to higher  $\text{Li}^+$  concentrations as the results of its high hydration), although lowering the molar metachor, does not contribute to the ionophoretic displacement of the spots towards the anode.

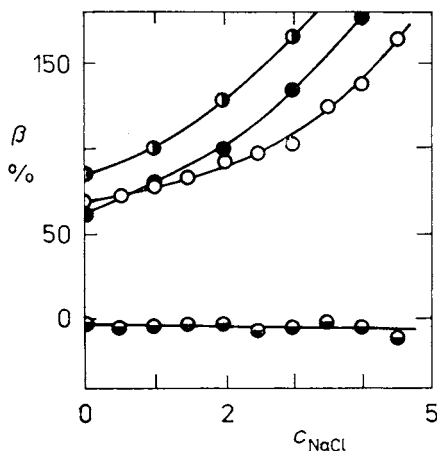


FIG. 1

Dependence of the degree of association  $\beta$  (%) of  $\text{CaCl}_2$  (●),  $\text{CdCl}_2$  (○),  $\text{UO}_2\text{Cl}_2$  (●) and  $\text{ZnCl}_2$  (○) in mixtures with  $\text{NaCl}$  on the concentration of the latter; the  $\beta$  values were calculated from Eq. (9) based on molar metachors measured in the mixed solutions at  $c(\text{Cl}^-) = 5 \text{ mol dm}^{-3}$  and a temperature of  $20^\circ\text{C}$

On the whole, it can be concluded that up to the highest concentrations, molar metachors of electrolytes in aqueous solutions provide information about the sum of free ionic charges per formula unit of the electrolyte both in one-electrolyte and in mixed aqueous solutions. Although not enabling conclusions to be drawn concerning the nature of bonds in associates or complexes, the molar metachor is a quantity which, being generally applicable, is able to offer specific views upon the constitution of highly concentrated aqueous solutions of electrolytes, in many cases not obtainable by other present-day experimental methods.

*The authors dedicate this paper to the memory of Prof. Stanislav Škramovský, who contributed so much to the very inception of the metachor concept.*

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