centration of the test acid after the addition of successive increments of standard base until the equivalence point is reached. The pK_a is calculated from the equation:

$$pK_a = pH + \log \frac{[HA] - \{H^+\}}{[A^-] + \{H^+\}}$$

where [HA] is the stoichiometric concentration of the undissociated acid molecule, $[A^-]$ is the stoichiometric concentration of the anion and $[H^+]$ is the activity of the hydrogen ion as calculated from the pH. The results are tabulated in Table II.

ACKNOWLEDGMENT

The authors thank the donors of the Petroleum Research Fund, Administered by the American Chemical Society, for partial support of this research.

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RECEIVED for review June 10, 1965. Accepted October 15, 1965. Based in part on dissertations submitted by J. P. Thole and R. D. Lingg to the Department of Chemistry of Xavier University in partial fulfillment of the requirements for the degree of Master of Science and Bachelor of Science, respectively.

Compound Formation in the Chloroform-Triethylamine System

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The phase diagram for the chloroform-triethylamine system has been determined from the results of cooling-curve experiments. Evidence has been found for a 1 to 1 compound which melts at 191° K. Eutectic compositions are at 0.38 and 0.78 mole fractions of triethylamine and 180° and 142° K.

RECENT equilibrium measurements (*1*) of the effect of chloroform on the mutual solubility of water and triethylamine have indicated strong interaction between chloroform and triethylamine. A variety of earlier investigations by others have also provided evidence for strong interactions of chloroform with triethylamine in all-liquid systems. Although there is general agreement that the observed deviations from ideal behavior can be attributed to hydrogen bonding and resulting formation of a complex or addition compound, no direct evidence for the existence of the proposed compound is available. This investigation was undertaken to provide direct evidence for or against the proposed compound.

EXPERIMENTAL

Cooling curves over the whole composition range from pure chloroform to pure triethylamine were determined with apparatus consisting of an evacuable Dewar, motor-driven stirring device, electric timer, calibrated platinum resistance thermometer, and Leeds and Northrup Type G-2 Mueller Bridge with Type HS galvanometer. Provision was made for passing a slow stream of dry air over the sample in the Dewar while measurements were being made. Cooling rates were controlled by adjusting the vacuum in the Dewar. The vacuum flask containing the sample to be investigated was immersed in a bath of liquid nitrogen.

Both chloroform and triethylamine were purified by distillation under reduced pressure. Boiling point and HCl titration measurements (*1*), as well as the freezing point data obtained in this investigation, confirm the purity of the triethylamine.

Because of the high viscosity of solutions containing more than about 60 mole % triethylamine, it was necessary to introduce seed crystals to prevent considerable supercooling. Several measurements made without the use of seed crystals indicated supercooling of more than 10° C., and in one experiment a temperature lower than the eutectic temperature was

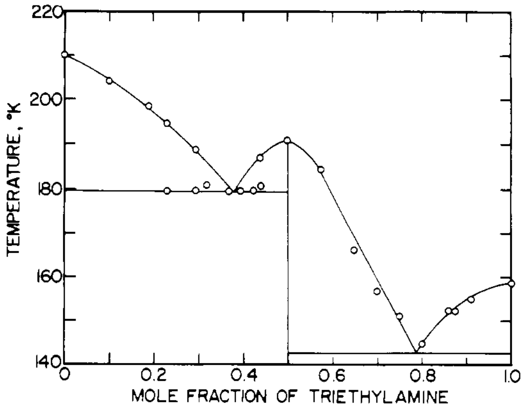

Figure 1. Phase diagram of chloroform and trimethylamine

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reached without obtaining crystals. Because of the great viscosity of the triethylamine-rich solutions at low temperatures, it was not possible to obtain a reliable eutectic halt for these solutions.

RESULTS

The results of this investigation are shown in the phase diagram in Figure 1, which provides direct evidence for a 1 to 1 compound of chloroform with triethylamine. This compound melts at 191° K. to form a nonideal mixture of chloroform and triethylamine. The eutectic on the chloroform-rich side is at 0.38 mole fraction of triethylamine and 180° K. The eutectic on the triethylamine-rich side is at 0.78 mole fraction of triethylamine and 142° K. Uncertainties in eutectic composition and temperature are less than ± 0.02 and $\pm 1°$ on the chloroform-rich side and ± 0.03 and $\pm 2°$ on the triethylamine-rich side.

Because of the obvious nonideality of the solutions in equilibrium with the 1 to 1 compound, no attempt was made to calculate the heat of formation of the compound from its components.

ACKNOWLEDGMENT

We thank the National Science Foundation for financial support, Paul R. Eisaman for his guidance in using the apparatus, and G. L. Bertrand for his assistance in preparing compounds and especially for his observations that led to our undertaking this investigation. The apparatus used in this work belongs to American Petroleum Institute Research Project No. 58B, and was kindly made available to us by A. J. Streiff.

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RECEIVED for review August 23, 1965. Accepted November 8, 1965.

Ternary Systems of Methanol

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Applications of methanol as a selective solvent or cosolvent for types of hydrocarbon are discussed. These include simple selective extraction of a mixture of paraffin isomers, use of methanol in small percentages to liquefy a low-melting organic crystalline solid such as o-nitrobiphenyl which has high selectivity, use of an anhydrous mixture of methanol and hydrogen chloride as a good solvent for cuprous chloride which dissolves light olefins selectively, and use of methano to extract aromatic hydrocarbon impurities from jet fuels diluted with carbon disulfide. Pertinent to these and to other attempted applications are 150 new observed ternary or quaternary system of methanol, as well as about the same number of published systems. The new systems are presented in this paper in concise form. Most of them include two or more liquid phases. Some of them show unusual types of graphs. The types include isopycnics, iso-optics, twin density lines, twin index lines, island curves, systems with two separate binodal curves, and those with three liquid phases. A novel type is one in which a twin density line terminates at a side line.

METHANOL is generally considered a relatively unselective solvent for different classes of hydrocarbons. For only one pair of hydrocarbon types—branched chain over straight chain paraffins—has pure methanol been recommended (*13*); and for that pair, only because no solvent has a very high selectivity.

On the other hand, the low cost, high stability, and convenient boiling point, 64.6°C., of methanol seemed to justify strenuous efforts to make it available as a selective solvent by the use of appropriate cosolvents. In many cases, these roles might be considered reversed—i.e., the properties of methanol may be exploited so that the selectivity of the other solvent becomes operable. For example, a low melting solid may be liquefied by solution in small percentages of methanol. These include highly polar organic crystalline solids such as *o*-nitrobiphenyl as well as inorganic salts such as lithium chloride.

In one example of this type (*14*), methanol seems to be much the best solvent for the purpose. Acid cuprous chloride is known to have a strong affinity for olefins over paraffins. However, the solubility of cuprous chloride in a preferred solution (*17*) is not over 17%, and this solution absorbs only a maximum of 0.224 mole of ethylene or 0.04 mole of propylene per mole of cuprous chloride in solution (*17*). Solutions of cuprous chloride in aqueous ammonia or alkylamines show still lower capacity for olefins.

By contrast, an anhydrous mixture of methanol and hydrogen chloride dissolves up to 34% total cuprous chloride (*11*, p. 101; *14*), as illustrated in graph 40 (in contact with copper turnings to keep it reduced and colorless). The solution is greenish black when a trace of cupric chloride is present. The cuprous chloride in solution absorbs molar amounts of ethylene or propylene (about 100 volumes per volume of solution) reversibly (in contrast to solutions of mercury salts) (*3*).

Ethyl and higher alcohols form similar complexes with cuprous chloride, with somewhat lower solubilities, and lower capacities for olefins; but they are unsatisfactory as selective solvents because the alcohol dissolves too much propane or ethane. Even methanol dissolves small amounts of propane. Glycols, ethoxyethanol, and especially hydroxypropionitrile (with hydrogen chloride) dissolve even larger concentrations of cuprous chloride than does methanol (graphs 41, 42), but these solutions absorb very little olefin. A small percentage of a glycol in a methanol solution greatly diminishes solution of propane. Solubility relations with some of these solvents are illustrated in graphs 40 to 45. $CuHCl_2$, a crystalline solid which is soluble in hydroxy compounds, is selected for plotting. However, the solid-solid relations of graph 43 were not in-

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