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# The Measurement of the Solubility of Metallic Mercury in Hydrocarbons by Means of the Cold-vapor Atomic Absorption Method

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**Synopsis.** The metallic mercury solubility in hydrocarbons (pentane, hexane, heptane, and octane) was determined in the temperature range from 5 to 40 °C by the cold-vapor atomic absorption method. The results, for pentane at 25 °C, were found to agree well with Kuntz's result obtained by means of the ultraviolet absorption method, while those for hexane, heptane, and octane were found to agree well with Spencer's results, which were obtained using a radioactivetracer technique in the above temperature range. The liquid-liquid distribution constant for metallic mercury between the above hydrocarbons and water was measured at 25 °C, and in each case was found to be equal to the ratio of the independent solubility in the hydrocarbon and in water.

The solubility of metallic mercury in water has been studied by many researchers. Early measurements of the solubility of mercury were made by means of the amalgamation[1)] or electrodeposition[2)] of the dissolved mercury. More recently, the measurements have been made using the radioactive tracer $Hg^{203}$, [3,4)] atomic absorption spectrometry,[5,6)] and neutron-activation analysis.[7)] Mercury solubility in hydrocarbons was studied by Spencer[4)] and by Kuntz.[8)] Spencer determined the solubility of mercury in hexane, heptane, and octane using a radioactive technique in the temperature range from 0 to 40 °C. Kuntz determined the solubility of mercury in pentane at 25 °C by combining optical data with a known mercury-solubility value.

In this work the mercury solubility in the above hydrocarbons was determined by the cold-vapor atomic absorption method. The liquid-liquid distribution constant of metallic mercury between these hydrocarbons and water was also investigated.

## Experimental

All the chemicals used were of an analytical reagent grade. The hydrocarbon solvents (pentane, hexane, heptane, and octane) were purified by passing them through activated alumina, and by distilling. The metallic mercury was purified in the usual manner.[5)]

The solubility experiments were conducted by shaking each hydrocarbon solvent with a drop of metallic mercury in a constant-temperature water bath, controlled to within ±0.1 °C. It was found that the mercury concentration was constant after about 24 h of shaking and thereafter remained constant over a period of several days. A solution of 0.5 $cm^3$ equilibrated was analyzed by the cold-vapor atomic absorption method, consisting of tin(II) chloride reduction, nitrogen bubbling (at a flow rate of 1.5 $dm^3\ min^{-1}$), and passing through a magnesium-perchlorate tube for mercury-vapor drying. The mercury concentration was determined from the area under the atomic absorption peak at 253.7 nm. A calibration curve was constructed by analysing a series of standard solutions from 0.1 to 1.5 ng of mercury in 100 $cm^3$ of water with the addition of 0.5 $cm^3$ of hydrocarbon. No effects of the amount of hydrocarbon added in the range from 0.1 to 1.0 $cm^3$ and of the type of the hydrocarbon on the calibration curve were seen. Also, Fujii[9)] has reported on the basis of the cold-vapor atomic absorption method, that these hydrocarbons have no effect on mercury analysis. Experiments were carried out in the temperature range from 5 to 40 °C.

Measurements of the liquid-liquid distribution constant of metallic mercury between the hydrocarbons and water were made by dissolving metallic mercury in the hydrocarbon solvents, shaking these solutions at 25 °C with distilled water containing 0.001 mol of phosphinic acid[3)] in order to prevent mercury oxidation, and determining the mercury concentrations of both phases.

## Results and Discussion

The temperature dependence of the mercury solubility in each hydrocarbon is shown in Fig. 1. The constants, A and B, that were found to satisfy Eq. 1 are shown in Table 1.

$$\mathrm{Log}\,X = A\,\mathrm{Log}\,T + B, \qquad (1)$$

where $X$ is the mole fraction of the solute and where $T$ is the absolute temperature. The results for pentane at 25 °C were found to agree well with Kuntz's result,[8)]

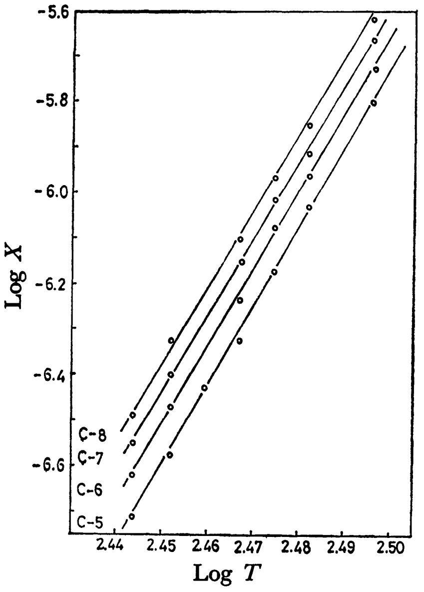

Fig. 1. Temperature dependence of the mercury solubility in hydrocarbons.
C-5: Pentane, C-6: hexane, C-7: heptane, C-8: octane.

Table 1. Constants of Eq. 1

| Solvent | A | B |
|---|---|---|
| Pentane | 17.375 | −49.169 |
| Hexane | 17.111 | −48.432 |
| Heptane | 17.250 | −48.705 |
| Octane | 16.500 | −46.800 |

which was obtained using the ultraviolet-absorption measurements at 256.0 nm, while for hexane, heptane, and octane the results agreed well with those of Spencer,⁴⁾ which were obtained using the radioactive tracer $\mathrm{Hg}^{203}$ in the temperature range from 5 to 40 °C. The mercury solubility in these hydrocarbons was estimated using the Hildebrand equation for regular solutions.¹⁰⁾ The agreement between the values calculated from the equation and the experimental measurements was a good approximation by an order of magnitude except in the case of water.

The liquid-liquid distribution constant for metallic mercury between each hydrocarbon and water is shown in Table 2. The distribution constant, $K$, is expressed by Eq. 2:

$$K = [\mathrm{Hg}]_{\mathrm{ag}}/[\mathrm{Hg}]_{\mathrm{hc}}, \qquad (2)$$

where $[\mathrm{Hg}]_{\mathrm{aq}}$ and $[\mathrm{Hg}]_{\mathrm{hc}}$ are the mercury concentrations in the aqueous solution and in the hydrocarbon respectively. Table 2 shows the $K$ values from this work in the first column and those from Moser's work³⁾ in the second column. The third column shows the values calculated from the ratio of the mercury solubility in the hydrocarbon and water at 25 °C. The mercury solubility in the water used was found to be $(3.0\pm0.1)\times10^{-7}\,\mathrm{mol\,dm^{-3}}$ at 25 °C in this work, in good agreement with the results of Glew⁵⁾ and Enat.⁶⁾ The distribution constant was found to be equal to the ratio of the independent mercury solubility in the hydrocarbon and in water.

Table 2. Distribution constants, $K$, at 25 °C

| | Measured | Reference³⁾ | Calculated |
|---|---|---|---|
| Pentane | 0.054 | — | 0.052 |
| Hexane | 0.048 | 0.048 | 0.048 |
| Heptane | 0.046 | — | 0.046 |
| Octane | 0.046 | — | 0.045 |

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