Specific ion effects on the surface tension and surface potential of aqueous electrolytes

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A B S T R A C T

The phenomena of electrolytes affecting the surface tension of aqueous solutions and producing measurable surface potentials are reviewed in the light of recent studies of them. The factual information presented includes the molar ionic surface tension increments $k_i = \lim(c_i \to 0)(d\sigma / dc_i)$ of many ions and the surface potential increments $\Delta\chi = \chi_E - \chi_W$ of electrolytes involving the cations H^+, Na^+, K^+, and NH_4^+ and various anions. Gaps in the data that invite filling and inconsistencies in reported data are pointed out. Correlations of k_i with several properties of the ions that should be relevant to their specific effects: their sizes, quantities representing their polarizabilities, their effects on the structure of the water and the binding of water molecules by them, are presented. Correlations of the surface potential increment $\Delta\chi$ with the electrolyte surface tension increments and with the differences between the cation and anion increments are shown. Models recently proposed for the rationalization of the observed phenomena and relevant theoretical developments are shown and discussed. The paradox of hydrogen ions not promoting significant charge separation at the interface but yielding large surface potentials is emphasized.

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1. Introduction

The specific effects of ions in biophysical phenomena depend inter alia on their molar surface tension increments (STIs) in aqueous solutions, which play an important role for the understanding of such phenomena [1,2]. For this purpose it is necessary to evaluate the STIs of individual ions from the measurable surface tension data of complete electrolytes. The surface tension of an aqueous electrolyte solution, σ_E, differs from that of pure water, σ_W, resulting in a surface tension increment, $\Delta\sigma$:

$$\Delta\sigma = \sigma_E - \sigma_W \qquad (1)$$

This increment may be positive (the general case for small ions constituting the electrolyte) or negative and depends on the electrolyte concentration. It turns out that $\Delta\sigma$ is proportional to the electrolyte concentration c_E:

$$\Delta\sigma = k_E c_E \qquad (2)$$

over a large range, from high dilutions up to at least 1 M (M = mol dm^{-3}). Hence, this relationship holds also at infinite dilution of the electrolyte, where additivity of the individual ionic values,

k_i, weighted by the stoichiometric coefficients, ν_i, necessarily takes place:

$$k_E = \sum \nu_i k_i \qquad (3)$$

From these ionic STIs, k_i, it is possible to obtain the enrichment or depletion of the ions in the surface layer of the solution relative to their bulk concentrations. This is governed by the Gibbs adsorption law that reads for an electrolyte as:

$$\Gamma_E = -(a_E/RT)(\partial\sigma_E/\partial a_E)_{T,P} \qquad (4)$$

where a_E is the thermodynamic activity of the electrolyte. If at a low concentration of the electrolyte this concentration is set equal to its activity, so that for individual ions $\partial\sigma_E/\partial a_E$ is replaced by their k_i values, the enrichment or depletion of the ion $\Gamma_i \approx -c_i k_i / RT$ may be evaluated (with $\Gamma_E = \sum \nu_i \Gamma_i$).

If the concentrations the constituent cations and anions of an electrolyte in the surface layer differ, $\sum \nu_+\Gamma_+ \neq \sum \nu_-\Gamma_-$, an electrostatic double layer results. The surface potential of the solution, χ_E, then differs from that of pure water, χ_W, i.e., $\Delta\chi = \chi_E - \chi_W \neq 0$, yielding a measurable voltage. Therefore, these subjects: the ionic STIs and the surface potentials, are closely connected.

It is the purpose of this review to present developments in these concepts of ionic surface tension increments and surface potentials of aqueous electrolyte solutions in recent years. The review is confined

to individual electrolytes up to moderate concentrations, 1 M, at ambient temperatures and pressures. Brines and concentrated electrolyte solutions and mixtures of electrolytes [3–6] are outside the scope of this review. The numerical values reported here pertain to 25 °C, although some have been obtained at near this temperature only.

2. Factual information

2.1. Individual ionic STIs

The recent book by Matubayashi [7] contains tables of surface tension data of aqueous electrolytes and should be a useful source of information. The most recently reported listing of individual molar ionic STIs, k_i values, is that by Marcus [8*], based on a fully annotated previous report by him [9]. The validity of the proportionality of Eq. (2) down to infinite dilution was discussed in [8*], whereas the additivity of the k_i values was demonstrated in [9]. The rest of this review leans heavily on the k_i values listed in [8*], hence, these are reproduced here in Table 1, with a few corrections and additions. The temperature dependence of k_i being rather small, the listed values are for as close temperatures to 25 °C as could be found in the literature [9] but may pertain to ambient temperatures in the range from 20 to 30 °C.

Following are comments on additions in Table 1 regarding the listing in [8*] and on reported data not shown in this Table and on altogether missing data that would be desirable to have. The value for Cu^{2+} derives from data for saturated aqueous solutions of $CuCl_2$ at 20 and 30 °C [10]. The mass percentages were converted by means of the provided densities to molarities and with the reported surface tensions the $k_E/mN\ m^{-1}\ M^{-1}$ at these temperatures were evaluated as 2.71 and 3.39. Their mean 3.05 is taken to represent the value at 25 °C, and deduction of twice the chloride value, 0.90 mN m^{-1} M^{-1} then yields the value 1.25 for Cu^{2+}. Association of the salt in the saturated solutions is ignored. A confirmation of the value is from the entry for the STI of aqueous $CuSO_4$ in [14], dσ/dm = 1.73 mN m^{-1} mol^{-1} kg. Conversion to the molar rather than molal scale and deduction of the sulfate value, 0.55 mN m^{-1} M^{-1} yielded the value for Cu^{2+}. The value for Zn^{2+} is from the temperature and molality dependence data of

the surface tension of aqueous $Zn(NO_3)_2$ solutions in [11], yielding dσ/dm = 2.08 mN m^{-1} mol^{-1} kg. Conversion to the molar scale and deduction of twice the nitrate value, 0.15 mN m^{-1} M^{-1} yielded the value for Zn^{2+} in Table 1. The entry in this table for Pb^{2+} corrects the misprinted value in [8*] by using the STI value 2.34 reported for $Pb(NO_3)_2$ in [9] and deduction of twice the nitrate value. Similarly, the entries for UO_2^{2+} and Cr^{3+} are from [9] for $UO_2(NO_3)_2$ and $Cr(NO_3)_3$, the former being preferred over that for UO_2SO_4, where association is to be expected.

Randles [12] provided values for the STI of aqueous KPF_6 at two concentrations, leading to $k_E/mN\ m^{-1}\ M^{-1}$ = 4.05 at 0.2 M and 3.78 at 0.4 M. The proportionality of $\Delta\sigma$ with c_E is thereby not well established, but a value of k_i = −2.6 ± 0.4 mN m^{-1} M^{-1} for the PF_6^- anion results on deduction of the value for K$^+$, and no more accurate value has been reported since.

Conspicuous for its absence from Table 1 is an entry for BF_4^- which is a favorite constituent of room temperature ionic liquids. In fact, there are two reports in the literature regarding the surface tension of aqueous $NaBF_4$ solutions, agreeing on its STI being negative, as expected in analogy with perchlorate solutions. The reports disagree, however, regarding to the magnitude of the effect. In the report by Imai et al. [15] the data appear as a figure of the surface tension against the salt molalities for NaBr and $NaBF_4$, the $k_E/mN\ m^{-1}\ kg\ mol^{-1}$ being + 0.30 and −0.22 respectively. The k_E is much too small for NaBr (expected 1.75 from the entries in Table 1), hence also for $NaBF_4$, so its value cannot be correct. In the paper by Fu et al. [16], on the contrary, the $k_E/mN\ m^{-1}\ kg\ mol^{-1}$ values for $BmimBF_4$ at 20 and 30 °C are −82.0 and −77.7, and for BmimBr they are −33.0 and 28.7 respectively. Therefore the differences that eliminate the effect of the imidazolium cation are Δk_E = (k_{BF4} − k_{Br}) = −49.0 mN m^{-1} kg mol^{-1} at both temperatures, a huge number that does not make sense.

The k_i value for $Fe(CN)_6^{3-}$, due to Jones and Ray [13] is comparable to that of PO_4^{3-} and is expected for this strongly water-structure-making complex ion [17]. On the other hand, the near zero value of k_i for $Fe(CN)_6^{4-}$ calculated from the $K_4Fe(CN)_6$ data in [13] is not expected, because this anion is also strongly structure making [17]. A reinvestigation of these more than 70 years old data is warranted.

STI data for hydrophobic ions with alkyl chains are not reproduced in Table 1, because they do not seem to be well established. The published data do show such ions to accumulate at the water/vapor interface: they have negative k_i values as expected, becoming more negative as the alkyl chain lengths increase, but there are inconsistencies in the reported magnitudes, as already commented on in [9]. Those for alkyl- and tetraalkylammonium cations, due to Tamaki [18–20] date to ≤1974 and have since been cited by other authors dealing with these ions, but not confirmed or otherwise by new investigations. It is noteworthy that their $\sigma_E = f(c_E)$ curves are non-linear (except for methyl-, ethyl-, and propylammonium chlorides), contrary to the cases dealing with smaller ions. Furthermore, it should be noted that tetraethylammonium chloride was reported to mildly increase the surface tension of its aqueous solution [20], k_E = 1.1, but the nitrate salt was reported to strongly decrease it [21], k_E = −3.1 (mN m^{-1} M^{-1}), whereas the opposite trend is expected from the contributions of chloride and nitrate anions. Thus, the data for the alkylammonium cations must also be viewed as requiring revision.

STI data for alkanoate anions larger than acetate are not shown in Table 1 either, because they have not been well established. The calculated values shown in [9], −2.95 for propanoate and −6.45 for butanoate (mN m^{-1} M^{-1}), are from the data reported for their sodium salts by Abramzon and Gaukberg [22] from single quite old sources that need confirmation.

It is deplorable that no valid STIs are available for the anions that are commonly used for room temperature ionic liquids (RTILs), including BF_4^-, $N(CN)_2^-$, $B(CN)_4^-$, $CF_3CO_2^-$, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, and $CH_3SO_4^-$. Such values could shed much light on the properties and behavior of RTILs, whether in a water-saturated or in a neat form.

Table 1
Individual ionic surface tension increments, k_i/mN m^{-1} M^{-1} of aqueous ions at ambient conditions, rounded to 0.05 units and with an uncertainty of ± 0.2 units, from [8*] or as noted and discussed in Section 2.1.a

Cation	k_i	Anion	k_i
H$^+$	−1.05	OH$^-$	1.05
Li$^+$	0.95	F$^-$	0.80
Na$^+$	1.20	Cl$^-$	0.90
K$^+$	1.10	Br$^-$	0.55
Rb$^+$	0.95	I$^-$	−0.05
Cs$^+$	0.80	SCN$^-$	−0.65
NH$_4^+$	0.70	NO$_3^-$	0.15
(CH$_3$)$_4$N$^+$	−0.10	ClO$_3^-$	0.00
C(NH$_2$)$_3^+$	0.04	BrO$_3^-$	0.35
Ag$^+$	0.70	IO$_3^-$	0.70
Tl$^+$	0.60	ClO$_4^-$	−0.70
Mg^{2+}	2.25	HCO$_2^-$	0.20
Ca^{2+}	2.10	CH$_3$CO$_2^-$	−0.25
Sr^{2+}	1.80	H$_2$PO$_4^-$	0.95
Ba^2	1.10	PF$_6^-$	−2.6^d
Mn^{2+}	1.35	CO$_3^{2-}$	0.30
Co^{2+}	1.65	SO$_4^{2-}$	0.55
Ni^{2+}	1.70	CrO$_4^{2-}$	0.85
Cu^{2+}	1.25^a	S$_2$O$_3^{2-}$	0.65
Zn^{2+}	1.85^b	PO$_4^{3-}$	1.10
Pb^{2+}	2.05^c	Fe(CN)$_6^{3-}$	1.10^e
UO$_2^{2+}$	2.10^c	Fe(CN)$_6^{4-}$	−0.05^e
Al^{3+}	2.65		
Cr^{3+}	3.70^c		
La^{3+}	3.20		

^{a} From [10]. ^{b}From [11]. ^{c}From [9]. ^{d}From [12]. ^{e}From [13].