THE METACHOR AS A CHARACTERISTIC OF THE ASSOCIATION OF ELECTROLYTES IN AQUEOUS SOLUTIONS

Jiří ČELEDA and †Stanislav ŠKRAMOVSKÝ

Department of Nuclear Fuel Technology and Radiochemistry,
Prague Institute of Chemical Technology, 166 28 Prague

Received March 3rd, 1982

Based on the earlier paper introducing a concept of the apparent parachor of a solute in the solution, we have eliminated in the present work algebraically the effect which is introduced into this quantity by the additivity of the apparent molal volumes. The difference remaining from the apparent parachor after subtracting the contribution corresponding to the apparent volume (for which the present authors suggest the name "metachor") was evaluated from the experimental values of the surface tension of aqueous solutions for a set of 1,1-, 1,2- and 2,1-valent electrolytes. This difference showed to be independent of concentration up to the very high values of the order of units mol dm^{-3} but it was directly proportional to the number of the free charges (with a proportionality factor 5 ± 1 cm^3 mol^{-1} identical for all studied electrolytes). The metachor can be, for this reason, a suitable characteristic for detection of the association of ions and formation of complexes in the solutions of electrolytes, up to high concentrations where other methods are failing.

Looking for methods applicable to detection and identification of the formation of complexes and association of the ions in the strongly concentrated solutions of electrolytes (the number of such methods is still unsufficient), one of the present authors has offered in his previous paper[1] a theoretical basis for the Sugden parachor of the individual liquid substances to which Sugden assigned the formula

$$P = (M/\varrho)\, \sigma^{1/y}\,, \qquad (1)$$

derived from the postulated independence of temperature (where M is the molecular mass of a substance, ϱ is its density and σ its surface tension at given temperature). It was shown that in this expression, the theoretically derived denominator of the exponent, y, approached in average the empirical value of Sugden, $y = 4$. Introducing approximations based on the same model, the author substantiated the additivity of the parachors of components in ideal liquid mixtures which is analogous to the additivity of the molal volumes. In a next step, he formulated[1] for the case of the non-ideal mixtures (as *e.g.* the aqueous solutions of electrolytes), a concept of the apparent parachor of a solute Π_1 – in analogy to the concept of the apparent molal volumes. Apparent parachor of a solute Π_1 represents that part of the parachor of the solution as a whole, $(\overline{M}/\varrho)\,\sigma^{1/y}$, remaining per one mol of the solute after subtraction of the parachor of the solvent which is taken as a pure free substance at given temperature, $x_0P_0 = x_0(M_0/\varrho_0)\,\sigma_0^{1/y}$. There, $\overline{M} = x_0M_0 + x_1M_1$ is the average molecular mass of the solution, ϱ is its density and σ is its surface tension. From the above definition, we obtained for evaluation of the apparent parachors of the electrolytes in aqueous solutions, Π_1 (using conversion of the molar fractions to mass percents q_1), a formula[1]

$$\Pi_1 = (M_1/q_1)\,[(100\sigma^{1/y}/\varrho) - \sigma_0^{1/y}(100 - q_1)/\varrho_0]\,. \qquad (2)$$

Indices 0 and 1 relate to the pure solvent and solute, respectively. Applying the same conversion, one gets an analogous expression also for the apparent volume of a solute[1].

$$\Phi_1 = (M_1/q_1)\,[(100/\varrho) - (100 - q_1)/\varrho_0]\,. \qquad (3)$$

This quantity includes all volume changes of the solvent resulting from the solvent interaction with particles of the dissolved substance. For evaluation of both quantities from the data measured in the solutions and in the pure solvent (ϱ, ϱ_0, σ, σ_0), it is convenient to modify (2) and (3) to a form

$$\Pi_1 = (M_1/q_1)\,[100(\sigma/\sigma_0)^{1/y}\,(\varrho_0/\varrho) - (100 - q_1)]\,P_0/M_0\,, \qquad (4)$$

where P_0 is the parachor of pure solvent and

$$\Phi_1 = (M_1/q_1)\,[100(\varrho_0/\varrho) - (100 - q_1)]\,V_0/M_0\,, \qquad (5)$$

where V_0 denotes the molal volume of pure solvent and the ratio V_0/M_0 is the specific volume per 1 kg of solvent.

Experimentally it was found that the apparent volumes of strong electrolytes in aqueous solutions increased linearly with the second root of concentration c. This fact is known as the "Masson square root rule"[2] and its validity was verified up to the highest concentrations by Geffcken[3], Scott[4], Root[5] and others. Since the contribution of surface tension of liquid compounds compensates in the parachors the temperature dependence of the corresponding molal volumes, it is reasonable to ask whether it does not also compensate the above described concentration dependence od apparent volumes in the solution, observed with strong electrolytes. The model used in the above cited paper[1] does not answer this question which can be solved only experimentally. This has been the first task of the present paper.

It is further known that apparent volumes of strong electrolytes in aqueous solutions, Φ_1^0, which were extrapolated using the Masson rule to an infinitely diluted solution can be additively divided into ionic volumes representing at given temperature a characteristic constant for each ion. As far as this point is concerned, one of the present authors has shown in an earlier paper[6] that similar additivity is observed also with apparent volumes Φ'_1 extrapolated to the "anhydrous" state of the electrolyte (*i.e.* to the curve $\Phi_1 c_1 = 1$, corresponding to a 100% filling of the solution with apparent volumes of the ions Φ'_1). These volumes represent (since under such conditions disappear the volume changes of the solvent in the field of the ions), the "true" volumes which the ions would have if they existed as a pure compound in the form in which they exist in a solution. In this way we came to the second question whether also the apparent parachors of the electrolytes Π_1^0, Π'_1, after extrapolation to the infinitely diluted solution and to the above mentioned "anhydrous" state can be divided into similar additive constant ionic contributions. One can also ask whether there is some correlation between the values of these ionic constants and chemical structure of the electrolyte which would permit to obtain some additional independent structural information, in addition to that obtained from the apparent volumes of the electrolytes[6]. At the present state of theory of the aqueous solutions of electrolytes, this problem, too, can be solved only experimentally which is thence the second task of the present work.

EXPERIMENTAL

Surface tension of the aqueous solutions of strong electrolytes was measured on samples with different percentual contents q_1 and the same solutions were used also for determination of the density ϱ, to ensure consistency of the results. We have taken advantage of the fact that quantities σ as well as ϱ appear for the solution and for the solvent (water) in equations (*4*) and (*5*) in a ratio. For this reason, we are able to use (without visibly affecting the results) uncorrected values for the surface tension σ' and density ϱ' of the solutions and water. The values were measured within short time intervals, with the same pycnometer and capillary and they were evaluated without correction for the atmospheric uplift pressure (respectively vapour tension). Only for evaluation of the coefficient following the broken bracket (related to a pure solvent), we have applied values σ_0 and ϱ_0 tabulated for given temperature.

Surface tension of the solutions was measured by the bubble method[7] modified in a same way as in the earlier works[8,9]. The solutions were prepared from redistilled water and reagent grade chemicals without further purification. The influence of surface active impurities was eliminated by their adsorption on preceding 10 bubbles; the 11th bubble was used for the measurement. Density ϱ' and ϱ'_0 were determined by the usual pycnometric method (ϱ'_0 was measured at the beginning and the end of each of the series of solutions, using the same pycnometer). All measurements with more concentrated solutions were carried out at 25°C. For diluted solutions, where even small temperature differences can lead to large differences in the resulting apparent parachors and volumes of the solute, we have chosen the temperature 20°C in order to reduce the temperature gradient. All parachor values were calculated with the Sugden value $y = 4$.

RESULTS AND DISCUSSION

In this work we are summarizing the results obtained for strong inorganic 1 – 1, 1 – 2 and 2 – 1 electrolytes. The experimental surface tension data and uncorrected values for density of the solutions are presented for the first two types in Tables I and II. As one can see, the parachors Π_1 evaluated from these data are not concentration-independent and their value increases linearly with the square root of concentration c, similarly to the apparent volumes. Hence follows that the surface tension contribution to the apparent parachor does not compensate the concentration dependence of the apparent molal volumes of the electrolytes. Examples are shown in Fig. 1. The left-hand side shows also the way in which concentration c' corresponding to the "anhydrous" state of the electrolyte is determined using graphical extrapolation of the apparent volumes to the curve $c'\Phi'_1 = 1$ (or 1 000 if the concentration is expressed in mol dm^{-3} and the apparent molal volumes in cm^3 mol^{-1}), as well as, the subsequent determination of the parachors of a solute in this "anhydrous" state Π'_1 (by means of the vertical dashed lines). The results have shown that in this way obtained experimental values of parameters Π'_1, as well as, values Π_1^0 extrapolated to the infinitely diluted solution can be divided into ionic contributions remaining constant within the experimental error. One of these constants has to be of course chosen arbitrarily. In the case of the apparent molal volumes, it is reasonable to select potassium chloride since it represents a combination of two particles of different size, yet, with an isoelectronic rare gas configuration, so that the volume can be distributed in proportion corresponding to the volume ratio calculated from their crystallographic radii[6,10].

Taking into account that molal volume of a substance M/ϱ, appears in the formula of its parachor (*1*) as a coefficient, we applied the same approach also for the apparent parachors of potassium chloride, dividing them in proportion to the ratio of the apparent volumes of considered ions (cm^3 mol^{-1}): $\Phi^0(K^+) = 5{\cdot}8$ and $\Phi^0(Cl^-) = 20{\cdot}0$ accepted from the above cited paper[10] as well as $\Phi'(K^+) = 11{\cdot}6$ and $\Phi'(Cl^-) = 26{\cdot}1$ from paper[6]. From these, in this way calculated, individual parachors of ions K^+ and Cl^-, we determined, by gradual subtraction from the experimental apparent parachors of other salts (applying least square analysis), the apparent parachors of other ions. Results are presented in Table III. Standard deviation between the experimentally obtained values of the apparent parachors of electrolytes Π_1^0, Π'_1 and the values formed additively from the ionic increments according to Table III is equal to $\pm 1{\cdot}0$ for the case of Π_1^0 and $\pm 0{\cdot}7$ for the case of Π'_1 (for Na^+ ions this degree of fitting is obtained with values calculated for the monoaquocomplex[6,12]).

From the above result it is evident that within the limits of attained accuracy of the measurement and extrapolation procedure, the additivity of the apparent ionic parachors of strong electrolytes holds in the whole concentration range (under the assumption that we compare values corresponding to the same "degree of filling"

TABLE I

Aqueous solutions of uni-univalent electrolytes

q_1	σ'	ϱ'	$10^3\Phi_1$	$10^3\Pi_1$	$10^3M_{\varepsilon,1}$
$NaCl^a$ 20°C					
0	73·40	0·99800	—	—	—
0·487	73·53	1·00155	15·9	62·2	5·3
0·511	73·53	1·00163	17·0	64·6	5·0
1·019	73·69	1·00519	17·5	67·5	5·6
NaCl 25°C					
0	72·58	0·9958	—	—	—
5·12	74·09	1·0328	17·6	68·0	5·7
9·90	75·34	1·0670	19·1	70·9	5·2
15·09	77·15	1·1063	19·8	73·6	5·4
19·93	79·33	1·1440	20·5	76·7	5·8
NaBr 20°C					
0	73·40	0·9972	—	—	—
1·80	73·63	1·0112	24·1	83·4	4·5
3·56	73·91	1·0252	24·1	84·8	5·0
NaBr 25°C					
0	72·58	0·9958	—	—	—
10·21	74·41	1·0793	25·0	90·0	5·8
20·17	76·05	1·1724	26·1	91·2	5·1
30·07	78·85	1·2797	27·1	95·3	5·6
40·37	81·89	1·4125	27·8	97·1	5·6
$NaNO_3$, 20°C					
0	73·40	0·9972	—	—	—
2·57	73·81	1·0146	28·3	96·2	4·5
5·06	74·20	1·0316	29·3	97·9	4·4
NH_4NO_3 25°C					
19·94	76·10	1·0797	49·0	155·9	4·4
29·72	77·79	1·1231	49·7	157·2	4·2
39·66	79·90	1·1705	50·1	158·4	4·1
49·68	81·95	1·2198	50·6	159·6	4·1

q_1	σ'	ϱ'	$10^3\Phi_1$	$10^3\Pi_1$	$10^3M_{\varepsilon,1}$
KCl 25°C					
5·56	73·67	1·0311	28·7	98·0	4·9
17·30	76·43	1·1107	30·1	102·5	5·0
22·44	78·18	1·1474	30·8	105·6	5·4
24·25	78·71	1·1580	31·6	108·0	5·4
KCl 25°C					
0	72·58	0·9958	—	—	—
10·82	73·98	1·0778	35·4	118·2	5·0
20·95	75·73	1·1659	36·2	120·9	5·2
30·22	77·53	1·2577	37·1	123·5	5·2
40·08	79·47	1·3699	38·0	125·5	5·0
KI 25°C					
19·84	74·19	1·1609	47·2	149·2	4·0
49·70	77·82	1·5362	49·3	153·2	3·8
57·54	79·64	1·6717	49·5	156·3	4·1
KIO_3 20°C					
2·02	73·53	1·0145	33·4	111·3	4·6
4·52	73·77	1·0365	34·4	117·6	5·7
$KClO_4$ 20°C					
0	73·40	0·9972	—	—	—
0·79	73·47	1·0023	49·4	156·8	4·2
KNO_3, 20°C					
0	73·40	0·9972	—	—	—
2·63	73·81	1·0139	38·0	126·8	5·3
5·18	74·18	1·0299	39·2	129·4	5·0
$NH_4NO_3{}^a$, 30°C					
0	71·90	0·9964	—	—	—
21·66	75·69	1·0840	50·4	159·6	4·4
34·38	77·74	1·1424	50·5	158·6	4·0
49·40	81·02	1·2160	51·0	160·3	4·0

TABLE I
(*Continued*)

q_1	σ'	ϱ'	$10^3\Phi_1$	$10^3\Pi_1$	$10^3M_{\varepsilon,1}$	q_1	σ'	ϱ'	$10^3\Phi_1$	$10^3\Pi_1$	$10^3M_{\varepsilon,1}$
		NH_4Cl, 20°C						NH_4Br, 25°C			
0	73·50	0·9970	—	—	—	19·76	75·72	1·1167	44·4	143·4	4·7
6·60	75·52	1·0165	38·0	127·2	5·4	20·46	76·16	1·1218	44·3	144·4	5·2
12·27	77·34	1·0342	37·9	126·7	5·4	24·77	76·76	1·1515	44·6	144·4	4·8
19·11	79·42	1·0533	38·6	128·2	5·2	30·29	77·93	1·1921	44·8	145·1	4·9
22·28	80·32	1·0620	38·9	128·6	5·1	40·11	80·20	1·2713	45·2	146·0	4·8
		KOH[a], 20°C						$KHCO_3$, 25°C			
0	72·75	0·9982	—	—	—	0	72·58	0·9958	—	—	—
4·09	74·18	1·0358	6·3	37·4	6·5	9·99	73·99	1·0630	36·9	120·9	4·6
9·32	76·29	1·0845	8·2	43·5	6·7	15·07	75·28	1·0990	37·8	126·6	5·5
13·92	78·52	1·1283	10·3	46·7	5·7	17·63	75·79	1·1172	38·5	128·5	5·5
18·69	80·12	1·1746	11·0	50·6	6·3	20·03	76·05	1·1351	38·9	128·6	5·2

[a] Data with the density corrected for atmospheric pressure.

of the solution with apparent volumes of the ions *i.e.* we take values corresponding to the same ratio c/c' in the range $0-1$), similarly as it was found for the apparent volumes[6,11,12]. Comparison of the apparent parachors which were obtained at mutually non-corresponding concentrations c_1 cannot serve (due to their large concentration dependence) as a basis for conclusions concerning the chemical structure of the electrolytes in solutions.

Table III shows that the values of the apparent parachors in aqueous solutions, Π_1^0, and, Π_1', increase, for identical charges, in proportion to the crystallographic dimensions of the ions. On contrary, the slope of the concentration increase of the parachor which is evaluated from the difference $\Pi_1' - \Pi_1^0$ increases sharply in the direction from the univalent to bivalent ions. This slope increases also with the hydration of the ions as it is possible to see on the sequence I^-—Br^-—Cl^-, or, on comparison of the halide ions with the more extensively hydrated[10] polar ions HCO_3^- and OH^- (in the case of univalent anions), or, on comparison of the bulky and thus less hydrated ions SO_4^{2-} with the smaller and therefore more strongly hydrated ions CO_3^{2-} (in the case of bivalent anions). From the slope of the concentration dependence of the apparent parachors of electrolytes in aqueous solutions (defined by equations (*2*) and (*4*)), it is thence possible to draw conclusions on the hydration of the electrolytes, as well as, on their association. This can be demonstrated on a case of potassium carbonate (which is fully dissociated to the 2nd degree), showing a much steeper concentration increase of the apparent parachor than $KHCO_3$ (dissociated practically only to the 1st degree), or, on the case of potassium hydroxide (Fig. 1, right-hand side) – in spite of the fact that the last one belongs to very strongly hydrated uni-univalent electrolytes. It is, of course, required that the parachor is measured in a wide concentration range.

Ammonium ion represents an anomaly since its apparent parachor is within the error limits independent of concentration. In comparison with other univalent cations, this ion behaves unusually also in other ways. Its apparent volume[13], equiva-

TABLE II
Uni-bivalent inorganic electrolytes

q_1	σ'	ϱ'	$10^3\Phi_1$	$10^3\Pi_1$	$10^3M_{\varepsilon,1}$
$(NH_4)SO_4$, 20°C					
0	73·40	0·9972	—	—	—
5·00	74·50	1·0270	55·6	190·6	9·6
$(NH_4)_2SO_4$, 25°C					
10·04	74·91	1·0547	58·8	200·5	9·9
15·45	75·97	1·0858	61·4	205·7	9·0
20·00	76·93	1·1120	63·3	210·1	8·7
24·89	78·46	1·1391	65·6	218·1	9·2
30·06	80·10	1·1696	67·0	223·0	9·4
34·98	82·14	1·1974	68·8	230·0	9·9
40·31	84·67	1·2224	71·6	240·0	10·5
Na_2SO_4, 20°C					
0	73·40	0·9972	—	—	—
2·46	74·01	1·0201	12·4	70·7	11·7
5·00	74·64	1·0436	15·8	76·8	10·5
$Na_2Cr_2O_7$[a] 20°C					
4·088	73·20	1·0296	66·7	223·2	9·8
5·893	73·37	1·0434	69·5	230·0	9·2
7·414	73·52	1·0554	70·6	232·5	9·0
K_2CO_3, 20°C					
2·32	74·03	1·0180	16·5	84·9	12·5
5·21	74·64	1·0439	19·6	88·5	10·6
K_2CO_3, 25°C					
0	72·58	0·9958	—	—	—
17·52	76·79	1·1574	28·2	110·4	9·7
24·89	79·16	1·2345	30·9	119·0	9·8
Na_2CO_3, 20°C					
0	73·40	0·9972	—	—	—
2·15	74·08	1·0196	−2·3	25·8	11·2
5·06	74·86	1·0502	+0·3	29·6	9·8
K_2CrO_4[a], 20°C					
1·954	73·10	1·0138	41·3	155·5	11·9
3·898	73·37	1·0301	40·0	147·1	10·4
6·688	73·85	1·0520	45·8	164·4	10·5
$K_2Cr_2O_7$[a] 20°C					
0	72·75	0·9982	—	—	—
5·48	73·40	1·0373	92·0	303·0	11·8
8·34	73·63	1·0585	93·4	302·8	10·3

[a] Density values corrected for atmospheric pressure.

lent conductance[14] and ionophoretic mobility[15] (determined for NH_4^+ ions isotopically labeled with nitrogen ^{15}N, in the solutions of non-labeled ammonium nitrate and ammonium chloride) are very little dependent on concentration. Decisive seems to be the different structure of the hydration sheath (resulting from the tetrahedrally arranged N–H bonds, fitting well the structure of liquid water to which the ions can be hydrogen-bonded without perturbing it).

It is worth to note that the parachors corresponding to the "anhydrous" states of the HCO_3^{1-} and CO_3^{2-} ions (in contradiction with their apparent volumes[6]) are mutually very different despite that their crystallographic radii are nearly the same. This difference cannot be, within reasonable limits, removed by another distribution of the apparent parachors between the cation and the anion. In order to bring the value of Π'_1 for CO_3^{2-} close to the value for the HCO_3^- anion, one would have

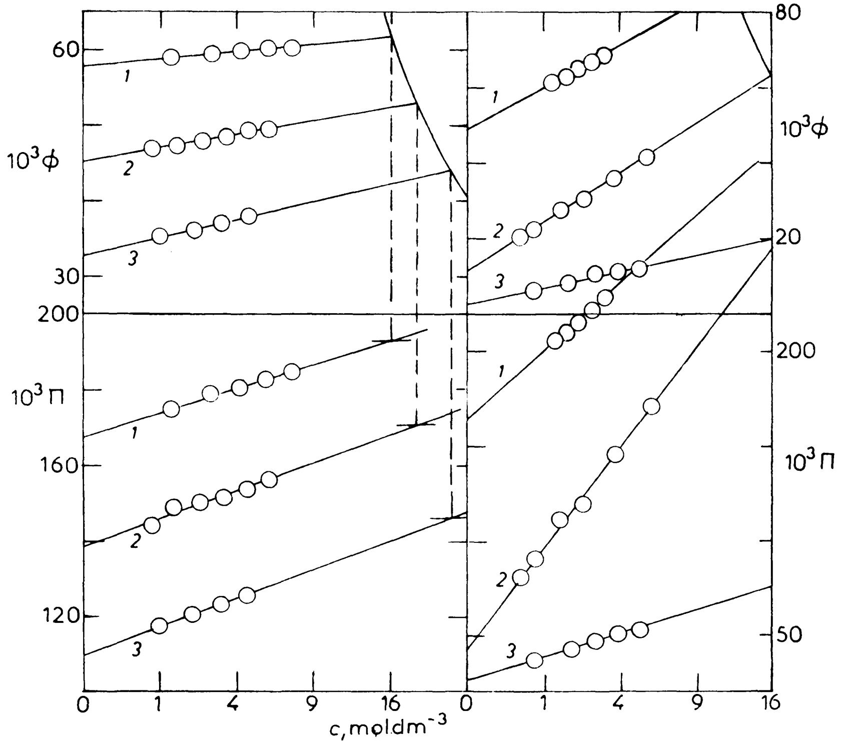

FIG. 1

Experimental apparent parachors Π_1 ($dm^3\ mol^{-1}\ (mN/m)^{1/4}$) (lower part) and apparent molal volumes Φ_1 ($dm^3\ mol^{-1}$) (upper part) of uni-univalent electrolytes: NH_4CNS (*1*), KI (*2*) and KBr (*3*) in aqueous solutions, 25°C (left section) and uni-divalent electrolytes: $(NH_4)_2SO_4$ (*1*) and K_2CO_3 (*2*) compared with potassium hydroxide (*3*) 25°C (right section) to increase the value of the apparent parachor for cation K^+ from 40 to 90 units. Consequently, the apparent parachor value of the much bulkier anion Cl^- would drop down to 40 units which is far below the correspondingly altered value for the K^+ ions. Such a low value is hard to accept from the physical point of view, independently of which model of surface tension of the solution we have selected.

This proves that also in the parachors corresponding to the "anhydrous" states of the ions remains preserved (independently on the effect of the ionic volume itself) the specific contribution of the surface tension. This contribution is visibly higher for the bivalent ion CO_3^{2-} than for the univalent ion HCO_3^-. From that we have concluded that apparent parachors of the electrolytes may provide information on constitution of the electrolytes in a solution, in addition to that obtained from the apparent volumes[6,10].

Since the concentration dependences of the apparent parachor and apparent volume of the electrolytes follow parallel trends, it was obvious that the most simple way how to separate the above effect of the dissociation state of the electrolytes on surface tension of their aqueous solutions was to calculate the mutual ratio od both these quantities Π_1/Φ_1. As follows from equation (*4*) and (*5*), this ratio eliminates the molecular mass of the solute and thus also the effect resulting from the additivity of the atomic masses. The only remaining interrelation is the dependence between the surface tension of a solution and its density.

It was observed that the values of ratio Π_1/Φ_1 (calculated from the data in Tables I, II) changed only slightly with concentration c. These changes were by one order of magnitude smaller than the changes of the values Π_1 and Φ_1 themselves and, in addition, they were quite irregular. For some electrolytes, the above ratio increased slightly with increasing concentration while with some other electrolytes it went

TABLE III

Individual ionic apparent parachors Π_i^0, Π_i' (dm^3 mol^{-1} mN$^{1/4}$ m$^{-1/4}$) in aqueous solutions

Ion	$10^3\Pi_i^0$	$10^3\Pi_i'$	$10^3(\Pi_i' - \Pi_i^0)$	Ion	$10^3\Pi_i^0$	$10^3\Pi_i'$	$10^3(\Pi_i' - \Pi_i^0)$
Na^{+a}	−10	8	18	CNS^-	119	145	26
K^+	20	40	20	NO_3^-	100	116	16
NH_4^+	49	48	−1	HCO_3^-	90	128	38
Cl^-	71	90	19	OH^-	7	59	52
Br^-	90	106	16	CO_3^{2-}	5	175	170
I^-	119	130	11	SO_4^{2-}	66	193	127

[a] Na^+ as NaH_2O^+.

slowly down and in some cases it fluctuated (within experimental error) around the mean value in a range ±1%. This approximate invariance of the ratio Π_1/Φ_1 with changing concentration allowed us to assume that this ratio would keep its value also in a hypothetical "pure state", in which the electrolyte (preserving its structure and the force interactions of its particles in the form in which they exist in a solution) would fill up the entire volume as a pure substance and the concentration of the solvent would drop to zero. In this "pure" component state, the apparent volume and apparent parachor should become identical with the true molal volume V and true parachor P of the above hypothetical "pure" substance – the structure and interaction of particles of which would correspond to the state in which the electrolyte exists in a solution.

From the definition of the parachor of a pure substance (*1*) (where the first coefficient signifies the molal volume of this substance), extrapolated ratio P/V should be equal to the y-root of surface tension σ_1 of the above described hypothetical form of the electrolytes in a "pure" state. Results are summarized in Table IV. The uncertainty in extrapolation to the zero content of water does not exceed ±2% for the values P/V and ±10% (for $y = 4$) for the values σ_1. It is surprising that quantity σ_1 is very little sensitive to a choice of parameter y in the formula of the parachor. In the range from $y = 1$ to $y = 8$ (which in direction up and down far exceeds the theoretically derived limits for the temperature invariance of the parachor[1]), the apparent parachor Π_1 evaluated from (*4*) changes its value within the range of two orders of magnitude, however, deviations of the calculated value of σ_1 from the mean value attain in average ±10%, close to the limits of accuracy of the extrapolation procedure.

The value of surface tension σ_1, determined in the above described way from the apparent parachor of the electrolyte in its aqueous solution can be therefore regarded as a characteristic of the state of the electrolyte in the solution, which, though it is evaluated from the values Π_1, unlike them is (within physically justifiable limits of variability of parameter y) practically independent on accuracy with which we know the correct value of Π_1. It is quite acceptable to take for all electrolytes a common, Sugden's value $y = 4$. The data given in Table IV were calculated using this value.

As one can see in this Table, it is impossible to find any univocal relation between the ratio Π_1/Φ_1 (respectively value σ_1) for different electrolytes and their apparent volumes Φ_1 (the values shown in the Table are presented for the value $c = 1 \text{ mol} . \text{dm}^{-3}$). In general, the only thing one can find out is that surface tension of the hypothetical substances corresponding to the dissolved form of strong electrolytes increases in direction from the salts with the bulky ions to the salts with ions with small radii. Bivalent anions shift the position of the electrolyte to a higher place in the sequence than one might expect from their crystallographic radii. This is in agreement with the Coulomb law: Separation energy of the particles of the substance, determining (as shown by the experimental data[1]) the surface tension of this substance in a liquid state, goes up with decreasing ionic radii and with increasing ionic charges. Both effects are, nevertheless, mixed together so that the region of 1,2-valent electrolytes considerably overlaps the region of 1,1-valent electrolytes. It is therefore impossible to determine unequivocally from the ratio Π_1/Φ_1 (in spite of its temperature invariance) the valence type of the electrolyte and thus also the degree of its association. As far as the values σ_1 are concerned, these seldom exceed the value of $2\sigma_0$ which indicates that the ionic contribution to surface tension of the solutions is based on mutual separation of the hydration sheaths of the ions and not on separation of the anhydrous ions themselves. The experimentally observed invariance of ratio Π_1/Φ_1 has shown that the concentration dependence of the apparent parachors Π_1 of strong electrolytes in aqueous solutions is overwhelmingly a result of the concentration dependence of their apparent volumes Φ_1. The inclusion of the surface tension does not contribute to the concentration dependence of Π_1 by any important additional effect. We could therefore assume that it should be possible to separate the contribution of the surface tension to the parachor of the electrolyte as a concentration invariant in which all effects included in the molal volume of the electrolytes (*i.e.* the concentration dependence, the additivity of atomic masses and volumes *etc.*) which make from the parachor a quantity of questionable diagnostic value in comparison with the molal volume itself[16], should be eliminated. As the result, one should get a pure effect of virial interaction ion-water and ion-ion, responsible for the changes in the surface tension of the solutions.

TABLE IV

Extrapolated ratios Π_1/Φ_1 and surface tensions of electrolytes in the hypothetical pure state

Electrolyte	t °C	$10^3\Phi_1$	Π_1/Φ_1	σ_1	Electrolyte	t °C	$10^3\Phi_1$	Π_1/Φ_1	σ_1
NH_4CNS	25°	58	3·10	92	$KHCO_3$	25°	37	3·30	119
$KClO_4$	20°	53	3·10	92	$NaNO_2$	20°	38	3·33	123
KI	25°	47	3·14	97	$(NH_4)_2SO_4$	25°	59	3·34	124
$Na_2S_2O_3$	25°	80	3·14	97	K_2SO_4	25°	44	3·35	126
NH_4NO_3	25°	48	3·15	99	KIO_3	20°	36	3·36	127
	30°	50	3·14	97	KCl	25°	29	3·41	135
KNO_3	25°	40	3·17	101	$NaNO_3$	20°	30	3·43	138
$NaClO_4$	20°	50	3·17	101	NaBr	25°	25	3·50	150
NH_4Br	25°	43	3·22	108	K_2CrO_4	20°	49	3·70	187
$K_2Cr_2O_7$	20°	103	3·24	110	NaCl	25°	18	3·80	209
$Na_2Cr_2O_7$	20°	73	3·25	112	$NaIO_3$	20°	26	3·85	220
KBr	25°	36	3·25	112	K_2CO_3	25°	19	3·93	239
NH_4Cl	20°	38	3·28	116	KOH	20°	7	(4·8)	(531)

We were able to carry out this separation in a purely algebraic way. Using appropriate transformation, we have derived from equations (*4*) and (*5*) an expression for a new quantity

$$M_{\varepsilon,1} = \Pi_1/\sigma_0^{1/y} - \Phi_1 = [(\sigma/\sigma_0)^{1/y} - 1]\, c^{-1}\,, \qquad (6)$$

where c (mol dm^{-3}), which was substituted for $(q_1/100)\,\varrho/M_1$ denotes the molar concentration of the electrolyte in a solution. For a pure liquid substance (where $\Pi_1 = P$, $\Phi_1 = V$ and $\sigma_0 = \sigma$), this quantity equals zero according to both the first and second formula in (*6*). If in the solutions of this substance, the above difference does not equal zero then its value represents the additional effect by which this substance contributes, by interaction of its particles, to the apparent parachor (contribution not included in its apparent volume in the solution). An appropriate name for the new quantity may be the "metachor", $M_{\varepsilon,1}$. This name and symbol will be used in the further text. The dimension of this function agrees with that of the molal volume, *i.e.* dm^3 mol^{-1}.

The values of the thus defined metachor, evaluated from the experimental data, are given in the last column of the Tables I and II. As one can see, the metachors for uni-univalent electrolytes range, in aqueous solutions, between 5·0 ± 1·0 cm^3 . . mol^{-1} while for uni-bivalent electrolytes they vary between 10·5 ± 1·5 cm^3 mol^{-1}, independently of the concentration of the electrolyte, the apparent volume and apparent parachor values and the crystallographic radii of the ions, *etc.* The ranges for the two valence types do not overlap and there is a wide, statistically significant gap between both of them which can be fully exploited for diagnostic purposes. This makes from the metachor a quantity which can be with convenience used for detection of the association of ions and formation of complexes in the solutions of electrolytes. Because of its concentration invariance, the metachor can be used up to the highest concentrations where other methods are failing. In addition, the metachor (as it is defined by equation (*6*)) has a preference of being independent on our knowledge of the exact value of density of a solution. As one can see from equations (*4*) and (*5*), even small errors in determination of density ϱ lead to deviations in the values of Π_1 and Φ_1 (especially then at low concentrations) but these errors are in the value of the metachor mutually compensated. This is very important for applications of the metachor as a structurally dependent characteristic of the electrolytes in aqueous solutions, if we consider that the metachor is a difference function evaluated from two values which are both by one order of magnitude larger. The right-hand side of equation (*6*) offers an explanation for that. There, density ϱ appears already only to such extent in which it participates in conversion of the mass percents q (which are known in the case that solutions were prepared by weighing of their components), to molar concentration c. Thus, *e.g.* determining the density of the solution with accuracy to the third decimal place, we obtain, by this procedure, the metachor values also with an error in the range $10^{-1}\%$. On contrary, the same accuracy of measurement can lead in diluted solutions to values Π_1 and Φ_1 which can be erroneous by 100% (or more), without visibly affecting the metachor value.

An example of applicability of the metachor for determination of the dissociation degree of the electrolytes in aqueous solutions can be illustrated on comparison of $KHCO_3$ and K_2CO_3. The metachor value of the former salt (which dissociates in the whole range of the studied concentrations practically only the to first degree) equals only to one-half of the value of the latter salt, dissociating to the second degree.

The described experimental observations led us to an attempt to investigate more closely the physical significance of the new quantity introduced in this paper which we have named the "metachor". The solution of this task was based on the coverage model used in previous papers[1,9]. According to this model: *a*) each particle forms in a solvent (from the point of view of the cohesion interactions) its own domain which can be in rough approximation represented by a spherical step-function model[14,17-21], *i.e.* as a sphere separated from the surrounding unaffected solvent by a sharp boundary, *b*) in the process of splitting of the column of the liquid, the surface-area proportion of these domains in the newly formed surface is equal to the volume proportion of these domains in the solution, *i.e.* cV_1' (there, V_1' – $dm^3\ mol^{-1}$ – is the overall volume of these "active" domains per 1 mol of the solute).

Denoting $\sigma_{0,1}$ the effective surface tension corresponding to the work connected with separation of the domains from the free solvent and σ_1 a similar quantity corresponding to separation of the domains from one side of the splitting plane from the domains in the opposite surface layer, we get for the resulting surface tension of the solution:

$$\sigma = (1 - cV_1')^2\,\sigma_0 + 2(1 - cV_1')\,cV_1'\sigma_{0,1} + (cV_1')^2\,\sigma_1 \tag{7}$$

or

$$\Delta\sigma = cV_1'(\Delta\sigma_1 - \delta) + (cV_1')^2\,\delta \tag{8}$$

in which we substituted $\Delta\sigma$ for the difference $\sigma - \sigma_0$, $\Delta\sigma_1$ for $\sigma_1 - \sigma_0$ and $\frac{1}{2}\delta$ for $\frac{1}{2}(\sigma_0 + \sigma_1) - \sigma_{0,1}$. Up to concentrations for which the product cV_1' does not exceed 10–15% of the total volume of the solution, the first coefficient in the quadratic term in (*8*) is at least ten times smaller than the coefficient in the linear term and it can be therefore, in approximation, omitted. In the ideal case, where $\sigma_{0,1}$ equals $\frac{1}{2}(\sigma_0 + \sigma_1)$, the value of δ becomes equal to zero, eliminating thus the whole quadratic term. In real cases, one can expect on the basis of simple electrostatic considerations that the gap between the separation energy "hydration sheath – hydration sheath" (σ_1) and the separation energy "hydration sheath – water" will be somewhat larger (though not very pronounced) than the gap between the latter energy ($\sigma_{0,1}$) and the separation energy "water–water" (σ_0). As a result, $\sigma_{0,1}$ does not lie exactly in the centre between σ_1 and σ_0 but slightly lower. We must therefore assume that coefficient δ in the quadratic term has a zero or positive value (nevertheless substantially smaller than $\Delta\sigma_1$ in the linear term). This shifts even further the concentration limits up to which one can omit in (*8*) the quadratic term against the linear term.

Ratio $(\sigma/\sigma_0)^{1/y}$ in (*6*) can be under these circumstances expanded in a series

$$(\sigma/\sigma_0)^{1/y} = 1 + (\Delta\sigma/\sigma_0)/y - (\Delta\sigma/\sigma_0)^2 (y - 1)/2y^2 . \qquad (9)$$

Starting with the third term, all terms become for Sugden's value $y = 4$, even for the highest commonly observed differences between σ and σ_0 (which for the aqueous solutions of strong electrolytes seldom exceed 20 mN m^{-1}), negligible in comparison with the second term. For this reason it is possible (due to the approximative character of the given model solution of the whole problem) to restrict the expansion up to the second term. Substituting the thus approximated expression (*9*) into (*6*) and replacing $\Delta\sigma$ with a similarly approximated expression (*8*) which was derived from the coverage model, one has partially compensated the omission of the positive, quadratic term in (*8*) by the omission of the negative, quadratic term in (*9*) so that the approximation degree of the resulting expression

$$M_{\varepsilon,1} = (V_1'/y)\,\Delta\sigma_1 \qquad (10)$$

providing the physical interpretation of the quantity "metachor" is further improved.

From equation (*10*) it is evident that the metachor should be (within the tolerances given by approximations inherent to the model and deviations connected with the omission of the higher-order terms) independent of concentration c – as far as the molal volume of the interaction spheres V_1' and the corresponding surface tension σ_1 are also concentration independent. This can be reasonably expected for concentrations at which some free solvent still exists in a solution, so that the form of the solvates, as well as, character of the force interactions between them is not visibly changing with increasing concentration.

Assuming that the Coulomb forces between the charges of the ions (respectively dipoles of the water molecules) represent the main contribution to the cohesive interactions in the aqueous solutions of strong electrolytes, we obtain direct proportionality between the radii of the active domains of the ions and the square root of their ion charge z (ref.[17]). This presentation of the problem leads to its solution in terms of the step-function model already mentioned[14,17–21]. We assume that the separation of each ionic hydration complex from the adjacent particles takes place in such a distance from its centre, r, in which the separation work drops, with decreasing field intensity, into the region of energies of the thermal motion, not depending on the charge z. The particles situated inside this critical boundary are exempt from the separation process due to their high separation work. The total number of separation events in the splitting plane per 1 mol of a z-valent ionic

TABLE V

The metachor values of some uni-univalent electrolytes in aqueous solutions up to high concentrations

LiCl, 20°C									NaCl, 25°C			NaClO$_4$, 20°C		
c	σ'	$10^3 M_{\varepsilon,1}$	c	σ'	$10^3 M_{\varepsilon,1}$	c	σ'	$10^3 M_{\varepsilon,1}$	c	σ'	$10^3 M_{\varepsilon,1}$	c	σ'	$10^3 M_{\varepsilon,1}$
0	73·40	—	2·46	77·18	5·1	5·15	83·27	6·2	0	72·58	—	0	73·40	—
0·48	74·10	5·0	2·49	77·37	5·3	5·43	83·33	5·9	1·25	74·53	5·1	2·64	77·55	5·2
0·83	74·58	4·8	2·86	77·92	5·3	5·90	84·17	5·9	2·00	75·85	5·5	3·49	79·10	5·4
0·98	74·90	5·2	3·25	79·05	5·8	6·10	85·46	6·4	2·50	76·84	5·7	4·41	80·45	5·3
1·23	75·38	5·4	3·62	79·37	5·5	6·53	86·53	6·4	3·00	78·46	6·6	5·30	81·26	4·8
1·60	75·80	5·1	3·85	80·40	6·0	7·00	87·68	6·5	3·50	79·13	6·2	6·21	82·75	4·9
1·65	76·06	5·4	4·05	80·17	5·5	7·04	86·88	6·1	4·00	80·07	6·2	7·04	83·32	4·6
1·99	76·58	5·4	4·50	81·26	5·7	7·33	88·62	6·6	4·50	80·94	6·1	7·86	85·47	4·9
2·05	76·40	4·9	4·93	82·27	5·9	8·23	90·48	6·5	5·00	82·00	6·2	8·79	86·50	4·8

species and thus also its active molal volume V_1' as well as the product $V_1' \Delta\sigma_1$ ($\Delta\sigma_1$ being independent of z) will then be proportional to the surface area of a sphere with radius r, *i.e.* to r^2; and, since the radii corresponding to identical field intensities are, according to Coulomb law, proportional to $z^{1/2}$, we thus obtain in (*10*), direct proportionality between $V_1' \Delta\sigma_1$ and z.

Considering also the direct proportionality to the number of the univalent counter-ions (z) which is then simply a matter of trivial additivity, we have come to a direct proportionality between the metachors of the electrolytes and the number of the charges in their molecules in the given state of dissociation. The experimentally found ratio between the metachors of the 1,1 and 1,2-valent electrolytes (given in Tables I and II) has in this way got its theoretical substantiation.

Basing on the earlier results obtained with the 1,1- and 1,2-valent electrolytes, we started to measure solutions of the 2,1-valent electrolytes. This time we concentrated directly on determination of the metachors $M_{\varepsilon,1}$. The right-hand side of equation (*6*) shows that, unlike with the apparent parachors and the apparent volumes, for the determination of the metachors one need not know the density of the solutions with great accuracy; it is sufficient to measure with an accuracy to the third decimal, which is quite acceptable for determination of the molal concentration c (for its evaluation from the ratio of the weighed components) and for determination of the surface tension by a bubble method. With respect to equation (*6*), we did not prepare any more the solutions by weighing the both components (salt and water) but we adjusted directly their molarities c by weighing the salt into a marked vessel (filling the solution up to the mark under temperature stabilized conditions, with subsequent analytical control). From the known c and σ values, we evaluated directly the metachors according to the right-hand side of equation (*6*), avoiding thus the roundabout way with the apparent parachor and apparent volume.

TABLE VI

The metachor values of some bi-univalent electrolytes in aqueous solutions up to high concentrations

$MgCl_2$ 25°C			$CaCl_2$ 20°C			$Mg(ClO_4)_2$ 25°C			$Ca(ClO_4)_2$ 25°C		
c	σ'	$10^3M_{\varepsilon,1}$	c	σ'	$10^3M_{\varepsilon,1}$	c	σ'	$10^3M_{\varepsilon,1}$	c	σ'	$10^3M_{\varepsilon,1}$
0	72·58	—	0	73·40	—	0	72·58	—	1·40	75·95	8·2
1·17	76·55	11·5	1·20	77·55	11·5	1·06	75·72	10·0	1·79	76·86	8·1
1·50	78·00	12·1	2·75	84·94	13·5	1·30	76·20	9·4	2·43	78·65	8·4
2·00	80·00	12·3	3·22	87·65	14·1	1·61	76·94	9·1	2·77	79·44	8·2
2·51	82·76	13·3	4·65	94·43	14·0	2·79	79·80	8·6	3·07	80·62	8·7

As a check, we have measured in the same way also the metachors of some uni-univalent electrolytes (Table V). Results obtained for bi-univalent electrolytes are summarized in Table VI. They support both earlier findings according to which: *a*) the metachor $M_{\varepsilon,1}$ is little (or not at all) dependent on the concentration of the strong electrolytes in aqueous solutions, *b*) the metachor is strongly dependent (within the experimental error even proportional to) on the number of the charges in the molecule of the electrolyte in its given dissociation state, irrespective of the volume differences between the small and large cations (Mg^{2+}, Ca^{2+}) or small and bulky anions (Cl^-, ClO_4^-). The metachor keeps both these properties up to the very high concentrations. This is important for detection of the association and complex formation in the strongly concentrated solutions of electrolytes where we still have a shortage of reliable and generally applicable methods. (At very high concentrations – from 3 to 9 mol dm^{-3} Cl^- – the metachor values of the chlorides are for both valency types increasing whereas the slightly lower values for perchlorates are evidently connected with partial association already setting in. The possibility to differenciate between both valency types is, however, not affected since the differences between the both types far exceed, even in these cases, the experimental error limits).

LIST OF SYMBOLS

c	molar concentration (mol dm^{-3})
c'	molar concentration in the extrapolated state corresponding to zero content of water (mol dm^{-3})
M	molar mass of the substance (kg mol^{-1})
M_1	molar mass of the dissolved electrolyte (kg mol^{-1})
M_0	molar mass of the solvent (kg mol^{-1})
P	parachor of the substance in pure liquid state (dm^3 mol^{-1} mN$^{1/4}$ m$^{-1/4}$)
P_0	parachor of the solvent at given temperature (dm^3 mol^{-1}mN$^{1/4}$ m$^{-1/4}$)
q_0	mass % of the solvent (kg per 100 kg solution)
q_1	mass % of the electrolyte (kg per 100 kg solution)
V	molal volume of the substance in pure liquid state, M/ϱ (dm^3 mol^{-1})
V_0	molal volume of the pure solvent at given temperature (dm^3 mol^{-1})
x	mole fraction (dimensionless)
y	dimensionless exponent denominator in the formula of the parachor
z	dimensionless ionic charge (a multiple of elementary charge unit)
$M_{\varepsilon,1}$	metachor of the electrolyte in the given solution (dm^3 mol^{-1})
Π_1	apparent parachor of the electrolyte in the given solution (dm^3 mol^{-1} mN$^{1/4}$ m$^{-1/4}$)
Π_1^0	apparent parachor of the electrolyte at infinite dilution (dm^3 mol^{-1} mN$^{1/4}$ m$^{-1/4}$)
Π_1'	apparent parachor extrapolated to zero content of water (dm^3 mol^{-1} mN$^{1/4}$ m$^{-1/4}$)
ϱ	density of the pure liquid substance and of the solution (kg dm^{-3})
ϱ'	experimental density non-corrected for atmospheric pressure (kg dm^{-3})
ϱ_0	density of the solvent at the given temperature (kg dm^{-3})
σ	surface tension of the pure liquid substance and of the solution (mN m^{-1})
σ_0	surface tension of the solvent at the given temperature (mN m^{-1})

σ_1 surface tension of the dissolved electrolyte in the hypothetical pure state (mN m^{-1})
Φ_1 apparent molal volume of the electrolyte in the given solution (dm^3 mol^{-1})
Φ_1^0 apparent molal volume of the electrolyte at infinite dilution (dm^3 mol^{-1})
Φ'_1 apparent molal volume extrapolated to zero content of water (dm^3 mol^{-1})

REFERENCES

1. Čeleda J.: This Journal *49*, 327 (1984).
2. Masson O.: Phil. Mag. (7) *8*, 218 (1929).
3. Geffcken W.: Z. Phys. Chem. (Leipzig) *A 155*, 1 (1931).
4. Scott A. F.: J. Phys. Chem. (Leipzig) *35*, 2315 (1931).
5. Root C. W.: J. Amer. Chem. Soc. *55*, 850 (1933).
6. Čeleda J.: Sb. Vys. Šk. Chemicko-Technol. Praze, Inorg. Technol. *5*, 17 (1964).
7. Glasstone S.: *Textbook of Physical Chemistry*, p. 489. Van Nostrand, New York 1946.
8. Škramovský S.: Čas. Česk. Lékárn. *11*, 105 (1944).
9. Čeleda J., Žilková J.: This Journal *42*, 2728 (1977).
10. Čeleda J.: Sb. Vys. Šk. Chemicko-Technol., Praze, FAT+FOT *3*, 15 (1959).
11. Čeleda J.: This Journal *48*, 1538 (1983).
12. Čeleda J.: This Journal *48*, 1680 (1983).
13. Čeleda J., Jedináková V.: This Journal *36*, 3885 (1971).
14. Čeleda J.: Sb. Vys. Šk. Chemicko-Technol. Praze, *B 11*, 5 (1967).
15. Jedináková V., Čeleda J., Hübner H.: Z. Physik. Chem. (Leipzig) *247*, 49 (1971).
16. Exner O.: This Journal *32*, 24 (1967).
17. Čeleda J.: Sb. Vys. Šk. Chemicko-Technol. Praze, Inorg. Technol. *1*, 401, 443 (1958).
18. Čeleda J., Žilková J.: See[17] *B 15*, 101 (1972).
19. Azzam A. M.: Can. J. Chem. *38*, 223, 993 (1960).
20. Conway B. E., Desnoyers J. E., Smith A. C.: Phil. Trans. Roy. Soc. London *A 256*, 389 (1964).
21. Čeleda J.: Sb. Vys. Šk. Chemicko-Technol. Praze, *B 26*, 9 (1981).

Translated by Z. Dolejšek.