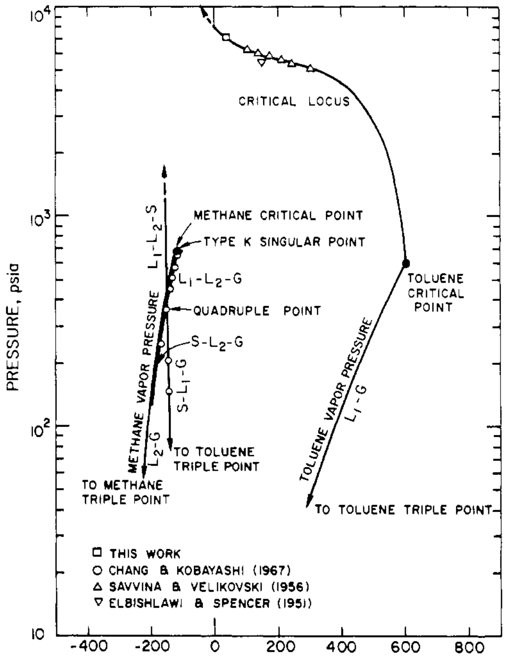

Figure 4. Pressure–temperature projection for the methane–toluene system.

the earlier data by Chang and Kobayashi (*2*) are attributed to sampling and/or analysis.

Acknowledgment

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Literature Cited

(1) Chang, H. L., Kobayashi, R., *J. Chem. Eng. Data*, **12**, 520 (1967).
(2) Chang, H. L., Kobayashi, R., *J. Chem. Eng. Data*, **12**, 517 (1967).
(3) Chen, R. J. J., Chappelear, P. S., Kobayashi, R., *J. Chem. Eng. Data*, **19**, 53 (1974).
(4) Chen, R. J. J., Chappelear, P. S., Kobayashi, R., *J. Chem. Eng. Data*, **19**, 58 (1974).
(5) Chen, R. J. J., Chappelear, P. S., Kobayashi, R., *J. Chem. Eng. Data*, **21**, 213 (1976).
(6) Elbishlawi, M., Spencer, J. R., *Ind. Eng. Chem.*, **43**, 1811 (1951).
(7) Exxon Production Research Co., Houston, Texas, private communication, 1977.
(8) Hwang, S.-C., Kobayashi, R., *J. Chem. Eng. Data*, **22**, 409 (1977).
(9) Hwang, S.-C., Lin, H.-M., Chappelear, P. S., Kobayashi, R., *J. Chem. Eng. Data*, **21**, 493 (1976).
(10) Mraw, S. C., Hwang, S.-C., Kobayashi, R., paper presented at the Cryogenic Engineering Conference, Boulder, Col., Aug 2–5, 1977.
(11) Mundis, C. J., Ph.D. Thesis, Oklahoma State University, Stillwater, Okla., 1976.
(12) Savvina, Y. D., Velikovski, A. S., *J. Phys. Chem. USSR*, **30**, 1596 (1956).
(13) Webber, C. E., *Trans. Am. Inst. Min. Metall. Pet. Eng.*, **136**, 192 (1940).
(14) Yarborough, L., *J. Chem. Eng. Data*, **17**, 129 (1972).

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Solubility of Chloromethylmercury(II) and Chloroethylmercury(II) in Water

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The solubilities of chloromethylmercury(II) (MMC) and chloroethylmercury(II) (EMC) in water have been carefully determined between 20 and 40 °C. The temperature dependence of the solubilities expressed as mole fraction, x_2, was given by the following equations: $\log x_{2(\mathrm{MMC})} = -1059/T + 0.176$; $\log x_{2(\mathrm{EMC})} = -1048/T - 0.612$. The thermodynamic parameters for converting MMC and EMC solids to a saturated aqueous solution were $\Delta\bar{H}_{2(\mathrm{MMC})} = 4711$ cal/mol, $\Delta\bar{S}_{2(\mathrm{MMC})} = 15.8$ eu, $\Delta\bar{H}_{2(\mathrm{EMC})} = 4642$ cal/mol, and $\Delta\bar{S}_{2(\mathrm{EMC})} = 15.6$ eu. The temperature dependence of the partial molal volume, $(\partial^2\bar{V}_2/\partial T^2)_P$, was negative in both MMC and EMC aqueous solutions.

Introduction

It is well known that trace amounts of organic mercury(II) compounds cause serious toxicity in mammals, especially humans. Increasing attention, therefore, is being paid to those compounds found naturally, e.g., in rivers and sea water. Accordingly, attention should be given to any redissolution of the compounds into natural water, for example, after soil reclamation and dredging harbors and contamination by industrial wastes containing an organic mercury(II) compound. For this reason, a fundamental study of the compounds is considered to be urgent for settling these problems.

Although many organic mercury(II) compounds are available, we studied the fundamental properties of MMC and EMC in this experiment, in which MMC is confirmed as the causal agent of so-called "Minamata disease" (*13–15*) and is widely analyzed among the organic mercury(II) compounds in natural occurence. EMC was chosen as the most related compound having the same toxicity as MMC.

Several authors have reported studies on the formation of CH_3Hg^+ with several ligands. Waugh et al. (*23*) obtained the solubility product of MMC only at 25 °C from the dissociation constant and solubility in water. Schwarzenbach and Schellenberg (*19*) reported formation constants and the thermodynamic values of CH_3Hg^+ with several ligands, and Budevsky et al. (*4*) studied in detail an interaction of CH_3Hg^+ with Cl^-. Hepler and Olofsson (*11*) also reviewed the thermodynamic properties,

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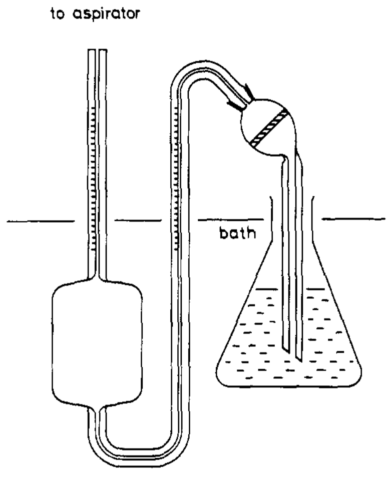

Figure 1. Handling of solution.

chemical equilibria, and standard potentials of the mercury(II) compounds. However, detailed solubilities of MMC and EMC over a large temperature range and thermodynamic parameters are not found in the literature.

The purpose of this investigation, therefore, was first to obtain accurate solubilities of MMC and EMC in water over a moderate range of temperatures and the values of enthalpy and entropy from the temperature dependence of the solubilities and then to study the dissolution of MMC and EMC into water from the temperature dependence of the partial molal volume of aqueous solution.

Experimental Section

MMC was obtained from Wako Co., Ltd., and recrystallized from absolute ethanol: mp 168 °C (reference values 168 (*8*) and 174 °C (*9*, *15*)), purity 99.1%. EMC was supplied from Tokyo Kasei Kogyo Co., Ltd., and also recrystallized from ethanol: mp 192 °C (reference value 192 °C (*16*), purity 99.3%. Inorganic mercury(II) as an impurity in a commercial product was detected before purification by a spot test of TLC with dithizone (*20*). After recrystallization, no color spot due to inorganic mercury(II) was observed. Other impurities were measured by a gas chromatography equipped electron capture detector (Yanagimoto, G-80); the degree of purity was evaluated. Water was carefully purified twice by distillation with potassium permanganate.

The saturated aqueous solutions of MMC and EMC were prepared using two thermostated baths for all experiments. The temperature of the first bath was maintained 3 °C higher than the desired temperature by continuous stirring; thus a saturated solution at higher temperature was primarily obtained. Constant temperature of the first bath was controlled by Pt-Hg regulator with ±0.05 °C accuracy. Then this solution was immersed in the second bath controlled at the desired temperature with a Pt-toluene-Hg regulator having an accuracy of ±0.01 °C. The temperature measurements in the baths were made by a Beckmann standard thermometer.

Determination of the concentration of a solute is often carried out by spectrophotometry. For the present solutes, since no absorption maxima are observed in the 200-300-nm region, even slight deviations of wavelength cause a large error in MMC and EMC contents. Furthermore direct gravimetry could not be applied because of some volatility and high toxicity of the solutes. Therefore, determination of the concentrations was performed in this experiment by density measurements of the solutions at a given temperature. A fairly linear relation having a high correlation coefficient ($\gamma = 0.999$) could be obtained between the mole fraction of the solutes and density of the solution in the 20-40 °C region. An extrapolation of a calibration curve, therefore, gave mole fraction of the solutes at a given temperature with high accuracy. Great care must be paid to deposition of the solutes with decreasing temperature of the solution and to handling of such a vigorous toxicant. Therefore, the apparatus in Figure 1 was used to lead the saturated solution directly into the pycnometer (ca. 20 mL capacity) without taking the sample solution from the bath. The pycnometer was joined via a glass filter (G-4, 5-10 μ) to the flask containing the thermostated solution and then filled with the solution by an aspirator.

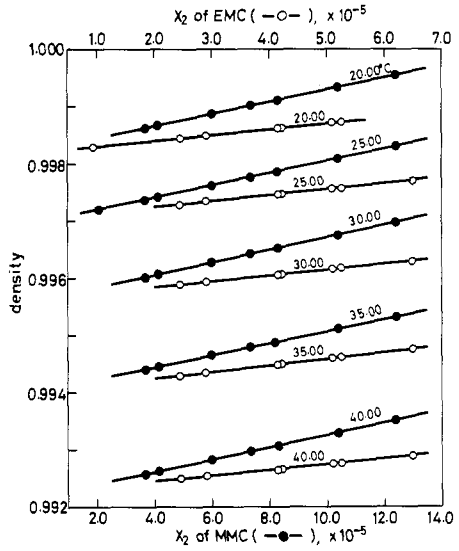

Figure 2. Density of solution as a function of mole fraction.

Table I. Temperature Dependence of Solubility

T, K	MMC $10^5 x_2$	EMC $10^5 x_2$
293.16	37.3 ± 0.5	6.5 ± 0.2
298.16	42.4 ± 0.5[a]	7.6 ± 0.3
303.16	46.8 ± 0.1	8.5 ± 0.1
308.16	54.8 ± 0.1	9.4 ± 0.2
313.16	63.4 ± 0.1	11.2 ± 0.2

[a] The value in ref 23 is 0.02 mol/L at 25 °C, which corresponds to $x_2 = 36.0 \times 10^{-5}$.

The partial molal volume was determined in this experiment using a dilatometer (Shibayama, simple type), because a gravity measurement with this pycnometer gave a somewhat low accuracy for a value of the partial molal volume. First, specific volume was determined by a dilatometer by measuring a volume of the solution containing a known amount of solute in weight percent between 20-40 °C at 2 °C intervals. In this experiment, the measurements of only three concentrations were made for both MMC and EMC, since, as mentioned above, fine linear relation could be obtained in advance between mole fraction of the solute and density of the solution. Then, partial molal volume at a given temperature was estimated using the data of the specific volume and weight percent. The cell capacity of the dilatometer was about 10 mL and diameter of capillary was 0.780 mm. Reading accuracy of a cathetometer was 0.01 mm. In order to minimize an error attributed to the accuracy of controlled temperature, at least six-ten readings, and generally more, were taken at each temperature.

Results and Discussion

The relation between density of the solution and mole fraction of MMC and EMC is illustrated in Figure 2, showing good linearity at every experimental temperature. The error in density, mainly originating from the weighing of the pycnometer, was ±0.000 05 g/cm^3. In Table I are presented the experimental values for the solubilities in water in the 20–40 °C region. These mole fractions were given by the equations from the least squares:

$$\log x_{2\,(\mathrm{MMC})} = -1059/T + 0.176 \qquad (\gamma = 0.997) \tag{1}$$

$$\log x_{2\,(\mathrm{EMC})} = -1048/T - 0.612 \qquad (\gamma = 0.998) \tag{2}$$

For the process of converting MMC and EMC solids to saturated solutions, the values of the partial molal enthalpy and entropy of solution are estimated from the data of temperature dependence of the solubility from the equations

$$\Delta\bar{H}_2 = RT\left(\frac{\partial \ln a_2}{\partial \ln x_2}\right)_{\mathrm{T}}\left(\frac{\partial \ln x_2}{\partial \ln T}\right)_{\mathrm{sat}} \tag{3}$$

$$\Delta\bar{S}_2 = \mathrm{R}\left(\frac{\partial \ln x_2}{\partial \ln T}\right)_{\mathrm{sat}}\left(\frac{\partial \ln a_2}{\partial \ln x_2}\right)_{\mathrm{T}} \tag{4}$$

where, a_2, $\Delta\bar{H}_2$, and $\Delta\bar{S}_2$ denote activity of solute, partial molal enthalpy, and entropy of solution, respectively. Though the value of a_2 was not determined in this experiment, it can be assumed that a_2 is nearly equal to x_2 by treating the system as an ideal solution because the system belongs to the "dilute solution". Accordingly, eq 3 and 4 can be converted to the following equations.

$$\Delta\bar{H}_2 \cong RT\left(\frac{\partial \ln x_2}{\partial \ln T}\right)_{\mathrm{sat}} \tag{3'}$$

$$\Delta\bar{S}_2 \cong R\left(\frac{\partial \ln x_2}{\partial \ln T}\right)_{\mathrm{sat}} \tag{4'}$$

From eq 3′ and 4′, the partial molal heat of solution for MMC and EMC was calculated to be $\Delta\bar{H}_{2(\mathrm{MMC})} = 4711$ cal/mol and $\Delta\bar{H}_{2(\mathrm{EMC})} = 4642$ cal/mol, and the partial molal entropy of solution was $\Delta\bar{S}_{2(\mathrm{MMC})} = 15.8$ eu and $\Delta\bar{S}_{2(\mathrm{EMC})} = 15.6$ eu, respectively.

The above discussion was made from an assumption that both solutes are nonelectrolytes. Schwarzenbach and Schellenberg (*19*), however, reported in detail an interaction of CH_3Hg^+ with Cl^- in water at 20 °C ($[CH_3HgCl]/[CH_3Hg^+][Cl^-] = 1.78 \times 10^5$, $\Delta\bar{G} = -7.0$ kcal/mol, $\Delta\bar{H} = -6.0$ kcal/mol, $\Delta\bar{S} = 3.6$ eu); namely, MMC seems to be a weak electrolyte. In order to estimate an effect of this slight dissociation, a dissociation constant and thermodynamic values for the dissociation process are calculated by using the above data as $[CH_3Hg^+][Cl^-]/[CH_3HgCl] = 5.62 \times 10^{-6}$ at 20 °C, $\Delta\bar{H}_{\mathrm{dis}} = 6.0$ kcal/mol, and $\Delta\bar{S}_{\mathrm{dis}} = -3.6$ eu, respectively. The influence of the calculated enthalpy and entropy change for this weak dissociation process will be negligibly small compared with the partial molal values obtained in this experiment. Although we have found no published value for the dissociation for EMC, it can be supposed that the dissociation of EMC will be less effective than that of MMC.

The dissolution of MMC and EMC into water was also studied in this experiment. Frank and Evans (*6*) described that, despite a small solubility of such hydrocarbons as higher alcohols in water, the heat of solution was small and an entropy of solution was negative. In order to rationalize this rather unusual situation, they postulated an ice formation which surrounds the dissolved hydrocarbon molecules and they proposed to call these phenomena the so-called "iceberg" formation. Afterward, many workers observed that in spite of small solubilities of the aliphatic hydrocarbons (*5*, *17*, *24*), aromatic hydrocarbons and their derivatives(*1*, *3*), and rare gases (*2*) in water, a value of the heat of solution was near zero and usually negative. In water, these phenomena are now considered to be general, while it is anomalous for the other solvents to exhibit these effects (*21*, *22*).

There are three experimental methods to judge iceberg forming or breaking: (a) by observing temperature dependence of partial molal volume (*10*), (b) by finding temperatures at which maximum density of solution is obtained (*7*, *25*, *26*), (c) by measurement of viscosity of solution (*12*, *18*).

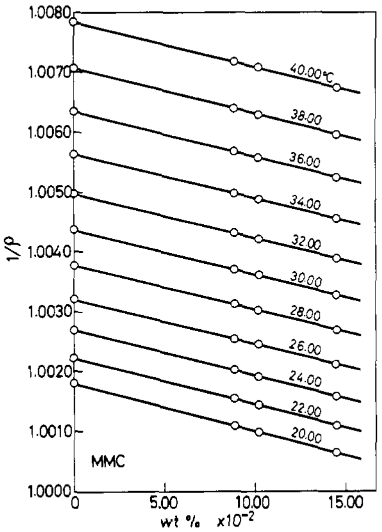

Figure 3. Plots of specific volume as a function of content of MMC in weight percent.

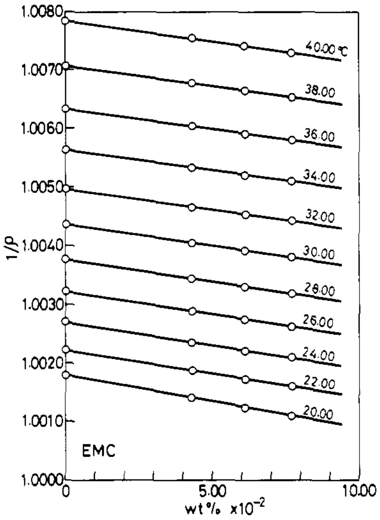

Figure 4. Plots of specific volume as a function of content of EMC in weight percent.

As far as the obtained thermodynamic parameters are concerned, both values were shown to be $\Delta\bar{H}_2 > 0$ and $\Delta\bar{S}_2 > 0$; therefore the present solutes seemed not to be "iceberg" forming but rather breaking. To confirm further this "iceberg" breaking, method (a) was applied by using the equation

$$\left(\frac{\partial \bar{C}_P}{\partial P}\right)_{\mathrm{T}} = -T\left(\frac{\partial^2 \bar{V}_2}{\partial T^2}\right)_{\mathrm{P}} \tag{5}$$

where $\bar{C}_P$ and $\bar{V}_2$ represent partial molal heat capacity and partial molal volume, respectively. Due to eq 5, structure-breaking leads to the prediction that $(\partial \bar{C}_P/\partial T^2)_P$ should be positive. On the basis of this reasoning and eq 5, it is seen that structure-breaking solutes should have negative $(\partial^2 \bar{V}_2/\partial T^2)_P$. Similar reasoning shows that positive $(\partial^2 \bar{V}_2/\partial T^2)_P$ should be associated with structure-making solutes. Figures 3 and 4 show the plots of specific volume (reciprocal density) against the contents of the solutes in weight percent. Thus partial molal volume at a respective temperature can be calculated by these graphs. Figures 5 and 6 represent the temperature dependence of the partial molal volume. The best fit curves are illustrated by treating with least squares. As is seen in the figures, $(\partial^2 \bar{V}_2/\partial T^2)_P$ was negative for both MMC and EMC. On the basis of the

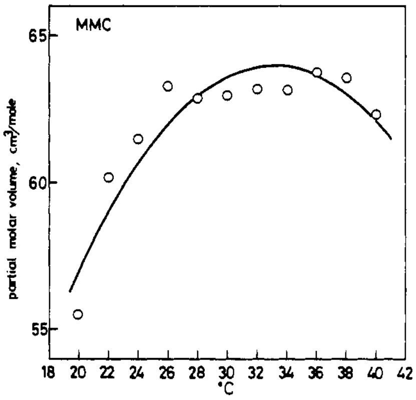

Figure 5. Temperature dependence of partial molal volume of MMC.

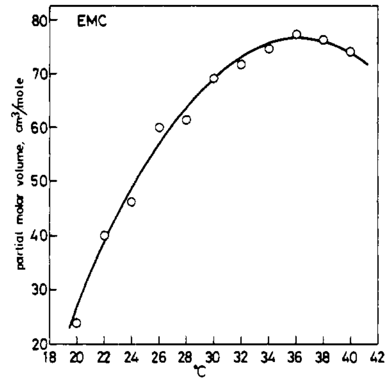

Figure 6. Temperature dependence of partial molal volume of EMC.

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.

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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.

Literature Cited

(1) Alexander, D. M., *J. Phys. Chem.*, **63**, 1021 (1959).
(2) Battino, R., Clever, H. L., *Chem. Rev.*, **66**, 395 (1966).
(3) Bohon, R. L., Claussen, W. F., *J. Am. Chem. Soc.*, **73**, 1571 (1951).
(4) Budevsky, O., Ingman, F., Liem, D. H., *Acta Chem. Scand.*, **27**, 1277 (1973).
(5) Claussen, W. F., and Polglase, M. F., *J. Am. Chem. Soc.*, **74**, 4817 (1952).
(6) Frank, H. S., Evans, M. W., *J. Chem. Phys.*, **13**, 507 (1945).
(7) Franks, F., Watson, B., *Trans. Faraday Soc.*, **63**, 329 (1967).
(8) Green, J. H. S., *Spectrochim. Acta, Part A*, **24**, 863 (1968).
(9) Goggin, P. L., Woodward, L. A., *Trans. Faraday Soc.*, **62**, 1423 (1966).
(10) Hepler, L. G., *Can. J. Chem.*, **47**, 4613 (1969).
(11) Hepler, L. G., Olofsson, G., *Chem. Rev.*, **75**, 585 (1975).
(12) Herskovits, T. T., Kelly, T. M., *J. Phys. Chem.*, **77**, 381 (1973).
(13) Irukayama, K., Kai, F., Kondo, T., Fujiki, M., *Kumamoto Med. J.*, **14**, 157 (1961).
(14) Irukayama, K., Kondo, T, Kai, F., Fujiki, M., *Kumamoto Med. J.*, **15**, 1 (1962).
(15) Irukayama, K., Kai, F., Fujiki, M., Kondo, T., *Kumamoto Med. J.*, **15**, 57 (1962).
(16) Kreevoy, M. M., Hansen, R. L., *J. Am. Chem. Soc.*, **83**, 626 (1961).
(17) Morrison, T. J., Billet, F., *J. Chem. Soc.*, 3819 (1952).
(18) Ruplei, J. A., *J. Phys. Chem.*, **68**, 2002 (1964).
(19) Schwarzenbach, G., Schellenberg, M., *Helv. Chim. Acta*, **48**, 28 (1965).
(20) Snell, F. D., Snell, C. T., "Colorimetric Methods of Analysis", George S. Ferguson, Philadelphia, Pa., 1958, p 136.
(21) Shinoda, K., *Kagaku Kogyo*, **21**, 1400 (1968).
(22) Shinoda, K., *J. Phys. Chem.*, **81**, 1300 (1977).
(23) Waugh, T. D., Walton, H. F., Laswick, J. A., *J. Phys. Chem.*, **59**, 395 (1955).
(24) Winkler, L. W., *Ber. Dtsch. Chem. Ges.*, **36**, 1408 (1901).
(25) Wada, G., Umeda, S., *Bull. Chem. Soc. Jpn.*, **35**, 646 (1962).
(26) Wada, G., Umeda, S., *Bull. Chem. Soc. Jpn.*, **35**, 1797 (1962).

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

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, ΔE_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 ΔE_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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