

# The Solubility of Ferrocene in Non-polar Solvents

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The solubility of ferrocene in perfluoroheptane, iso-octane, heptane, cyclohexane, carbon tetrachloride, bromotrichloromethane, carbon disulphide, and 1,4-dioxane has been determined at 25 °C. Several of the determinations were also carried out at 10 °C and 40 °C. The data are analyzed in terms of the Scatchard-Hildebrand theory. The problems in calculating solubilities of solids with high melting points are discussed.

The Scatchard-Hildebrand theories have led to an understanding of the theory of the thermodynamic properties of solutions of non-electrolytes, including the solubility of solids. Hildebrand and Scott<sup>1,2</sup> have carefully examined the solubility of iodine, sulphur, stannic iodide, phosphorus, and a few other, *e.g.* naphthalene and anthracene, are roughly discussed. Latest Victoria and Walkley<sup>3</sup> have presented the solubility of tetraphenyltin.

In the prediction of the solubility of solids in non-polar solvents the following equation can be used

$$\ln x_2 = \ln x_2^i - v_2 \Phi_1^2 (\delta_1 - \delta_2)^2 / RT \quad (1)$$

where  $x_2$  and  $x_2^i$  are the solubility and the ideal solubility expressed in mol fractions,  $\Phi_1$  the volume fraction and  $\delta$  the solubility parameter. Index 2 refers to the solute and index 1 to the solvent.

The solubility of ferrocene in eight solvents has been determined and some problems in the theoretical calculation of the solubility of ferrocene are discussed, and it is shown that ferrocene fulfils the assumptions in the solubility parameter theory. The deviations between predicted and experimental values are for seven of the solvents within the usual order of magnitude, but for heptane the predicted value is about 2.5 times smaller than the experimental.

## EXPERIMENTAL

### Materials

*Ferrocene* was of same origin and purity as described earlier.<sup>4</sup>

*Perfluoroheptane* was purified for hydrocarbons as described by Glew and Reeves.<sup>5</sup> Gas-chromatographic analysis showed an amount of impurity of about 6 %. Determination of the boiling point gave 82.48–82.53 °C. Glew and Reeves found 82.34 °C. A part of the material was further purified by preparative gaschromatography. The boiling point was now 82.38–82.40 °C, and a gaschromatographic analysis showed impurities about 0.5 %. The solubility of ferrocene in the two products differed by about 9 %. Only the result from the purest product was used.

*Iso-octane*, *cyclohexane*, and *carbon disulphide* were of the same origin and purity as described by Thomsen.<sup>6</sup>

*Heptane* was of the same origin and purity as described by Thomsen and Gjaldbæk.<sup>7</sup>

*Carbon tetrachloride* (zur Analyse, Merck) showed an amount of about 0.6 % impurity by GLC analysis. The boiling point was 76.67 °C and  $n_D^{20} = 1.4606$ , Nilsson.<sup>8</sup> Timmermans<sup>9</sup> states 76.75 °C and 1.46023–1.46044, respectively. It was used without any purification.

*Bromotrichloromethane* (Aldrich) was purified by fractional distillation and the purity examined by Harsted.<sup>10</sup> The boiling point was 104.62 °C and  $n_D^{20} = 1.5065$ . Davidson and Sullivan<sup>11</sup> found 105.2 °C and Stevels<sup>12</sup> found 1.5061. A GLC analysis showed impurities of about 0.1 %.

*1,4-Dioxane* (zur Analyse, Merck) was kept with sodium and distilled before use. The distilled dioxane showed no content of peroxide.

### Measurements

Saturated solutions of ferrocene in the different solvents were established in a water thermostat kept within  $\pm 0.02$  °C. The great differences in the solubilities of ferrocene in the solvents employed demanded the use of different methods in the determination of the concentration of ferrocene in the saturated solutions.

In the experiments with *cyclohexane*, *iso-octane*, and *heptane* as solvents, a part of the saturated solutions were diluted in a known scale with the solvent. The optical density of these solutions were measured and the concentration of ferrocene was found by using calibration curves. This method was earlier used by Glew and Hildebrand<sup>13</sup> on the iodine-perfluoroheptane system.

In *carbon disulphide*, *dioxane*, *carbon tetrachloride*, and *bromotrichloromethane*, the solvents of samples taken were removed by vacuum evaporation and the residue of ferrocene was weighed. All work with solutions of ferrocene in the two last mentioned solvents took place in the dark; cf. below.

In *perfluoroheptane* the solvent was removed in the same way and the residue of ferrocene determined by a micro-quantitative titration used by Renger and Jenik.<sup>14</sup>

Spectra of solutions of ferrocene in the solvents used in this work (except carbon disulphide) were recorded with a Beckman DK-2 spectrophotometer in the range 3000–6000 Å. Only the solutions in silicone tetrachloride, carbon tetrachloride, and bromotrichloromethane showed spectra different from that in cyclohexane, with the absorption of ferrocene at 3500 and 4400 Å. Moreover the solutions in CCl<sub>4</sub> and CBrCl<sub>3</sub> showed changes with the time after the solutions were placed in daylight. Earlier Brand and Snedden<sup>15</sup> observed that solutions of ferrocene in carbon tetrachloride and in bromotrichloromethane are stable in darkness, but react on irradiation with the formation of phosgene and ferric chloride. They have suggested that the absorption at 307 mμ is attributed to intermolecular charge transfer in which ferrocene serves as the electron donor.

## RESULTS AND DISCUSSION

The results of the solubility experiments are given in Table 1 expressed in mol fraction

(100  $x_2$ ), with the uncertainties stated. Each determination given is the average of 4–6 experiments.

The measured solubilities of ferrocene at 25 °C show, in most cases, the expected increase with increasing value of the solubility parameter of the solvent,  $\delta_1$ .

The ideal solubility of ferrocene,  $x_2^i$ , was calculated from

$$d \ln x_2^i / dT = \Delta H^{\text{fus}} / RT^2 \quad (2)$$

where  $\Delta H^{\text{fus}}$  is the heat of fusion. Using the heat of fusion and heat capacities for solid and liquid ferrocene, determined in an earlier work,<sup>4</sup> the ideal solubility of ferrocene,  $x_2^i = 0.140$ , was found. Since our determination of the molal heat capacity of liquid ferrocene was carried out only between 448 and 485 K, we used an empirical value 0.1 for  $dC_p/dT$  in calculating the heat of fusion at 25 °C. Values of  $dC_p/dT$  were calculated for about 20 liquids using  $c_p$  given by Timmermans.<sup>9</sup> It turned out that the value 0.1 can be considered as a first rough estimation of the temperature coefficient even over large intervals of temperature.

The solubility parameter,  $\delta_2$ , for ferrocene was calculated from

$$\delta_2 = [(\Delta H^{\text{vap}} - RT)/v_2]^{1/2} \quad (3)$$

where the heat of vaporization,  $\Delta H^{\text{vap}}$ , at 25 °C was calculated as the difference between the heat of sublimation at 25 °C, 17.53 kcal per mol found by Edwards and Kingston,<sup>16</sup> and the heat of fusion at 25 °C calculated in the same way as the calculation for the ideal solubility.  $\delta_2 = 10.8$  was found.

Table 1. Solubilities of ferrocene. Experimental values expressed in mol fractions (100 $x_2$ ). The ratio ( $f$ ) between experimental values and values calculated by means of eqn. (1) (25 °C).

Solvent	$v_1$	$\delta_1$	10 °C	25 °C	40 °C	$f$
1. Perfluoroheptane	226	5.85		0.044 ± 0.001		0.83
2. Iso-octane <sup>b</sup>	166	6.9	1.50 ± 0.04	2.28 ± 0.02	3.34 ± 0.03	0.51
3. Heptane	148	7.4	1.65 ± 0.02	2.62 ± 0.06	3.79 ± 0.04	2.5
4. Silicone tetrachloride	115	7.6		2.17 <sup>a</sup>		1.5
5. Cyclohexane	109	8.2	2.43 ± 0.02	3.88 ± 0.03	5.62 ± 0.04	1.1
6. Carbon tetrachloride	97	8.6	5.04 ± 0.01	6.92 ± 0.06	9.61 ± 0.08	1.3
7. Bromotrichloromethane	99	8.8		9.40 ± 0.02		1.4
8. Carbon disulphide	61	10.0	4.51 ± 0.08	6.69 ± 0.10		0.52
9. 1,4-Dioxane	86	10.0		6.83 ± 0.07		0.54

<sup>a</sup> Uhlig and Hüttenrauch.<sup>17</sup> <sup>b</sup> i.e. 2,2,4-trimethylpentane.

The molal volume,  $v_2$ , of liquid ferrocene extrapolated to 25 °C is required in the calculations. Determinations of the density of molten ferrocene were carried out by the pycnometer method. Six experiments carried out between about 177 and 206 °C resulted in the following equation for the density ( $\rho$ )

$$\rho_t = 1.4055 - 0.0011104 t$$

resulting in the value  $v_2 = 135$  ml at 25 °C. Although the extrapolation is carried out over an interval of about 150 °C the error in the value of  $v_2$  is considered to be small since the density changes only slightly with the temperature.

The calculated ratio ( $f$ ) between experimental values and values calculated by means of eqn. (1) (25 °C) are shown in Table 1. Using this equation the usual maximum error is  $\pm 0.3$  in  $\log x_2$ , i.e. the ratio  $f$  should lie between 0.5 and 2. This is fulfilled for all the experiments except for the solubility in heptane. Large discrepancies in the calculated solubility in heptane have earlier been observed, see e.g. Refs. 18, 19. An empirical value ( $\delta_1 = 8.1$ ) for heptane was used in these two papers in order to get better agreement with the solubility measurements.

If  $\delta_2$  is calculated from eqn. (1) using the experimental values for the solubilities at 25 °C we get the mean value 10.78, which is accidentally identical with the theoretical value 10.8. However there are large discrepancies from the mean value for some of the  $\delta_2$ 's. In heptane we thus calculate  $\delta_2 = 10.18$ , while using the empirical value (8.1) we get  $\delta_2 = 10.88$ . The theory which has resulted in eqn. (1) is too rough to use for an interpretation of these discrepancies.

It should be pointed out that very carefully made heat capacity measurements are necessary in the calculations of solubilities of solids. If such measurements do not exist, a constant enthalpy of fusion in eqns. (2) and (3) can be used as a first approximation.

In the calculation of the ideal solubility, the molal volume, and the solubility parameter long extrapolations of heat capacities and densities of the melted solid are necessary. This will in many cases introduce a considerable uncertainty in the theoretical calculation of the solubility of solids.

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