THE METACHORS OF POLYVALENT AND ASSOCIATED ELECTROLYTES IN AQUEOUS SOLUTIONS

Jiří ČELEDA, †Stanislav ŠKRAMOVSKÝ and Jana ŽILKOVÁ

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

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The quantity "metachor" introduced in the preceding paper was evaluated from the experimental data on surface tension of the aqueous solutions for a set of polyvalent and weak electrolytes. The almost complete concentration independence of the metachor and its direct proportionality to the number of the free charges in a dissociated molecule (observed and theoretically substantiated in the above cited paper for strong 1,1-, 1,2- and 2,1-valent electrolytes) has been verified in the present paper also for electrolytes of the higher valency types. The metachor values of fully dissociated 1,1-, 1,2-, 1,3- and 1,4-valent electrolytes follow a ratio (5 ± 1) : (10 ± 1·5) : 15 : 22 $cm^3 mol^{-1}$. Association of the electrolytes decreases correspondingly the metachor value as one can see on the case of electrolytes with bulky ions (NH_4SCN, KCH_3COO, $Na_2S_2O_3$, hexacyanoferrates(II)) or with the free acids H_2SO_4, H_2CrO_4, H_3PO_4 *etc.* A weak, in the investigated concentration range negligibly dissociated oxalic acid, consisting of small hydrated hydrophilic molecules, exhibits metachor values close to zero. Dibasic organic acids with a larger number of hydrophobic CH_2 groups reach very high negative metachor values, however, their salts again possess metachor values close to 10 $cm^3 mol^{-1}$ — in accordance with the values found for strong 1,2-valent electrolytes. The metachors of $ZnCl_2$ and $CdCl_2$ decrease sharply from the last mentioned value, with increasing concentration while the metachor value of zinc perchlorate remains unchanged at the level corresponding to the fully dissociated salt. This is in agreement with the well known sequence of tendency of the d^{10}-cations to form complexes with the Cl^- and ClO_4^- anions. All these facts have verified that the metachor can be, in principle, applied for a diagnostics of the dissociation states of the electrolytes in aqueous solutions.

In the previous paper[1], we have formulated on the both theoretical and experimental basis, a concept of the metachor $M_{\varepsilon,1}$, defined by the formula

$$M_{\varepsilon,1} = [(\sigma/\sigma_0)^{1/4} - 1]\, c^{-1}\,, \qquad (1)$$

as a subtractional molal quantity given by the difference between the apparent parachor of the electrolyte in a solution (reduced to a unit surface tension of the solvent) and its apparent volume in the same solution. This quantity is practically independent (or without significance) of the molal volume of the electrolyte as well as of its concentration, up to the very high values of the order of units mol dm^{-3}. On the other hand, this quantity is proportional to the number of the free charges z in the molecule of the electrolyte in a given dissociation state, with a proportionality factor $0{\cdot}005 \pm 0{\cdot}001\ \text{dm}^3\ \text{mol}^{-1}$ found experimentally for the strong 1,1-, 1,2- and 2,1--valent electrolytes. (In the above definitions, σ, σ_0 mN m^{-1} are the surface tension of the solution and water at given temperature, c mol dm^{-1} denotes the concentration of the electrolyte and z is the number of charges of one sign in the molecule, expressed as a multiple of elementary charge). The method of the metachor is applied in the present paper to the electrolytes of higher valency types as well as to the electrolytes which are considerably associated.

EXPERIMENTAL

The experimental approach and the purity grade of the chemicals used were identical with the preceding paper[1]. The solutions were prepared from weighed components (with a correction for the analytically determined content of crystal and hygroscopic water in the samples), with a subsequent conversion to molar concentration c — applying the density values determined experimentally with an accuracy $\pm 0{\cdot}001\ \text{kg dm}^{-3}$. Such accuracy is quite sufficient both for the above conversion as well as for determination of the surface tension by a bubble method[1]. Deviations caused by omission of the correction for a vacuum in Eq. (*1*) are, within the range of the σ values found in the experiment, mutually compensated. Solutions of $ZnCl_2$, $ZnClO_4$ and $CdCl_2$ were prepared by weighing the corresponding salts into a calibrated vessel, filling up to the mark with water at controlled temperature, in a thermostat. The sample of $Zn(ClO_4)_2$ was prepared by dissolution of the weighed-in amount of ZnO, in a slight excess of $HClO_4$, followed by evaporation and re-crystallization of the crystalline product. The corresponding metachors were evaluated from formula (*1*). Simultaneously, we have evaluated from the experimental data also the values of the apparent parachors of electrolytes Π_1, and of their apparent volumes Φ_1. Nonetheless, since the density is determined with lesser accuracy, the above values are of purely qualitative value, serving exclusively for confrontation of their large variation compared with the small variability of the metachor and with its regular charge dependence substantiated theoretically[1].

RESULTS AND DISCUSSION

The experimental values of the surface tension σ (mN/m), density ϱ (kg/dm^3) and the hence evaluated values of the metachors $M_{\varepsilon,1}$ (dm^3/mol) as well as the approximate values of the apparent parachors Π_1 ($\text{dm}^3\ \text{mol}^{-1}\ \text{mN}^{1/4}\ \text{m}^{-1/4}$) and apparent volumes Φ_1 (dm^3/mol) of the solute are shown in dependence on concentration c (mol/dm^3) in Tables I–IV.

From the first part Table I summarizing the data obtained for first part for four electrolytes with bulky ions (known for their tendency to form ion pairs), it is possible to see that the metachor values of the 1,1-valent electrolytes are in majority of cases smaller than $0{\cdot}005\ \text{dm}^3\ \text{mol}^{-1}$ – which is the value observed for this valency type in a state of full dissociation[1]. Also the value found for $Na_2S_2O_3$ is smaller than the average value $0{\cdot}010\ \text{dm}^3\ \text{mol}^{-1}$ obtained with the fully dissociated species of the 1,2-valent electrolytes. These results indicate a formation of the ion pairs $H^+(aq)\ HSO_4^-$ in the

TABLE I

Aqueous solutions of associated inorganic electrolytes

c	σ	ϱ'	$10^3\Pi_1$	$10^3\Phi_1$	$10^3M_{\varepsilon,1}$
NH_4SCN, 25°C					
0	72·58	0·9958	—	—	—
1·31	72·96	1·0184	175	59·0	1·0
2·80	73·95	1·0420	179	59·7	1·7
2·82	73·92	1·0424	179	59·7	1·6
4·15	74·98	1·0632	181	59·9	2·0
5·72	76·70	1·0874	183	60·2	2·4
7·29	78·66	1·1107	185	60·4	2·8
$Na_2S_2O_3$, 25°C					
0	72·58	0·9961	—	—	—
0·47	73·61	1·0341	250	78	7·4
0·96	74·30	1·0717	250	79	6·1
1·40	75·24	1·1047	254	81	6·5
1·46	75·06	1·1090	253	81	5·8
2·01	76·49	1·1494	259	82	6·6
2·64	77·68	1·1930	264	84	6·5
H_2SO_4, 19°C					
0	73·55	0·9974	—	—	—
1·61	74·70	1·0980	111	36	2·4
3·09	75·40	1·1840	116	38	2·0
CrO_3[a], 25°C					
0	72·58	0·9972	—	—	—
0·23	72·61	1·0147	78	26	0·5
0·40	72·67	1·0257	97	32	0·8
0·64	72·75	1·0417	108	36	0·9
0·79	72·84	1·0513	114	38	1·1
H_3PO_4[a], 20°C					
0	73·36	0·9983	—	—	—
0·30	73·62	1·0148	140	45	3·0
0·60	73·90	1·0302	145	47	3·1
0·96	73·19	1·0500	143	46	2·9

TABLE I
(*Continued*)

c	σ	ϱ'	$10^3\Pi_1$	$10^3\Phi_1$	$10^3M_{\varepsilon,1}$
		KH_2PO_4[a], 20°C			
0	73·40	0·9983	—	—	—
0·28	74·02	1·0247	141	41	7·6
0·46	74·36	1·0417	143	42	7·1
0·63	74·70	1·0574	145	43	7·0
0·77	75·08	1·0690	151	44	7·4
		K_2HPO_4[a], 20°C			
0·23	74·12	1·0315	114	28	10·8
0·34	74·47	1·0480	117	29	10·6
0·47	74·77	1·0650	121	32	9·9
0·59	75·12	1·0819	124	32	9·8
		NH_4NaHPO_4[a], 20°C			
0	73·40	0·9982	—	—	—
0·19	73·98	1·0184	109	27	10·3
0·38	74·49	1·0384	114	29	9·6
		K_3PO_4[a], 20°C			
0	73·40	0·9983	—	—	—
0·14	74·06	1·0268	81	13	15·2
0·29	74·75	1·0551	95	17	15·8
0·39	75·22	1·0741	101	19	15·7
0·51	75·62	1·0954	103	20	14·8

[a] Densities ϱ corrected for a vacuum.

case of sulphuric acid; with CrO_3 — most probably even of larger agglomerates consisting of partially dissociated polychromic acids, in a mixture with their undissociated species. Formation of such ion pairs necessarily decreases the intensity of the electrostatic field of the resulting products of ion association (and thus also of the corresponding energy of attractive forces between them and water, as well as, between thermselves mutually) in comparison with the free ions. This leads to a decrease of the surface tension of the solutions and consequently, according to (*1*), also of the metachor value of the solute.

In term of this interpretation, we may expect that the decrease of metachor should become more pronounced with increasing concentration, in correspondence with

TABLE II

Cyanoferrates and the salts of monobasic carboxylic acids

c	σ	ϱ'	$10^3\Pi_1$	$10^3\Phi_1$	$10^3M_{\varepsilon,1}$
		K_3 $Fe(CN)_6$, 20°C			
0	73·40	0·997	—	—	—
0·16	74·09	1·026	487	152	14·6
0·21	74·17	1·034	488	154	12·3
		$Na_4Fe(CN)_6$, 20°C			
0	73·20	0·997	—	—	—
0·10	73·64	1·021	267	77	14·5
0·20	74·04	1·041	287	84	14·4
		K_4 $Fe(CN)_6$, 20°C			
0	73·40	0·997	—	—	—
0·08	73·94	1·018	405	116	22·1
0·12	74·05	1·027	414	124	17·9
0·16	74·15	1·037	407	123	15·6
		HCOONa, 20°C			
0	73·50	0·997	—	—	—
0·76	74·77	1·030	91	26	5·7
1·23	75·45	1·049	92	26	5·4
		HCOOK, 18°C			
0	74·00	0·997	—	—	—
1·28	76·09	1·058	128	37	5·4
8·00	85·08	1·342	134	41	4·4
		CH_3COOK, 20°C			
0	73·40	0·997	—	—	—
0·30	73·65	1·014	126	40	2·9
0·65	74·08	1·034	131	41	3·6
1·87	75·00	1·084	160	52	2·9

TABLE III

Dibasic organic acids and their salts at 20°C

c	σ	ϱ'	$10^3\Pi_1$	$10^3\Phi_1$	$10^3M_{\varepsilon,1}$
		Oxalic acid			
0	73·50	0·997	—	—	—
0·20	73·38	1·006	130	47	−2·0
0·40	72·95	1·015	123	47	−4·7
		Malonic acid			
0	73·40	0·997	—	—	—
0·23	72·12	1·005	150	70	−19·0
0·24	72·25	1·006	144	66	−16·6
0·50	70·95	1·016	152	66	−17·0
0·75	70·00	1·026	148	66	−15·7
		Maleinic acid			
0·21	71·48	1·006	129	75	−30·9
0·45	69·96	1·015	144	76	−26·8
		Succinic acid			
0·21	71·15	1·005	130	81	−36·7
0·43	69·40	1·013	145	82	−32·2
		Tartaric acid			
0·17	73·37	1·009	234	80	−0·6
0·34	73·49	1·020	243	82	+0·9
0·51	73·47	1·032	243	83	+0·5
		Na-oxalate			
0	73·40	0·997	—	—	—
0·11	73·71	1·010	97	24	9·5
0·23	74·10	1·023	102	25	10·1
		K-Oxalate			
0·20	74·04	1·021	164	45	10·9
0·38	74·70	1·042	173	48	11·6

TABLE III
(*Continued*)

c	σ	ϱ'	$10^3\Pi_1$	$10^3\Phi_1$	$10^3M_{\varepsilon,1}$
		Na-malonate			
0·15	73·82	1·014	132	36	9·6
0·32	74·38	1·032	144	39	10·3
		Na-tartrate			
0	73·40	0·997	—	—	—
0·11	73·80	1·013	193	54	12·3
0·17	74·00	1·020	202	57	12·1
0·23	74·10	1·028	202	58	10·6
0·34	74·40	1·042	205	60	10·1
		NaK-tartrate			
0	73·40	0·997	—	—	—
0·18	73·90	1·023	226	68	9·2
0·37	74·62	1·049	239	71	11·1

a more extensive association. Nothing like that is observed. For H_2SO_4 the values of $M_{\varepsilon,1}$ go down only slightly, for $Na_2S_2O_3$ they stay roughly at the same level, while with the remaining two electrolytes, we can see a marked increase. These results can be, possibly, explained by a superposition of the decrease of the metachor values due to association, with the positive concentration effects on the metachors of the ions and their association products (where the magnitude of the latter effect is enhanced by increasing concentration). Such a view is supported by orientational measurements in the solutions of K_2CO_3, carried out at high concentrations from 8 to 11 mol dm^{-3} K^+. These measurements showed an increase from the original metachor values[1] around $10 \,.\, 10^{-3}$ dm^3 mol^{-1}, to 14 or even $16 \,.\, 10^{-3}$ dm^3 mol^{-1}. This can be caused by several reasons. One of them is a simple dehydration occurring with large ions at high concentrations, since, under such circumstances, the solution is almost completely filled-up with the volumes of all present ions and the content of water (and its activity) are thus strongly reduced. The decrease of mean radii of the hydration sheaths leads to an increase of the interaction energy of the ions with the water and with the counter-ions, which results in the increase of surface tension of the solution and of the metachor value of the solute.

Another possible reason can be connected with the non-linear dependence of surface tension of the solution on volume concentration of the free charges. From the equations for surface tension of the solution derived[1] theoretically on basis of the coverage model, one gets for the metachor of the solute (using expansion to a power series) – in second approximation – an expression

$$4M_{\varepsilon,1}/V_1' = (\Delta\sigma_1 - \delta)/\sigma_0 + cV_1'[(\delta/\sigma_0) - \tfrac{3}{8}(\Delta\sigma_1 - \delta)^2/\sigma_0^2]\,, \qquad (2)$$

where V_1' is the molal volume of the interaction domains of ions in the solution participating in its surface tension; $\Delta\sigma_1$ is the difference between the hypothetical surface tension σ_1 which would correspond to the ions alone if they were as a pure substance in the same state in which they exist in the solution and, the surface tension of water σ_0. The correction term represents the difference

$$\delta = (\sigma_1 - \sigma_{01}) - (\sigma_{01} - \sigma_0)\,, \qquad (3)$$

where $\sigma_{0,1}$ signifies the surface tension which would, for a given solution, correspond to the mean interaction energy water–ion. In an ideal case where energy σ_{01}

Table IV

Metachor values for some salts of divalent d^{10}-ions up to high concentrations, at 25°C

c	σ	$10^3M_{\varepsilon,1}$	c	σ	$10^3M_{\varepsilon,1}$
	$Zn(ClO_4)_2$			$CdCl_2$	
1·56	77·45	10·5	0	72·58	—
2·08	78·62	9·7	0·49	74·02	10·0
2·50	80·26	10·2	0·75	74·32	7·9
2·60	82·00	11·9	1·00	74·25	5·7
			1·50	75·00	5·5
	$ZnCl_2$		2·00	75·65	5·2
			2·50	76·22	4·9
1·96	78·22	9·6	2·96	76·91	4·9
2·45	79·18	9·0	3·04	76·36	4·2
2·95	79·60	7·9	3·50	77·29	4·5
3·44	80·33	7·5	4·00	78·14	4·7
3·89	80·58	6·8	4·47	78·83	4·7
4·46	81·60	6·7			
4·90	81·97	6·3			

(ion–water) lies in the middle between the energy σ_1 (ion–ion) and energy σ_0 (water–water), the value of δ becomes zero and the concentration-dependent term in (2) almost disappears (since its quadratic component represents only a negligible correction of the metachor value). However, in real cases, one can expect for the "ion–ion" interactions relatively higher energies than those corresponding to the linear extrapolation of the step from the interactions "water–water" to interaction "water–ion" – which consequently leads to positive values for the parameter δ. In the concentration dependence of the surface tension of the solutions, we get then a positive quadratic term and in the metachor of the dissociated forms appears a new term whose value is increasing with concentration c. This term can compensate or even exceed the decrease of $M_{\varepsilon,1}$ caused by association of the ions with increasing concentration. This might explain why the low metachor value of the associated electrolyte does not further decrease with the increasing concentration, or, why it eventually visibly goes up (as in the case of NH_4SCN). The mentioned effect is independent of the degree of filling of the solution with proper volumes of the ions and it can therefore, at high concentrations, become significant even for electrolytes consisting of small ions.

Reduced and at the same time concentration-independent, or slightly dependent metachor values (in comparison with the fully dissociated 1,1-valent electrolytes) can be seen in the lowest section of Table I also for the phosphoric acid, dissociating to the first degree. Dissociation to the second degree is suppressed by hydrogen ions released in the first dissociation step. The observed decrease of metachor value relates to the bulky anion $H_2PO_4^-$, respectively to its ion pairing with the large hydronium cations.

The metachor of the primary phosphate has somewhat larger values than those corresponding to the dissociation to the first degree, possibly as the result of a hydrolysis and partial dissociation to the second degree (coordinative disproportionation). Both processes, in this case, are no more suppressed by the high concentration of hydrogen ions, as it was in the case of the free phosphoric acid. The metachor values of the secondary phosphates K_2HPO_4 and NH_4NaHPO_4 appear well in the range observed for the dissociated uni-divalent electrolytes, whereas the metachor of the tertiary phosphate is in good agreement with the value corresponding to the completely dissociated 1,3-valent electrolytes (a triple of the metachor value found for most of the fully dissociated uni-univalent electrolytes[1]).

Based on the above results, we decided to extend, in a next step of this study of the metachor, our investigation onto the electrolytes of still higher valency types and on the salts of the organic acids (Table II). The metachor of potassium hexacyanoferrate(III), at a concentration $0{\cdot}1\ \text{mol dm}^{-3}$ correlates (related to K_3PO_4) with almost complete dissociation to the 3rd degree and its decrease with increasing concentration indicates partial ion pairing of the anions $Fe(CN)_6^{3-}$ with cations K^+. For hexacyanoferrates(II), the metachor of the potassium salt amounts, at the lowest studied concentration, roughly to a quadruple of the mean value of the fully dissociated uni-univalent electrolytes, as it is possible to expect for a dissociation to the fourth degree. However with increasing concentration this value rapidly diminishes to a value corresponding to association to the ion pair $K^+[Fe(CN)_6]^{4-}$. The existence of this species, in this concentration range, was proved by a number of other methods and has been generally accepted. The metachor value of the sodium salt fits in with the value for a dissociation to the third degree in the whole concentration range.

Alkaline salts of the lowest monobasic carboxylic acids have metachor values corresponding to the strong uni-univalent electrolytes and exhibit a usual decrease when passing from formiates to a bulkier acetate. A decrease of the potassium formiate metachor value, at a concentration 8 mol dm^{-3} which is observed instead of the expected increase due to dehydration, points at extensive association.

The metachors of dibasic organic acids shown in the upper section of Table III (which, according to their tabulated dissociation constants are within the investigated concentration range almost completely present as undissociated molecules) evidence that these acids act, in aqueous solution, as surface active substances decreasing the surface tension of the solution. This consequently results in negative values of the metachors. Surface tension σ_1 of the hypothetical liquid (in which the interactions of the particles are identical with those of the solute in a solution) has, if it is determined from the extrapolated ratio of the apparent parachor and apparent volume of the solute[1], in most cases lower values than the surface tension of water. The smallest effect is observed with the oxalic acid and the effect increases with the number of hydrophobic groups in the molecule. A substitution of two hydrogen atoms on the links of the chain with hydrophilic OH groups changes the large negative metachor values for succinic acid, to the values close to zero for the tartaric acid.

All the above facts permit to formulate a following conclusion: the undissociated molecules not containing distinct hydrophobic groups (*e.g.* electroneutral inorganic complexes), as well as, the molecules for which the hydrophobic effects are compensated with the hydrophilic effects, both possess metachor values near to zero. Dissociation increases the above value in average by $5 . 10^{-3}$ dm^3 mol^{-1} per each dissociation degree. This is supported by the measurements carried out with normal alkaline salts of the above dibasic acids, as it is shown in the lower section of Table III. The widely differing negative values of metachors of the free acids (for which the differences amount to tens of units 10^{-3} dm^3 mol^{-1}) are all uniformly transformed after the neutralization to positive values around +10 units— in complete correspondence with the earlier data[1] on fully dissociated uni-divalent electrolytes. A possible explanation for that can be as follows: the electrostatic field of the formed free anions overcomes (as long a length of the hydrocarbon chain does not exceed the critical length which is characteristic for the detergents and soaps) the hydrophobic solute–water interactions, arising from the short-range van der Waals forces and interruption of the hydrogen bonds between the water molecules. This dominant effect of Coulombic ion-dipole forces rearranges the adjacent water molecules to a radially oriented hydration sheath. The organic hydrophobic molecules are thus changed into hydrated anions affecting the surface tension in a same way as the hydrated anions of inorganic acids and they have for this reason also the same metachor value.

The metachor values permit a distinct detection of between the formation of the complexes. This is illustrated on a case of the chlorocomplexes of d^{10}-ions which are known for their large stability (Table IV). While the metachor of zinc perchlorate remains, up to concentrations 5 mol dm^{-3} ClO_4^-, at the value corresponding to the strong electrolytes[1], the metachor of cadmium chloride quickly drops from this value, with increasing concentration, to a level corresponding to a dissociation to the first degree; the metachor of zinc chloride comes at 10 mol dm^{-3} Cl^- close to this value. The above data evidence formation of the monochlorocomplexes, where subsequent association to the electroneutral dichlorocomplex is evidently supressed by the process of coordinative disproportionation $2\,MeCl_2 \rightleftharpoons Me^{2+} + MeCl_4^{2-}$ or, possibly, by direct disproportionation proceeding already in the stage of the monochlorocomplex: $2\,MeCl^+ + 2\,Cl^- \rightleftharpoons Me^{2+} + MeCl_4^{2-}$. Both these reactions are connected with the well known stability of tetrahedric tetrachlorocomplexes of the d^{10}-ions with the hybrid sp^3-bonds, which is enhanced by the dative effects at d-orbitals of the central ion. The total number of the free charges in the solution is unaffected by this process and remains at a value corresponding to the monochlorocomplex – in accord with the values obtained for the metachor.

Summarizing, one can conclude that the metachor values of the electrolytes in aqueous solutions are predominantly determined by a number of the charges of the free ions into which the electrolyte is split. The metachor is roughly proportional to the number of these charges, independently of the structure of the ions themselves, of the apparent parachor of the electrolyte and of its apparent volume. (As evident from Tables I–III, the values of the latter quantities are spread over a wide range so that they do not permit to draw conclusive information relating to the ion association).

REFERENCES

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