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SOLUBILITY AND ENTROPY OF SOLUTION OF IODINE IN ETHANOL-CYCLOHEXANE SOLUTIONS

Koichiro NAKANISHI and Sotō ASAKURA
Department of Industrial Chemistry, Kyoto University, Kyoto

The solubility of iodine in ethanol-cyclohexane solutions has been measured at 15.0, 25.0 and 35.0°C and the entropy of solution has been evaluated. It is found that the iodine complex formed in the mixed solutions is more stable than that in pure ethanol.

In the course of study on the diffusivity of iodine in various kinds of mixed solvents,[1)] it became necessary to consider thermodynamic data on iodine in these solvents. The simplest method to get such informations is to measure the solubilities of iodine in pure and mixed solvents.[2)] We have designed a new solubility apparatus and now obtained reliable solubility data in ethanol-cyclohexane solutions, from which the entropy of solution has been calculated.

Figure 1 illustrates our solubility apparatus. It was placed on a water-sealed magnetic stirrer immersed in a thermostat which was controlled within ±0.03°C. Solutions saturated with iodine were allowed to stand for a few hours under agitation to attain solubility equilibrium. The saturated solutions were first sucked into a syringe. The syringe was then slightly pulled up, turned, and the solutions were poured into the sampling container(10 x 10 x 40 mm). The sampled solutions were then transfered from the apparatus, diluted with water, and titrated with 1/50N sodium thiosulphate solution. With this operation, possible error due to the temperature change during the sampling was completely avoided.

In Table I are shown the solubilities of iodine s (mol%) in ethanol-cyclohexane solutions at 15.0, 25.0 and 35.0°C and the values of R(d log s/d log T) at 25.0°C. The latter can be approximately regarded as the entropy of solution of iodine. Iodine forms a strong charge-transfer complex with ethanol and the solubility is about five times larger than that in cyclohexane. The present data indicate that the solubility enhanced appreciably when ethanol is diluted with inert component.

Table I. Solubility and Entropy of Solution of I_2 in EtOH-c-C_6H_{12} Solutions

x_{EtOH}	s (mol%)			$R\frac{d \log s}{d \log T}$
	15.0°C	25.0°C	35.0°C	(cal/deg.mol)
0	0.613	0.901	1.33	22.5
		0.918[2)]		22.2[2)]
0.2	1.87	2.47	3.13	15.7
0.4	3.22	3.96	4.59	10.8
0.6	4.75	5.17	5.90	7.4
0.8	6.01	6.78	7.26	5.8
0.9	5.03	5.66	6.26	6.4
1	4.15	4.69	5.62	7.7
		4.71[2)]		7.4[2)]

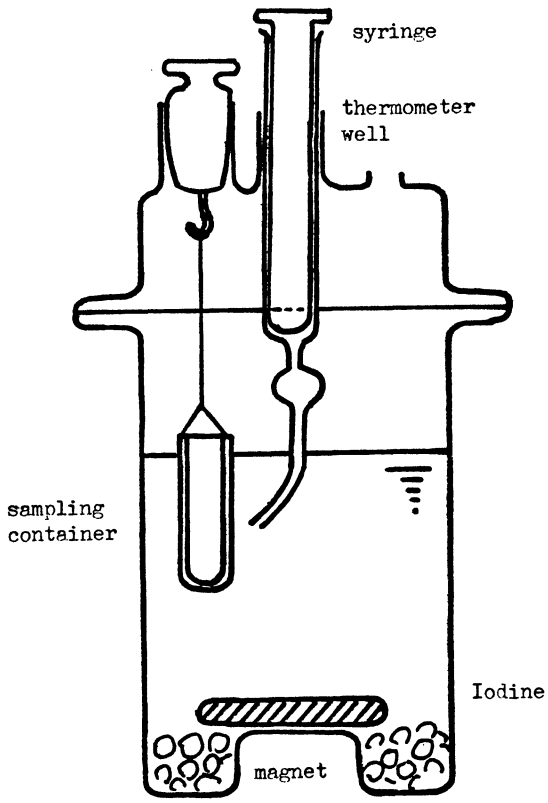

Figure 1. Solubility apparatus

The solubility parameter theory[2)] predicts such an enhancement of solubility only when the solubility parameter δ of solute comes between those of two solvents. Since $\delta(I_2) = 14.1$, $\delta(c\text{-}C_6H_{12}) = 8.2$, and $\delta(\text{EtOH}) = 13.0$[3)], no maximum solubility may be expected from this theory.

Of special interest in our data is the small values of entropy of solution in mixed solvents. The lowest value (ca. 5.5 cal/deg.mol) at $x_{EtOH} = 0.8$ is even smaller than that in pure ethanol (ca. 7.5 cal/deg.mol). This fact indicates that the iodine complex in ethanol-rich regions of the mixed solution is more stable than that in pure ethanol. This is a strong support to our interpretation to the relative decrease of diffusion coefficients in the same mixed solution.[1)]

We are obtaining further solubility data for various kinds of solvent pairs.

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