

THE HEAT OF SOLUTION OF IODINE IN SOME ORGANIC SOLVENTS

BY K. HARTLEY AND H. A. SKINNER

Received 20th March, 1950

Values are reported for the heat of solution of solid iodine in 15 organic solvents. The heats of solution are examined in relation to the theory of regular solutions as developed (in particular) by Hildebrand, and approximate values are obtained for the heats of complex formation of iodine with various organic substances.

In the course of some measurements of the heats of iodination of metallic alkyls ^{1, 2} we required to know the solution heats of solid iodine in various organic solvents. The literature contains heat of solution data due to Pickering ³ and Waentig ⁴ which are, however, not always in close agreement, e.g. Pickering gave -6.0 kcal. mole⁻¹, and Waentig -4.7 kcal. mole⁻¹ for the heat of solution of I₂ in benzene. In this paper we report new measurements on the heat of solution of solid iodine in 15 common organic solvents. These heats were measured by the direct method.

Experimental

The heats of solution were measured in a Dewar vessel calorimeter, similar to that described by Pritchard and Skinner.⁵ Temperature changes were followed by the change in resistance of a thermistor element; the iodine was contained in weighed glass ampoules, which were broken as required on a polytetrafluoroethylene platform immersed in the solvent inside the Dewar vessel.

TABLE I.—HEATS OF SOLUTION AND COLOUR OF IODINE SOLUTIONS

Solvent	Conc. I ₂ g./l.	Heat of Solution kcal. mole ⁻¹	Colour of Solution
Cyclohexane . . .	2.5	-5.8 ± 0.2	Blue
Carbon tetrachloride . . .	2.0	-5.8 ± 0.2	Blue
Chloroform * . . .	2.0	-5.1 ± 0.2	Blue
Chlorobenzene . . .	6.7	-4.75 ± 0.05	Blue
Benzene	6.7	-4.25 ± 0.05	Blue
Toluene	7.8	-3.85 ± 0.05	Blue-brown
Methyl benzoate . . .	5.7	-3.9 ± 0.1	Brown
Ethyl acetate	5.7	-3.1 ± 0.1	Brown
Methyl acetate	5.7	-2.45 ± 0.1	Brown
Methyl alcohol	7.6	-2.07 ± 0.05	Brown
1 : 4-Dioxan	7.8	-1.85 ± 0.1	Brown
Diethyl ether	7.5	-1.80 ± 0.1	Brown
Nitrobenzene	6.7	-1.70 ± 0.1	Brown
Ethyl alcohol	7.7	-1.65 ± 0.05	Brown
Pyridine	2.5	3.6 ± 0.1	Yellow

* The chloroform contained 1½ % ethyl alcohol.

¹ Carson, Hartley and Skinner, *Proc. Roy. Soc. A.*, 1949, **195**, 500.

² Carson, Hartley and Skinner, *Trans. Faraday Soc.*, 1949, **45**, 1159.

³ Pickering, *J. Chem. Soc.*, 1888, **53**, 865.

⁴ Waentig, *Z. physik. Chem.*, 1909, **68**, 512.

⁵ Pritchard and Skinner, *J. Chem. Soc.*, 1950, 272.

The solution heats in most solvents are negative, and it was possible to balance the negative heat of solution by simultaneously passing a measured amount of electrical energy through a calibration heater, so that the measurements were conducted under virtually isothermal conditions. In each experiment, the iodine was dissolved in 300 ml. of solvent. Corrections for small heat losses (evaporation, stirring) were made graphically.

The solvents were dried and fractionated prior to use, and A.R. iodine was used throughout. The results are summarized in Table I. The heats of solution are given in units of the kcal. mole.⁻¹ = 4.1833×10^3 int. joules mole.⁻¹.

Discussion

The close parallelism between the *colour* of iodine solutions and the *heat of solution* is apparent from the results of Table I. Hildebrand⁶ has previously shown that the solubility curves for iodine in solvents giving blue solutions form a regular family whose deviation from ideality can be related to differences of internal pressure (or cohesive energy density). The solubility curves of the brown solutions do not fall into a regular family of any kind, and the deviations are probably to be attributed to the formation of iodine-solvent complexes.

In the case of iodine forming an *ideal* solution, there is no heat and excess entropy of mixing of the liquid iodine with the solvent, and the heat of solution of solid iodine in this ideal case is negative and equal to the molal latent heat of fusion L_f of iodine. The solubility relationships holding for the blue iodine solutions are typical of so-called regular solutions, which deviate from the ideal only in that the heat of mixing is no longer zero. Hildebrand and Wood,⁷ and Scatchard⁸ have related the molal heat of mixing at constant volume ΔE_v for regular solutions to the concentrations of the components and their respective internal pressures, by the equation

$$\Delta E_v = \frac{x_1 V_1 x_2 V_2}{x_1 V_1 x_2 V_2} (d_2 - d_1)^2, \quad . \quad . \quad . \quad (1)$$

where x_1 , x_2 , and V_1 , V_2 are the respective mole fractions and molar volumes of the two components, and d_1 , d_2 are the internal pressures. These latter are defined by

$$d_1 = (\Delta E_1/V_1)^{\frac{1}{2}}; \quad d_2 = (\Delta E_2/V_2)^{\frac{1}{2}}, \quad . \quad . \quad . \quad (2)$$

where ΔE = molal internal energy of vaporization.

Accordingly, in the blue (regular) solutions, the overall heat of solution of solid iodine should be more negative than L_f , i.e. more negative than -3.74 kcal. mole.⁻¹ (Frederick and Hildebrand⁹). In the non-regular brown solutions, a positive heat of combination due to iodine-solvent complex formation is likely to participate and render the overall heat of solution more positive than is calculated from internal pressure considerations alone.

For the regular solutions, the heat of solution is given by

$$Q_{\text{soln.}} = -L_f - q_R \quad . \quad . \quad . \quad (3)$$

in which q_R is related to eqn. (1) and (2). If the deviations from regular behaviour in the brown solutions are primarily due to the formation of iodine-solvent complexes, then the difference between an observed $Q_{\text{soln.}}$ and a calculated $-(L_f + q_R)$, would give a rough measure of the heat of this complex formation.

⁶ Hildebrand, *Solubility of Non-electrolytes* (Reinhold, New York, 1936), 2nd ed.

⁷ Hildebrand and Wood, *J. Chem. Physics*, 1933, **1**, 817.

⁸ Scatchard, *Chem. Rev.*, 1931, **8**, 321.

⁹ Frederick and Hildebrand, *J. Amer. Chem. Soc.*, 1938, **60**, 1436.

We have not attempted to evaluate the terms in q_R , as there are not data available on the volume changes accompanying the mixing of liquid iodine with the various solvents. These data would be required in order to compare the observed heats of solution at constant pressure with calculated values of ΔE_v at constant volume. Rather, we have examined the general relationship expressed in eqn. (1), (2) and (3) between $Q_{\text{soln.}}$ and the internal pressure term $(d_2 - d_1)^2$. The plot of $Q_{\text{soln.}}$ against $(d_2 - d_1)^2$ is shown in Fig. 1. It is seen that the solvents C_6H_{12} , CCl_4 ,

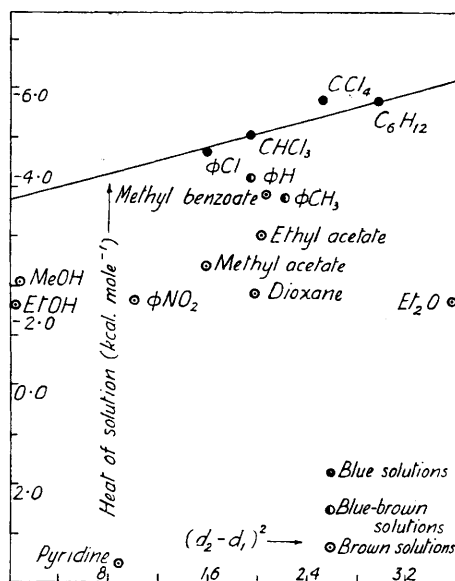


FIG. 1.

CHCl_3 , and $\text{C}_6\text{H}_5\text{Cl}$ give points which lie reasonably close to a straight line intercepting the ordinate at $Q_{\text{soln.}} = -L_f$ when $(d_2 - d_1)^2 = 0$.

These solvents give blue solutions, and there is no evidence from other studies of complex formation in these instances. The solvents C_6H_6 and $\text{C}_6\text{H}_5 \cdot \text{CH}_3$, which give blue or near-blue solutions, fall off the straight-line, toluene more so than benzene. We would interpret these deviations as evidence of I_2 -benzene and I_2 -toluene complex formation, and may refer to the work of Benesi and Hildebrand¹⁰ confirming this conclusion. The brown solutions without exception deviate markedly from the straight line plot.

The values used for the internal pressures of the various solvents are listed in Table II. They were obtained, where possible, from experimental heats of vaporization; in some cases reliable heats of vaporization are not available and these are bracketed, but for the most part the data given in Table II should be accurate within a few per cent.

The internal pressure of liquid iodine was calculated from the value $\Delta E_{\text{vap.}} = 11.2$ kcal. mole⁻¹ given by Hildebrand,⁵ and the molar volume $V = 59.0$ ml. mole⁻¹ obtained by extrapolation of the data of Drugman and Ramséy.¹⁹ In the final column of Table II, the derived values of $(d_2 - d_1)^2$ are listed, d_2 being the internal pressure of iodine and d_1 referring to the solvent.

The large deviations of all the brown solutions from the simple linear dependence on $(d_2 - d_1)^2$, as shown by Fig. 1, strongly point to positive

¹⁰ Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

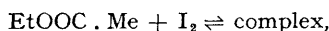
TABLE II.—INTERNAL PRESSURES AT 20° C

Compound	$\lambda_{\text{vap}}^{20}$ (kcal. mole ⁻¹)	V^{20} (ml. mole ⁻¹)	$\Delta E/V$ (cal. ml. ⁻¹)	$(\Delta E/V)^{\frac{1}{2}}$	$(d_2 - d_1)^2$
Diethyl ether . . .	6.65 ¹¹	103.7	58.5	7.65	35.4
Cyclohexane . . .	7.91 ¹²	108.7	67.3	8.2	29.1
CCl ₄ . . .	7.85 ¹²	97.1	74.7	8.65	24.6
Toluene . . .	9.08 ¹²	106.8	79.4	8.9	22.0
Methyl benzoate . .	(10.8)	125.1	(81.5)	9.05	20.7
Ethyl acetate . . .	8.70 ¹³	97.8	83.0	9.1	20.1
Dioxane . . .	(8.7)	96.9	84.1	9.17	19.6
Benzene . . .	8.12 ¹⁴	88.9	84.8	9.2	19.3
Chloroform . . .	7.47 ¹²	80.2	85.3	9.25	19.0
Methyl acetate . .	7.96 ¹⁵	79.3	93.1	9.65	15.6
Chlorobenzene . .	—	101.7	(93.4) ⁸	9.65	15.5
Pyridine . . .	9.71 ¹⁶	80.7	113.2	10.65	8.75
Nitrobenzene . . .	(11.7) ¹⁷	102.0	(109.0)	10.44	9.98
Ethyl alcohol . . .	10.33 ¹⁸	58.2	171.0	13.1	0.27
Iodine . . .	—	59.0 ¹⁹	190.0	13.6	0.0
Methyl alcohol . .	9.01 ¹²	40.4	208.7	14.45	0.72

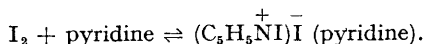
values for the heats of complex formation in these solvents. The magnitudes of the heats of complex formation can be obtained from the simple assumption that they are equal to the deviations from the linear plot of Fig. 1. The estimated values are then obtained as follows (in kcal./mole):

Benzene + 0.85; toluene + 1.45; methyl alcohol + 1.7; ethyl acetate + 2.05; ethyl alcohol + 2.1; methyl acetate + 2.4; nitrobenzene + 2.75; dioxane + 3.25; diethyl ether + 4.4; pyridine + 7.95.

Little is known from other sources of the heats of iodine-solvent complex formation; in case of iodine-ethyl acetate, Hildebrand and Glascock²⁰ measured the equilibrium constant at 12° C and 28° C of the reaction



from which they were able to calculate the heat of the reaction as + 3.06 kcal./mole. Independent evidence for the formation of iodine-solvent complexes has been given by Hildebrand and Glascock for nitrobenzene and ethyl alcohol, and by Audrieth and Birr²¹ with I₂-pyridine. Our data suggest that the I₂-pyridine complex is one of the most stable of the iodine-solvent complexes, and one is tempted in this instance to postulate salt-formation, in the manner



¹¹ Faust and Littman, *Z. physik. Chem.*, 1924, **113**, 482.

¹² *Selected Values of Chemical Thermodynamic Properties* (Bureau of Standards, Washington), 1948-49.

¹³ de Kolosowsky and Alimow in *Landolt-Bornstein* (1936).

¹⁴ Fiock, Ginnings and Holton, *J. Bur. Stand. Res.*, 1931, **6**, 881.

¹⁵ Roth and Müller in *Landolt-Bornstein* (1936).

¹⁶ Hieber and Woerner, *Z. Elektrochem.*, 1934, **40**, 252.

¹⁷ Toral and Moles, *Ann. Soc. Españ. Fis. Quim.*, 1923, **31**, 735.

¹⁸ Bartoszewicz, *Rocz. Chem.*, 1931, **11**, 90.

¹⁹ Drugman and Ramsey, *J. Chem. Soc.*, 1900, **77**, 1228.

²⁰ Hildebrand and Glascock, *J. Amer. Chem. Soc.*, 1909, **31**, 26.

²¹ Audrieth and Birr, *ibid.*, 1933, **55**, 668.

The values quoted above for the heats of complex formation are, it should be emphasized, not strict measures of these heat quantities: nevertheless, they show a trend which is probably correct, even if the absolute values given are less reliable.

The authors wish to express their thanks to Prof. M. G. Evans, F.R.S., for his interest in this work and for his assistance in the interpretation of the results.

*Department of Chemistry,
Manchester University.*
