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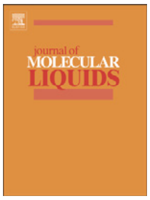

Prediction of salting-out and salting-in constants

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ABSTRACT

An expression is established to predict the Setchenow salting constants of solid and liquid organic compounds from aqueous solutions by electrolytes. It employs the conventional standard partial molar volumes and the intrinsic molar volumes of the ions. It also uses properties for the non-electrolytes that are foreign to their aqueous solution behavior: their molar volumes and either the Kamlet/Taft polarity/polarizability indexes or the Hildebrand solubility parameters. The expression is tested on data not included in the correlations used to establish it.

1. Introduction

The solubility of non-electrolytes in aqueous salts solutions is of importance in several fields of chemistry, such as marine chemistry, recovery of synthesis products from aqueous solutions, and petroleum production. The observed quantities are generally correlated by means of the Setchenow equation [1]:

$$\log(s_{N0}/s_N) = k_{N,E}c_E \tag{1}$$

Here s_{N0} and s_N are the molar solubilities of the non-electrolyte (subscript $_N$) in pure water and in a c_E molar solution of the electrolyte (subscript $_E$), and $k_{N,E}$ is the salting constant (the Setchenow constant). The latter is generally positive (for salting-out), but in certain cases it is negative (for salting-in). Eq. (1) is generally valid up to c_E of the aqueous electrolyte of several mol L^{-1}.

It is of interest to be able to predict the value of $k_{N,E}$ for an arbitrary non-electrolyte and an arbitrary electrolyte from independent properties of these substances. Ni and Yalkowsky [2] did indeed propose a predictive expression for one electrolyte, namely sodium chloride, which is the main salt constituent of sea water. They applied it to Setchenow constants of 101 non-electrolytes at ambient temperatures with the expression:

$$k_{N,E} = 0.114 + 0.040\log K_{Now} \tag{2}$$

Here $\log K_{Now}$ is the logarithm of the distribution constant of the non-electrolyte between 1-octanol and water. The adjusted correlation coefficient squared is $r^2_{adj} = 0.7717$ and the standard error of the fit is $\sigma_{fit} = 0.041$. The values correlated by this expression were mostly gleaned from the review by Xie et al. [3] (for 20–25 °C) but included also data from other annotated sources. It should be noted, however, that the $k_{N,E}$ values for a given non-electrolyte and a given electrolyte in these sources have a considerable spread between those reported by various authors. This is seen, e.g., for the values reported for toluene and aqueous sodium chloride, ranging from 0.195 to 0.270 [3], from among which 0.210 was selected as representative. An even worse case is naphthalene salted out from aqueous sodium chloride, where the spread of the reported $k_{N,E}$ is from 0.213 to 0.620.

No expression has so far been proposed to predict the salting properties of organic compounds by electrolytes other than sodium chloride. However, in the case of gaseous substances (subscript $_G$) such predictions were proposed by Weisenberger and Schumpe [4] by means of the empirical expression:

$$k_{G,E} = \Sigma_I\ \nu_I\left[k_{G,I} + k_{G,25} + h_G\left((t/^\circ C) - 25\right)\right] \tag{3}$$

The index $_I$ pertains to the individual ions of the salting-out electrolyte E (including mixed electrolytes), $k_{G,I}$ is an ion specific parameter that is relatively independent of the temperature, and $k_{G,25}$ and h_G are gas specific parameters. Weisenberger and Schumpe reported conventional numerical values for the $k_{G,I}$ for many ions on the basis that $k_{G,I}(H^+)^{conv} = 0$, shown in Table 1.

In spite of the successful correlation by Eq. (2) for the salting of solid and liquid organic compounds by sodium chloride, a reservation may be made that it employs quantities, $\log K_{Now}$, already representative of the solution behavior of the non-electrolytes in water. Thus, it is not completely independent of the salting behavior it is supposed to predict.

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Table 1
Properties of ions and the Setchenow constants for the salting of benzene and of gases at 25 °C.

Ion	r_c [20]	$V_I^{\infty\ \mathrm{conv}}$ [8]	V_{Iintr}	ΔV_I	$k_{\mathrm{PhH,I\ expt}}$ [3,6]	$k_{\mathrm{PhH,I\ calc}}$ Eq. (8)	$k_{\mathrm{G,I}}$ [4]
	nm	cm^3/mol	cm^3/mol	cm^3/mol	L/mol	L/mol	L/mol
Li^+	0.069	−0.9	1.3	−2.2	0.063	0.057	0.075
Na^+	0.102	−1.2	4.3	−5.5	0.106	0.075	0.114
K^+	0.138	9.0	10.6	−1.6	0.077	0.054	0.092
Rb^+	0.149	14.1	13.3	0.8	0.061	0.041	0.084
Cs^+	0.170	21.3	12.4	8.9	0.009	−0.002	0.076
NH_4^+	0.148	17.9	13.0	4.9	0.024	0.019	0.056
Me_4N^+	0.280	89.6	55.4	34.2	−0.183	−0.139	
Et_4N^+	0.337	149.1	96.5	52.6	−0.246	−0.238	
Pr_4N^+	0.379	214.4	137.3	77.1	−0.373	−0.370	
Bu_4N^+	0.413	275.7	158.6	117.1	−0.568	−0.585	
Mg^{2+}	0.072	−21.2	1.5	−22.7	0.143	0.167	0.169
Ca^{2+}	0.100	−17.9	4.0	−21.9		0.163	0.176
Sr^{2+}	0.113	−18.2	5.8	−24.0	0.145	0.174	0.189
Ba^{2+}	0.136	−12.5	10.1	−22.6	0.207	0.166	0.217
F^-	0.133	−1.2	9.5	−10.7	0.151	0.103	0.092
Cl^-	0.181	17.8	23.8	−6.0	0.084	0.077	0.032
Br^-	0.196	24.7	30.3	−5.6	0.054	0.075	0.027
I^-	0.220	26.2	26.9	−0.7	−0.006	0.011	0.004
SCN^-	0.213	35.7	24.4	11.3	0.004	−0.016	0.063
NO_3^-	0.200	26.2	20.2	6.0	0.018	0.013	0.013
ClO_3^-	0.195	36.7	32.2	4.5	0.020	0.021	0.135
ClO_4^-	0.240	44.1	34.9	9.2	−0.005	−0.004	0.049
HCO_2^-	0.204	26.2	34.1	−7.9	0.065	0.087	
$MeCO_2^-$	0.232	40.5	50.2	−10.3	0.064	0.100	
SO_4^{2-}	0.230	14.0	61.5	−47.5	0.310	0.301	0.112

The two tasks that were undertaken in the present study were to establish an expression to predict the salting properties of solid and liquid organic compounds by electrolytes other than sodium chloride and one that employs only data for the non-electrolyte foreign to its aqueous solution properties.

2. Prediction of the salting properties of electrolytes

Eq. (1) is a proportionality with respect to the concentration of the electrolyte, hence should be valid at infinite dilution. Therefore, $k_{\mathrm{N,E}}$ should be additive with regard to the ions. This is contrary to the assertion by Poulson et al. [5] concerning ionic non-additivity for the salting out of toluene. However, such results quoted by them could be ascribed to the choice of the $k_{\mathrm{PhMe,E}}$ values (PhMe stands for toluene) tested for additivity from among the reported values that have considerable spreads.

Xie et al. [3] reported the $k_{\mathrm{PhH,E}}$ values (PhH stands for benzene) at 25 °C for a large number of electrolytes, including hydrochloric and perchloric acids. Conventional ionic values $k_{\mathrm{PhH,I}}^{\mathrm{conv}}$ could then be established on the basis that $k_{\mathrm{PhH,I}}(H^+)^{\mathrm{conv}}=0$. The resulting ionic values are shown in Table 1. For the tetraalkylammonium ions corresponding values are available from Desnoyers et al. [6], also shown in Table 1.

Of the several theoretical expressions relating the Setchenow constants to the properties of the ions, the present treatment found the internal pressure/electrostriction approach of McDevit and Long [7] to be the most appropriate in a qualitative sense. Its operative quantity is the difference ΔV_I between the conventional standard partial molar volume of the ion, $V_I^{\infty\ \mathrm{conv}}$ (based on $V_I^{\infty\ \mathrm{conv}}(H^+)=0$), and its intrinsic volume, V_{Iintr}. The former values were taken from Millero [8], shown in Table 1. The latter were calculated by the expression suggested by Mukerjee [9]: $V_{\mathrm{Iintr}}=2522(1.213r_I)^3$, where $2522=(N_A 4\pi/3)$ for r_I, the ionic radius, in nm and the resulting volume in cm^3 mol^{-1}. This expression takes care of the voids between the water molecules in the hydration shell of the ions and is appropriate for the monatomic ions but was also applied to NH_4^+, ClO_3^-, HCO_2^-, and $CH_3CO_2^-$. For the poorly hydrated large ions, the polyatomic SCN^-, NO_3^-, and ClO_4^-, as well as for Cs^+ and I^- the bare intrinsic volumes were used: $V_{\mathrm{Iintr}}=2522r_I^3$, assuming that no need for recognition of the voids exists. For the well hydrated SO_4^{2-} anion the values suggested by Glueckauf [10], again taking into account the voids in the hydration shell, was used. These values of V_{Iintr} as well as the resulting ΔV_I values are shown in Table 1. The plot of $k_{\mathrm{PhH,I}}^{\mathrm{conv}}$ vs. ΔV_I is shown in Fig. 1 to be expressed well by the straight line:

$$k_{\mathrm{PhH,I}}^{\mathrm{conv}}=(0.045\pm0.006)\text{–}(0.00538\pm0.00016)\Delta V_I \tag{4}$$

with an adjusted correlation constant squared $r_{\mathrm{adj}}^2=0.9795$ and a standard error of the fit $\sigma_{\mathrm{fit}}=0.026$ for $n=24$ ions.

According to the additivity principle $k_{\mathrm{PhH,E}}=\Sigma_I\ \nu_I k_{\mathrm{PhH,I}}^{\mathrm{conv}}$, and this should hold, therefore, also for other solutes for which extensive data for various electrolytes are available. Plots of $k_{\mathrm{N,E}}$ vs. $\Delta V_E=\Sigma_I\ \nu_I\Delta V_I$ should produce straight lines, as is, indeed the case for $k_{\mathrm{PhH,E}}$, $k_{\mathrm{PhMe,E}}$, and $k_{\mathrm{Nphth,E}}$ (Nphth stands for naphthalene). The expressions for these lines are as follows:

$$k_{\mathrm{PhH,E}}=0.046\text{–}0.0065\Delta V_E \quad n=30 \quad r_{\mathrm{adj}}^2=0.9635 \quad \sigma_{\mathrm{fit}}=0.044 \tag{5}$$

$$k_{\mathrm{PhMe,E}}=0.057\text{–}0.0087\Delta V_E \quad n=27 \quad r_{\mathrm{adj}}^2=0.9490 \quad \sigma_{\mathrm{fit}}=0.048 \tag{6}$$

$$k_{\mathrm{Nphth,E}}=0.008\text{–}0.0098\Delta V_E \quad n=25 \quad r_{\mathrm{adj}}^2=0.9098 \quad \sigma_{\mathrm{fit}}=0.071 \tag{7}$$

The fits become worse on going from benzene to toluene to naphthalene as do the qualities of the data (larger spreads in reported values) but the fits are still well acceptable. The salting-in of benzene and naphthalene by $HClO_4$, LiSCN, CsSCN, Me_4NBr, and Et_4NBr noted by Xie et al. [3] is corroborated by Eqs. (5) and (7), though for the tetraalkylammonium bromides only qualitatively, the data being rather uncertain. The more accurate data for benzene salting-in by tetraalkylammonium bromides of Desnoyers et al. [6] confirm the predictions by Eq. (5) well.

3. Prediction of the salting properties of liquid and solid organic compounds

The ionic $k_{\mathrm{N,I}}$ being additive for the three aromatic hydrocarbons tested, it stands to reason that whatever is established for sodium chloride should be valid also for other electrolytes. Therefore, only

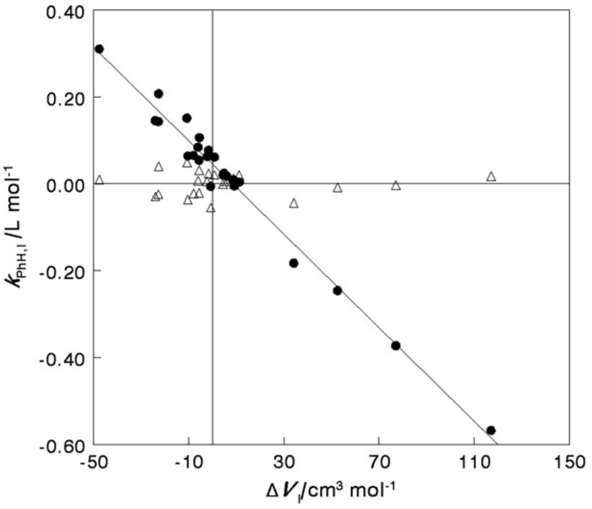

Fig. 1. Conventional ionic salting constants for benzene (filled circles) and the difference between the experimental and calculated ones (from Eq. (4), empty triangles) plotted against the difference between the conventional ionic standard molar volume and the ionic intrinsic volume.