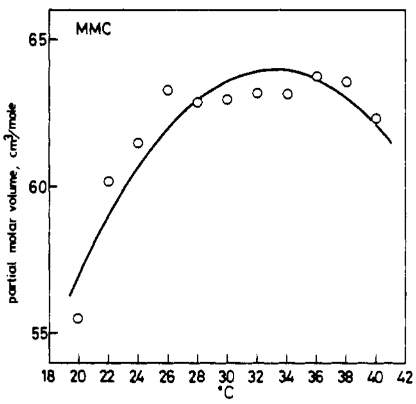

**Figure 5.** Temperature dependence of partial molal volume of MMC.

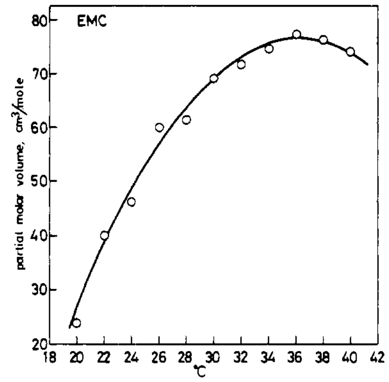

**Figure 6.** Temperature dependence of partial molal volume of EMC.

present results and the signs of the thermodynamic values, it can be possibly concluded that both solutes in aqueous solution appear to be "iceberg" breakers. This behavior presumably can be explained as hydrogen bonding formation between chloride in the solutes and hydrogen of water, considered to be weak, would interrupt "iceberg" formation.

### Acknowledgment

The authors wish to express their thanks to the staffs of Faculty of General Education of Kumamoto University, for their valuable discussion, and to Dr. H. Sassa, chief of the Institute, for his encouragement throughout the work.

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Received for review November 1, 1977. Accepted March 7, 1978.

**Supplementary Material Available:** Tables of density and mole fraction values and reciprocal densities (4 pages). Ordering information is given on any current masthead page.

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# Solubility of Hydrocarbons in Cyclohexylamine

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**Measurements are reported of the solubility of methane, ethane, propane, and ethylene in cyclohexylamine. These hydrocarbons form regular solutions in cyclohexylamine; the solubilities give normal correlations with energies of vaporization at the boiling point and with temperature.**

In determining the kinetic acidities of several volatile hydrocarbons with cesium cyclohexylamide in cyclohexylamine (CHA) (*6*, *8*), it was necessary to measure solubilities in CHA in order to correct for the proportion of hydrocarbon in the vapor phase. Hildebrand (*4*) has found excellent correlations of gas solubilities with the energy of vaporization at the boiling point, $\Delta E_b{}^v$. This quantity is taken as a measure of the forces of attraction between the molecules of the gas. Dymond (*2*) and Miller (*7*) have found that the solubilities of 17 different gases in cyclohexane at 25 °C give an excellent correlation with $\Delta E_b{}^v$ of the gases. In addition, they have found that the entropies of solution form an excellent correlation with $-R \ln x_2$ ($x_2$ = mole fraction of dissolved gas). If these relationships are valid in the solvent cyclohexylamine, measurement of a few solubility values should allow prediction of solubility values at similar temperature for other hydrocarbon gases which might be desired in the future. Dymond (*2*) found that the gases may be grouped into three different families. One correlation is provided by inert gases, another by fluorocarbons, and a third by aliphatic hydrocarbons. An investigation was therefore undertaken to determine if a similar correlation could be established for the solubilities of aliphatic hydrocarbons in cyclohexylamine.

### Experimental Section

The apparatus generally reported for measurement of gas solubilities is complex and expensive (*3*). We found that results

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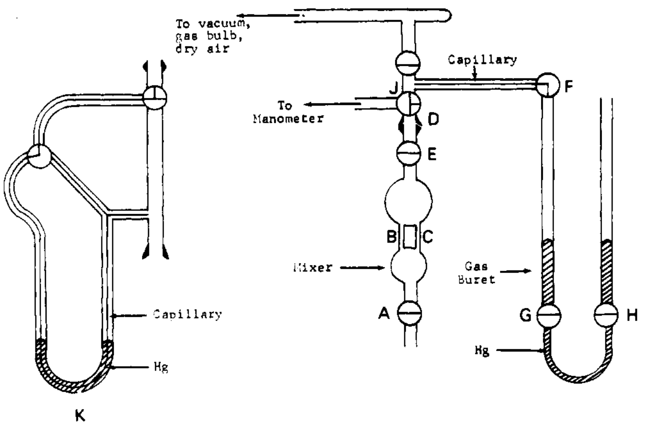

**Figure 1.** Gas solubility apparatus.

of adequate precision for the present purpose could be obtained by the simpler apparatus described below. The accuracy of values obtained by this technique was confirmed by comparison of solubility values for methane in cyclohexane with the values reported by Dymond (*2*). The technique was then applied to a study of the solubility behavior of a series of gases in cyclohexylamine as a function of temperature.

The apparatus employed is shown in Figure 1. The basic elements are a mixer, where the gas and liquid may be equilibrated at a constant temperature, a gas buret to allow introduction of a known molar amount of gas, and a vacuum manifold, which allows evacuation to 1 $\mu$, introduction of dry air, connection to a gas storage bulb, and accurate measurement of the pressure. A solubility measurement was conducted in the following manner.

Degassed cyclohexylamine, previously dried over lithium cyclohexylamide, was admitted under its own vapor pressure to the evacuated mixer, via the lower stopcock A, and the liquid level was allowed to rise until the meniscus was in the calibrated region of the central capillaries, B and C. The volume of solvent at 25 °C was then simply determined by comparing the meniscus height to a calibration chart. The mixer was then attached to the vacuum manifold at D, and the degassed alkane was rapidly admitted from the gas buret via the upper stopcock E with stopcocks F, G, and H open, and three-way stopcock J as shown in Figure 1. Since the gas buret and manifold were at atmospheric pressure and temperature before and after admission of gas, the molar amount of gas swept in was known. The mixer was then detached from the vacuum manifold and slowly rotated, while immersed in the water constant temperature bath, about a horizontal axis orthogonal to the plane of the capillaries B and C. Efficient mixing of gas and liquid phases occurred, and equilibrium was established within 0.5 h. The mixer was then reattached to the vacuum manifold at D but with the balancing manometer K interposed. By suitable manipulation of the stopcocks the pressure inside the mixer was balanced by dry air, and the air pressure was measured using the main manometer, and corrected by any imbalance in the capillary manometer K. All mercury heights were measured with a cathetometer. Using this minimum volume (2.4 mL) manometer, reliable and reproducible data were obtained. Earlier attempts using larger manometers gave large systematic errors. Successive values of the solubility could be obtained without admitting fresh alkane, by evacuating the manometer after closing stopcock E, reestablishing equilibrium in the mixer, and measuring the new gas pressure as above. Alternatively, additional alkane could be swept into the mixer between such readings, so long as the pressure inside the mixer was less than 1 atm. It was found convenient to determine the alkane solubility at four temperatures, without intermediate change of the solvent, starting at the upper temperature so that additional alkane could be added as the solubility increased with decreasing temperature.

Table I. Solubility of Hydrocarbons in Cyclohexylamine[a]

| Hydrocarbon | Temp, °C | $10^4 x_2$ | Molarity, M | $\Delta E_b^V$, kcal mol$^{-1}$ |
|---|---|---|---|---|
| Methane | 30.0 | 19.2 | 0.017 | 1.77 |
| Ethane | 25.2 | 145 | 0.129 | 3.15 |
| Ethane | 30.0 | 139 | | |
| Ethane | 35.0 | 130 | | |
| Ethane | 39.7 | 124 | | |
| Propane | 25.2 | 537 | 0.469 | 4.03 |
| Propane | 30.0 | 497 | | |
| Propane | 34.9 | 455 | | |
| Propane | 39.9 | 421 | | |
| Ethylene | 24.9 | 105 | 0.094 | 2.9 |

[a] Solubilities calculated for 1.0 atm partial pressure of the gas.

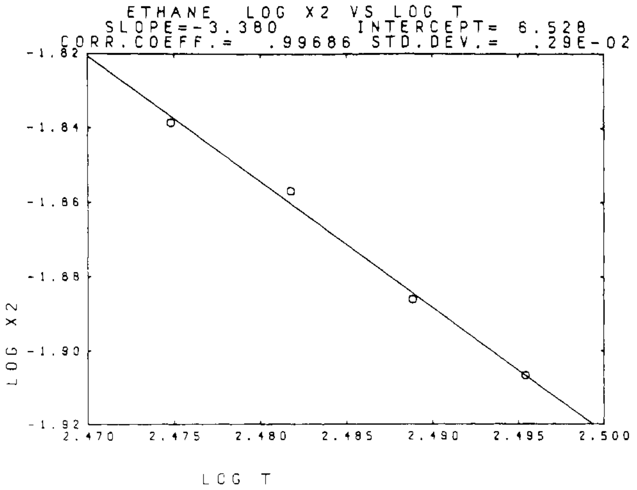

**Figure 2.** Solubility of ethane in cyclohexylamine as a function of temperature.

It was found that the volumes of both solvent and gas could be obtained to a precision of 0.5%. The final solubility values showed standard deviations below 1.0%. The technique does not give the high accuracy and precision of more complex apparatus, (*3*) but for the interpretation of kinetic data, these values are more than sufficient.

## Results and Discussion

The results obtained with this technique are collected in Table I. These hydrocarbons are found to be significantly less soluble in cyclohexylamine than they are in cyclohexane. This is not surprising, as the more polar cyclohexylamine would be expected to have a higher degree of intermolecular bonding than would the nonpolar cyclohexane.

The temperature dependence studies for ethane and propane enable a determination of the entropies of solution for these compounds. Since these sparingly soluble gases should obey Henry's law, eq 1 should apply, where $\bar{S}_2$ = the entropy of the dissolved gas, and $\bar{S}_2^{g}$ = the entropy of the compound in the gaseous state.

$$\Delta\bar{S}_2 = \bar{S}_2 - \bar{S}_2^{g} = R(\partial \ln x_2/\partial \ln T) \qquad (1)$$

A good indication of the reliability and internal consistency of the data obtained in these experiments is the linearity of the plots of log $x_2$ vs. log $T$. These are shown for ethane and for propane in Figures 2 and 3, where it can be seen that the correlation coefficients are greater than 0.99 in each case. These plots give values of −6.7 and −10.1 eu deg$^{-1}$ for ethane and propane, respectively. These compare with the values of −8.7 and −12.2 eu deg$^{-1}$ for ethane and propane in cyclohexane found by Dymond (*2*).

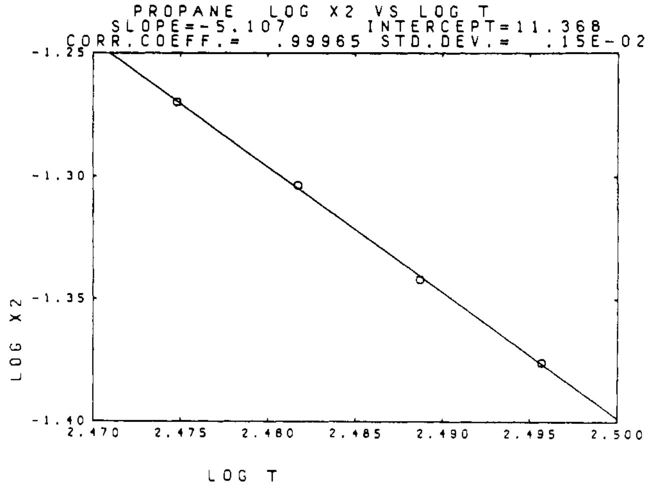

**Figure 3.** Solubility of propane in cyclohexylamine as a function of temperature.

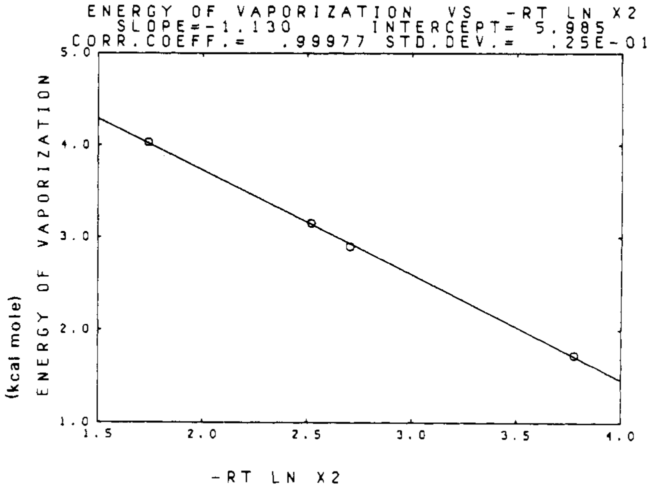

**Figure 4.** Correlation of solubilities at 25 °C of methane, ethane, propane, and ethylene with $\Delta E_b^v$; $\Delta E_b^v = -1.156(RT \ln x_2) + 6.035$.

For related systems a linear relation has been shown generally to obtain between $\Delta \bar{S}_2$ and $R \ln x_2$ (*5*). The data for ethane and propane correspond to eq 2. This equation in a series of successive approximations provided the short extrapolation for

$$\Delta \bar{S}_2 = 1.319(-R \ln x_2^{25\ °C}) - 17.8 \qquad (2)$$

methane at 25 °C, $x_2 = 19.7 \times 10^{-4}$. The derived value of $\Delta \bar{S}_2$ for methane is small, −1.5 eu deg$^{-1}$, and the temperature coefficient is also small.

The solubility parameter, $\delta_1$, of cyclohexylamine is calculated to be 8.7 cal$^{1/2}$ mL$^{-1/2}$ using the vapor pressure data of Carswell and Morrill (*1*). This value and the correlations of Hildebrand and Scott (*5*) between $\delta_1$ and log $x_2$ for methane and ethane give predicted values −2.60 and −1.72, respectively; the experimental values for log $x_2$ at 25 °C are −2.71 and −1.84, respectively. This close agreement provides further evidence that aliphatic hydrocarbons form regular solutions in cyclohexylamine. A further demonstration is provided by the linearity of the plot of solubility values for the four hydrocarbons in Table I at 25 °C with the corresponding values of $\Delta E_b^v$ in Figure 4. This correlation indicates that the solubilities of other hydrocarbons should be accurately predicted by the respective $\Delta E_b^v$ values.

## Acknowledgment

We are indebted to Professors J. H. Hildebrand and J. M. Prausnitz for valuable advice.

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Received for review November 21, 1977. Accepted April 17, 1978. This research was supported in part by USPH NIH Grant No. GM-12855.