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Surface Tension of Aqueous Electrolytes and Ions

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Values of the surface tension increments by electrolytes in aqueous solutions, $d\Delta\gamma/dc_2$, reported in the literature have been critically examined and are presented. The additivity of the ionic contributions to these increments has been tested and confirmed within ± 0.2 $mN \cdot m^{-1} \cdot mol^{-1} \cdot dm^3$. A set of ionic increments $d\Delta\gamma/dc_i$ is proposed and tabulated.

Introduction

The surface tension of aqueous electrolytes has become recently of interest with respect to the effects of ions on biomolecules.[1,2] The surface layer of the aqueous solutions, of thickness ~1 nm, has air (or dilute water vapors) on the one side and bulk water on the other. Ions may be positively or negatively sorbed in this layer, depending on whether they decrease or increase the surface tension, γ, of water. According to the Gibbs adsorption law:

$$\Gamma_2 = -(a_2/RT)(\partial\gamma/\partial a_2)_{T,P} \qquad (1)$$

where Γ_2 denotes the number of moles of electrolyte (subscript $_2$) sorbed per unit increase of the surface energy and a_2 is the activity of the electrolyte. The surface tension increment, $(\partial\gamma/\partial c_2)_{T,P}$, where at low molar concentrations c_2 the latter approximates the activities a_2, is thus a key quantity in dealing with the role of ions at surfaces.

There appears to be no comprehensive critical compilation of surface tension increments in the literature, but one recent paper reports averaged values for 46 electrolytes.[3] Three relatively recent publications[4−6] do contain a large number of data that ought to be examined. They are presented for constant (ambient) pressure P at constant temperatures T, so that the partial derivatives can be replaced by ordinary ones. The first set of three papers by Abramzon and Gaukhberg[4] presents values of γ or $\Delta\gamma = \gamma - \gamma_{water}$ as functions of c_2, m_2 (molality), w'_2 (mass percent), or x_2 (mole fraction) of the electrolytes. The second set of two papers by Weissenborn and Pugh[5] presents $d\Delta\gamma/dc_2 = d\gamma/dc_2$ data directly. The maximal bubble-pressure method (mbp), as applied by Weissbron and Pugh[5] pertaining to a 1.5 s growth, appears to be a reliable method, with an expected data uncertainty of ± 0.1 $mN \cdot m^{-1} \cdot mol^{-1} \cdot dm^3$. Henry et al.[6] measured the surface tension by means of the maximal bubble-pressure method of 28 electrolytes at 20 °C, taking the error in the measurements of $d\gamma/dc_2$ to be 10 %. The present paper puts all of the data on a common basis: $d\gamma/dc_2$ in $mN \cdot m^{-1} \cdot mol^{-1} \cdot dm^3$ at (20 to 30) °C (preferably 25 °C). The temperature dependence over this range is smaller than ± 0.1 $mN \cdot m^{-1} \cdot mol^{-1} \cdot dm^3$.

The values for the individual ions need to be extracted from the electrolyte data, because any discussion of the role of the ions on aqueous biomolecules in terms of the ionic properties requires dealing with single ions rather than with electrolytes. It is necessary for this purpose to ascertain that the effects of ions are additive at low concentrations, as they are at infinite dilution for many thermodynamic quantities. This is done in this paper, and a splitting of electrolyte data into the ionic contributions is suggested.

Results

The results of the critical examination of the data for the surface tension increments of aqueous electrolytes at (20 to 30) °C are presented in Table 1. This table also includes the averaged data reported by Pegram and Record,[3] over the temperature range (15 to 30) °C, converted from $d\gamma/dm_2$ to $d\gamma/dc_2$ as shown below. Recent data from Matsubayashi et al.[16−18] and older values not included in Abramzon and Gaukhberg's compilation[4] are also presented in this table. The sources all show that over considerable ranges of composition (molarity, molality, etc.) the derivatives of the surface tension increment $\Delta\gamma$ (hence of γ itself) with the composition (c_2, m_2, w'_2, x_2) are quite linear up to at least 1 $mol \cdot dm^{-3}$ (1 $mol \cdot kg^{-1}$, etc) and in many cases well farther. The first $d\gamma/dc_2$ column contains more reliable data, preferably those obtained at concentrations $c_2 < 1$ $mol \cdot dm^{-3}$. However, there are quite appreciable differences between the values reported by diverse authors using the same, not to say, various methods. The capillary rise method may suffer from the effect of a wetting layer in very fine capillaries (in which the rise or fall of the level is large and more easily measurable). Thus, the seemingly very accurate values by Jones and Ray[7] at very high dilutions are not valid $d(\gamma/\gamma_{water})/dc_2$ values, since they include the effect of the zeta potential.[8] Let us remember in this connection the fiasco of so-called "polywater".

Data expressed as $\gamma(w'_2)$ (a function of the mass percent of the electrolyte)[4] were first converted to $\gamma(m_2)$ by means of:

$$m_2/mol \cdot kg^{-1} = (1000/M_2)w'_2/(100 - w'_2) \qquad (2)$$

where M_2 is the molar mass of the electrolyte in $g \cdot mol^{-1}$. Those data expressed as $\gamma(x_2)$ (a function of the mole fraction of the electrolyte)[4] were first converted by means of:

$$m_2/mol \cdot kg^{-1} = (1000/M_1)x_2/(1 - x_2) \qquad (3)$$

where $M_1 = 18.015$ $g \cdot mol^{-1}$ is the molar mass of water. Further conversion from the molal basis to the molar one was effected by $d\gamma/dc_2 = d\gamma/dm_2 \cdot dm_2/dc_2$, noting that

$$m_2/mol \cdot kg^{-1} = c_2/\rho_{water}(1 - c_2V_{\varphi,2}/1000) \qquad (4)$$

Here ρ_{water} is the mass density of water at the relevant

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Table 1. Surface Tension Increments, $\mathrm{d}\gamma/\mathrm{d}c_2$ ($\mathrm{mN \cdot m^{-1} \cdot mol^{-1} \cdot dm^3}$), of Aqueous Strong Electrolytes at (20 to 30) °C[a]

electrolyte	$\mathrm{d}\gamma/\mathrm{d}c_2$	method, ref	$\mathrm{d}\gamma/\mathrm{d}c_2$	method, ref	$\mathrm{d}\gamma/\mathrm{d}c_2$	method, ref	$\mathrm{d}\gamma/\mathrm{d}c_2$, ref 3	additivity
HCl	−0.27	mbp, 5	−0.25	mbp, 6	−0.20	cr, dv, 4	*−0.28*	−0.15
HBr	−0.47	cr, 4	−0.46	mbp, 6			*−0.50*	−0.40
HNO_3	−0.83	mbp, 5	−0.45	mbp, 6	−0.74	pd, 10	*−0.82*	−0.90
$HClO_4$	−2.15	mbp, 5	−1.70	mbp, 6	*−1.04*	cr, 4	*−1.88*	−1.85
$H(HSO_4)$	0.44	mbp, 5	0.59	mbp, 6	*0.53*	?, 4	*−0.51*	
$LiOH$	1.67	cr, 4			*1.26*	dc, 4	*1.65*	2.00
$LiCl$	1.98	mbp, 5			1.70	cr, dp, 4	*1.68*	1.85
$LiBr$	*1.24*	cr, 4					*1.34*	1.60
LiI	0.78	cr, 4					*0.83*	1.00
$LiNO_3$	1.14	dv, 11			1.24	cr, dp, 4	*1.26*	1.10
$LiClO_4$	0.27	mbp, 5					*0.31*	0.15
$LiCH_3CO_2$	0.84	mbp, 5					*0.87*	0.70
Li_2SO_4	*2.48*	dv, 12	*2.49*	dv, 13	2.65	cr, 4	*3.17*	2.44
$NaOH$	*2.17*	mbp, 4	2.03	mbp, 6			*1.86*	2.25
NaF	1.83	mbp, 5			*2.40*	rdf, 13	*1.81*	2.00
$NaCl$	2.08	mbp, 5	1.76	mbp, 6	*1.71*	mbp, 4	*1.77*	2.10
$NaBr$	1.83	mbp, 5	1.71	mbp, 6	1.50	mbp, 4	*1.51*	1.85
NaI	1.23	mbp, 5			1.00	cr, dv, 4	*1.18*	1.25
$NaSCN$	0.50	?, 2					*0.50*	1.10
$NaNO_3$	*1.09*	mbp, 4	1.35	mbp, 6	1.13	dv, 11	*1.25*	1.35
$NaClO_3$	0.89	mbp, 5	0.72	mbp, 6			*0.79*	0.90
$NaClO_4$	0.22	mbp, 5	0.32	mbp, 6	0.49	mbp, 4	*0.27*	0.40
$NaHCO_2$	*1.08*	mbp, 4			1.59	?, 14		1.05
$NaCH_3CO_2$	0.93	mbp, 5	1.41	mbp, 6	*0.53*	mbp, 4	*0.97*	0.95
$NaC_2H_5CO_2$	−2.03	mbp, 4						
$NaC_3H_7CO_2$	−5.56	mbp, 4						
NaH_2PO_4	2.03	dv, 4						2.15
Na_2CO_3	2.60	cr, dv, 4			*2.64*	dv, 15	*2.72*	2.75
Na_2SO_4	2.90	mbp, 5	2.99	mbp, 6	2.71	mbp, 4	*2.84*	2.95
Na_2CrO_4	4.20	dv, 4						3.25
$Na_2S_2O_3$	3.21	dv, 4			1.92	?, 14		3.25
Na_3PO_4	2.85	mbp, 4						4.70
KOH	1.98	mbp, 5	1.75	mbp, 6	*2.17*	cr, 4	*1.90*	2.15
KF	*1.89*	rdf, 4			1.97	pd, 10	*1.82*	1.90
KCl	1.85	mbp, 5	1.68	mbp, 6	*1.57*		*1.64*	2.00
KBr	1.97	?, 4	1.74	mbp, 6	*139*	dv, 15	*1.40*	1.75
KI	1.07	pd, 10			0.84	mbp, 4	*1.21*	1.15
KNO_2	*0.62*	mbp, 4						
KNO_3	1.03	mbp, 4			1.10	dv, 11	*1.12*	1.25
$KClO_3$	0.72	mbp, 6					*0.50*	0.80
$KHCO_2$	1.36	?, 14					*0.81*	0.95
KCH_3CO_2	0.76	mbp, 5	0.75	mbp, 6	0.85	?, 14		0.85
KH_2PO_4	2.13	?, 14						2.05
K_2CO_3	3.57	cr, dp, 4			*4.32*	dv, 4	*3.09*	2.55
K_2SO_4	2.51	cr, dv, 4	*2.35*	dv, 13	*2.36*	dv, 12	*2.66*	2.75
K_2CrO_4	*3.16*	mbp, 4						3.05
K_2HPO_4	2.90	?, 14						
K_3PO_4	4.42	?, 14						4.40
$RbCl$	*1.37*	mbp, 4						1.85
$CsCl$	*1.69*	dv, 15			1.52	mbp, 4	*1.64*	1.70
$CsCH_3CO_2$	1.12	mbp, 5					*1.20*	0.55
Cs_2SO_4	3.02	mbp, 5	*2.87*	dv, 13	*2.89*	dv, 12	*3.21*	2.15
NH_4Cl	1.59	mbp, 5	1.78	mbp, 6	*1.28*	mbp, 4	*1.45*	1.50
NH_4Br	1.22	cr, 4			*1.24*	dv, 17	*1.34*	1.25
NH_4I	0.74	cr, 4			*0.67*	dv, 17	*0.78*	0.65
NH_4SCN	0.59	?, 14						0.60
NH_4NO_3	1.15	mbp, 5	1.17	mbp, 6	*1.09*	dv, 4	*1.13*	0.75
$(NH_4)_2SO_4$	*1.81*	mbp, 4			*2.13*	dv, 17	*2.44*	1.75
$C(NH_2)_3HCl$							*0.79*	0.95
$C(NH_2)_3HBr$							*0.69*	0.70
$(C(NH_2)_3H)_2SO_4$							*1.03*	0.65
$(CH_3)_4NCl$	0.94	mbp, 5						0.80
$(CH_3)_4NCH_3CO_2$	−0.51	mbp, 5						−0.35
$AgNO_3$	*0.83*	dv, 4						0.85
$TlOH$	*1.63*	dv, 4						1.55
$MgCl_2$	4.06	mbp, 5	3.73	mbp, 6	3.51	cr, 4		4.05
$Mg(NO_3)_2$	2.98	mbp, 5	*2.01*	dv, 13				2.55
$Mg(ClO_4)_2$	0.99	mbp, 6						0.65
$Mg(CH_3CO_2)_2$	0.48	mbp, 5						1.75
$MgSO_4$	2.44	mbp, 5	2.37	mbp, 6	2.06	?, 4		2.80
$CaCl_2$	4.02	mbp, 5	3.64	mbp, 6	3.44	dv, 4		3.90
$Ca(NO_3)_2$	2.47	mbp, 5	2.64	mbp, 6				2.40
$Ca(ClO_4)_2$	1.25	mbp, 6						0.50
$Ca(CH_3CO_2)_2$	0.70	mbp, 6						1.10
$SrCl_2$	3.41	cr, 4			*3.64*	mbp, 4		3.60
$Sr(NO_3)_2$	*2.69*	mbp, 4						2.10

Table 1. Continued

electrolyte	$d\gamma/dc_2$	method, ref	$d\gamma/dc_2$	method, ref	$d\gamma/dc_2$	method, ref	$d\gamma/dc_2$, ref 3	additivity
$Ba(OH)_2$	2.93	dc, 4						3.60
$BaCl_2$	*3.20*	mbp, 4			*2.82*	mbp, 4		3.30
$Ba(NO_3)_2$	2.00	dv, 4						1.80
$Ba(HCO_2)_2$	1.64	dv, 4						1.20
$MnCl_2$	2.96	cr, 4						3.15
$MnSO_4$	2.10	?, 4						1.90
$FeSO_4$	1.53	mbp, 4						
$CoSO_4$	2.21	mbp, 4						2.20
$NiSO_4$	2.23	cr, 4						2.25
$CuSO_4$	*3.65*	mbp, 4						
$Pb(NO_3)_2$	2.34	rpf, 4						
$UO_2(NO_3)_2$	2.41	mbp, 4						
UO_2SO_4	*2.04*	cr, 4						
$LaCl_3$	5.91	mbp, 5						5.90
$Cr(NO_3)_3$	4.13	mbp, 5						
$Al_2(SO_4)_3$	6.94	mbp, 4						6.95

[a] Values converted from $d\gamma/dm_2$ ($mN \cdot m^{-1} \cdot mol^{-1} \cdot kg$) to $d\gamma/dc_2$ are in *italics*. A question mark in the method column means that the method was not specified in the source paper. Methods: mbp = maximal bubble pressure, dv = drop volume, cr = capillary rise, rpf = ring pulling force, pd = plate detachment (Wilhelmy).

Table 2. Examples of the Additivity of $d\gamma/dc_i$ ($mN \cdot m^{-1} \cdot mol^{-1} \cdot dm^3$) Values[a]

anion	Na^+-Li^+	Na^+-K^+	cation	Cl^--Br^-	$Cl^--NO_3^-$
OH^-	0.50	0.19	H^+	0.20	0.56
Cl^-	0.10	0.23	Li^+	0.74	0.84
Br^-	0.59	−0.14	Na^+	0.25	0.99
I^-	0.45	(0.39)	K^+	−0.12	0.82
NO_3^-	−0.01	0.10	NH_4^+	0.37	(0.44)
$CH_3CO_2^-$	0.09	0.17	1/2 Mg^{2+}		0.54
ClO_4^-	−0.05		1/2 Ca^{2-}		0.88
1/2 CO_3^{2-}		(−0.49)	1/2 Sr^{2+}		(0.36)
1/2 SO_4^{2-}	(−0.79)	0.20	1/2 Ba^{2+}		0.60
1/2 CrO_4^{2-}		(0.52			
average	0.23	0.13	average	0.29	0.75

[a] The averages disregard the values in parentheses.

Table 3. Ionic Surface Tension Increments of Aqueous Ions, $d\gamma/dc_i$ ($mN \cdot m^{-1} \cdot mol^{-1} \cdot dm^3$), at (20 to 30) °C[a]

cation	$d\gamma/dc_i$	anion	$d\gamma/dc_i$	ref 2	ref 4
H^+	−1.35	OH^-	1.35		*2.00*
Li^+	0.65	F^-	1.10	*1.60*	
Na^+	0.90	Cl^-	1.20	*1.63*	*1.57*
K^+	0.80	Br^-	0.95	*1.31*	*1.26*
Rb^+	(0.65)	I^-	0.35	*1.02*	*0.80*
Cs^+	0.50	SCN^-	0.20	*0.54*	*0.40*
NH_4^+	0.40	NO_2^-		*1.18*	
$(CH_3)_4N^+$	−0.40	NO_3^-	0.45		*1.23*
$C(NH_2)_3H^+$	−0.24	ClO_3^-	(0.00)	*0.55*	*0.70*
Ag^+	(0.40)	ClO_4^-	−0.50		
Tl^+	(0.30)	HCO_2^-	0.15		
Mg^{2+}	1.65	$CH_3CO_2^-$	0.05	*0.93*	
Ca^{2+}	1.50	KH_2PO_4	1.25		
Sr^{2+}	1.20	CO_3^{2-}	0.95	*1.35*	*1.90*
Ba^2	0.90	SO_4^{2-}	1.15	*1.37*	*1.13*
Mn^{2+}	0.75	CrO_4^{2-}	1.45		
Fe^{2++}		$S_2O_3^{2-}$	(1.45)		*1.45*
Co^{2+}	(1.05)	PO_4^{3-}	(2.00)		
Ni^{2+}	(1.10)				
Pb^{2+}	(1.80)				
UO_2^{2+}	1.40				
Al^{3+}	(1.75)				
Cr^{3+}					
La^{3+}	(2.30)				

[a] Values in parentheses were derived from a single salt. Values in *italics* are $d\gamma/dc_i$ from refs 2 and 4.

temperature, and $V_{\varphi,2}$ is the apparent molar volume of the electrolyte in $cm^3 \cdot mol^{-1}$. The factor of 1000 arises from the choice of the units of the variables. Within the experimental error of the determinations of the surface tension slopes, the derivative dm_2/dc_2 is well-approximated by $m_2(c_2 = 1)$ (with the units of these quantities mentioned above). Such values can be interpolated from $m_2(c_2)$ tables[9] or by using in eq 4 $V_{\varphi,2} = V_2^{\infty} + 1.85\ cm^3 \cdot mol^{-1}$; the first term is the additive standard partial molar volume, obtainable from the conventional ionic volumes in tables,[10] and the latter is the Debye−Hückel slope (as $1.85c_2^{1/2} = 1.85\ cm^3 \cdot mol^{-1}$ for $c_2 = 1\ mol \cdot dm^{-3}$ for 1:1 electrolytes).

The additivity of the ionic contributions to $d\gamma/dc_2$ could be approximately established, within ± 0.2 $mN \cdot m^{-1} \cdot mol^{-1} \cdot dm^3$ at best, from the available data in Table 1. Noting that data for salts with Na^+ cations and salts with Cl^- anions are most abundant, examples of the additivities obtained are shown in Table 2. Ionic values $d\gamma/dc_i$ have then been derived on the *arbitrary* but plausible basis that $d\gamma/dc_i$ in $mN \cdot m^{-1} \cdot mol^{-1} \cdot dm^3$ are 0.90 for Na^+ and 1.20 for Cl^- and are shown in Table 3. The justification of this choice is that given the additivity of the ionic values (within ± 0.2 $mN \cdot m^{-1} \cdot mol^{-1} \cdot dm^3$), the additively calculated sums for entire electrolytes, $d\gamma/dc_2 = \sum_i d\gamma/dc_i$, rounded to 0.05 $mN \cdot m^{-1} \cdot mol^{-1} \cdot dm^3$ and shown in the last column of Table 1, represent the experimental values as well as possible.

Discussion

The data presented in Table 1 pertain to strong electrolytes, presumed to be fully dissociated into ions. Therefore, the value for aqueous sulfuric acid pertains to $H(HSO_4)$ rather than to H_2SO_4, whereas those for aqueous acetic and phosphoric acids and for $CdCl_2$, and so forth, are not included there.

Abramzon and Gaukhberg[4] and LoNostro et al.[1] took it for granted that only anions have any effect on the surface tension of aqueous solutions. Their reported values for the anions are shown in Table 3. However, it is clear from examination of the data in Table 1 that for electrolytes with any given anion the values of the surface tension increment $d\gamma/dc_2$ differ among various cations. Therefore, the anionic values presented by these authors are not valid.

The ionic values of $d\gamma/dc_i$ in Table 3 exhibit some clear trends that are independent of the arbitrary assumption of the values for Na^+ (and/or Cl^-) since they pertain to sequences among cations separately from those among anions. It is difficult to perceive a reason why in the series of alkali metal cations, alkaline earth cations, and halide anions the ionic values should not change smoothly with a parameter such as ionic size. This fact forms one criterion for the critical examination of the reported dγ/dc_2 values.

One feature is obvious: negative values of dγ/dc_i are rare, meaning that most (small) ions are desorbed from the surface layer and their concentration in it is lower than in the bulk solution. Outstanding cases of negative values are H^+ and $(CH_3)_4^+$ among the cations and large singly charged anions, such as ClO_4^-. Indeed, the (dγ/dc_i)/mN·m^{-1}·mol^{-1}·dm^3 values for propionate, −2.95, and butanoate, −6.45,[4] and even more of butylammonium, −18, dibutylammonium, −49, and tri- or tetrabutylammonium, −136, as chlorides,[19] show clearly the effect of large hydrophobic groups of favoring sorption of such ions into the surface layer. (It should be noted that the extremely large negative values for the butyl-substituted ammonium ions may be incorrect. This follows from the large effect of the accompanying anions: the value for the tetrabutylammonium chloride is −136, that for the bromide is −201, and that for the iodide is −365.) The hydrogen ion is unique among small cations in that it is favorably sorbed in the surface layer of water, but of course, it is not an individual cation but a part of the hydrogen bonded network of the water molecules.[20]

Another trend that emerges from the data is that the positive values of dγ/dc_i tend to increase with the ionic charge, whether positive or negative, but there are exceptions. The higher the charge, the stronger the ions are hydrated, and the larger their centrally symmetric hydration spheres are. They are then less well-accommodated in the nonisotropic hydrogen-bonded structure of the surface layer.

The trend among ions of the same charge class is to have smaller values of dγ/dc_i the larger the size of the ion (the weaker then its hydration and the fewer strongly bonded water molecules in the hydration shell are). However, there appear to be exceptions concerning the first members of the alkali metal and the halide sequences: the value for Li^+ is smaller than for Na^+, and that for F^- is smaller than for Cl^-. This statement must be taken cautiously, because the uncertainty of the individual ionic values is no better than ± 0.2 mN·m^{-1}·mol^{-1}·dm^3 and the reversals are within this uncertainty. Furthermore, the reported values for electrolytes involving Cs^+ diverge considerably among electrolytes and authors (methods), making the alkali metal series trend rather uncertain.

It is not the purpose of this paper to discuss the consequences of the relative values of the surface tension increment on biomolecules in aqueous solutions, nor is it the discussion of models for the prediction of surface tension effects of ions or their theoretical interpretation. It is important, however, to point out that the well-known Hofmeister series of ions is not absolutely followed by the ionic surface tension increments,[2] as far as the presently available data can be used for their determination.

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