

## Solubility of Caesium Hexachlororhenate(IV) and Hexabromorhenate(IV) in Water and in Mixed Aqueous Solvents

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The enthalpies of solution of caesium hexachlororhenate(IV) and hexabromorhenate(IV) in water have been determined, from the temperature variation of their solubilities, as +88 and +96 kJ mol<sup>-1</sup> respectively. Hence the single-ion enthalpies of hydration of the (gaseous) hexachlororhenate(IV) and hexabromorhenate(IV) anions have been estimated, using the assumption that the single-ion hydration enthalpy of the proton is -1 091 kJ mol<sup>-1</sup>, as -845 and -786 kJ mol<sup>-1</sup> respectively. Attempts to correlate the solubility of caesium hexachlororhenate(IV) in mixed aqueous solvents with various empirical solvent parameters are described.

SINGLE-ION hydration enthalpies have been estimated and reported for a generous number of cations, but for a rather smaller range of anions.<sup>1</sup> Values for hydration enthalpies of anions containing transition metals are, with one exception, restricted to oxo-anions. The

<sup>1</sup> See, for example, (a) N. N. Greenwood, 'Ionic Crystals, Lattice Defects, and Non-stoichiometry,' Butterworths, London, 1968, p. 27; (b) C. S. G. Phillips and R. J. P. Williams, 'Inorganic Chemistry,' vol. 1, Oxford University Press, 1965, p. 160.

exception is the hexachlororhenate(IV) anion, for which a single-ion hydration enthalpy can be derived from published thermochemical data on the enthalpy of solution of potassium hexachlororhenate(IV).<sup>2</sup> One reason for the paucity of thermochemical data relating to halogeno-anions of transition metals is that these

<sup>2</sup> R. H. Busey, H. H. Dearman, and R. B. Bevan, *J. Phys. Chem.*, 1962, **66**, 82.

complexes are often substitution labile. However, the hexachloro- and hexabromo-rhenate(IV) anions, where rhenium is in the normally kinetically inert  $d^3$  configuration, are sufficiently long lived in solution<sup>3</sup> for measurements of solubilities and of enthalpies of solution to be made. In the present paper we report the determination of enthalpies of solution of the sparingly soluble caesium salts of the hexachlororhenate(IV) and hexabromorhenate(IV) anions. From these enthalpies of solution, single-ion hydration enthalpies of the two anions can be estimated. That for the hexachloro-anion is in good agreement with the value estimated

sufficiently sparingly soluble for the estimation of their respective enthalpies of solution from the temperature variation of solubility products to be reasonable, but therefore too sparingly soluble for direct calorimetric determination of their enthalpies of solution. In contrast, potassium hexachlororhenate(IV) is sufficiently soluble in water for its enthalpy of solution to be measured calorimetrically with ease. It is thus too soluble for the determination of its enthalpy of solution from the temperature variation of its solubility to be at all satisfactory without the ancillary determination of activity coefficients.<sup>10</sup>

TABLE I

Measured anion concentrations and calculated (concentration) solubility products ( $K_s$ ) for saturated aqueous solutions of caesium hexachlororhenate(IV) and hexabromorhenate(IV)

T/K	Cs <sub>2</sub> [ReCl <sub>6</sub> ]		T/K	Cs <sub>2</sub> [ReBr <sub>6</sub> ]	
	10 <sup>5</sup> [ReCl <sub>6</sub> <sup>2-</sup> ]/ mol dm <sup>-3</sup>	10 <sup>13</sup> K <sub>s</sub> / mol <sup>3</sup> dm <sup>-9</sup>		10 <sup>5</sup> [ReBr <sub>6</sub> <sup>2-</sup> ]/ mol dm <sup>-3</sup>	10 <sup>13</sup> K <sub>s</sub> / mol <sup>3</sup> dm <sup>-9</sup>
273.2	7.10	14.3	273.2	3.28	1.4
273.2	7.25	15.3	274.2	3.38	1.6
276.0	7.60	17.5	275.2	3.23	1.4
276.3	8.55	25.0	277.8	3.03	1.1
278.2	8.70	26.4	280.0	4.14	2.8
281.2	10.23	42.8	280.4	4.65	3.8
281.3	9.47	33.9	282.6	3.64	1.9
281.7	9.47	33.9	284.6	4.55	3.8
284.0	10.92	52.0	285.2	4.95	4.8
284.2	10.84	50.9	286.5	5.56	6.9
284.3	11.76	65.0	288.8	5.66	7.2
286.1	12.14	71.5	290.9	7.47	16.7
287.0	12.75	82.9	292.4	7.58	17.4
287.9	12.37	75.6	293.5	7.83	19.2
289.8	14.50	122.0	295.4	8.89	28.1
290.2	12.67	81.4			
292.3	17.18	202.7			
293.2	16.41	176.8			
295.1	19.24	284.7			

from direct calorimetric measurements of the enthalpy of solution of potassium hexachlororhenate(IV); that for the hexabromo-anion is the first estimate to be published for this anion.

The second part of this paper deals with the solubility of caesium hexachlororhenate(IV) in a range of aqueous-organic binary-solvent mixtures. The possibility of correlating these solubilities with various empirical solvent parameters, such as the kinetically based  $Y$ ,<sup>4</sup> spectroscopically based  $Z$ <sup>5</sup> and  $E_T$ ,<sup>6</sup> and generally based  $S$  values,<sup>7</sup> or with solvent composition<sup>8</sup> or solvent dielectric constant, has been examined. Solubilities of caesium hexachlororhenate(IV) correlate tolerably well with those of sodium hexahydroxoantimonate(V)<sup>9</sup> in the solvent mixtures used.

#### RESULTS AND DISCUSSION

*Solubility in Water.*—The least-soluble alkali-metal salts of the hexachlororhenate(IV) and hexabromorhenate(IV) anions are those of caesium. They are both

\* These error limits represent the estimated standard errors of the cited means.

<sup>3</sup> J. Burgess, R. D. Peacock, and A. M. Petric, *J.C.S. Dalton*, 1972, 903.

<sup>4</sup> E. Grunwald and S. Brownstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846.

<sup>5</sup> E. M. Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253.

The measured anion concentrations and the solubility products thence derived for caesium hexachlororhenate(IV) and hexabromorhenate(IV) in aqueous solution over a range of temperatures are reported in Table I. Plots of logarithms of these solubility products against reciprocal temperatures are straight lines. Least-mean-squares computations of the two sets of results in Table I gave enthalpies of solution of  $+87.8 \pm 3.6$  \* and  $+95.5 \pm 8.4$  \* kJ mol<sup>-1</sup> for the hexachloro- and hexabromo-complex respectively, assuming that the activity coefficients do not vary with temperature. The mean ionic-activity coefficient at 298.2 K can be estimated<sup>11</sup> as 0.97 for each salt; the variation of this with temperature seems unlikely<sup>12</sup> to make a difference of more than 1 kJ mol<sup>-1</sup> to the enthalpies of solution cited above. Short extrapolations from the results in

<sup>6</sup> K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Annalen*, 1963, **661**, 1.

<sup>7</sup> S. Brownstein, *Canad. J. Chem.*, 1960, **38**, 1590.

<sup>8</sup> Ya. I. Korenman, *Russ. J. Phys. Chem.*, 1973, **47**, 140.

<sup>9</sup> M. J. Blandamer, J. Burgess, and R. D. Peacock, *J.C.S. Dalton*, 1974, 1084.

<sup>10</sup> A. T. Williamson, *Trans. Faraday Soc.*, 1944, **40**, 421.

<sup>11</sup> R. B. Heslop, 'Numerical Aspects of Inorganic Chemistry,' Elsevier, Amsterdam, 1970, p. 138.

<sup>12</sup> *cf.*, For example, R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' 2nd edn., Butterworths, London, 1965, pp. 480—481.

Table 1 gave values for the solubility products of caesium hexachlororhenate(IV) and hexabromorhenate(IV) in water at 298.2 K of  $3.4 \times 10^{-11}$  and  $3.2 \times 10^{-12}$  mol<sup>3</sup> dm<sup>-9</sup>. From these numbers and the assumed mean ionic-activity coefficients of 0.97, the standard free-energy changes,  $\Delta G^\circ$ , of the solids to the hypothetical solution standard of  $m = 1$  mol kg<sup>-1</sup>, are +60 and +66 kJ mol<sup>-1</sup>. Thence the respective temperature-entropy products  $T\Delta S^\circ$  are +28 and +30 kJ mol<sup>-1</sup> for the hexachloro- and hexabromo-complexes respectively. To derive single-ion hydration enthalpies from these estimated enthalpies of solution it is necessary to calculate the lattice energies and thence enthalpies of the salts, and then to separate sums of pairs of ionic-hydration enthalpies into single-ion values. Both these steps require the making of assumptions, as detailed in the following paragraphs.

Caesium hexachlororhenate(IV) and hexabromorhenate(IV) both crystallise with the K<sub>2</sub>[PtCl<sub>6</sub>] (anti-fluorite) structure, with four molecules per unit cell. The unit-cell parameters are  $a_0 = 10.260$  and  $10.685$  Å respectively.<sup>13</sup> From this information the lattice energies of these two salts can be calculated in a variety of ways.\* We chose to use the Born-Mayer equation,<sup>14</sup> with a value for  $\rho$  of 0.345 Å and a Madelung constant<sup>15</sup> of 5.03879. Thence the estimated lattice energies are -1 453 and -1 399 kJ mol<sup>-1</sup> respectively, and the lattice enthalpies at 298.2 K are -1 460 and -1 406 kJ mol<sup>-1</sup>. From these calculated lattice enthalpies and measured enthalpies of solution, the sums of the enthalpies of hydration of the (gaseous) constituent ions are -1 372 kJ mol<sup>-1</sup> for caesium hexachlororhenate(IV) and -1 312 kJ mol<sup>-1</sup> for caesium hexabromorhenate(IV).

These sums of ionic-hydration enthalpies cannot be separated into their individual ion constituents without making an assumption. We chose to use the assumption that the single-ion hydration enthalpy of the proton is -1 091 kJ mol<sup>-1</sup>.<sup>16</sup> Thence the single-ion hydration enthalpy for the caesium cation is -264 kJ mol<sup>-1</sup>, and those for the hexachlororhenate(IV) and hexabromorhenate(IV) anions are -845 and -784 kJ mol<sup>-1</sup> respectively. This value of -845 kJ mol<sup>-1</sup> for the chloro-anion compares favourably with that of -827 kJ mol<sup>-1</sup> derived from direct calorimetric determination<sup>2</sup> of the enthalpy of solution of potassium hexachlororhenate(IV). It is impossible to put statistically meaningful uncertainty limits to the preceding single-ion hydration enthalpies for the hexachlororhenate(IV) and hexabromorhenate(IV) anions. The uncertainties in these values which derive from our experimental determination of enthalpies of solution are less than  $\pm 10$  kJ mol (see above). The uncertainties derived from the absolute value used for the single-ion hydration enthalpy for the proton are *ca.*  $\pm 10$  kJ mol<sup>-1</sup>.<sup>15</sup> In the

\* Methods of calculating lattice energies for compounds of the type M<sub>2</sub>AX<sub>6</sub> have recently been discussed, with the consequences of the use of various formulae and assumptions fully described (M. Webster and P. H. Collins, *J.C.S. Dalton*, 1973, 588; M. W. Lister, S. C. Nyburg, and R. B. Poyntz, *J.C.S. Faraday I*, 1974, 70, 685).

present state of knowledge concerning the calculation of lattice energies for salts of this type it is impossible to assess the uncertainties from this source. However comparisons between these results and those for other anions, especially of similar type (*cf.* following paragraph), will be valid provided that the lattice energies are calculated by similar methods.

Although few values for single-ion hydration enthalpies of polyatomic anions of the type [MX<sub>6</sub>]<sup>n-</sup> (X = halogen) are quoted in reviews and textbooks, it is possible to estimate these for several such anions from published solubility data and known crystal structures. We carried out this procedure for some hexachloro- and hexabromo-metallates which are closely related to the hexahalogenorhenates(IV) which form the subject of this paper. The solubility data used in calculating enthalpies of solution are quoted in Table 2; the calculations of enthalpies of solution were carried out on the assumption that activity coefficients for these sparingly soluble salts are invariant with temperature. All the salts listed in Table 2 crystallise with the K<sub>2</sub>[PtCl<sub>6</sub>] structure;

TABLE 2  
Computed enthalpies of solution ( $\Delta H_{\text{soln}}$ ) of salts A<sub>2</sub>MX<sub>6</sub> in water

Salt	Ref.	T/K	<i>n</i> <sup>a</sup>	$\Delta H_{\text{soln}}$ <sup>b/</sup> kJ mol <sup>-1</sup>	Standard error of the mean/ kJ mol <sup>-1</sup>
Cs <sub>2</sub> [ReCl <sub>6</sub> ]	<i>c</i>	273.2—295.1	19	+88	4
Cs <sub>2</sub> [ReBr <sub>6</sub> ]	<i>c</i>	273.2—300.7	15	+96	8
Cs <sub>2</sub> [PtCl <sub>6</sub> ]	<i>d</i>	273.2 and 373.2	2	+70	
K <sub>2</sub> [PtCl <sub>6</sub> ]	<i>e</i>			+56	
K <sub>2</sub> [PtBr <sub>6</sub> ]	<i>e</i>			+51	
[H <sub>4</sub> N] <sub>2</sub> [PtCl <sub>6</sub> ]	<i>f</i>	273.3—372.2	12	+62	1
[H <sub>4</sub> N] <sub>2</sub> [PtBr <sub>6</sub> ]	<i>f</i>	273.4—372.2	12	+54	2
[H <sub>4</sub> N] <sub>2</sub> [IrCl <sub>6</sub> ]	<i>f, g</i>			+61 <sup>h</sup>	

<sup>a</sup> Number of solubility determinations. <sup>b</sup> Assuming that activity coefficients do not vary with temperature. <sup>c</sup> This work. <sup>d</sup> 'Handbook of Chemistry and Physics,' 53rd edn., ed. R. C. Weast, Chemical Rubber Co., Cleveland, Ohio, 1973, pp. B63 *et seq.* <sup>e</sup> 'Handbook of Chemistry,' 10th edn., ed. N. A. Lange, McGraw-Hill, New York, 1967. <sup>f</sup> E. H. Archibald and J. W. Kern, *Trans. Roy. Soc. Canada*, 1917, 11, 7. <sup>g</sup> E. Rimbach and F. Korten, *Z. anorg. Chem.*, 1907, 52, 406. <sup>h</sup> Mean value.

their lattice parameters are listed in Table 3. Lattice energies, again calculated using the Born-Mayer equation<sup>14</sup> with  $\rho = 0.345$  Å and a Madelung constant<sup>15</sup> of 5.03879, are also given in Table 3. From the respective lattice enthalpies and enthalpies of solution, single-ion hydration enthalpies for the various hexahalogeno-anions were calculated in the manner, and using the assumptions, described above for the hexahalogenorhenates(IV). The ranges of values for the single-ion hydration enthalpies of the [MCl<sub>6</sub>]<sup>2-</sup> and [MBr<sub>6</sub>]<sup>2-</sup> anions are small, since the radius of each hexahalogeno-anion is dominated by the large chlorides

<sup>13</sup> H. J. Berthold and G. Jakobson, *Angew. Chem. Internat. Edn.*, 1964, 3, 445.

<sup>14</sup> W. E. Dasent, 'Inorganic Energetics,' Penguin, London, 1970, p. 75.

<sup>15</sup> Ref. 1(a), p. 19.

<sup>16</sup> H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, 1963, 59, 1126; D. R. Rosseinsky, *Chem. Rev.*, 1965, 65, 467.

or bromides. Indeed the uncertainties in the individual anion values are comparable with the range, and it is therefore not possible to tell whether the expected trend of anion-hydration enthalpies with anion radius obtains.

There do not appear to be any other published single-ion hydration enthalpies for rhenium-containing complex

TABLE 3  
Unit-cell parameters and calculated lattice energies ( $U_L$ )  
for salts  $A_2MX_6$

Salt	$a/\text{\AA}$	$U_L/\text{kJ mol}^{-1}$
$\text{Cs}_2[\text{ReCl}_6]$	10.260 <sup>a</sup>	-1 453
$\text{Cs}_2[\text{ReBr}_6]$	10.685 <sup>a</sup>	-1 399
$\text{Cs}_2[\text{PtCl}_6]$	10.215 <sup>b</sup>	-1 459
$\text{K}_2[\text{ReCl}_6]$	9.840 <sup>a</sup>	-1 506
$\text{K}_2[\text{PtCl}_6]$	9.755 <sup>b</sup>	-1 521
$\text{K}_2[\text{PtBr}_6]$	10.270 <sup>b</sup>	-1 451
$[\text{H}_4\text{N}]_2[\text{PtCl}_6]$	9.858 <sup>b</sup>	-1 507
$[\text{H}_4\text{N}]_2[\text{PtBr}_6]$	10.370 <sup>b</sup>	-1 439
$[\text{H}_4\text{N}]_2[\text{IrCl}_6]$	9.870 <sup>b</sup>	-1 505

<sup>a</sup> From ref. 13. <sup>b</sup> R. W. G. Wyckoff, 'Crystal Structures,' 2nd edn., Interscience, New York, 1964, vol. 3.

anions with which to compare our results for the two hexahalogenorhenates(IV). One can estimate a value for the perrhenate anion from the published solubility data and crystal structure of potassium perrhenate. There is disagreement in the literature over the enthalpy of solution of potassium perrhenate in water. An early calorimetric determination (at 21.7 °C) gave +13.8 kcal mol<sup>-1</sup> (58 kJ mol<sup>-1</sup>);<sup>17</sup> subsequent estimates from the temperature variation of solubility gave 7.63 (ref. 18) and 7.68 (ref. 19) kcal mol<sup>-1</sup> (31.9 and 32.1 kJ mol<sup>-1</sup> respectively). Unfortunately, these authors plotted logarithms of solubilities rather than of solubility products against reciprocal temperatures, and are therefore a factor of two in error; more unfortunately these erroneous values rather than the earlier calorimetric determination are quoted in a current monograph on rhenium chemistry.<sup>20</sup> We computed an enthalpy of solution of potassium perrhenate in water of  $64.5 \pm 1.3$  kJ mol<sup>-1</sup> from the values given in ref. 18 and  $61.2 \pm 1.1$  kJ mol<sup>-1</sup> from some earlier independent solubility data,<sup>21</sup> both of which estimates are in tolerable agreement with the calorimetric value which we shall use here. Potassium perrhenate crystallises in the scheelite ( $\text{CaWO}_4$ ) lattice, with four molecules in the unit cell and dimensions of  $a = 5.680$  and  $c = 12.703$  Å.<sup>22</sup> Each rhenium has four nearest potassium ions at 4.016 Å, and four potassiums and four rheniums at 4.260 Å. Using the value of 4.016 Å for  $r_c + r_a$  in Kapustinskii's equation,<sup>23</sup> a lattice energy of -547 kJ mol<sup>-1</sup> was calculated. Thence by the procedures used above, a single-ion hydration enthalpy of -172 kJ mol<sup>-1</sup> was estimated for the perrhenate anion. In accord with an electrostatic model for ion hydration, this value is somewhat smaller

<sup>17</sup> W. A. Roth and G. Becker, *Z. phys. Chem.*, 1932, **A159**, 27.

<sup>18</sup> W. T. Smith, *J. Amer. Chem. Soc.*, 1946, **68**, 394.

<sup>19</sup> W. T. Smith and S. H. Long, *J. Amer. Chem. Soc.*, 1948, **70**, 354.

<sup>20</sup> R. Colton, 'The Chemistry of Rhenium and Technetium,' Interscience, Sydney, 1965, p. 38.

than that for the permanganate ion<sup>1</sup> and much less than those reported above for the hexahalogenorhenates(IV). In turn these latter hydration enthalpies are smaller than those for the considerably smaller sulphate anion.<sup>1</sup>

*Solubilities in Mixed Aqueous Solvents.*—We have previously tried to correlate the solubility of sodium hexahydroxoantimonate(V) in a range of water-rich mixed aqueous solvents with Grunwald-Winstein solvent  $Y$  values.<sup>9</sup> In that case there was a moderately satisfactory correlation ( $3.49 \geq Y > ca. 1$ ), though the correlation line was curved rather than linear. We decided to investigate the solubility of caesium hexachlororhenate(IV) in the same range of mixed aqueous solvents, as a better and more linear correlation might be expected here; this anion resembles more closely the

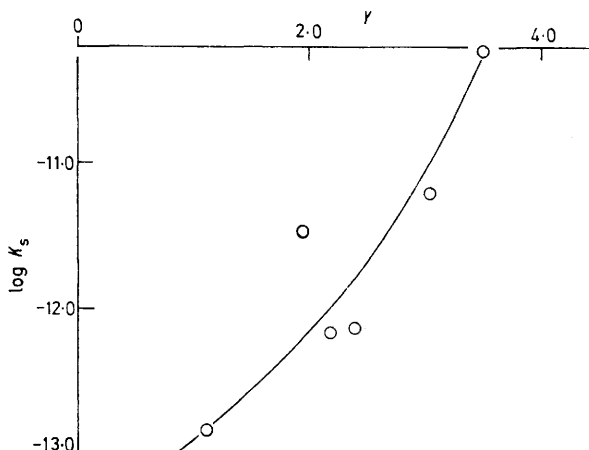
TABLE 4

Single-ion hydration enthalpies ( $\Delta H_{si}$ ) for some  $[\text{MX}_6]^{2-}$  anions

Anion	Counter ion	$\Delta H_{si}/\text{kJ mol}^{-1}$	Mean $\Delta H_{si}/\text{kJ mol}^{-1}$	$M^{4+}$ Radius */Å
$[\text{ReCl}_6]^{2-}$	$\text{Cs}^+$	-845	-836	0.72
$[\text{ReCl}_6]^{2-}$	$\text{K}^+$	-827		
$[\text{IrCl}_6]^{2-}$	$\text{NH}_4^+$	-834	-834	0.64
$[\text{PtCl}_6]^{2-}$	$\text{Cs}^+$	-868		
$[\text{PtCl}_6]^{2-}$	$\text{K}^+$	-829	-844	0.65
$[\text{PtCl}_6]^{2-}$	$\text{NH}_4^+$	-834		
$[\text{ReBr}_6]^{2-}$	$\text{Cs}^+$	-784	-784	0.72
$[\text{PtBr}_6]^{2-}$	$\text{K}^+$	-764	-769	0.65
$[\text{PtBr}_6]^{2-}$	$\text{NH}_4^+$	-774		

\* B. R. Eggins, 'Chemical Structure and Reactivity,' Macmillan, London, 1972, p. 85.

chloride ion whose solvation determines the reactivities that define solvent  $Y$  values. We also investigated whether the solubilities of caesium hexachlororhenate(IV)



Dependence of the decadic logarithm of the solubility product of caesium hexachlororhenate(IV) ( $\log K_s$ ) on solvent  $Y$  values in water and in mixed aqueous solvents (data from Table 5)

correlate with other solvent parameters, and indeed with solubilities of sodium hexahydroxoantimonate(V).

Measured concentrations of hexachlororhenate(IV)

<sup>21</sup> H. Holemann and W. Kleese, *Z. anorg. Chem.*, 1938, **237**, 172.

<sup>22</sup> J. C. Morrow, *Acta Cryst.*, 1960, **13**, 443.

<sup>23</sup> Ref. 1 (a), p. 35.

and derived (concentration) solubility products are reported, with appropriate values for the various solvent parameters, in Table 5. The plot of logarithms of solubility products against solvent  $Y$  values (Figure) was curved, but the points fell tolerably close to a common curve. Plots of logarithms of solubility products against other solvent parameters gave poorer correlations, whose relative curvature and scatter could be roughly judged from the computed standard errors of least-mean-squares straight lines. These standard errors were 33% for the attempted correlations with  $E_T$ , 36%

3.7 Å for  $[\text{Sb}(\text{OH})_6]^-$ ; cation radii are 1.69 Å for  $\text{Cs}^+$ , 0.95 Å for  $\text{Na}^+$  (ref. 24).

#### EXPERIMENTAL

Caesium hexachlororhenate(IV) and hexabromorhenate(IV) were prepared by reducing solutions of ammonium or potassium perrhenate with iodide ions and then precipitating with caesium chloride or bromide respectively.<sup>25</sup> Saturated solutions of these salts were prepared by equilibrating an excess of solid with the appropriate solvent in a well stirred, thermostatted, reaction vessel. Equilibration times for the hexabromo-complex had to be less than

TABLE 5

Measured anion concentrations and calculated (concentration) solubility products ( $K_s$ ) for saturated solutions of caesium hexachlororhenate(IV) in binary mixed aqueous solvents at 298.2 K; the empirical solvent parameters ( $E_T, S, Y$ ), mol fraction ( $x_2$ ), and dielectric constant ( $D$ ) are listed for each solvent mixture

Non-aqueous component (% by volume)	$x_2$	$D^a$	$E_T^b$	$S^c$	$Y^d$	$10^5[\text{ReCl}_6^{2-}]$ mol dm <sup>-3</sup>	$10^{13}K_s$ mol <sup>3</sup> dm <sup>-9</sup>
Water	1.000	78.5	63.1	0.154	3.493	24.72	604.1
Methanol (40)	0.229	63.42	59.2	0.129	2.391	5.77	7.7
Ethanol (20)	0.072	69.35	60.0	0.144	3.051	11.67	63.6
(40)	0.171	58.47	56.6	0.126	2.196	5.57	6.9
(60)	0.317	46.44	55.0	0.097	1.124	3.34	1.5
Dioxan (40)	0.124	43.84	55.6	0.110	1.945	9.54	34.8

<sup>a</sup> J. Timmermans, 'The Physicochemical Constants of Binary Systems in Concentrated Solutions,' Interscience, London, 1959, vol. 1. <sup>b</sup> C. Reichardt, 'Lösungsmittelleffekte in der Organischen Chemie,' Verlag Chemie, Weinheim, 1968. <sup>c</sup> S. Brownstein, *Canad. J. Chem.*, 1960, **38**, 1590. <sup>d</sup> E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846.

for the dielectric-constant function  $(D - 1)/(2D + 1)$ , 37% for mol fraction, 42% for  $S$ , and 47% for  $D$ . A plot of logarithms of solubility products for caesium hexachlororhenate(IV) against those of sodium hexahydroxoantimonate(V) gave better results; \* the standard error of 13% arises mainly from the slight curvature of the correlation line. The gradient of this last-named plot was  $1.5 \pm 0.2$ ; the solubility of caesium hexachlororhenate(IV) is more sensitive to solvent variation than that of sodium hexahydroxoantimonate(V). This difference may presumably be attributed primarily to the 2- charge on the hexachlororhenate(IV) anion {estimated anion radii are 4.2 Å for  $[\text{ReCl}_6]^{2-}$ ,

ca. 1 h, so that aquation of this complex was negligible. Anion concentrations in the saturated solutions were determined spectrophotometrically. For the hexachloro-anion, the optical density at the frequency of maximum absorption at  $35\,340\text{ cm}^{-1}$  ( $\epsilon\ 13\,100\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ) † was monitored; for the hexabromo-anion, the maximum absorption frequency is at  $28\,330\text{ cm}^{-1}$  ( $\epsilon\ 9\,900\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ).

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\* Correlations between the solubilities of several aromatic compounds in aqueous-organic binary-solvent mixtures have recently been described and used as the basis of a new empirical solvent parameter  $g(S)$  (P. Letellier, *Bull. Soc. chim. France*, 1973, 1569; P. Letellier and R. Gaboriaud, *J. Chim. phys. Physiochim. Biol.*, 1973, **70**, 941).

† Cf.  $\epsilon = 12\,750\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$  at  $35\,500\text{ cm}^{-1}$  (V. W. Meloche and R. L. Martin, *Analyt. Chem.*, 1956, **28**, 1671).

<sup>24</sup> Ref. 1 (a), pp. 40–41.

<sup>25</sup> R. D. Peacock, 'The Chemistry of Technetium and Rhenium,' Elsevier, Amsterdam, 1966, p. 28.