These experiments indicate that the basic pyridine molecule orients water molecules such that acidic and neutral salts cause more salting out than basic ones. The opposite effect was observed for the case of acidic nonelectrolytes.

An acid salt such as ammonium chloride may form a complex ion with pyridine. Formation of such a complex causes a decrease in the effective pyridine concentration and would result in the salting in of pyridine.

LITERATURE CITED

(1) Bogart, M., Brunjes, A. S., *Chem. Eng. Progr.* **44**, 95 (1948).
(2) Debye, P., McAuley, J., *Physik. Z.* **26**, 22 (1925).
(3) Fogg, E. T., Ph.D. thesis, University of Pennsylvania, 1953.
(4) Garwin, L., Hutchison, K. E., *Ind. Eng. Chem.* **42**, 727 (1950).
(5) Glasstone, S., Pound, A. J., *J. Chem. Soc.* **127**, 2660 (1925).
(6) Gross, P. M., *Chem. Revs.* **13**, 91 (1933).
(7) Gross, P., Iser, M., *Monatsh.* **55**, 329 (1930).
(8) Gross, P., Schwarz, K., *Ibid.*, **55**, 287 (1930).
(9) Guyer, A., Guyer, A., Jr., Johnson, B. K., *Helv. Chim. Acta* **38**, 946 (1942).
(10) Harned, H. S., Owen, B. B., "Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1942.
(11) Johnson, A., Furter, W., *Can. J. Technol.* **34**, 413 (1957).
(12) Jost, W., *Chem.-Ing.-Tech.* **23**, 65 (1951).
(13) Long, F. A., McDevit, W. F., *Chem. Revs.* **51**, 119 (1952).
(14) Novella, E. C., Tarraso, J. M., *Anales real soc. espan. fis. y quim. (Madrid)* **48B**, 441 (1952).
(15) Philip, J. C., *J. Chem. Soc.* **91**, 711 (1907).
(16) Rieder, R. M., Thompson, A. R., *Ind. Eng. Chem.* **42**, 379 (1950).
(17) Tammann, G., *Physik. Z. Chem.* **11**, 676 (1893).
(18) Tursi, R. R., Thompson, A. R., *Chem. Eng. Progr.* **47**, 304 (1951).
(19) Yamamoto, Y., others, *Chem. Eng. (Japan)* **16**, 166 (1952).

Received for review June 28, 1957. Accepted March 3, 1958.

Boiling Point – Composition Diagrams for the Systems 2-Ethoxyethanol–Ethyl Acetate and 2-Ethoxyethanol–Propyl Acetate

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In an investigation of the solvent properties of mixtures of 2-ethoxyethanol-ethyl acetate and 2-ethoxyethanol-propyl acetate in which moderately active metal salts were to be electrolyzed, it seemed desirable to determine the boiling point-composition diagrams for these systems. Especially because azeotrope formation has been noted in the 2-ethoxyethanol-butyl acetate system (*1,4*) it was of interest to determine whether azeotropes would form between 2-ethoxyethanol and ethyl or propyl acetate solutions.

MATERIALS

C.P. ethyl and propyl acetate were purified by the procedure of Hurd and Strong (*3*) and distilled twice from a 3-foot, all-glass column (*7*); in each case the center fraction was taken. The refractive indices at 25° for ethyl and propyl acetate, respectively, were $n_D^{25} = 1.3698$ and $n_D^{25} = 1.3821$.

C.P. 2-ethoxyethanol was fractionally distilled twice from a 3-foot, all-glass column and the center fractions were retained. The refractive index at 25° was found to be $n_D^{25} = 1.4059$.

ANALYTICAL METHODS

Vapor and liquid samples were analyzed by means of index of refraction, using a Bausch & Lomb refractometer with a sodium lamp as the source of illumination. The composition of the samples was determined from a refractive index-composition curve determined from samples of known composition. Standard samples were prepared by direct weighing in glass-stoppered flasks. The refractometer cell was maintained at a constant temperature of 25° ± 0.05° by pumping water from a constant temperature bath through the instrument. Four or five measurements were taken on each sample and the average refractive index was taken.

PROCEDURE

The determinations were carried out in an Othmer equilibrium still (*5*) manufactured by the Emil Greiner Co. The pressure was maintained at 760 mm. of mercury by means of

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Table I. Boiling Point-Composition Data for 2-Ethoxyethanol-Ethyl Acetate System at 760 Mm. of Mercury Pressure

B.P., °C.	Composition, Mole % of 2-Ethoxyethanol	
	Vapor	Liquid
77.1	0.0	0.0
80.6	3.75	18.75
82.3	5.0	26.25
84.2	6.25	33.5
87.1	8.75	42.0
90.5	13.25	54.75
95.4	18.25	65.25
97.6	21.0	68.5
106.8	34.25	80.7
113.1	47.0	86.7
119.3	59.1	91.75
125.9	74.0	95.0
128.6	80.4	96.8
130.6	83.75	98.0
135.0	100.0	100.0

Table II. Boiling Point-Composition Data for 2-Ethoxyethanol-Propyl Acetate System at 760 Mm. of Mercury Pressure

B.P., °C.	Composition, Mole % of 2-Ethoxyethanol	
	Vapor	Liquid
101.6	0.0	0.0
103.1	4.75	11.0
104.0	6.5	15.75
105.3	11.0	20.5
107.2	15.75	37.5
109.55	21.5	48.5
111.8	27.0	59.0
114.6	34.5	68.75
117.5	42.5	76.5
120.6	48.6	81.5
126.3	67.6	90.4
129.5	77.0	93.75
131.4	84.1	96.4
133.85	95.6	98.5
135.0	100.0	100.0

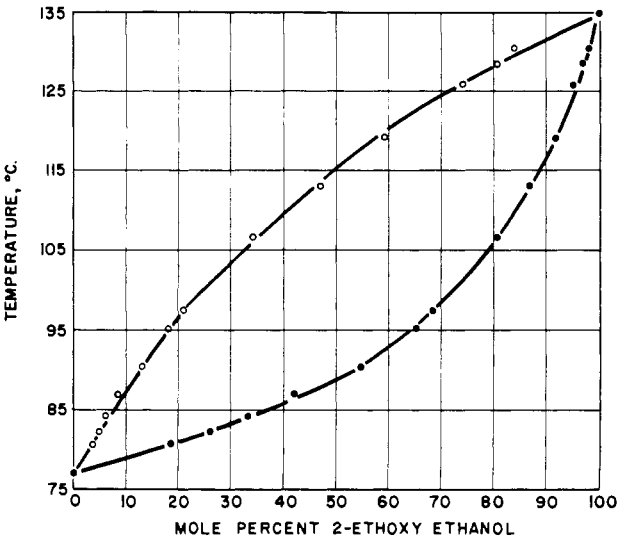

Figure 1. Boiling point-composition diagram for system 2-ethoxyethanol-ethyl acetate

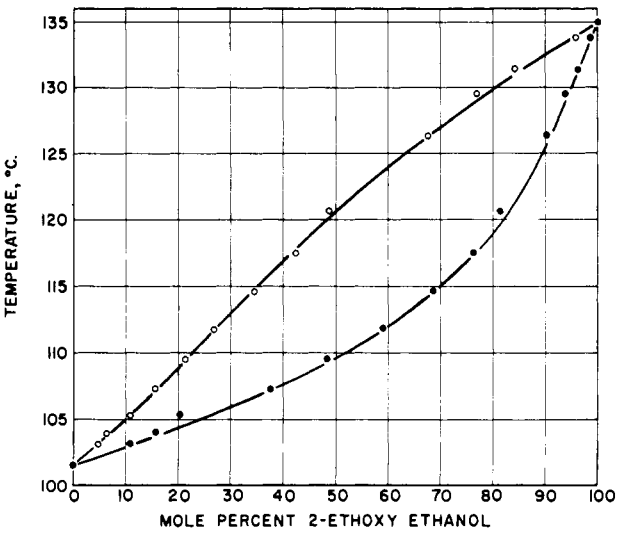

Figure 2. Boiling point-composition diagram for system 2-ethoxyethanol-propyl acetate

a manostat similar to that previously described (*6*). Positive pressure on the still was provided by dry nitrogen. The thermometer was calibrated against several pure liquid standards.

RESULTS

The experimental results are shown in Tables I and II and graphically in Figures 1 and 2. The activity coefficient, γ, of 2-ethoxyethanol in ethyl and propyl acetate has been calculated using the relation

$$\gamma = \frac{py_1}{p_1 x_1}$$

where p signifies total gas pressure, 760 mm., y_1 the mole fraction of 2-ethoxyethanol in the vapor phase, x_1 the mole fraction of 2-ethoxyethanol in the liquid phase, and p_1 the vapor pressure of pure 2-ethoxyethanol. Values for p_1 were calculated using the Antoine equation,

$$\log p_1 = A - B/t + C$$

with constants approximated from the experimental data of Gardner (*2*).

The average value for γ in 2-ethoxyethanol-ethyl acetate solutions above 82.3° is calculated as 1.09 with the average deviation from the mean in this range ± 0.05. The average value for γ in 2-ethoxyethanol-propyl acetate solutions above 105.3° is calculated as 0.99 with average deviation from the mean in this range ± 0.02. In both of these systems there is a gradual increase in activity coefficient of 2-ethoxyethanol in the high acetate concentration range. Although there are no azeotropes in these systems, appreciable deviation from ideality does exist in dilute solutions of 2-ethoxyethanol in ethyl and propyl acetate, as indicated by the increase in the activity coefficient in this concentration range.

The refractive index-composition curve for the 2-ethoxyethanol-propyl acetate system gives a curve bowed slightly downward; in the 2-ethoxyethanol-ethyl acetate system a straight-line relation was obtained.

LITERATURE CITED

(1) Carbide and Carbon Chemicals Corp., "Cellosolve and Carbitol Solvents," Jan. 1, 1947.
(2) Gardner, G. S., *Ind. Eng. Chem.* **32**, 226–31 (1940).
(3) Hurd, C. D., Strong, J. S., *Anal. Chem.* **23**, 542 (1951).
(4) Miller, K. J., *J. Phys. Chem.* **62**, 512 (1958).
(5) Othmer, D. F., *Ibid.*, **20**, 763–6 (1948).
(6) Piret, E. L., Hall, M. W., *Ind. Eng. Chem.* **40**, 661–72 (1948).
(7) Todd, F., *Ind. Chem., Anal. Ed.* **17**, 175–81 (1945).

Received for review April 3, 1957. Accepted January 10, 1958.

Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behavior of the Methane-Cyclohexane System

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Quantitative information concerning the volumetric and phase behavior of hydrocarbon mixtures is often of value in connection with the production and refining of petroleum. Such equilibrium data are also essential to the evaluation and application of information concerning molecular transport in which deviations from equilibrium are encountered. No information was found by the authors concerning the volumetric or phase behavior of mixtures of methane and cyclohexane. Because of the absence of such experimental information, a study was made of the volumetric behavior of four mixtures of methane and cyclohexane at pressures up to 10,000 p.s.i. and at temperatures between 70° and 340° F. Significant thermal rearrangement of the cyclohexane occurred at higher temperatures, thus limiting the range of temperatures investigated.

The volumetric behavior of cyclohexane has been studied in detail near atmospheric pressure and was critically reviewed by Rossini (*14*). More recently the effect of pressure and temperature upon the molal volume of cyclohexane liquid has been determined (*9*). The latter investigation included