Inorganica Chimica Acta, 58 (1981) 135–142
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Enthalpies of Solution and Solubilities of Tin(IV) Iodide and of Germanium(IV) Iodide

J. BURGESS and J. KIJOWSKI
Chemistry Department, University of Leicester, Leicester LE1 7RH, U.K.

Received June 22, 1981

Enthalpies of solution of tin(IV) iodide and of germanium(IV) iodide are reported for a variety of polar and non-polar solvents. Correlations with Gutmann donor numbers and enthalpies of vaporisation are discussed. Solubilities of tin(IV) iodide and of germanium(IV) iodide are reported in a range of non-polar solvents, at 298.2 K. These and earlier results, for these compounds and for silicon(IV) iodide and iodine, are discussed by regular solution theory in terms of Hildebrand's solubility parameter δ. Entropies of solution have been calculated for tin(IV) iodide dissolving in non-polar solvents.

Introduction

The solubility of tin(IV) iodide has been measured in a range of liquids, organic [1–16] and inorganic [17, 18], at a variety of temperatures by various authors, and much discussed [19]. Enthalpies of solution have attracted very much less attention. A value for dissolution in carbon tetrachloride was reported in 1925 [20] and a second, somewhat different, determination reported in 1977 [21]. Enthalpies of solution (reaction) have been measured for dimethyl sulphoxide [22] and for formamide [23]. Both for intrinsic interest and in view of possible relevance to lamp manufacture we have determined enthalpies of solution of tin(IV) iodide in a range of aprotic solvents, and enthalpies of interaction with a few polar solvents. We have also measured some solubilities, to complement and extend available data. We have, for comparison purposes, carried out a parallel series of measurements on the much-less-studied germanium(IV) iodide. Our results are compared with published results for silicon(IV) iodide and for iodine, and discussed in relation to such solvent parameters as Gutmann donor numbers, *DN*, for enthalpies [24, 25] and Hildebrand's δ parameter for solubilities [26].

Experimental

Tin(IV) iodide was prepared by the published procedure [27] and recrystallised from dichloromethane (m.p. 417–419 K; lit. 417–418 K [28]). Germanium(IV) iodide (Pierce Inorganics) was also recrystallised from dichloromethane (m.p. 418 K; lit. 417 K [29] or 419 K [30]). Solvents were purified by standard procedures [31].

The calorimeter assembly used has been described previously [32]. It was calibrated periodically against the enthalpy of solution of potassium chloride in water (17.31 kJ mol^{-1} [33]). Solubilities were determined by equilibrating pure solvent and an excess of tin(IV) or of germanium(IV) iodide at 298.2 K in the dark. Concentrations of the resultant saturated solutions were estimated spectrophotometrically and by evaporation of aliquots to dryness. It was necessary to determine molar extinction coefficients for each solvent, as these quantities are known to be solvent-dependent for these compounds [34] (our results are included in Table III below). Kinetic experiments were carried out in the thermostatted cell compartment of a Pye-Unicam SP800 spectrophotometer.

Results

Enthalpies of solution of tin(IV) iodide and of germanium(IV) iodide in a range of hydrocarbon and halogenated organic solvents are reported in Table I. This Table also includes relevant published values [4, 20, 21] and estimated solution enthalpies calculated from the reported temperature dependence of solubilities [5, 9, 10, 35]. These van't Hoff estimates are all somewhat lower than our direct calorimetric measurements, but there are no dramatic differences. Enthalpies of interaction, in other words of solution and of subsequent reaction, of tin(IV) iodide and of germanium(IV) iodide in some polar solvents are reported in Table II [36–39]. These values do not depend on amounts used (typically samples of between 0.03 and 0.08 g were used, with 35 cm^3 solvent). There is satisfactory agreement between our results and the earlier published value [22] in the case of dissolution of tin(IV) iodide in dimethyl

TABLE I. Enthalpies of Solution, kJ mol^{-1}, of Tin(IV) Iodide and of Germanium(IV) Iodide, in Non-polar Solvents at 298.2 K.

Solvent	SnI_4		GeI_4	
	Calorimetric[a]	Van't Hoff[b]	Calorimetric[a]	Van't Hoff[b]
CCl_4	27.1 ± 0.5[c]	22.9[d], 23.4[e], 26.2[f]	32.7 ± 2.5	28.2[g]
$CHCl_3$	29.4 ± 0.4	23.4[d]	27.2 ± 2.1	
CH_2Cl_2	45.6 ± 1.4			
$CCl_2{:}CCl_2$	26.3 ± 0.2		21.0 ± 0.7	
$CHCl{:}CCl_2$	24.8 ± 0.6			
t-$CHCl{:}CHCl$	36.4 ± 1.2			
CH_3CCl_3	25.3 ± 1.5			
$CHCl_2CHCl_2$	22.9 ± 0.7			
$CH_2ClCHCl_2$	24.6 ± 0.8		26.3 ± 1.2	
CH_3CHCl_2			36.2 ± 0.8	
CH_2ClCH_2Cl	27.9 ± 1.7		29.2 ± 2.8	
$CHBr_3$	23.5 ± 1.2	19.0[e]		
CH_2Br_2	33.8 ± 2.9			
$CHBr_2CHBr_2$	15.0 ± 0.9			
CH_2BrCH_2Br	24.2 ± 0.2	20.4[d]		
CH_3CH_2Br	61.6 ± 0.8		50.2 ± 1.0	
CH_3I	33.2 ± 1.2		45.0 ± 1.3	
CH_3CH_2I	21.3 ± 1.5			
n-C_6H_{14}	39.5 ± 2.0			
n-C_7H_{16}	25.8 ± 0.9			13.0[g]
n-C_8H_{18}	23.9 ± 0.9			
iso-C_8H_{18}	32.1 ± 2.6			
c-C_6H_{12}	27.9 ± 2.0	27.0[f]		
C_6H_6	33.6 ± 2.3	21.1[d], 25.9[f]		25.5[g]
$C_6H_5CH_3$	23.6 ± 0.9	19.3[d]		23.9[g]

[a] This work, at 298.2 K, means of six estimates, quoted uncertainties are 90% confidence limits. [b] From the temperature dependence of published solubilities. [c] 15.9 kJ mol^{-1} (temperature unspecified) [20]; 21.8 kJ mol^{-1} [21]; 22.0 kJ mol^{-1} (295.4 K) [4]. [d] Ref. [5]. [e] Ref. [9]. [f] Ref. [10]. [g] Ref. [35].

sulphoxide; less satisfactory agreement was obtained for formamide [23].

Solubilities of tin(IV) iodide and of germanium(IV) iodide in organic solvents are reported in Table III. We give solubilities in three different units to facilitate comparisons with the assorted published data. In the systems where direct comparison is possible, for solubilities in carbon tetrachloride and in chloroform, agreement with published results [5] is good.

The determination of enthalpies of solution and of solubilities proved impossible in some cases. 1,1-Dichloroethene decomposed too rapidly on removal of inhibitor; several other potential solvents (*e.g.* n- and i-pentane) proved too volatile. Tin(IV) bromide has an inconvenient melting point (304 K) and could not be loaded cleanly into ampoules for calorimetry. Enthalpies of solution could not be measured for tin(IV) iodide in acetonitrile or in propylene carbonate due to low solubilities and consequent excessively slow dissolution (for propylene carbonate a rough estimate of –60 kJ mol^{-1} was obtained). Low solubilities in some N-donor solvents also lead to difficulties arising from reaction with residual water; dissolution of tin(IV) iodide in 2,6-lutidine gave significant amounts of the hydriodide of the solvent. Problems with N-heteroaromatic basic solvents have been mentioned before, for example by Onyszchuk in connection with determining enthalpies of solution of MX_4 ($M = Si$, Ge, or Sn; $X = F$, Cl, or Br) in pyridine [41].

Discussion

Enthalpies of Solution: Non-polar Solvents

Tin(IV) iodide and germanium(IV) iodide dissolve in the solvents included in Table I without

TABLE II. Enthalpies of Solution, kJ mol^{-1}, of Tin(IV) Iodide and of Germanium(IV) Iodide in Polar Solvents, at 298.2 K (uncertainties quoted are 90% confidence limits).

Solvent	*DN*	SnI_4	GeI_4	*Cf.* I_2^{a}
Acetone	17.0	+48 ± 1	(+1)^{b}	
Methanol	23.5	−38 ± 3		+8.7
Ethanol	30.0	−43 ± 2	−30 ± 1	
i-Propanol		−60 ± 2		
Formamide^{c}	24.7	−113 ± 4^{d}		
Dimethyl sulphoxide	29.8	−151 ± 1^{e}	−188 ± 3	
Pyridine	33.1	−191 ± 3		−15.1
2,6-Lutidine	^{f}	−226 ± 5	−305 ± 5	
2,4,6-Collidine	^{f}	−233 ± 10	−303 ± 5	
Hexamethylphosphoramide	38.8^{g}	−298 ± 4		

[a] From ref. [36]. [b] Dissolution is a two-stage process; the value cited here is for the first stage, which presumably corresponds to solution of GeI_4 as the $GeI_4(acetone)_2$ adduct. [c] It is not possible to measure a simple enthalpy for DMF, *cf.* refs. [37] and [38]. [d] Cf. −75 kJ mol^{-1} [23]. [e] *Cf.* −141 kJ mol^{-1} [22]. [f] Donor numbers for these solvents are not yet available (V. Gutmann, personal communication), though there are some calorimetric data for the reaction of $SbCl_5$ with substituted pyridines in carbon tetrachloride rather than in 1,2-dichloroethane [39]. [g] Ref. [40].

TABLE III. Solubilities of Tin(IV) Iodide and of Germanium(IV) Iodide, at 298.2 K.

Solvent	δ_1^{a}	Tin(IV) iodide					Germanium(IV) iodide solubility		
			solubility^{b}						
		ϵ	wt.%	g dm^{-3}	$100x_2$	δ_2	wt.%	g dm^{-3}	$100x_2$
CCl_4	8.6		5.9^{c}	96	1.51	11.5	5.3	87	1.46
$CHCl_3$	9.2	6040	8.1^{c}	125	1.65	12.0	7.6	117	1.65
CH_2Cl_2	9.8		8.3	115	1.21	12.8	8.9	124	1.40
$CCl_2:CCl_2$	9.3	8640	6.7	112	1.87	12.0	6.8	115	2.05
$CHCl:CCl_2$		8620	9.2	140	2.07				
t-$CHCl:CHCl$	9.0	8020	9.2	121	1.54	11.9	9.2	123	1.66
CH_3CCl_3	8.5		4.6	63	1.02	11.6			
$CH_2ClCHCl_2$			5.9	87	1.31		5.5	82	1.32
CH_3CHCl_2	9.1		5.4	65	0.90	12.3	5.5	67	0.98
CH_2ClCH_2Cl	9.9	8800	6.8	88	1.13	13.0	6.8	89	1.22
CH_3CH_2Br	8.9		12.6	198	2.45	11.5	12.7	200	2.65
$CHBr_2CHBr_2$		6640	16.9^{d}	511	10.1				
CH_3I	9.9		35.5	954	11.1	10.2	39.0	1054	13.5
CH_3CH_2I	9.4		25.2	560	7.7	10.8			

[a] From ref. [19]. [b] Gravimetric determinations. Consistent values were obtained spectrophotometrically for those solvents whose ϵ values are quoted. Published data on solubilities in other solvents can be found in refs. [1] to [16]. [c] Compare values of 5.7 and 8.3 for CCl_4 and $CHCl_3$ respectively in ref. [5], and similar values in CCl_4 at 295.6 K and in $CHCl_3$ at 301.2 K [4]. [d] Spectrophotometric method only (solvent too involatile for accurate gravimetric determination).

chemical change, though there are marked interactions with the aromatic solvents [34]. Enthalpies of solution are all positive, covering the relatively small range of +15 to +62 kJ mol^{-1}. Values for germanium(IV) iodide are greater than those for tin(IV) iodide; though as one might expect there is a fairly good correlation of values for these two compounds. There is also some correlation of these solution enthalpies with those for iodine [35, 42], but here a few values do lie a long way from the best correlation line. Comparisons with silicon(IV) iodide are extremely limited; enthalpies of solution of 23.0 and

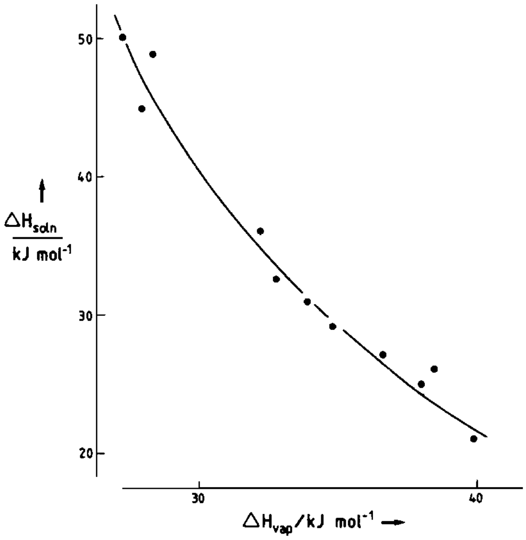

Fig. 1. Correlation of enthalpies of solution (ΔH_{soln}) of germanium(IV) iodide in non-polar solvents with enthalpies of vaporisation (ΔH_{vap}) of the respective solvents.

40.2 kJ mol^{-1} for carbon tetrachloride and for n-heptane may be estimated from the published dependence of solubilities on temperature [43]. Tetraiodide–tetrabromide–tetrachloride comparisons are almost impossible for enthalpies of solution of these Group IV elements in non-polar solvents due to the paucity of data. However an early investigation of enthalpies of solution in carbon tetrachloride revealed that the value for tin(IV) bromide was some 3 kJ mol^{-1} smaller than that for tin(IV) iodide, and the value of tin(IV) chloride about 17 kJ mol^{-1} less than that for the bromide [20]. The enthalpy of solution of tin(II) iodide in carbon tetrachloride, 15.9 kJ mol^{-1} [20], is considerably smaller than that of tin-(IV) iodide (Table I).

One might expect enthalpies of solutions in this type of system to correlate with some simple solvent properties, for example enthalpy of vaporisation, boiling point, or viscosity. In fact the correlation of enthalpies of solution for germanium(IV) iodide with enthalpies of vaporisation is, for these non-polar solvents, good (Fig. 1). A similar graph for the considerably more extensive data for tin(IV) iodide looks at first sight less satisfactory, but can in fact be analysed into parallel trends for chloro-, bromo-, iodo-, hydrocarbon, and aromatic solvents.

Enthalpies of Solution: Polar Solvents

Enthalpies of solution of tin(IV) iodide and of germanium(IV) iodide in polar solvents are generally negative, in contrast to the small positive values for non-polar solvents. But, as for the non-polar solvents, there is a correlation between values for these two iodides. Favourable solution enthalpies for polar solvents may be ascribed to strong solvation of these solutes. For several solvents of this type, octahedral solvento-adducts $MX_4(solv)_2$ are well characterised [44]. Examples include adducts with dimethyl sulphoxide [22, 45], formamide [23], dioxan [46], tetrahydrofuran [47], and a variety of amines and ketones [44, 48]. Enthalpies of solution of tin(IV) iodide correlate fairly well with Gutmann donor numbers (*DN*, [24, 25]), as shown in Fig. 2. Thus the solvation characteristics here are similar to those of Gutmann's closely related reference solute, antimony(V) chloride. Interestingly, enthalpies of solution of indium(III) and gallium(III) chlorides and iodides appear to correlate less well with *DN* values [49].

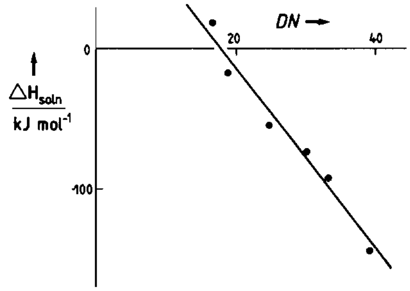

Fig. 2. Correlation of enthalpies of solution (ΔH_{soln}) of tin-(IV) iodide with Gutmann donor numbers (*DN*).

It is not possible to establish an order of solution enthalpies for the tetraiodides of tin, germanium, and silicon, firstly because there are extremely few values relating to silicon tetraiodide and secondly because although most values for the germanium compound are more negative (less positive) than for the tin compound this order is not universal. It is therefore impossible to tie in enthalpies of solution sequences with the Lewis acidity orders established for Group IV tetrahalides [50]. The dependence of solution enthalpy on halide nature can be illustrated for dimethyl sulphoxide, where solution enthalpies of −180 and *ca.* −150 kJ mol^{-1} for tin-(IV) chloride and tin(IV) bromide [51] may be compared with the Table II value of −151 kJ mol^{-1} for tin(IV) iodide. The enthalpy of solution of tin-(II) iodide in dimethyl sulphoxide, −95 kJ mol^{-1} [52], where again a disolvato-species is the likely product, is considerably smaller.

We have measured the enthalpy of solution of the adduct $SnI_4(py)_2$ [53] in pyridine, obtaining a value of +50 kJ mol^{-1}. We can thus estimate the enthalpy of addition of pyridine to tin(IV) iodide:

$$SnI_4 + 2py \rightarrow SnI_4(py)_2$$

to be −241 kJ mol^{-1}. This is a much more favourable process than the addition of tetrahydrofuran:

$SnI_4 + 2THF \rightarrow SnI_4(THF)_2$

for which the enthalpy change is -17 kJ mol^{-1} in benzene solution [47, 54]; tin(IV) iodide–benzene interaction is claimed to be negligible [47, 55]. In the dissolution of tin(IV) bromide and of tin(IV) chloride in dimethyl sulphoxide, the enthalpy pattern is similar to tin(IV) iodide–pyridine, with a large negative enthalpy of addition of two molecules of solvent to the tetrahalide indicating a very favourable process and an almost thermo-neutral dissolution of the bis-solvento-adduct in solvent [51].

Although tin(IV) iodide and germanium(IV) iodide dissolve simply as $MI_4(solv)_2$ in many of the solvents included in Table II, in some cases there are subsequent solvolysis and redox reactions, as for example in the case of water [56], primary alcohols [57], and acetone. In these cases our reported enthalpies of solution, which are measured as quickly as possible (within one minute) for technical reasons associated with the calorimeter design, refer to the initially formed species $MI_4(solv)_2$. We have conducted preliminary kinetic studies of the subsequent reactions in some cases, specifically for ranges of dichloromethane + alcohol, water + alcohol, and water + acetone solvent mixtures. The disappearance of the tin(IV) iodide charge-transfer band, monitored by repeat scan spectra, followed first-order kinetics closely in all cases. For alcohols ROH, in 3 to 50% by volume solution in dichloromethane, observed first-order rate constants are all in the range 0.5 to 2.7×10^{-3} s^{-1} (*i.e.* the half-life lies within the range 300 to 1000 s) at 298.2 K for R = Me, Et, Pr^i, Pr^n, Bu^i, Bu^s, Bu^t. Adding a little water results in a small decrease in rate. Reaction is slower in acetone-containing mixtures, rate constants being in the range 0.8 to 2.8×10^{-4} s^{-1} for tin(IV) iodide, this time measured at 308.2 K. Germanium(IV) iodide reacts about an order of magnitude more rapidly. These kinetic results are useful in giving an idea of the decomposition timescale. We felt unable to continue with a detailed kinetic study as we were not able to characterise and quantify the products. These included, *inter alia,* hydriodic acid, tin(II) iodide, tetra-alkoxy tin(IV) compounds from the alcohols, and monoiodoacetone from acetone.

Solubilities

Solubilities of tin(IV) iodide and germanium(IV) iodide (Table III) correlate well, as shown in Fig. 3. The point for methyl iodide lies far to the top right of Fig. 3, but lies close to the correlation line indicated. The best straight line for germanium(IV) iodide values (y axis) plotted against tin(IV) iodide values (x axis) has a slope 1.07 ± 0.07, suggesting that the solubility of the germanium compound is slightly more sensitive to solvent variation than the tin compound. The solubility of silicon(IV) iodide [43, 58] is much more sensitive to solvent nature, a plot of silicon(IV) iodide solubilities against tin(IV) iodide solubilities having a slope of 2.72 ± 0.23. Correlation with solubilities of iodine is less close. Such comparisons are affected by the different extents of interaction and complex formation between the tetraiodides and iodine and aromatic solvents; omission of data for these solvents leads to a better, though not linear, correlation. In almost all solvents, solubilities decrease in the order $SiI_4 \gg GeI_4 > SnI_4 > I_2$. Transition metal tetraiodides, *e.g.* TiI_4 [59], are generally less soluble.

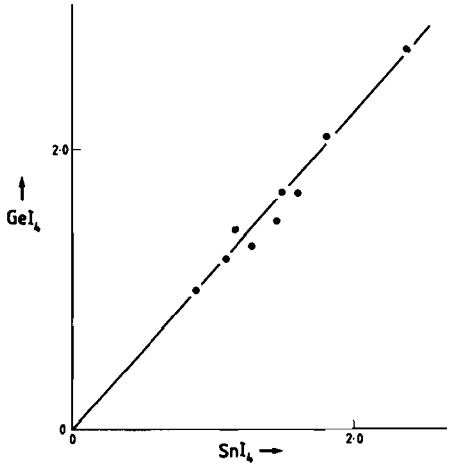

Fig. 3. Correlation of solubilities (mol percent) of tin(IV) and germanium(IV) iodide.

Tin(IV) iodide and related compounds are covalent non-electrolytes, and are suitable substrates for using and testing theories of regular solutions. It is well established that solubilities of tin(IV) iodide can be correlated by the use of Hildebrand's solubility parameter, δ [19, 26]. This is defined in terms of the enthalpy of vaporisation, ΔH_V, and molal volume (V_m):

$$\delta = \left(\frac{\Delta H_v - RT}{V_m}\right)^{1/2} \qquad (1)$$

For regular solutions of solids in liquids, the Hildebrand solubility parameters, δ_2 and δ_1 respectively, are inter-related and related to the activity (a_2), molal volume (V_2), and mole fraction (x_2) of the solute, and the volume fraction (ϕ_1) of the solvent by:

$$\ln a_2 = \ln x_2 + \frac{V_2\phi_1^2(\delta_2 - \delta_1)^2}{RT} \qquad (2)$$

The activity of the solute (a_2) can be calculated from its enthalpy of fusion (ΔH_m) at the melting point (T_m), and the difference (ΔC_p) between the molal heat capacities of the liquid and solid:

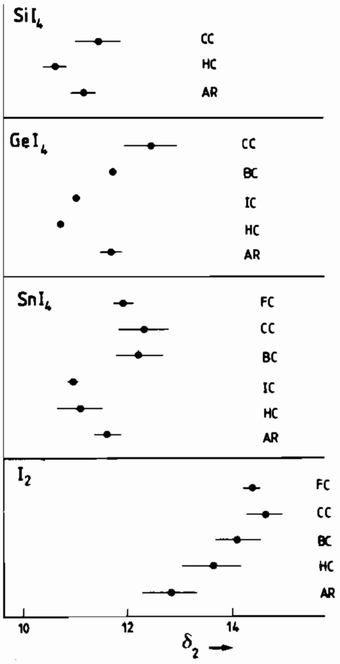

Fig. 4. Mean δ_2 values with their ranges (standard deviations) for solutions of Group IV tetraiodides and for iodine in various classes of solvent; FC = fluorocarbons, CC = chlorocarbons, BC = bromocarbons, IC = iodocarbons, HC = hydrocarbons (aliphatic), AR = aromatic solvents.

$$\ln a_2 = -\frac{\Delta H_m}{R}\left(\frac{T_m - T}{T_m T}\right) + \frac{\Delta C_p}{R}\left(\frac{T_m - T}{T}\right) - \frac{\Delta C_p}{R}\ln\left(\frac{T_m}{T}\right) \qquad (3)$$

The activities of tin(IV) iodide and silicon(IV) iodide are 0.130 and 0.194 at 298.2 K, based on Negishi's data for the former [60] and Kurosawa's data for the latter [61]. The activity of germanium(IV) iodide cannot be calculated, as ΔH_m and ΔC_p are not known, but can be interpolated as 0.16 from the tin(IV) and silicon(IV) iodide activities. Molal volumes of tin(IV) iodide and silicon(IV) iodide are 151 cm^3 [19] and 157 cm^3 [58] respectively, whence a value of 154 cm^3 may be interpolated for germanium(IV) iodide. Using these numbers and δ_1 (solvent) values from Hildebrand's compilation [19]*, values of δ_2 for tin(IV) iodide and germanium(IV) iodide were calculated using equation (2); these δ_2 values are included in Table III. In a perfect world the value of δ_2 for a given solute would be independent of solvent. The degree of non-ideality of solutions of the tetraiodides of this paper, and of iodine, is represented in Fig. 4. This shows the average value and the standard deviation for each compound in each type of solvent. The overall mean (all solvents) for each compound, with the respective standard deviation and confidence limits, is shown in Table IV. From Table IV and Fig. 4 it appears that the δ_2 values for the three tetraiodides are not statistically different, but that δ_2 for iodine is significantly larger.

TABLE IV. Mean δ_2 Values for Group IV Tetraiodides and for Iodine, for All Solvents, with Standard Deviations and 90% Confidence Limits.[a]

	SnI_4	GeI_4	SiI_4	I_2
Mean δ_2/cal$^{1/2}$ cm$^{-3/2}$	11.81	12.01	10.99	14.12
Standard deviation	0.64	0.72	0.44	0.73
90% Confidence limits	0.19	0.36	0.29	0.26

[a] The data used for this Table and for Fig. 4 are tabulated in ref. [63]; this reference points out that there are a few minor errors in relevant δ values given in ref. [19].

Hildebrand δ_2 values have been reported at various times for a variety of inorganic solutes. In Table V [64–76] we put our mean values for δ_2 for the three Group IV tetraiodides and for iodine into the context of the available range of values, for inorganic solutes and for some representative organic solutes and solvents. Iodine has the highest value yet reported for an inorganic solute, whereas the tetraiodides have intermediate values. It is difficult to detect general trends in the inorganic δ_2 values in Table V. There are many variations of compound and structure type; the elucidation of factors underlying these δ_2 values would seem to require the establishment of series of values for related series of compounds, so that various contributory factors could be isolated. The dissection of δ values for organic compounds into components, *e.g.* dispersion, polar, and hydrogen-bonding, has been attempted several times, with three [76] and even four [73] component equations being suggested. It is not possible to use these approaches for the Table V inorganic values, as the required physical data for the dissection of these δ values is not available (or even, in some cases, not obtainable) for the majority of these compounds. These dissections of δ values are much more appropriate for volatile organic solvents; it is noteworthy that Barton's comprehensive review of solubility parameters [76], which discusses various contributory factors to δ values, makes no direct mention of any inorganic solutes. One might add that the

---

*The following additional δ_1 values were calculated using equation (1). $CHCl{=}CCl_2$ 9.2; $CHCl_2CHCl_2$ 9.7; $CH_2ClCHCl_2$ 9.6; CH_2Br_2 10.7; $CHBr_2CHBr_2$ 10.9. Relevant solvent data are given in ref. [62].

TABLE V. Values of the Hildebrand Solubility Parameter δ_2 ($\mathrm{cal}^{1/2}\ \mathrm{cm}^{-3/2}$)[a] for a Selection of Inorganic Compounds, Listed in Order of δ_2 Values, and δ Values for Reference Organic Compounds.

I_2	14.1	GeI_4	12.0	$TiCl_4$	9.0	HCHO	19.2[k]
S_4N_4	13.7[b]	SnI_4	11.8	UF_6	8.9	CH_3OH	14.5[k]
S_7NH	12.7[c]	$Cu(acac)_2$	11.6[e]	$SnCl_4$	8.7	$(CH_3)_2SO$	12.0[k]
S_8	12.7	$Fe(acac)_3$	11.6[f]	$GeCl_4$	8.1	$C_6H_5CO_2H$	11.9[l]
OsO_4	12.6	SiI_4	11.0	$SiCl_4$	7.6	n-$C_{25}H_{52}$	10.5[m]
NH_2Cl	12.3[d]	$M(acac)_3$[g]	10.7–9.7[h]	SF_6	6.2[j]	n-C_4H_{10}	7.1[n]
Al_2Br_6	11.9	$Th(acac)_4$	10.6[i]	SiMe4	6.2	CCl_4	8.6
						C_7F_{16}	5.9

[a] From Table IV and ref. [19] unless otherwise indicated. [b] Ref. [64]. [c] Ref. [65]. [d] Ref. [66]. [e] Ref. [67]. [f] Ref. [68]; δ_2 values for the dibenzoylmethane and dipivaloylmethane analogues are 10.0 and 9.9 respectively. [g] M = Al, Cr, Co. [h] Ref. [69]; and, for $Cr(acac)_3$ only, also ref. [70]. [i] Ref. [71]. [j] Ref. [72]. [k] Ref. [73]. [l] Ref. [74]. [m] Ref. [75] for n-$C_{25}H_{52}$ down to n-C_5H_{12}. [n] Ref. [76].

TABLE VI. Enthalpies of Solution (kJ mol^{-1}), Gibbs Free Energies of Solution (kJ mol^{-1}), and Entropies of Solution (J $\mathrm{mol}^{-1}\ \mathrm{K}^{-1}$) of Tin(IV) Iodide, at 298.2 K.

Solvent	ΔH	ΔG	ΔS
CCl_4	27.1	4.7	75
$CHCl_3$	29.4	4.0	85
CH_2Cl_2	45.6	4.2	139
$CCl_2{:}CCl_2$	26.3	4.3	74
$CHCl{:}CCl_2$	24.7	3.7	71
t-$CHCl{:}CHCl$	36.4	4.1	109
CH_3CCl_3	25.3	5.7	66
$CHCl_2CHCl_2$	22.9	4.6	61
$CH_2ClCHCl_2$	24.6	4.9	66
CH_3CHCl_2	52.1	5.6	156
CH_2ClCH_2Cl	27.9	4.8	77
CH_2Br_2	34.8	0.9	114
$CHBr_2CHBr_2$	15.0	0.5	49
CH_3CH_2Br	61.6	2.8	197
CH_3I	33.2	−1.0	115
CH_3CH_2I	21.3	0.3	70

situation with respect to δ_1 values for inorganic solvents can hardly be considered satisfactory, when entropies of solution (Table VI). Enthalpies and values between 17.6 [74] and 23.4 [77] have been given for water.

Entropies

Gibbs free energies of solution can be calculated from measured solubilities, and from these and measured enthalpies of solution we have calculated entropies of solution (Table VI). Enthalpies and entropies of solution for tin(IV) iodide correlate, and, as so often, compensate and leave Gibbs free energies as small resultants. The situation is similar for germanium(IV) iodide.

Acknowledgements

The authors are grateful to Thorn Lighting Limited, the Royal Society, and S.R.C. for their support.

References

1 Sneider, *Pogg. Ann.*, *127*, 624 (1866).
2 J. W. Retgers, *Z. Anorg. Chem.*, *3*, 253, 344 (1893).
3 H. Arctowski, *Z. Anorg. Chem.*, *11*, 272 (1895).
4 F. A. McDermott, *J. Am. Chem. Soc.*, *33*, 1963 (1911).
5 M. E. Dorfman and J. H. Hildebrand, *J. Am. Chem. Soc.*, *49*, 729 (1927).
6 M. E. Dice and J. H. Hildebrand, *J. Am. Chem. Soc.*, *50*, 3023 (1928).
7 E. P. McLaughlin and R. L. Scott, *J. Am. Chem. Soc.*, *76*, 5276 (1954).
8 E. P. Doane and H. G. Drickamer, *J. Phys. Chem.*, *59*, 454 (1955).
9 E. B. Smith and J. Walkley, *Trans. Faraday Soc.*, *56*, 220 (1960).
10 S. K. Suri and V. Ramakrishna, *Canad. J. Chem.*, *47*, 3049 (1969).
11 P. N. Kunur and S. N. Vyas, *Indian Chem. J.*, *9*, 20 (1975).
12 W. E. Acree and G. L. Bertrand, *J. Phys. Chem.*, *81*, 1170 (1977).
13 A. Purkayastha and J. Walkley, *Canad. J. Chem.*, *50*, 834 (1972).
14 J. H. Hildebrand, *J. Am. Chem. Soc.*, *51*, 66 (1929).
15 F. Gaizer and M. T. Beck, *J. Inorg. Nucl. Chem.*, *29*, 21 (1967).
16 F. G. Thomas and I. M. Kolthoff, *J. Electroanal. Chem. Interfac. Electrochem.*, *31*, 423 (1971).

17 J. H. Hildebrand and R. Negishi, *J. Am. Chem. Soc., 59,* 339 (1937).

18 R. F. Adamsky and C. M. Wheeler, *J. Phys. Chem., 58,* 225 (1954).

19 J. H. Hildebrand and R. L. Scott, 'Regular Solutions', Prentice-Hall, New Jersey (1962), and refs. therein.

20 G. T. Morgan, S. R. Carter and W. F. Harrison, *J. Chem. Soc.,* 1917 (1925).

21 Yu. G. Stenin, G. A. Kokovin and N. N. Zhamskaya, *Izvest. Sib. Otd. Nauk SSSR, Ser. Khim. Nauk,* 81 (1977).

22 R. C. Paul, P. Singh, K. S. Dhindsa and S. L. Chadha, *Indian J. Chem., 8,* 1014 (1970).

23 R. C. Paul, K. S. Dhindsa, S. C. Ahluwalia and S. P. Narula, *Indian J. Chem., 8,* 549 (1970).

24 V. Gutmann, *Fortschr. Chem. Forsch., 27,* 59 (1972).

25 W. J. DeWitte and A. I. Popov, *J. Solution Chem., 5,* 231 (1976); and references therein.

26 J. H. Hildebrand, J. M. Prausnitz and R. L. Scott, 'Regular and Related Solutions', Van Nostrand Reinhold, New York (1970).

27 D. M. Adams and J. B. Raynor, 'Advanced Practical Inorganic Chemistry', p. 38, Wiley, New York (1965).

28 See p. 125 of ref. [19].

29 'Handbook of Chemistry and Physics', 58th edn., edited by R. C. Weast, p. B115. CRC Press, Cleveland, Ohio (1977).

30 E. G. Rochow, in 'Comprehensive Inorganic Chemistry', edited by J. C. Bailar, H. J. Emeléus, R. Nyholm and A. F. Trotman-Dickenson, vol. 2, p. 23. Pergamon, Oxford (1973).

31 A. J. Gordon and R. A. Ford, 'The Chemist's Companion', Wiley, New York (1972).

32 J. Burgess, I. Haigh and R. D. Peacock, *J. Chem. Soc. Dalton Trans.,* 1062 (1974).

33 V. B. Parker, 'Thermal Properties of Aqueous Uni-univalent Electrolytes', U.S. Dept. of Commerce, NSRDS-NBS2 (1965).

34 J. F. Murphy and D. E. Baker, *Canad. J. Chem., 43,* 1272 (1965).

35 G. M. Kurdyumov, V. B. Strizhkov and I. V. Korobov, *Khim. Prom. (Moskva), 48,* 310 (1972).

36 K. Hartley and H. A. Skinner, *Trans. Faraday Soc., 46,* 621 (1950).

37 A. Vertes, F. Gaizer and M. T. Beck, *Acta Chim. Acad. Sci. Hung., 80,* 343 (1974).

38 U. Mayer and V. Gutmann, *Monatsh., 101,* 997 (1970).

39 R. C. Paul, M. L. Lakhanpal, P. S. Gill and J. Singh, *Indian J. Chem., 2,* 262 (1964).

40 Y. Ozari and J. Jagur-Grodzinski, *J. Chem. Soc. Chem. Commun.,* 295 (1974).

41 J. M. Miller and M. Onyszchuk, *J. Chem. Soc. A,* 1132 (1967);
G. Vandrish and M. Onyszchuk, *ibid.,* 3327 (1970).

42 C. M. Blair and D. M. Yost, *J. Am. Chem. Soc., 55,* 4489 (1933);
J. H. Hildebrand, *ibid., 59,* 2083 (1937);
G. Kortüm and M. Kortüm-Seiler, *Z. Naturforsch., 5A,* 544 (1950).

43 L. V. McCarty, L. C. Landauer and J. M. Binkowski, *J. Chem. Eng. Data, 5,* 365 (1960).

44 I. R. Beattie, *Q. Rev. Chem. Soc., 17,* 382 (1963).

45 M. F. Lappert and J. K. Smith, *J. Chem. Soc.,* 3224 (1961).

46 H. Rheinbolt and R. Boy, *J. Prakt. Chem., 129,* 268 (1931).

47 A. Vértes and I. N. Czakó, *Magy. Kem. Foly, 82,* 200 (1976);
A. Vértes, I. N. Czakó and K. Burger, *J. Phys. Chem., 80,* 1314 (1976).

48 I. R. Beattie and L. Rule, *J. Chem. Soc.,* 3267 (1964).

49 J. Burgess and J. Kijowski, *J. Inorg. Nucl. Chem.,* accepted for publication.

50 J. A. Daniels, J. R. Jennings, P. G. Huggett and K. Wade, *Inorg. Nucl. Chem. Lett., 14,* 445 (1978);
P. G. Huggett, K. Manning and K. Wade, *J. Inorg. Nucl. Chem., 42,* 665 (1980).

51 R. Makhija and A. D. Westland, *Inorg. Chim. Acta Lett., 29,* L269 (1978).

52 R. A. Geanangel, *J. Inorg. Nucl. Chem., 40,* 603 (1978).

53 A. G. Dimitrion, *Praktika, 2,* 496 (1927);
K. G. Huggins, F. W. Parrett and H. A. Patel, *J. Inorg. Nucl. Chem., 31,* 1209 (1969).

54 A. Vértes and C. I. Nagyné, *Magy. Kem. Foly., 82,* 200 (1976).

55 M. L. Huggins, *Polymer, 12,* 389 (1971).

56 M. Cartwright and A. A. Woolf, *J. Chem. Soc. Dalton Trans.,* 829 (1976).

57 T. Karantassis, *Ann. Chem., 8,* 78 (1927).

58 I. R. Krichevskii, G. F. Ivanovskii and E. F. Safronov, *Doklady Akad. Nauk SSSR, 122,* 400 (1958).

59 E. G. M. Tornqvist and W. F. Libby, *Inorg. Chem., 18,* 1792 (1979).

60 G. R. Negishi, *J. Am. Chem. Soc., 58,* 2293 (1936).

61 T. Kurosawa, R. Hasegawa and T. Yagihashi, *Trans. Jap. Inst. Metals, 6,* 229 (1965).

62 J. Kijowski, *Ph.D. Thesis,* University of Leicester (1981); see Appendix 1.

63 See pp. 162–4 of ref. [62].

64 S. Hamada, Y. Kudo and M. Kawano, *Bull. Chem. Soc. Japan, 48,* 719 (1975).

65 S. Hamada, Y. Kudo and M. Kawano, *Bull. Chem. Soc. Japan, 48,* 2963 (1975).

66 Y. G. Rao and D. S. Viswanath, *J. Chem. Eng. Data, 20,* 29 (1975).

67 H. Koshimura, *J. Inorg. Nucl. Chem., 38,* 1705 (1976); *39,* 148 (1977).

68 H. Koshimura, *J. Inorg. Nucl. Chem., 40,* 865 (1978).

69 M. Yamamoto and Y. Yamamoto, *Analyt. Chim. Acta, 87,* 375 (1976).

70 K. Saitoh and N. Suzuki, *Bull. Chem. Soc. Japan, 51,* 116 (1978).

71 B. Allard, *J. Inorg. Nucl. Chem., 39,* 694 (1977).

72 H. Jaster and P. G. Kosky, *J. Chem. Eng. Data, 21,* 66 (1976).

73 B. L. Karger, L. R. Snyder and C. Eon, *Analyt. Chem., 50,* 2126 (1978).

74 Y. Fujii, K. Sobue and M. Tanaka, *J. Chem. Soc. Faraday Trans. I, 74,* 1467 (1978).

75 S. P. Sokolova and A. N. Pereverzev, *Russ. J. Phys. Chem., 51,* 750 (1977).

76 A. F. M. Barton, *Chem. Rev., 75,* 731 (1975).

77 M. H. Abraham and J. Liszi, *J. Chem. Soc. Faraday Trans. I, 74,* 1604 (1978).