Solubilities and Setchenow Coefficients for $[Fe(bipy)_2(CN)_2]$ and $[Fe(5NO_2\text{-}phen)_2(CN)_2]$† in Aqueous Salt Solutions

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Solubilities of the title complexes in aqueous solutions of alkali-metal and tetra-alkylammonium bromides and chlorides at 298.2 K are reported. Setchenow coefficients have been derived from these data, and compared with those for the ligands 2,2′-bipyridyl and 5-nitro-1,10-phenanthroline, for the complex $[Co(NH_3)_3(NO_2)_3]$, and for a selection of organic and simple inorganic non-electrolyte solutes.

NEARLY a century ago Setchenow [1] established that the effects of added salts on the solubility of carbon dioxide in water could be represented by equation (1). This

$$\log(S_0/S) = k_S c \qquad (1)$$

equation has subsequently become known by his name, and values of k_S are termed Setchenow coefficients. In equation (1), S is the solubility in salt solution, S_0 the solubility in water, and c the concentration of carbon dioxide (or dissolved non-electrolyte in general). An equation of the same form as (1) was also proposed over half a century ago to correlate salt effects on solubilities of proteins.[2] The topic was fully reviewed by Long and McDevit in 1952,[3] and later (1965) by Sergeeva; [4] more recent developments can be traced in a paper by Masterton *et al.*[5] Originally applications were to non-polar solutes, but subsequently polar solutes were also treated in like manner. Interest in Setchenow analysis and coefficients continues to the present day, but remains concentrated on organic solutes. Setchenow analysis for inorganic solutes is restricted to oxygen, hydrogen, and the noble gases,[4] and, in the field of transition-metal complexes, to $[Co(NH_3)_3(NO_2)_3]$.[6] The requirements of zero charge and kinetic inertness are very restricting for complexes, but are met for a few low-spin iron(II) complexes. In the present paper we report solubilities of two such complexes, $[Fe(bipy)_2(CN)_2]$ and $[Fe(5NO_2\text{-}phen)_2(CN)_2]$ (bipy = 2,2′-bipyridyl, $5NO_2$-phen = 5-nitro-1,10-phenanthroline), in aqueous solution of alkali-metal and tetra-alkylammonium bromides and chlorides. Our results can be linked to the established pattern for organic solutes *via* reported solubilities of the ligands bipy and $5NO_2$-phen in a few aqueous salt solutions.

EXPERIMENTAL

The complexes $[Fe(bipy)_2(CN)_2]$ [7] and $[Fe(5NO_2\text{-}phen)_2(CN)_2]$ [8] were prepared by published methods. In the case of the latter complex we ensured that complete reaction occurred and that the intermediate $[Fe(5NO_2\text{-}phen{\cdot}CN)_2(5NO_2\text{-}phen)]$ had been fully converted into the required product. The chlorides and bromides used were of the best quality commercially available. Solubilities were determined by equilibrating a large excess of the solid complex with the salt solution; aliquots were withdrawn at intervals and complex concentrations therein estimated spectrophotometrically (Unicam SP 800; at 298.2 K). Both iron complexes exhibit solvatochromic behaviour,[9] but this is significant in mixed aqueous and non-aqueous media rather than in salt solutions. We have found that the change in molar absorption coefficient for our two complexes is not significant over the concentration range employed here by checking absorbances in water and in strong salt solutions. This is a necessary precaution in view of established (although small) variations in medium Z [10] and g(S) [11] parameters with salt concentration.

RESULTS

Measured solubilities of $[Fe(bipy)_2(CN)_2]$ and of $[Fe(5NO_2\text{-}phen)_2(CN)_2]$ in aqueous solutions of 1 : 1 electrolytes at 298.2 K are reported in Tables 1 and 2.

TABLE 1

Solubilities * of $[Fe(bipy)_2(CN)_2]$ in aqueous salt solutions at 298.2 K

	[salt]/mol dm^{-3}						
Salt	0.05	0.10	0.20	0.375	0.50	0.75	1.00
KCl	1.9	1.9	1.9	2.0	2.1	2.1	
KBr	1.9	1.9	2.0	2.1	2.2	2.3	2.4
CsBr					2.5		2.7
$[NMe_4]Br$					3.8		5.6
$[NEt_4]Br$					5.6		10
$[NBu^n_4]Br$	2.3	3.3	4.2	7.3	13	19	36

* In 10^{-4} mol dm^{-3}. Solubility in water 1.82×10^{-4} mol dm^{-3} at 298.2 K.

TABLE 2

Solubilities * of $[Fe(5NO_2\text{-}phen)_2(CN)_2]$ in aqueous salt solutions at 298.2 K

	[salt]/mol dm^{-3}			
Salt	0.10	0.20	0.375	0.50
LiBr	2.7	2.9	3.2	3.6
NaBr	2.5	2.7	2.9	3.2
KBr	2.9	3.2	3.9	4.7
CsBr	2.9	3.6	4.7	5.7
$[NMe_4]Br$	3.2	3.6	5.4	6.4
$[NEt_4]Br$	3.2	3.9	6.1	7.5
$[NBu^n_4]Br$	5.0	10	26	

* In 10^{-5} mol dm^{-3}.

DISCUSSION

Our solubility results for the two iron complexes can be satisfactorily accommodated by the Setchenow equation (1) above. The precision of the solubilities in Tables 1 and 2 are better than ±5% for the alkali-metal halide solutions. Reproducibility of solubility measurements in the tetra-alkylammonium bromide solutions was less good, with uncertainties increasing from *ca.* 5% in dilute $[NMe_4]Br$ and $[NEt_4]Br$ to *ca.* 10% in the strongest $[NBu^n_4]Br$ solution. This level of accuracy does not warrant analysis of our results by the multi-

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† Bis(2,2′-bipyridyl)dicyanoiron(II) and dicyanobis(5-nitro-1,10-phenanthroline)iron(II) respectively.

parameter equation developed elsewhere[12] to cover small deviations from linearity at low and at high salt concentrations. The dependence of the solubilities of the iron(II) complexes on salt concentration is illustrated in Figure 1. For comparison an analogous graph for benzene[3] (same scale) is shown in Figure 2. The slopes of the lines on these plots give the Setchenow coefficients for the various salts used. A comparison of Figures 1 and 2 reveals a great similarity of pattern between the iron(II) complexes and benzene, even including the order $\text{Li}^+ > \text{Na}^+ < \text{K}^+$. However, the benzene diagram has effectively to be rotated clockwise about the origin in order to match the previous diagrams for the iron complexes. Ethylene, which is 'salted-out' (positive Setchenow coefficient) by most alkali-metal halides, but 'salted-in' by caesium iodide as well as by tetra-alkylammonium halides,[13] represents an intermediate situation. Figure 3 (*a*) and (*b*) shows that the solubilities of the ligands 2,2′-bipyridyl[14] and 5-nitro-1,10-phenanthroline[15] in aqueous salt solutions exhibit similar patterns.

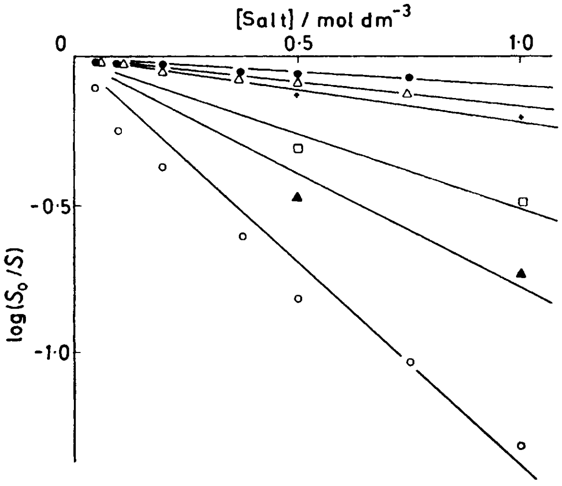

FIGURE 1 Plot of the logarithm of S_0/S against salt concentration for [Fe(bipy)$_2$(CN)$_2$]. Aqueous solutions: KCl (●); KBr (△); CsBr (+); [NMe$_4$]Br (□); [NEt$_4$]Br (▲); [NBu$^n_4$]Br (○)

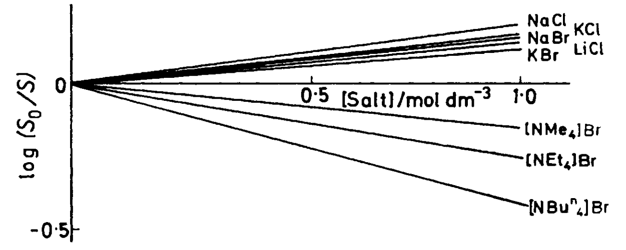

FIGURE 2 Plot of the logarithm of S_0/S against salt concentration for benzene (data from ref. 3)

Setchenow coefficients for the iron(II) complexes are given in Table 3, where they are compared with values for a selection of organic solutes, both non-polar and polar, for the sole inorganic complex, [Co(NH$_3$)$_3$(NO$_2$)$_3$], and for a couple of simple non-polar inorganic solutes. Several comments can be made on various aspects of the collation of results in Table 3. Comparison of the iron(II) complexes with [Co(NH$_3$)$_3$(NO$_2$)$_3$] shows that alkali-metal halides 'salt-in' (negative Setchenow coefficient) all three complexes, in contrast to most organic non-electrolytes being 'salted-out' by most alkali-metal halides, and to simple inorganic gases. The inclusion of a nitro-substituent leads to more negative Setchenow coefficients, for iron(II) complexes as for aromatic compounds such as benzene, phenol, or aniline.[4] The effect of a nitro-substituent in an aliphatic compound is less clear-cut, to judge from the very few comparisons possible between k_S values for nitromethane[16] and methane.[17] The replacement of $\cdots$CH$\cdots$ by $\cdots$N$\cdots$ in an aromatic ring does not seem to have much effect on Setchenow coefficients, to judge from comparison of 2,2′-bipyridyl with biphenyl (Table 3).

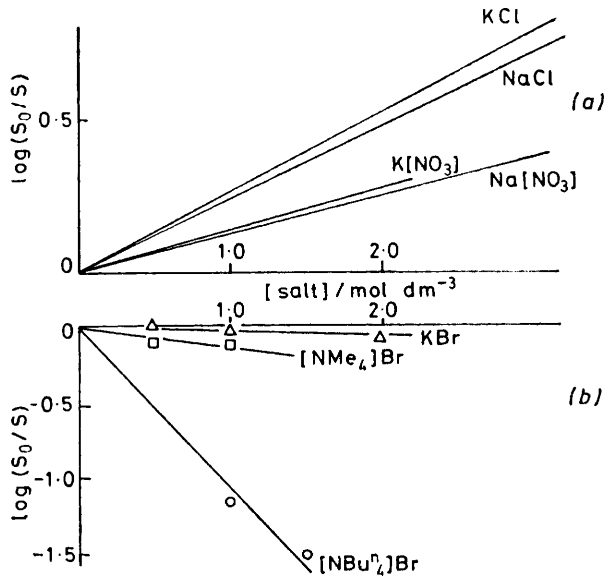

FIGURE 3 Plot of the logarithm of S_0/S against salt concentration for heteroaromatic di-imines (*a*) 2,2′-bipyridyl and (*b*) 5-nitro-1,10-phenanthroline

Considerable success has been achieved in correlating k_S values with molar volumes of, for example, hydrocarbons[4,18,19] and alcohols,[12] but a simple correlation could not cover the whole range of compound types included in Table 3. The dissection of Setchenow coefficients into contributions from molecular units, as carried out successfully for amides,[20] and subsequent generalisation to a multi-parameter equation might work, but we have too many disparate units at present for a useful application of this approach. However some correlation with characteristic volumes can be carried out on our results for [Fe(bipy)$_2$(CN)$_2$] and [Fe(5NO$_2$-phen)$_2$(CN)$_2$]. It has been suggested[21] that the solubilities S_0 and S of non-electrolytes in water and in aqueous salt solutions respectively can be related to the characteristic volumes, V_x, of the non-electrolytes by equation (2).

$$\log_{10}(S_0/S) + \text{any interaction terms} = -V_x(0.65\,[\text{H}_2\text{O}]_0 - 0.65\,[\text{H}_2\text{O}]_s - 1.35\,I) \qquad (2)$$

The concentration of water $[\text{H}_2\text{O}]_0$ refers to the solution

TABLE 3

Setchenow coefficients for $[Fe(bipy)_2(CN)_2]$, $[Fe(5NO_2\text{-phen})_2(CN)_2]$, bipy, $5NO_2$-phen, and some other non-electrolytes in aqueous salt solutions at 298.2 K

Non-electrolyte	LiCl	NaCl	KCl	LiBr	NaBr	KBr	CsBr	$[NMe_4]Br$	$[NEt_4]Br$	$[NBu^n_4]Br$	Ref.
C_6H_6	0.141	0.198	0.166		0.155	0.119		−0.15	−0.25	−0.41	2, 21 *a,b*
$C_6H_5NO_2$			0.075					−0.17			3
C_6H_5OH			0.133								3
p-$O_2NC_6H_4OH$		0.106	0.050								*c*
$C_{10}H_8$	0.180	0.260	0.204		0.169			−0.27 [d]			*e*
$C_6H_5C_6H_5$	0.218	0.276	0.295		0.209						*e*
bipy	0.26	0.25									19
phen		*f*									*f*
$5NO_2$-phen						0.05		*ca.* −0.2		−1.1	20
$[Fe(bipy)_2(CN)_2]$			−0.12			−0.15	−0.25	−0.55	−0.8	−1.5	*g*
$[Fe(5NO_2\text{-phen})_2(CN)_2]$				−0.31	−0.17	−0.54	−0.72	−0.85	−1.0	−2.9	*g*
$[Co(NH_3)_3(NO_2)_3]$		−0.16	−0.24								3, 13
O_2	0.230	0.312	0.298			0.250					4
Ar	0.226	0.314	0.270			0.263					4

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in water, $[H_2O]_s$ to the salt solution, and I is the (molar) ionic strength of the salt solution. Equation (2) may be rewritten as (3), where c_S is the concentration of the salt,

$$\log_{10}(S_0/S) + \text{any interaction terms} = c_S V_x(1.35\,\Sigma z^2 - 36\,000\,\bar{V}_S) \quad (3)$$

z^2 is the product of the charges of the ions constituting the added electrolyte, and $\bar{V}_S$ its partial molar volume.

TABLE 4

Relations between the solubilities of $[Fe(bipy)_2(CN)_2]$ in water (S_0) and in aqueous salt solutions (S), the concentration (c_S) and partial molar volume ($\bar{V}_S^0$) of the added salt, and the characteristic volume (V_x) of the complex; concentrations in mol m^{-3}. The constant k_c is 2×10^{-3} m^3 mol^{-1} for alkali-metal halides, zero for tetra-alkylammonium halides (see text)

Salt	[salt]/mol m^{-3}	$\log\left(\frac{S_0}{S}\right)$	$\log\left(\frac{S_0}{S}\right) + \log(1 + k_c c_s)$	$c_s V_x(2.7 - 36\,000\bar{V}_s^0)$
KCl	50	−0.02	0.02	0.02
	100	−0.02	0.06	0.05
	200	−0.02	0.13	0.10
	375	−0.06	0.18	0.19
	500	−0.06	0.24	0.25
	750	−0.06	0.34	0.37
KBr	50	−0.01	0.03	0.02
	100	−0.01	0.07	0.04
	200	−0.05	0.10	0.09
	375	−0.07	0.17	0.16
	500	−0.08	0.22	0.21
	750	−0.12	0.28	0.32
CsBr	500	−0.14	0.16	0.15
	1 000	−0.17	0.31	0.30
$[NMe_4]Br$	500	−0.32		−0.18
	1 000	−0.49		−0.38
$[NEt_4]Br$	500	−0.49		−0.51
	1 000	−0.74		−1.02
$[NBu^n_4]Br$	50	−0.10		−0.12
	100	−0.25		−0.23
	200	−0.37		−0.47
	375	−0.60		−0.87
	500	−0.84		−1.16
	750	−1.02		−1.74
	1 000	−1.30		−2.32

In Table 4 values of $\log_{10}(S_0/S) + \log_{10}(1 + k_c c_S)$ are compared with $c_S V_x(2.7 - 36\,000\bar{V}_S)$ for $[Fe(bipy)_2(CN)_2]$, for which $V_x = 2.865 \times 10^{-4}$ m^3 mol^{-1} if the suggested value of 0.291×10^{-4} m^3 mol^{-1} is used for the iron.[22] Partial molar volumes at infinite dilution are $\bar{V}_s^0(KCl) = 2.681 \times 10^{-5}$, $\bar{V}_s^0(KBr) = 3.373 \times 10^{-5}$, and $\bar{V}_s^0(CsBr) = 4.619 \times 10^{-5}$ m^3 mol^{-1}.[13] For these added

TABLE 5

Relations between the solubilities of $[Fe(5NO_2\text{-phen})_2(CN)_2]$ in water (S_0) and in aqueous salt solutions (S), the concentration (c_S) and partial molar volume ($\bar{V}_s^0$) of the added salt, and the characteristic volume (V_x) of the complex; concentrations in mol m^{-3}. The constant k_c is 3×10^{-3} m^3 mol^{-1} for alkali-metal halides, zero for tetra-alkylammonium halides (see text)

Salt	[salt]/mol m^{-3}	$\log\left(\frac{}{S}\right)$	$\log\left(\frac{S_0}{S}\right) + \log(1 + k_c c_s)$	$c_s V_x(2.7 - 36\,000\bar{V}_s^0)$
LiBr	100	−0.03	0.08	0.06
	200	−0.06	0.14	0.13
	375	−0.11	0.21	0.24
NaBr	100	0	0.11	0.06
	200	−0.03	0.17	0.13
	375	−0.06	0.26	0.24
	500	−0.11	0.29	0.32
KBr	100	−0.06	0.05	0.05
	200	−0.11	0.09	0.10
	375	−0.20	0.12	0.19
	500	−0.27	0.13	0.26
CsBr	100	−0.06	0.05	0.03
	200	−0.16	0.04	0.07
	375	−0.27	0.05	0.14
	500	−0.36	0.04	0.18
$[NMe_4]Br$	100	−0.11		−0.05
	200	−0.16		−0.10
	375	−0.33		−0.17
	500	−0.41		−0.27
$[NEt_4]Br$	100	−0.11		−0.12
	200	−0.20		−0.25
	375	−0.39		−0.46
	500	−0.48		−0.62
$[NBu^n_4]Br$	100	−0.30		−0.28
	200	−0.60		−0.56
	375	−1.02		−1.06

salts, agreement between the two columns (Table 4) is satisfactory.

A similar analysis of our results in tetra-alkylammonium halide solutions (also Table 4) leads to less good agreement. We have used $\bar{V}_s^0(NMe_4Br) = 1.114 \times 10^{-4}$, $\bar{V}_s^0(NEt_4Br) = 1.737 \times 10^{-4}$, and $\bar{V}_s^0(NBu^n{}_4Br) = 3.004 \times 10^{-4}$ m^3 mol^{-1} in our calculations.[23] The constant k_c quantifies direct interactions between the non-electrolyte and the added salt.[19] Its value here appears to be 2×10^{-3} m^3 mol^{-1} for alkali halides, but close to zero for tetra-alkylammonium halides. A similar treatment for $[Fe(5NO_2\text{-}phen)_2(CN)_2]$ solubilities is set out in Table 5. Here agreement between the two right-hand columns is less good than for the $[Fe(bipy)_2(CN)_2]$ results; indeed agreement is somewhat better for the tetra-alkylammonium halides than for the alkali-metal halides for $[Fe(5NO_2\text{-}phen)_2(CN)_2]$. Strong ion-solvent interaction has recently been proposed between tetra-alkylammonium ions and nitrobenzene.[24] Presumably it is the nitro-substituent which is upsetting the looked-for correlations; the rather unusual properties of aqueous solutions of tetra-alkylammonium halides [25] must also be invoked in the case of the $[Fe(bipy)_2(CN)_2]$ solubilities.

While the above treatment, and indeed many other authors' treatments, have concentrated on volume effects, there has also been some discussion of dipole moments in determining k_S values for polar non-electrolytes.[26] Dispersive and dipole interactions make opposing contributions to salting-in and salting-out of polar non-electrolytes by halides of small and large cations; [26] hydrophobic interactions are important when tetra-alkylammonium salts are involved.[27] These hydrophobic interactions might be expected to be particularly advantageous when a large complex with a predominantly hydrophobic exterior is the non-electrolyte; this expectation is qualitatively realised in the particularly large salting-in observed for these iron(II) complexes by the tetra-alkylammonium bromides, particularly by the tetra-n-butylammonium bromide (Tables 1 and 2). The structural influences of the solutes are compatible here.[28]

We have for some time been interested in salt effects [15,29] on kinetics of substitution reactions, and their analysis into initial-state and transition-state components. The establishment of Setchenow coefficients for transition states might be of interest in this connection; they have indeed been obtained for t-butyl chloride solvolysis.[30] Unfortunately substitution at the present iron(II) complexes takes place impossibly slowly at 298 K, but we hope eventually to find an iron(II) complex whose kinetic properties permit an investigation of the Setchenow coefficients of initial and transition states.

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