Solubilities of Caesium Hexachlororhenate(IV), Hexabromorhenate(IV), and Tetraoxorhenate(VII) in Alcohol–Water Mixtures, and their Relation to Cosolvent Characteristic Volume

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Solubilities of $Cs_2[ReCl_6]$ in methanol–, ethanol–, and t-butyl alcohol–water mixtures, and of $Cs_2[ReBr_6]$ and $Cs[ReO_4]$ in methanol–water mixtures, are reported. Correlation of these solubilities with various solvent and solubility parameters is discussed; a simple correlation of solubilities with solvent composition and cosolvent characteristic volume is remarkably satisfactory.

The solubility of caesium hexachlororhenate(IV) has been measured in a few binary aqueous solvent mixtures;[1] the solubilities obtained were found to correlate only poorly with the respective Grunwald–Winstein solvent Y values.[2] In the present paper we report solubilities of $Cs_2[ReCl_6]$ in a wider range of alcohol–water mixtures, and of caesium hexabromorhenate(IV) and caesium tetraoxorhenate(VII) in several methanol–water mixtures. We also discuss attempted correlations of these results with a range of solvent and solubility parameters. Correlations between solubilities and solvent composition and cosolvent characteristic volumes, previously demonstrated for several simple electrolytes,[3] are also satisfactory for the compounds and mixed-solvent series examined here.

EXPERIMENTAL

Caesium hexachlororhenate(IV) and caesium hexabromorhenate(IV) were prepared, and their solubilities determined, as described previously.[1] Caesium tetraoxorhenate(VII) was precipitated from a solution of the potassium salt by the addition of caesium chloride solution. Concentrations of $[ReO_4]^-$ were determined spectrophotometrically at 206 (ε 6 060) or 228 nm (ε 3 610 dm^3 mol^{-1} cm^{-1}).[4]

RESULTS

Solubilities of $Cs_2[ReCl_6]$, $Cs_2[ReBr_6]$, and $Cs[ReO_4]$ in alcohol–water mixtures are reported in Table 1. For the first two salts, the amount of organic cosolvent which can be used is limited by the increasing rate of solvolysis of the anions as the proportion of organic cosolvent increases.[5] This restriction is much more severe for $Cs_2[ReBr_6]$ than for its chloro-analogue.

DISCUSSION

In an earlier paper we attempted to correlate a few solubilities of $Cs_2[ReCl_6]$ with values of the Grunwald–Winstein kinetically based empirical solvent parameter Y.[2] This choice of solvent parameter was prompted by the similarity of the periphery of the $[ReCl_6]^{2-}$ anion here to the leaving Cl^- anion whose solvation behaviour effectively determines solvent Y values. However, a plot of solubility against Y for this salt gave a curved plot about which the experimental points were widely scattered. We therefore wished to seek a more satisfactory correlation, and have determined solubilities under a rather wider range of conditions in order to make a better test of the proposed correlations.

Table 1

Solubilities (S) of caesium hexachlororhenate(IV), hexabromorhenate(IV), and tetraoxorhenate(VII) in binary aqueous mixtures at 298.2 K

Cosolvent	Solvent composition [a]	$10^5 S$/mol dm^{-3}		
		$Cs_2[ReCl_6]$	$Cs_2[ReBr_6]$	$Cs[ReO_4]$
	0	24.6	10.4	2 210
Methanol	10	18.6		
	20	12.0	6.4	1 730
	30	8.9	4.4	1 610
	40	5.8 [b]	2.5 [b]	1 360
Ethanol	10	18.7		
	20	11.7 [b]		
	30	9.9		
	40	5.6 [b]		
	50	4.7		
	60	3.4 [b]		
t-Butyl alcohol	10	16.8		
	20	12.2		
	30	9.6		
	40	6.1		

[a] Volume % non-aqueous component. [b] From ref. 1.

A generous selection of empirical solvent parameters exists, based on a range of spectroscopic, kinetic, and thermodynamic solvent and solution properties.[6] Our measured solubilities of caesium salts of rhenium-containing anions do not correlate satisfactorily with widely used spectroscopically based solvent parameters such as Kosower's[7] Z or Reichardt's[8] E_T; nor do they correlate well with the solubility based parameter $g(S)$.[9] Correlation of electrolyte solubilities with reciprocal dielectric constants ($1/D$) of aqueous solvent mixtures has been proposed,[10] despite an earlier demonstration

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[2] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846.

[3] J. C. McGowan, *Nature*, 1974, **252**, 296.

[4] A. Carrington and M. C. R. Symons, *J. Chem. Soc.*, 1957, 659.

[5] J. Burgess, R. D. Peacock, and A. M. Petric, *J.C.S. Dalton*, 1973, 902.

[6] C. Reichardt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 29.

[7] E. M. Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253.

[8] K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Annalen*, 1963, **661**, 1.

[9] P. Letellier and R. Gaboriaud, *J. Chim. phys.*, 1973, **70**, 941; P. Letellier, *Bull. Soc. chim. France*, 1973, 1569.

[10] A. Watanabe, *Nagoya Kogyo Guutsu Shikendo Hokoku*, 1965, **14**, 1.

that the solubility products of silver bromate and calcium iodate show no correlation whatsoever with the dielectric properties of binary aqueous mixtures (eight or nine cosolvents).[11] We have found that a plot of solubility against $1/D$ for $Cs_2[ReCl_6]$ in alcohol–water mixtures is only approximately linear.

Attempts to generate general correlations to cover solubilities of inorganic electrolytes in binary aqueous solvent mixtures [12] have often met with limited success. However, many decades ago Rothmund [13] showed that Setchenow's [14] treatment of the effects of added electrolytes on the solubility of non-electrolytes in water could also be applied to the complementary effect of added non-electrolytes on the solubility of inorganic salts in water. Rothmund's treatment has subsequently been refined and generalised by incorporating the characteristic volume V^* of the added non-electrolyte.[3] The solubilities of a salt in a series of binary aqueous mixtures, S_X, were related to its solubility in pure water, S_0, and the concentration of non-electrolyte, c_S, by expression (1).

$$\log_{10} S_0 = \log_{10} S_X + K_S' V^* c_S \qquad (1)$$

Here K_S' is a constant characteristic of the electrolyte. This equation holds well for a variety of inorganic salts, *e.g.* $K[BrO_3]$, $K_2[SO_4]$, $Li_2[CO_3]$, and $Pb[SO_4]$, in a range of binary aqueous mixtures where the cosolvents include alcohols, acetone, acetonitrile, methyl acetate, and phenol. Equation (1) breaks down when the salt is significantly soluble in the organic cosolvent, or when there are specific ion–organic cosolvent interactions, as in the case of silver(I) salts in acetonitrile–water mixtures. Values of K_S' [equation (1)] seem to be determined primarily by the charges on the ions in the electrolyte concerned. Thus K_S' is *ca.* 0.7 for 1 : 1 electrolytes, *ca.* 1.0 for 2 : 1 and 1 : 2 electrolytes, and 1.6 for the 2 : 2 electrolyte lead(II) sulphate (Table 2).[3] A similar dependence of solubility trends in aqueous ethanol solvent mixtures on electrolyte charge product is apparent from Korenman's treatment of solubilities.[15]

The standard error of the gradient of a plot of the decadic logarithm of the solubility products for $Cs_2[ReCl_6]$ (Table 1) against $V^* c_S$ [equation (1)] is *ca.* 3%. This is very much better than the standard errors of 9, 11, 12, and 12% for analogous plots against solvent Y values, reciprocal dielectric constants, Kosower Z values, and $g(S)$ values respectively. Plots of the decadic logarithm of the solubility products of $Cs_2[ReBr_6]$ and of $Cs[ReO_4]$ against $V^* c_S$ are also satisfactory, although this observation is much less significant here, where the results are only available for methanol as cosolvent. Nonetheless it seems that a satisfactory solubility correlation can be obtained for these rhenium-containing salts with a function involving only the characteristic volume of the cosolvent and its concentration.

Values of K_S' for $Cs_2[ReCl_6]$, $Cs_2[ReBr_6]$, and $Cs[ReO_4]$ are compared in Table 2 with values established earlier for some simple oxo-anion salts (*cf.* above) and with values calculated for some halides and some salts containing complex anions or cations from published solubility data. It is clear from Table 2 that the dependence of K_S' on electrolyte charge product apparent for simple oxo-anion salts does not apply to many of the salts included in Table 2, although the fact that not all the solubilities refer to 25 °C introduces an element of complication. Moreover, although equation (1) applies satisfactorily to the salts in this Table, it does not apply to the solubilities of some salts with large cations, for example $[Fe(phen)_3][ClO_4]_2$ (phen = 1,10-

TABLE 2

Values of K_S' [*cf.* equation (1)] for electrolytes in binary aqueous mixtures, at 298 K unless otherwise stated

Compound	Cosolvents [a]	K_S'	Ref.
1 : 1 Electrolytes			
NaCl	E	0.4 [b]	*c*
KCl	E	0.5	*c*
NaF	M, E	0.9_5	*d*
$K[BrO_3]$	Numerous	0.8	3
$Ag[BrO_3]$	M, E, P, A	0.6	3
$Na[Sb(OH)_6]$	E, B, A, D	*ca.* 0.7	*h*
$Cs[ClO_4]$	M, E	0.4	17
$K[ClO_4]$	M	0.3	*e*
$Cs[ReO_4]$	M	0.2	*l*
$[Co(en)_2Cl_2][ClO_4]$ [m]	Numerous [k]	0.1_5	*n*
2 : 1 Electrolytes			
$K_2[SO_4]$	Numerous	1.0	3
$Ag_2[SO_4]$	Numerous	1.1	3
$Li_2[CO_3]$	Numerous	1.0_5	3
$K_2[S_2O_8]$	M	0.7	*e*
$K_2[PtCl_6]$	M, E	1.0 [f]	*g*
$K_2[SiF_6]$	M, E	1.3 [i]	*j*
$Cs_2[ReCl_6]$	M, E, B [k]	0.7	*l*
$Cs_2[ReBr_6]$	M	0.6	*l*
1 : 2 Electrolyte			
$[Co(NH_3)_5Cl]Cl_2$	E [k]	0.7	*o*

[a] M = Methanol, E = ethanol, P = n-propanol, B = t-butyl alcohol, A = acetone, D = 1,4-dioxan, numerous = five or more cosolvents. [b] Values for KBr, KI, and $[NH_4]Cl$ in ethanol–water mixtures are similar (footnote *c*). [c] H. E. Armstrong, J. V. Eyre, A. V. Hussey, and W. P. Paddison, *Proc. Roy. Soc.*, 1907, **79**, 564. [d] H. K. Zhadanov, *J. Gen. Chem.* (*U.S.S.R.*), 1954, **24**, 762; F. Winkler, D. Dümk, M. Fortsch, K. Schneider, and R. Trögen, *Z. Chem.*, 1971, **11**, 293. [e] J. Burgess and R. I. Haines, unpublished observation. [f] At 293 K. [g] E. H. Archibald, W. G. Wilcox, and B. G. Buckley, *J. Amer. Chem. Soc.*, 1908, **30**, 747. [h] M. J. Blandamer, J. Burgess, and R. D. Peacock, *J.C.S. Dalton*, 1974, 1084. [i] At 287 K. [j] M. Pierrat, *Compt. rend.*, 1921, **172**, 1041. [k] Results in glycol–water and in glycerol–water (see footnote *p*) mixtures do not fit the general correlation. [l] This work. [m] en = Ethylenediamine. [n] E. M. Strel'tsova, N. K. Markova, and G. A. Krestov, *Russ. J. Phys. Chem.*, 1974, **48**, 992; *Zhur. fiz. Khim.*, 1976, **50**, 264. [o] E. M. Strel'tsova, N. K. Markova, and G. A. Krestov, *Izvest. Vyssh. Ucheb. Zaved. Khim. i Tekhnol.*, 1973, **16**, 694; *Russ. J. Phys. Chem.*, 1974, **48**, 804. [p] Interestingly, solubilities of calcium iodate in glycerol–water mixtures were considered exceptional many years ago (ref. 11).

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[12] See, for example, A. Seidell, 'Solubilities of Inorganic and Metal Organic Compounds,' 3rd edn., van Nostrand, New York, 1940, vol. 1.

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[14] J. Setchenow, *Z. phys. Chem.*, 1889, **4**, 117; *Ann. Chim. phys.*, 1891, **25**, 226.

[15] Ya. I. Korenman, *Russ. J. Phys. Chem.*, 1973, **47**, 140.

phenanthroline).[16] Indeed, although results for Cs[ClO$_4$] can be incorporated satisfactorily into Table 2, those for tetrapropylammonium perchlorate cannot.[17] It would be interesting to know whether such simple compounds as silver(I) or thallium(I) halides followed the pattern of the simple oxo-anion salts. Unfortunately this is impossible to determine as the solubilities of such salts in binary aqueous mixtures are affected both by specific cation–cosolvent interactions in some cases, and by the formation of complexes (*e.g.* [Ag$_2$I]$^+$ and [AgI$_2$]$^-$) in several aqueous mixtures.[18]

We therefore conclude that, in many cases, the solubilities of electrolytes in binary aqueous mixtures can be correlated with simple volume characteristics, but that the magnitude of the dependence cannot yet be satisfactorily rationalised.

[7/207 *Received, 7th February,* 1977]

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