METACHORS AND DISSOCIATION OF SALTS OF OXO ACIDS OF GROUP VI HEAVY METALS IN AQUEOUS SOLUTIONS

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The background of the previously introduced concept of the metachor is outlined. This concept is applied to aqueous solutions of Se, Te, Mo, and W oxo acids and their sodium and potassium salts for which the metachors, calculated from the experimental surface tension values, are used to gain insight into their dissociation state in solution. The normal salts with mononuclear and binuclear anions (Me_2XO_3, Me_2XO_4, and $Me_2X_2O_7$ types) in aqueous solutions at concentrations of $0 \cdot 1 - 0 \cdot 5$ mol dm^{-3} are completely dissociated in the 2nd step and their metachors are about 10 cm^3 mol^{-1}, whereas $KHSeO_4$ and $Na_2W_3O_{10}$ with its bulky trinuclear anion are dissociated in the 1st step only and their metachors at the above concentrations lie in the 4·5 to 5·5 cm^3 mol^{-1} range (at concentrations as low as $0 \cdot 025$ mol dm^{-3} for the latter). The metachor of the free acid H_2SeO_4 is as low as $2 \cdot 5 - 1 \cdot 5$ cm^3 mol^{-1}, corresponding to an appreciable association in the 1st dissociation step. The metachor only reflects the "chemical" association due to short-range forces, whereas it is indifferent to physical outer-sphere ion pairing.

The concept of the quantity which Sudgen has given the name "parachor" has recently been subjected to a theoretical analysis by one of us[1]. This quantity, which is based on the experimental surface tension, has been introduced to compensate for the temperature changes in the experimental molar volumes of substances, used for the elucidation of their chemical constitution. In the study[1], a model relying on the approximative concept of a "triangle-well" potential[30-32] was used and the exponent of 1/4 in Sudgen's formula for the parachor was substantiated theoretically as a mean value in which the effect of the substance polarity (which tends to increase the exponent) and the effect of the finite gradient of repulsive forces (which tends to lower the exponent) compensate each other completely or at least partly.

It has been also shown[1] that the sensitivity of the molar volume to the structure characteristics of the substance (multiple bonds, chain cyclization, *etc.*) is lowered by the introduction of the surface tension because both the surface tension and the density shift in the same direction as the molecular characteristics are changed, although the shift of the surface tension is smaller. This should theoretically apply also to solutions, for which the concept of the apparent parachor Π_1 has been introduced in analogy with that of the apparent molar volume of solute Φ_1, and a formula has been derived[1] for its calculation from the experimental data measured in solutions at a given solute concentration c or a given solute weight content of the solution q.

The theoretically deduced response of the surface tension of solution to changes in the structure of solute suggests that the two quantities might be combined into a function, where the role of the molar volume (and thus of its temperature and, more important, its concentration changes caused by solvation effects which are considerable particularly in solutions of strong electrolytes)

would be completely eliminated to leave the net effect of the solute structure on the surface tension of the solution.

Based on the formulae derived for the apparent volume and apparent parachor, such a function has actually been set up[2] as $\Pi_1/\sigma_0 - \Phi_1$, where σ_0 is the surface tension of solvent; the Π_1 and Φ_1 values refer to a given concentration. The term "metachor" has been suggested for this quantity by the authors, to denote the entity that in the apparent parachor lies beyond the limits of the apparent molar volume and is independent of it.

It turned out that on the transformation of the solute per cent fraction or mole fraction to its volume concentration c_1 (in mol dm^{-3}), the solution density ϱ is completely eliminated from the combined function, and the metachor of solute (labelled by subscript 1) can be written[2] as

$$M_{\varepsilon,1} = [(\sigma/\sigma_0)^{1/4} - 1]/c_1 , \tag{1}$$

where the surface tension of solution, σ, is the only quantity to be determined experimentally. Adopting a simplified model[1] we have found[2] that theoretically the metachor so calculated for aqueous solutions of electrolytes should be independent or only slightly dependent on concentration over a wide concentration region (of the order of magnitude of units of mol dm^{-3} at which the free water between the spheres significantly affected by the electrostatic field of the ions is still present), and that, provided that none of the ions acts as a surfactant accumulating in the surface layer, the metachor should be approximately proportional to the number of free charges of one sign (z) into which the molecule (the formula unit) of the electrolyte is split at the given concentration. This renders the metachor a simple, universal means for (a crude) determination of the dissociation state of electrolytes, usable up to high concentrations. This approach is particularly convenient if the surface tension is determined by some expeditious method such as the drop or the bubble method since only moderate demands are placed on the accuracy of the value obtained, in view of the approximative nature of the theory.

The theoretical conclusions have been verified on data obtained by the bubble method for a set of strong electrolytes of various valency types[2,3]. The value of 5 ± 1 cm^3 mol^{-1} has been found for the factor of proportionality between the number of charges z and the metachor.

In the present work the metachor approach is applied to oxo acids of Group VI heavy metals and their alkali salts for which few data concerning their dissociation state are available and these are often in a mutual disagreement.

EXPERIMENTAL

The data used were partly measured by one of us (S. Š.) and partly were taken from the thesis[4] elaborated under his supervision.

The experimental methods were as described previously[2,3]. The solutions were prepared from chemicals of reagent grade purity and redistilled water. Na_2SeO_3, $K_2TeO_3.2 H_2O$, and $Na_2WO_4.2 H_2O$ were additionally purified by crystallization from aqueous solutions and precipitated with methanol or ether; Na_2SeO_4, K_2SeO_4, $KHSeO_4$, H_2SeO_4 80%, $Na_2TeO_4.4 H_2O$ or $Na_2H_4TeO_6.2 H_2O$, $Na_2MoO_4.2 H_2O$, K_2MoO_4, $Na_2Mo_2O_7.4 H_2O$, $Na_2WO_4.2 H_2O$, $K_2WO_4.H_2O$, and $Na_2W_3O_{10}.4 H_2O$ were obtained by routine methods described in the literature. All the products were subjected to analytical control using Treadwell's gravimetric methods both for the alkali and the heavy metals. The concentrations of the solutions were corrected for the crystal and adsorption water found in the product.

With regard to the low solubility of some of the substances under study, the concentrations used were not very high, usually below 0·5 mol dm^{-3}. For the density and surface tension measurements[2,3], the temperature was held constant at 20°C to within $\pm 0\cdot1$°C for eliminating

the effect of the temperature gradient with respect to the environment. Still, the variance of the results, arising from their high sensibility to minor inaccuracies in the measurements at the low concentrations used is considerably higher than in the previous work[2,3]. This is nevertheless tolerable in view of the high differences in the metachor values for the consecutive dissociation steps of the electrolytes.

The pycnodilatometer for the density measurements was calibrated with redistilled water making allowance for the atmospheric uplift pressure and air humidity, the capillary for the surface tension determination by the bubble method was calibrated with redistilled water and benzene. The experimental densities, ϱ', and surface tensions, σ', were not reduced to vacuum with regard to the fact that the corrections are nearly cancelled at the low concentrations at which the differences $\varrho - \varrho_0$ and $\sigma - \sigma_0$ are very low[2].

RESULTS AND DISCUSSION

The results for the selenium compounds, as a typical case, are fully presented in Table I along with the calculated apparent parachors Π and apparent volumes Φ of solute. For the remaining VIA and VIB Groups compounds, the mean metachor values along with their standard deviations are given in Tables II and III, respectively. The statistical distribution of the deviations from the mean M_ε values is random and does not exhibit any statistically significant dependence on concentration. For the apparent quantities (Π, Φ) as well as for the concentrations, c, only the lower and upper limits of their ranges are given. The lower density limit was $1 \cdot 005 - 1 \cdot 015$ kg dm^{-3}, the upper limit was $1 \cdot 05 - 1 \cdot 09$ kg dm^{-3}; the surface tension of the solutions increased with increasing solute concentration up to $73 \cdot 0 - 74 \cdot 2$ mN m^{-1}. The data for the selenium compounds (Table I) and for the sulphur and chromium compounds studied previously[2,3] are also statistically treated for a comparison.

The metachors of the selenates and selenites (Table I) all lie near 10 cm^3 mol^{-1} over the entire concentration range of $0 \cdot 1 - 0 \cdot 5$ mol dm^{-3}, thus indicating complete dissociation in the 2nd step[2], although the apparent parachors and apparent volumes increase considerably. This also applies to the mononuclear and binuclear chromates, molybdates, and tungstates as well as to the sulphates, tellurates, and tellurites (Tables II and III). The KHSeO$_4$ acid salt is completely dissociated in the 1st step only; its metachor is a half of that of the normal salts over the entire concentration range. Sodium tritungstate exhibits the same M_ε values, giving evidence of its complete dissociation to the NaW$_3$O$_{10}$ species. The lowest metachors, considerably lower than as corresponds to the complete dissociation in the 1st step, are observed for the free acids. This indicates that the dissociation is incomplete even in the 1st step. For H$_2$CrO$_4$ and H$_2$SeO$_4$, polycondensation to polynuclear anions,

$$n \, \text{H}^+ \, + \, n \, \text{HXO}_4^- \, \rightarrow \, \text{H}^+ \, + \, \text{HX}_n\text{O}_{3n+1}^- \, + \, (n-1) \, \text{H}_2\text{O} \, ,$$

is also feasible; by this process the sum of the free charges in the solution (with the unchanged complete dissociation of the dibasic acid in the 1st step) decreases n times.

TABLE I

Experimental densities ϱ' (kg dm^{-3}) and surface tensions σ' (mN m^{-1}) and calculated apparent parachors Π (dm^3 mN$^{1/4}$ mol^{-1} m$^{-1/4}$), apparent volumes Φ (dm^3 mol^{-1}), and metachors M_ε (dm^3 mol^{-1}) of selenium compounds at 20°C for various solute concentrations q (% (m/m)) or c (mol dm^{-3})

q	c	ϱ'	σ'	$10^3\Pi$	$10^3\Phi$	$10^3 M_\varepsilon$
			Na$_2$SeO$_3$ ($M_r = 172{\cdot}94$)			
0	0	0·9973	72·69	—	—	—
2·6117	0·155	1·0234	73·13	41·3	4·2	10·0
4·1315	0·248	1·0381	73·37	52·1	8·4	9·4
6·0581	0·370	1·0571	73·74	61·8	11·5	9·7
7·0117	0·433	1·0669	73·92	63·6	12·0	9·7
7·9712	0·496	1·0766	74·03	65·4	13·1	9·2
			Na$_2$SO$_4$ ($M_r = 188{\cdot}94$)			
0	0	0·9975	72·65	—	—	—
1·9540	0·105	1·0158	72·99	75·6	14·7	11·1
3·0053	0·163	1·0251	73·14	87·7	19·7	10·3
3·9583	0·217	1·0340	73·30	89·9	20·4	10·3
5·9829	0·333	1·0524	73·64	100·5	24·2	10·2
7·0439	0·396	1·0623	73·82	103·6	25·3	10·2
8·0641	0·458	1·0723	74·01	104·3	25·5	10·2
			K$_2$SeO$_4$ ($M_r = 221{\cdot}16$)			
0	0	0·9970	72·68	—	—	—
2·5642	0·118	1·0193	73·06	126·2	31·9	11·5
3·9804	0·186	1·0310	73·34	146·6	37·9	12·2
6·0039	0·285	1·0483	73·66	154·1	40·9	11·8
7·0051	0·335	1·0570	73·72	153·7	41·95	10·6
7·0607	0·338	1·0573	73·64	152·8	42·56	9·7
7·8088	0·376	1·0653	74·78	145·0	39·58	10·0
			KHSeO$_4$ ($M_r = 183{\cdot}07$)			
0	0	0·9975	72·70	—	—	—
2·1039	0·117	1·0149	72·85	112·1	33·9	4·4
3·1190	0·174	1·0228	72·96	125·8	37·9	5·1
4·1817	0·236	1·0314	73·08	130·8	39·2	5·5
6·7327	0·387	1·0519	73·19	137·2	42·6	4·3
8·2500	0·480	1·0643	73·32	141·1	43·8	4·4

TABLE I
(*Continued*)

q	c	ϱ'	σ'	$10^3\Pi$	$10^3\Phi$	10^3M_ε
		H_2SeO_4 ($M_r = 144\cdot98$)				
0	0	0·9973	72·66	—	—	—
1·9900	0·139	1·0141	72·74	76·8	24·3	2·0
3·3843	0·240	1·0257	72·82	84·6	26·6	2·3
6·0305	0·435	1·0467	72·89	97·5	31·5	1·8
7·0871	0·516	1·0555	72·88	98·4	32·2	1·5
8·0186	0·588	1·0632	72·91	100·6	32·9	1·4

Comparing the M_ε values with the Π and Φ values in Tables II and III we see that the apparent parachors on their own do not have such explanatory power, just because here the differences in the interaction force effects on the surface tension of the solutions are obscured by the much higher differences in the own volumes of the ions and in the concentration-dependent hydration contractions.

For verifying the validity of Eq. (*1*), where the metachor should be a concentration-independent constant[2] (to a first approximation at least), the curves of the theoretical dependence of the surface tension of aqueous solutions σ' on the solute concentration c_1 were evaluated using the empirically found mean value of $\sigma_0' = 72\cdot68$ mN m^{-1} for $M_\varepsilon = 10 \cdot 10^{-3}, 5 \cdot 10^{-3}$, and 0 dm^3 mol^{-1} corresponding to completely dissociated uni-bivalent electrolytes, completely dissociated uni-univalent electrolytes, and nondissociated electrolytes, respectively. The results are shown in Figs 1 and 2, where the points denote the experimental values for selected electrolytes for which the surface tension was measured at a number of concentrations in the low-concentration region (Fig. 1), or where the measurements were extended to concentrations higher than 0·6 mol dm^{-3} (Fig. 2). For the salts, the experimental points approach the theoretical curves for complete dissociation in the 2nd or the 1st step, for the free acids they lie below the theoretical curve for the 1st step. In the case of H_2SO_4 the points shift towards the nondissociated-state straight line with increasing concentration, which agrees qualitatively with the conclusions derived from the Raman[5] and NMR spectra[6] although quantitative differences occur. For chromic acid the metachor lies on this straight line starting from the lowest concentrations; in fact, extensive polycondensation is indicated also by the intense colour of the substance and the bathochromic shift in the absorption spectrum in the visible region.

The explanatory power of the metachor can be, of course, only assessed by a com-

parison with the results obtained by other methods. This, however, poses quite a problem. The Bjerrum[7] and Fuoss–Kraus[8] theory of ionic association, accounting for the departures of the activity coefficients of strong electrolytes in dilute solutions from the Debye–Hueckel theory and for the departures of the conductivity of these

TABLE II

Regions of concentrations c (mol dm^{-3}), apparent parachors Π (dm^3 mN$^{1/4}$ mol^{-1} m$^{-1/4}$) and apparent volumes Φ (dm^3 mol^{-1}) and values of the metachor M_ε (dm^3 mol^{-1}) and its standard deviation for compounds of VIA Group elements

Compound	c	$10^3\Pi$	$10^3\Phi$	$10^3 M_\varepsilon \pm \Delta$	
H_2SO_4	1·61—3·09	111—116	36—48	2·2	0·2
H_2SeO_4	0·14—0·59	77—101	24—33	1·8	0·4
$KHSeO_4$	0·12—0·48	112—141	34—44	4·7	0·5
Na_2SO_4	0·17—0·35	71— 77	12—26	11·1	0·4
$(NH_4)_2SO_4$	0·75—3·00	200—240	59—72	9·5	0·6
Na_2SeO_4	0·11—0·46	76—104	15—26	10·4	0·4
K_2SeO_4	0·12—0·38	126—145	32—40	11·0	1·0
Na_2SeO_3	0·16—0·50	41— 65	4—13	9·6	0·3
K_2TeO_3	0·12—0·33	97—129	23—35	9·5	0·5
Na_2TeO_4	0·03—0·07	110—145	29—49	9·9	0·5

TABLE III

Regions of concentrations c (mol dm^{-3}), apparent parachors Π (dm^3 mN$^{1/4}$ mol^{-1} m$^{-1/4}$) and apparent volumes Φ (dm^3 mol^{-1}) and values of the metachor M_ε (dm^3 mol^{-1}) and its standard deviations for compounds of VIB Groups elements

Compound	c	$10^3\Pi$	$10^3\Phi$	$10^3 M_\varepsilon \pm \Delta$	
CrO_3	0·23—0·79	78—114	26—38	0·8	0·3
Na_2CrO_4	0·12—0·52	75— 88	16—21	9·8	0·7
K_2CrO_4	0·10—0·48	132—155	34—44	10·1	0·4
$Na_2Cr_2O_7$	0·09—0·30	206—222	60—65	11·0	0·9
$K_2Cr_2O_7$	0·07—0·30	257—285	78—87	10·2	0·6
Na_2MoO_4	0·12—0·35	36— 52	3— 6	10·1	1·4
K_2MoO_4	0·07—0·29	97—116	24—31	11·3	1·6
$Na_2Mo_2O_7$	0·06—0·21	139—180	37—50	11·2	2·1
Na_2WO_4	0·07—0·36	60—124	12—30	11·8	1·8
K_2WO_4	0·07—0·27	133—173	34—49	11·0	1·0
$Na_2W_3O_{10}$	0·03—0·11	175—246	53—78	5·5	0·8

solutions from the Debye–Hueckel–Onsager theory (as described by the Fuoss––Kraus equation[8,9] which by its five parameters introduces a considerable uncertainty into the results) by ion pairing, are only applicable up to concentrations at which these activity and conductivity theories hold true; these are about 0.1 mol dm^{-3} for the potentiometric method (including the Hueckel empirical salting-out term) and about 10^{-3} mol dm^{-3} for the conductivity method for uni-univalent electrolytes, and much lower for polyvalent electrolytes. Even in this high dilution range, however, the results are sensitive to the small differences between the various evaluation procedures. Association constants differing as much as an order of magnitude are obtained for a given electrolyte within a given concentration region.

As an example, compare the stability constants for the $Cd^{2+}.I^-$ ion pair at 25°C obtained by using the potentiometric method by Pope and coworkers[10] (91 dm^3 . . mol^{-1}), by Golub[11] (910 dm^3 mol^{-1}), and by Votínský[12], who obtained the value of $K = 186$ dm^3 mol^{-1} by the Hedström evaluation procedure for $c_{Cd^{2+}} = 0.03$ mol . . dm^{-3} and $c_{I^-} = 0-2.7$ mol dm^{-3}, and by using the densimetric method[13], where no association was observed in molar volume measurements up to $c_{I^-} = 0.1$ mol .
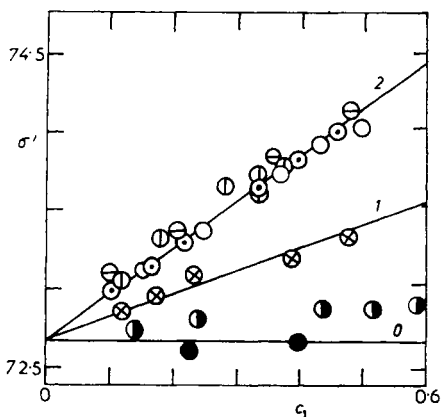

FIG. 1

Theoretical curves of the surface tension of aqueous solutions σ' (mN m^{-1}) at 20°C for solute concentrations c_1 up to 0.6 mol . . dm^{-3}. *0* undissociated state, *1* completely dissociated uni-univalent electrolytes, *2* completely dissociated uni-bivalent electrolytes. Experimental points: ○ Na$_2$SeO$_3$, ⊙ Na$_2$.SeO$_4$, ⦶ K$_2$SeO$_4$, ⊗ KHSeO$_4$, ◗ H$_2$SeO$_4$, ⊖ K$_2$CrO$_4$, ● CrO$_3$ (25°C)
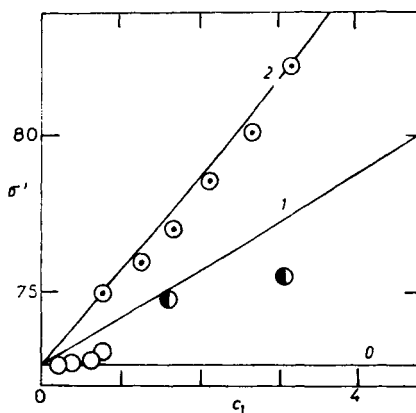
FIG. 2

Theoretical curves of the surface tension of aqueous solutions σ' (mN m^{-1}) at 20°C for solute concentrations c_1 exceeding 0.6 mol . . dm^{-3}. *0* undissociated state, *1* completely dissociated uni-univalent electrolytes, *2* completely dissociated uni-bivalent electrolytes. Experimental points: ⊙ (NH$_4$)$_2$SO$_4$, ◐ H$_2$SO$_4$, ○ CrO$_3$

. dm^{-3}, and only above this limit a sharp change appeared in the molar volume of the Cd^{2+} ion corresponding to a stability constant of CdI$^+$ of $20 \pm 6\,dm^3$ . . mol^{-1}. The association of the SO$_4^{2-}$ ion to the Cd^{2+} ion in the outer coordination sphere appears in the molar volume only indirectly, by shifting the $K(CdI^+)$ value. A long-range physical interaction seems to be involved in the former cases; the electrostatic fields of the paired ions are in a simple mutual superposition, similarly as with the free ions, without affecting the molar volume of water in these fields. In the latter case, on the other hand, the I$^-$ anion enters the inner coordination sphere of the Cd^{2+}ion giving rise to a chemical bond, which alters the electrostatic action of the formed complex on the neighbouring water, thereby inducing its volume changes. A number of examples can be found in the well-known tables of stability constants and in the classic monographs on ionic interactions in solutions (see, *e.g.*, refs[14−17]).

One of us has subjected this problem to theoretical analysis verified on experimental data[18]. It turned out that the classical methods of detection of ionic association (potentiometric, conductometric, extraction, *etc.*) lose their detection ability for the Bjerrum ion pairing with increasing electrolyte concentration, because as the volume fraction of the free water, nonbonded by hydration, decreases in the solution, the competitive ion–water interaction plays an increasing role, and this, not allowed for by the Debye–Hueckel or Onsager theories, obscures the manifestation of the association effects in terms of these theories.

For instance, it was found[19,20] that the continuing decrease in the molar conductivity of strong electrolytes at concentrations above 0·1 mol dm^{-3}, which disagrees with the Onsager theory even if allowance is made for the Bjerrum ion pairing, can be adequately explained so that decrease in the mean distance between the oppositely charged ions is accompanied by an increase in the overlap of the spheres within which the activation energy of transition of the water molecules from one equilibrium position to the other is substantially increased, whereupon the mutual displacement of oppositely charged ions whose distance has decreased below the critical limit is virtually blocked. Only those ions that have remained in the holes of the blocked ion network then participate in the charge transfer. The volume fraction of the holes should decrease exponentially[19,21,22] with increasing concentration of the electrolyte. This implies that the dependence of the molar conductivity of strong electrolytes should also be exponential, and this has been verified experimentally[19] with a high precision for medium and high concentrations (5 mol dm^{-3} and more).

Ion pairs formed by long-range electrostatic forces are automatically included in the blocked network and thus eliminated from the conductivity balance together with the remaining ions of the network without affecting its electrostatic field. Only those of them appear in the conductivity decrease that have remained isolated in the free space of the blocked network in equilibrium with the free ions of both signs, the total concentrations of which in the solution drop rapidly due to the formation

of the blocked network. This implies that the ions pairing constants, determined by the conductivity method in highly dilute solutions, must drop rapidly to zero in the range above 10^{-1} mol dm^{-3}. This theoretical conclusion has also been fully confirmed by experimental data[18,19]. Strong electrolytes of the same valency type (except for electrolytes with an anomalous structure of the hydration shell[23]) exhibit, over the region of $1-5$ mol dm^{-3}, identical slopes of the exponential conductivity decrease irrespective of their ion pairing constants (which often differ considerably) found by the potentiometric and conductometric methods based on the Bjerrum theory of ionic association. Within this concentration region, only the formation of chemical bonds between the ions manifests itself to a significant extent, altering the electron density distribution and thereby modifying the electrostatic field of the associate and the volume fraction of the blocked ionic network in the solution. This has been observed[13,24,25] also for the molar volumes of electrolytes in solution, even starting from the lowest concentrations.

Now, this rises the question as to what position, within this hierarchy of methods and the wide span of association constants, is assumed by the metachor, introduced by the authors of this work as a criterion for the dissociation state of strong electrolytes in aqueous solutions. Typically, normal alkali salts of dibasic oxo acids of Group VI elements are regarded as strong electrolytes, fully dissociated at any actual concentration. No significant chemical changes are revealed by their absorption spectra, and ion pairing, which in some instances is inferred from the potentiometric and conductometric measurements (which actually are scarce for compounds of Group VI heavy metals), does not manifest itself in their chemical behaviour or reactions. For the hydrogen salts at concentrations above the limit of starting dissociation of the acid in the 2nd step, dissociation is currently considered to follow the strong 1,1-electrolyte pattern, independent of any further ion pairing. Tables I − III and Fig. 1 document that the experimental metachors are entirely consistent with these "classical chemical" concepts and are indifferent to purely physical long-range interactions, associated with the electrostatic forces between the ions. In this sense, we are obliged to correct and refine the conclusions of our earlier work[2,3].

This can be explained easily. The energy of the ion pairing, as assumed by the Bjerrum and Fuoss-Kraus theory of ionic association, lies in the range of thermokinetic energies, of the order of kT (about 2·5 kJ mol^{-1} at room temperature). On the other hand, within the simplified model of the liquid column tearing[1] without allowing for the surface accumulation or expulsion of ions, only those interactions between the ions and water or between the ions mutually can manifest themselves in the surface tension whose energy is comparable with the separation work of H_2O molecules in liquid water, which is more than an order of magnitude higher (tens of kJ mol^{-1}). The Bjerrum ion pairing contributes quite a negligible fraction to the energy balance.

Sodium tritungstate is a special case. Its metachor corresponds, over the entire region of its solubility, to the prevailing occurrence of the univalent $NaW_3O_{10}^-$ ion which might be interpreted, in terms of the Bjerrum theory, as $Na^+(aq).W_3O_{10}^{2-}$. .(aq) ion pair. However, according to all the above results, the metachor rather indicates that the $NaW_3O_{10}^-$ anion is, in analogy with $HSeO_4^-$, a chemical entity with the $W_3O_{10}^{2-}$ ligand strongly bonded by short-range forces to one of the Na^+ cations as the central atom. This is consistent with the general knowledge about the formation of associates of cations possessing a rare gas configuration with very bulky anions (*e.g.*, $K[Fe(CN)_6]^{3-}$), where often even a low solubility indicates that this species is a link in an anhydrous crystal lattice (such as $KClO_4$). According to the above criterion (competition of ion–ion and ion–H_2O dipole bonds), these species in solution can be regarded as genuine chemical compounds. Formation of similar associates between cations of A-metals (in the Philipps-Williams classification) and "hard" bulky anions in highly concentrated solutions has been proved even by the conductivity and ionophoresis methods which in this region — as mentioned — no more respond to ion pairing; for instance, for microconcentrations of ions of radioactive Cs (which lie many orders of magnitude below the solubility product of $CsClO_4$) in highly concentrated solutions of $NaClO_4$ and $Ca(ClO_4)_2$ ($c_{ClO_4^-} = 5-10$ mol dm^{-3}), by the significant negative deviations from the $\log \Lambda$ *vs* c straight lines and even by the reversed direction of migration of Cs^+ during the ionophoretic treatment[18], which give evidence of the formation of the "chemical" $Cs(ClO_4)_2^-$ complex. This did not appear with smaller univalent ions, despite their often high experimental ion pairing constants in dilute solutions. For polyvalent cations of A-metals, such and similar[26,27] ionophoretic evidence of the formation of "chemical" complexes is supported also by the molar volume changes for the salts in solutions[24].

Taking into account all the above comparisons, it can be claimed that the metachor can serve as a tool for discriminating between the two types of interaction, "physical" and "chemical", as two qualitatively different levels of motion of matter, which thus find additional support for their revitalization. One cannot but appreciate the bright remark of Sillén's[28], made more than a quarter of a century ago, that the favourably developing study of the chemical forms of electrolytes in aqueous solutions was overshadowed for many decades by the "superb results" of physical theories (Debye and Hueckel 1923, Bjerrum 1926), which actually meant a reduction of the chemistry of electrolyte solutions to pure physics, where "deviations of the laws of ideal solutions can be interpreted in terms of long-range interactions between the ions instead of their association"[17].

"... most chemists forgot what McBain and Van Rysselberghe[29] correctly stressed in 1928 that'it must remain a primary aim [of the study of electrolyte solutions] to determine the actual molecular species and their real concentrations"[17]. We believe that the concept of the metachor, introduced by us, could be of assistance in pursuing this goal.

REFERENCES

1. Čeleda J.: This Journal *49*, 327 (1984).
2. Čeleda J., Škramovský S.: This Journal *49*, 1061 (1984).
3. Čeleda J., Škramovský S., Žilková J.: This Journal *49*, 1079 (1984).
4. Kunzlová-Velická I.: *Thesis*. Charles University, Prague 1953.
5. Young T. F., Maranville L. F., Smith H. M. in the book: *The Structure of Electrolyte Solutions* (J. M. Austin, R. A. Matheson, R. N. Parton, Eds), Chapter 4. Wiley, New York 1959.
6. Hood G. C., Redlich O., Reilly C. A.: J. Chem. Phys. *22*, 2067 (1954); *23*, 2229 (1955).
7. Bjerrum N.: Kgl. Danske Videnskab. Selskab., Mat. Fys. Medd. (9) *7*, 1 (1926).
8. Fuoss R. M., Kraus C. A.: J. Amer. Chem. Soc. *55*, 1019 (1933); *79*, 3304 (1957).
9. Fuoss R. M.: J. Amer. Chem. Soc. *79*, 3301 (1957).
10. Pope D., Josif E., Lice C.: Rev. Roum. Chim. *12*, 169 (1967).
11. Golub A. M.: Ukr. Khim. Zh. *19*, 205 (1953).
12. Votinský J.: *Thesis*. Institute of Chemical Technology, Pardubice 1968.
13. Jedináková V., Čeleda J.: J. Inorg. Nucl. Chem. *31*, 2793 (1969).
14. Gurney R. W.: *Ionic Processes in Solutions*. McGraw-Hill, New York 1953.
15. Nancollas G. H.: *Interactions in Electrolyte Solutions*. Elsevier, Amsterdam 1966.
16. Davies C. W.: *Ionic Association*. Butterworths, London 1962.
17. Beck M. T.: *Chemistry of Complex Equilibria*. Van Nostrand-Reinhold, London 1970.
18. Čeleda J.: Sb. Vys. Šk. Chemicko-Technol. Praze B *26*, 9 (1981).
19. Čeleda J.: Sb. Vys. Šk. Chemicko-Technol. Praze B *11*, 5, 29 (1967).
20. Jedináková V., Čeleda J., Hübner H.: Z. Phys. Chem. (Leipzig) *247*, 49 (1971).
21. Čeleda J.: Sb. Vys. Šk. Chemicko-Technol. Praze FAT+FOT *1*, 401 (1958).
22. Čeleda J., Žilková J.: Sb. Vys. Šk. Chemicko-Technol. Praze B *15*, 101 (1972).
23. Čeleda J.: This Journal *48*, 1680 (1983).
24. Čeleda J.: Sb. Vys. Šk. Chemicko-Technol. Praze FAT *5*, 17 (1964).
25. Čeleda J., Tuck D. G.: J. Inorg. Nucl. Chem. *36*, 373 (1974).
26. Šmirous F., Čeleda J., Palek M.: This Journal *36*, 3891 (1971).
27. Čeleda J., Holub J., Šmirous F.: This Journal *39*, 3559 (1974).
28. Sillén L. G.: J. Inorg. Nucl. Chem. *8*, 176 (1958).
29. McBain J. W., Van Rysselberghe P. J.: J. Amer. Chem. Soc. *50*, 3009 (1928).
30. Reed R. D.: J. Chem. Phys. *43*, 1078 (1965).
31. Feinberg M. J., De Rocco A. G.: J. Chem. Phys. *41*, 3439 (1964).
32. Fowler R. H., Graben H. W., De Rocco A. G., Feinberg M. J.: J. Chem. Phys. *43*, 1083 (1965).

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