Solubility of Sodium Hexahydroxoantimonate in Water and in Mixed Aqueous Solvents

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The enthalpy of solution of sodium hexahydroxoantimonate in water has been determined, from measurements of its solubility as a function of temperature, as +33 kJ mol^{-1}. Hence the enthalpy of hydration of the (gaseous) hexahydroxoantimonate anion has been estimated as -124 kJ mol^{-1} (assuming an enthalpy of hydration of -1091 kJ mol^{-1} for the proton). The variation of the solubility of sodium hexahydroxoantimonate with solvent composition in a range of binary mixed aqueous solvents has been determined.

SODIUM HEXAHYDROXOANTIMONATE, $Na[Sb(OH)_6]$,[1] is one of the few sodium salts which are sparingly soluble in water. Quantitative information regarding its solubility appears limited to values of 0·03 g/100 cm^3 at 12·3 °C and 0·3 g/100 cm^3 at 100 °C.[2] We have now determined the solubility of this salt in water at several temperatures in the range 298·2—353·2 K, in order to estimate its enthalpy and entropy of solution. Thence we have estimated values for the enthalpy and entropy of hydration of the (gaseous) hexahydroxoantimonate anion.

We have also investigated the variation of the solubility of sodium hexahydroxoantimonate with solvent composition in several series of mixed aqueous solvents. Solubilities in methanol–, ethanol–, acetone–, and dioxan–water mixtures have been compared with several empirical solvent parameters,[3] and a reasonable correlation with the kinetically based Grunwald–Winstein Y values [4] found. As some properties of solutes in t-butyl alcohol–water mixtures are particularly sensitive to solvent composition,[5] we have determined the solubility of sodium hexahydroxoantimonate in a range of such solvent mixtures to discover whether a similar sensitivity is shown by the solubility of this salt. Hydrogen peroxide–water mixtures are also of some current interest, in view of the fact that these mixtures are almost isodielectric,[6] and characterised by a negative excess molar Gibbs function of mixing, G^E. [In contrast the other solvent mixtures referred to above are all characterised by a positive G^E (ref. 7).] Furthermore added hydrogen peroxide has an unusual effect on reactivities, as for instance recently reported for t-butyl chloride solvolysis.[8] Solubilities of sodium hexahydroxoantimonate in hydrogen peroxide–water mixtures have now been shown to exhibit unusual features similar to those established in the kinetic studies.

RESULTS AND DISCUSSION

Solubility in Water.—The sodium salt is the least soluble of the alkali metal hydroxoantimonates. At room temperature the solubility trend is $Cs^+ > Rb^+ > K^+ > Na^+ < Li^+$; the lithium salt is only slightly more soluble than the sodium salt. Solubilities of the sodium salt at temperatures in the range 298—353 K (at ambient pressure) are reported in Table 1. A plot of logarithms of these solubilities, or of the solubility products, against reciprocal temperature is a good straight line. The published value [2] for the solubility of sodium hexa-

TABLE 1

The solubility of sodium hexahydroxoantimonate in aqueous solution

Temperature/K	298·2	308·2	323·2	343·2	353·2
10^3 Solubility/mol dm^{-3}	3·3	4·4	6·0	8·4	9·3

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[1] N. Schrewelius, *Z. anorg. Chem.*, 1938, **238**, 241.

[2] 'Handbook of Chemistry and Physics,' 53rd edition. ed. R. C. Weast, Chemical Rubber Company, Cleveland, Ohio, 1972, p. B-136.

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

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

[5] See, *e.g.*, M. J. Blandamer and M. F. Fox in 'Water—a Comprehensive Treatise,' ed. F. Franks, vol. 2, Plenum Press, New York, 1973, ch. 8.

[6] P. M. Gross and R. C. Taylor, *J. Amer. Chem. Soc.*, 1950, **72**, 2075.

[7] F. Franks and D. S. Reid, ch. 5 of ref. 5.

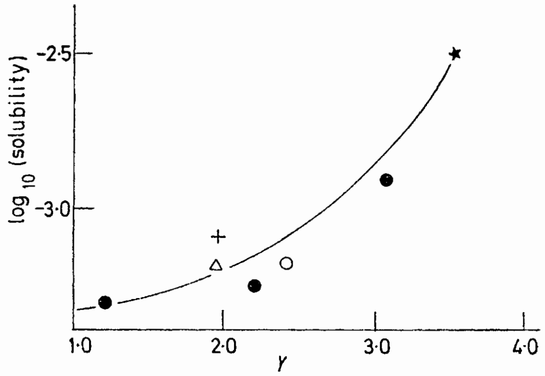
[8] M. J. Blandamer and J. R. Membrey, *J.C.S. Chem. Comm.*, 1973, 514.

hydroxoantimonate at 373·2 K falls on this line, but that at 285·5 K does not.

The enthalpy of solution of sodium hexahydroxoantimonate can be estimated[9] from the variation of logarithms of solubility products with reciprocal temperature. A least-mean-squares treatment of the results of Table 1 yields an enthalpy of solution of $+33{\cdot}1$ kJ mol^{-1}. The 90% confidence limits[10] for this value are $\pm 3{\cdot}3$ kJ mol^{-1}. This treatment assumes that the mean ionic activity coefficient does not vary with temperature. In fact the mean ionic activity coefficient at 298 K can be estimated[11] as 0·94; the variation of the activity coefficient with temperature is unlikely[12] to make a difference of more than 2 kJ mol^{-1} in the estimated enthalpy of solution. From the measured solubility at 298·2 K and an assumed mean ionic activity coefficient of 0·94, we calculate that the standard free energy change ΔG° (solid $\longrightarrow$ solution) for sodium hexahydroxoantimonate is $+29$ kJ mol^{-1}. Here the solution standard state is taken as the hypothetical solution where $\gamma_{\pm} = 1{\cdot}0$ and $c = 1$ mol dm^{-3}. The entropy of solution of this salt can be estimated to be $+13$ J K^{-1} mol^{-1}.

Sodium hexahydroxoantimonate crystallises in a tetragonally distorted modification of the sodium chloride structure, with four molecules in the unit cell, whose dimensions are $a_0 = b_0 = 8{\cdot}01$ Å and $c_0 = 7{\cdot}88$ Å.[13] The lattice energy can be calculated by the use of the Born–Mayer equation[14] as -557 kJ mol^{-1}; the lattice enthalpy at 298·2 K as -562 kJ mol^{-1}.[15] From this value and our experimentally determined value of $+33$ kJ mol^{-1} for the enthalpy of solution of sodium hexahydroxoantimonate, we can deduce a value of -529 kJ mol^{-1} for the sum of the enthalpies of solvation of the (gaseous) constituent ions. In order to separate this sum into individual enthalpies of solvation of the ions it is necessary to make some basic assumption about the enthalpy of solvation of some reference ion, for example the proton.[16] We shall assume an enthalpy of hydration of the proton of -1091 kJ mol^{-1};[17] the enthalpy of hydration of the sodium ion is then -405 kJ mol^{-1}.[18] Hence the enthalpy of hydration of the hexahydroxoantimonate anion is -124 kJ mol^{-1}. In general the magnitudes of enthalpies of hydration of ions decrease as ionic radii increase (at constant charge). It is not, therefore, surprising that the magnitude of the enthalpy of hydration of the hexahydroxoantimonate anion is smaller than those reported[18] for the smaller mononegative anions perchlorate (-208 kJ mol^{-1}) and permanganate (-229 kJ mol^{-1}).

Solubility in Mixed Aqueous–Organic Solvents.—There have been few systematic studies of the solubility of inorganic compounds in mixed aqueous solvents. We are interested to see whether solubilities correlate with any of the numerous empirical solvent parameters.[3] In particular, we are interested in using solubility data in the analysis of the kinetics of inorganic substitution reactions in mixed aqueous solvents. Thus a variation in thermodynamic activation parameters with change in solvent yields information concerning the changes in energy differences between initial and transition states. In principle, the variation in solubilities of a salt with solvent can provide information about the changes in initial state energies. Therefore it should be possible to calculate, by difference, the changes in transition state energies and so the complete details of the kinetics will emerge. Our first test was to discover whether solubilities in mixed solvents could be correlated with Grunwald–Winstein Y values[4] which have proved so valuable in the analysis of kinetic data, in inorganic[19] as well as in organic systems.



Solubility of Na[Sb(OH)$_6$], at 298 K, as a function of solvent Y values for aqueous–organic solvent mixtures. Cosolvents: ○, methanol (40%); ●, ethanol (20, 40, 60%); △, acetone (40%); +, dioxan (40%); ★, water. The units of the solubilities are mol dm^{-3}

Solubilities of sodium hexahydroxoantimonate in a range of mixed aqueous solvents have been measured; the results are plotted against the respective solvent Y values[3,4] in the Figure. There is a tolerable correlation, albeit a curved rather than a rectilinear one.

Plots of a variety of spectroscopic, thermodynamic, and kinetic parameters against mole fraction composition for t-butyl alcohol–water mixtures show marked changes of slope or extrema, often at a mole fraction of around

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[9] Iw. Schroder, *Z. phys. Chem.*, 1893, **11**, 449; A. T. Williamson, *Trans. Faraday Soc.*, 1944, **40**, 421.

[10] See, *e.g.*, E. S. Swinbourne, 'Analysis of Kinetic Data,' Nelson, London, 1971, pp. 7—9.

[11] R. B. Heslop, 'Numerical Aspects of Inorganic Chemistry,' Elsevier, Amsterdam, 1970, p. 138.

[12] *Cf.*, *e.g.*, R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' 2nd edn., Butterworths, London, 1965, pp. 480—481.

[13] R. W. G. Wyckoff, 'Crystal Structures,' 2nd edn., Wiley, New York, 1965, vol. 3, p. 329.

[14] N. N. Greenwood, 'Ionic Crystals, Lattice Defects, and Nonstoichiometry,' Butterworths, London, 1968, p. 28.

[15] T. C. Waddington, in 'Advances in Inorganic Chemistry and Radiochemistry,' vol. 1, Academic Press, New York, 1959, pp. 158—221.

[16] D. R. Rosseinsky, *Chem. Rev.*, 1965, **65**, 467.

[17] H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, 1963, **59**, 1126.

[18] These enthalpies of hydration are derived from p. 27 of ref. 14, but with the values cited there amended to refer to an enthalpy of hydration of the proton of -1091 kJ mol^{-1} (ref. 17).

[19] See, *e.g.*, C. H. Langford, *Inorg. Chem.*, 1964, **3**, 228; J. Burgess, *J.C.S. Dalton*, 1973, 825; 'Inorganic Reaction Mechanisms,' ed. J. Burgess, Chem. Soc. Specialist Periodical Report, London, 1972, vol. 1, pp. 202—203, and 1974, vol. 3 in the press; and refs. therein.

0·035 and/or 0·1 of t-butyl alcohol (at 298·2 K).[5] The trend of the solubility of sodium hexahydroxoantimonate with solvent composition (Table 2) shows no such marked features.

TABLE 2

The solubility of sodium hexahydroxoantimonate in water–t-butyl alcohol mixtures, at 298·2 K

Mole fraction Bu^tOH	0	0·02	0·04	0·07	0·10	0·15
10^3 Solubility/mol dm^{-3}	3·3	2·5	2·0	1·2	0·9	0·6

Solubility in Water–Hydrogen Peroxide Mixtures.—The reactivity trend for the solvolysis of t-butyl chloride in water–hydrogen peroxide mixtures is the opposite from the trends reported for solvolysis of this substrate in water–organic cosolvent mixtures. Only in the water–hydrogen peroxide system does the rate constant increase as the mole fraction of the non-aqueous component increases.[8] We therefore wished to ascertain whether this kinetic anomaly was paralleled by a similar initial-state property anomaly, in other words whether solubility patterns are different in the two types of mixed aqueous solvents. For all the organic cosolvents mentioned in the previous section, the solubility of sodium hexahydroxoantimonate decreases as the proportion of organic cosolvent increases. In contrast, the results quoted in Table 3 show that the solubility of this salt increases as the proportion of hydrogen peroxide increases; the solubility mirrors the kinetic pattern described above.

Although this is insufficient information on which to base a general conclusion, it does prompt the suggestion that the dependence of solubility on the composition of a mixture could be related to the sign and magnitude of G^E as well as the solubility differences in the two pure components. Further work will be necessary to test this simple hypothesis.

TABLE 3

The solubility of sodium hexahydroxoantimonate in water–hydrogen peroxide mixtures, at 298·2 K

Mole fraction H_2O_2	0	0·017	0·034	0·052
10^3 Solubility/mol dm^{-3}	3·3	4·1	4·8	5·8

EXPERIMENTAL

Samples of sodium hexahydroxoantimonate were prepared by the addition of antimony pentachloride to dilute aqueous solutions of sodium hydroxide. Solvent mixtures were prepared from AnalaR materials. The concentration of hydrogen peroxide in mixtures of this solvent with water was checked by iodometric analysis.[20] Concentrations of dissolved sodium hexahydroxoantimonate were estimated by flame photometric determination of the sodium, with great care being lavished on the use of appropriate blanks and reference solvent mixtures. The standard deviations of the results cited in Tables 1—3 are 5% or less; each value in these Tables represents the mean of at least three independent determinations.

We are grateful to Mrs. C. M. Stokes for much experimental assistance.

[3/2350 *Received, 16th November, 1973*]

[20] A. I. Vogel, ' Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1961, p. 363.