

Isobaric Vapor-Liquid Equilibrium Data

System: Ethylene Dichloride-*n*-Butanol

D. SUBRAMANIAN, G. D. NAGESHWAR, and P. S. MENE
Laxminarayan Institute of Technology, Nagpur, India

Vapor-liquid equilibrium data have been determined between 723 and 729 mm. of Hg for the system ethylene dichloride-*n*-butanol. The activity coefficient data are correlated with Chao's modified Redlich-Kister equation. The experimental data meet the thermodynamic requirements, checked by Herington's area test. The system does not form an azeotrope.

VAPOR-LIQUID equilibrium data for the binary system ethylene dichloride-*n*-butanol are not available in the literature and are reported here at isobaric condition.

EXPERIMENTAL

The vapor-liquid equilibrium data were determined by an Othmer-type vapor recirculating still (5). *n*-Butanol, A.R. grade, supplied by M/S British Drug House Co., Bombay, and ethylene dichloride supplied by M/S E. Merck AG, Darmstadt, Germany, were redistilled in a laboratory-packed distillation column having a diameter of 32 mm. and a height of 480 mm., packed with 2-mm. Raschig rings. The boiling point was measured by a calibrated mercury-in-glass thermometer. The atmospheric pressure was measured by a Fortin's barometer. The density was

determined with a locally made pycnometer, which gave the density of water at 40°C. as 0.9926 [literature (2) value = 0.9922] and the refractive index was measured by Abbe's refractometer. The physical properties of the chemicals, used along with the literature values, are given in Table I.

Table II shows the specific gravity composition data. They were determined by keeping the pycnometer in the constant-temperature bath at 40° ± 0.1°C. for one hour. A large graph was drawn, and the composition of the unknown mixture was determined from this.

The liquid phase activity coefficient was determined from the relation

$$\gamma_i = \frac{y_i P}{x_i P_i^0}$$

The vapor imperfection, if it existed, is ignored, as the pressure is nearly 1 atm.

The vapor pressure data for *n*-butanol (4) at various temperatures were calculated from the equation $\log P^0$ (mm. of Hg) = 9.136 - (2442.8)/*T*. Range, -75° to 117.7°C. For ethylene dichloride (4), the data were obtained from the graph of vapor pressure vs. temperature.

Table I. Physical Properties of the Chemicals

Reagent	B.P., ° C., 760 Mm. of Hg	Density, Grams/Ml., 25° C.	Refractive Index, 25° C.	Ref.
Ethylene dichloride	83.5 ± 0.2 (83.5) ^a	1.2448 (1.2453)	1.4423 (1.4425)	(7)
<i>n</i> -Butanol	117.7 ± 0.2 (117.726)	0.8051 (0.8057)	1.3973 (1.3974)	(7)

^a Literature values are shown in parentheses; the boiling points were obtained by *dt/dP* correction.

Table II. Specific Gravity Composition Data, 40° ± 0.1°C.

Ethylene Dichloride, Mole Fraction, <i>x</i> ₁	Specific Gravity
0.0000	0.7996
0.0528	0.8200
0.0991	0.8401
0.1536	0.8579
0.2034	0.8769
0.2523	0.8976
0.2916	0.9155
0.3562	0.9365
0.4027	0.9558
0.4494	0.9751
0.5041	0.9981
0.5501	1.0183
0.6005	1.0399
0.6537	1.0636
0.7005	1.0853
0.7473	1.1058
0.7991	1.1313
0.8521	1.1566
0.9111	1.1836
0.9508	1.2046
1.0000	1.2325

Table III. Experimental Vapor-Liquid Equilibrium Data

Pressure, Mm. of Hg	B.P., ° C.	<i>x</i> ₁	<i>y</i> ₁	<i>y</i> ₁ , Calcd.	<i>γ</i> ₁	<i>γ</i> ₂
723.5	108.15	0.069	0.316	0.3170	2.314	0.999
726.4	106.80	0.085	0.366	0.3168	2.259	0.997
726.7	104.35	0.110	0.440	0.4380	2.224	0.996
724.6	103.40	0.120	0.462	0.4610	2.190	0.999
725.2	101.95	0.138	0.498	0.5000	2.132	1.013
727.0	101.70	0.143	0.508	0.5089	2.124	1.008
725.1	100.00	0.163	0.547	0.5467	2.076	1.018
726.9	99.40	0.175	0.568	0.5681	2.055	1.010
725.4	98.50	0.185	0.585	0.5824	2.044	1.015
727.0	97.35	0.206	0.613	0.6134	1.973	1.024
727.1	96.30	0.224	0.636	0.6372	1.909	1.033
725.5	94.55	0.256	0.670	0.6674	1.857	1.041
723.9	92.20	0.315	0.718	0.7200	1.708	1.064
726.0	90.35	0.373	0.758	0.7576	1.599	1.082
724.0	88.90	0.424	0.784	0.7843	1.502	1.116
727.3	87.90	0.468	0.806	0.8044	1.438	1.140
725.5	86.40	0.543	0.830	0.8285	1.327	1.236
727.8	85.30	0.621	0.856	0.8554	1.231	1.327
724.1	84.40	0.692	0.879	0.8740	1.158	1.420
728.1	83.90	0.754	0.897	0.8972	1.096	1.561
726.3	83.55	0.808	0.909	0.9085	1.053	1.810
726.7	82.95	0.846	0.922	0.9218	1.027	1.967
724.7	82.55	0.898	0.940	0.9430	1.006	2.327
726.5	82.20	0.938	0.958	0.9620	0.979	2.724
724.7	81.80	0.974	0.981	0.9820	0.978	2.972

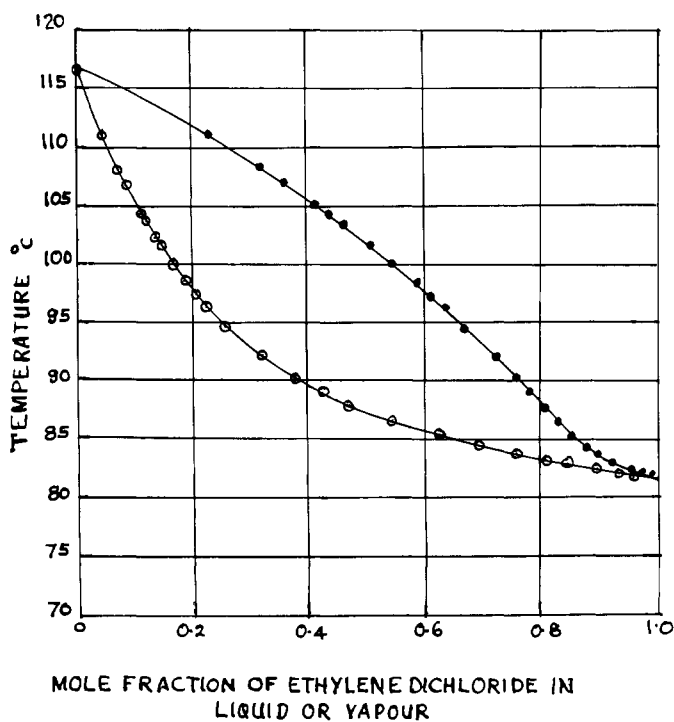


Figure 1. t - x - y Diagram
 ○ Liquid ● Vapor

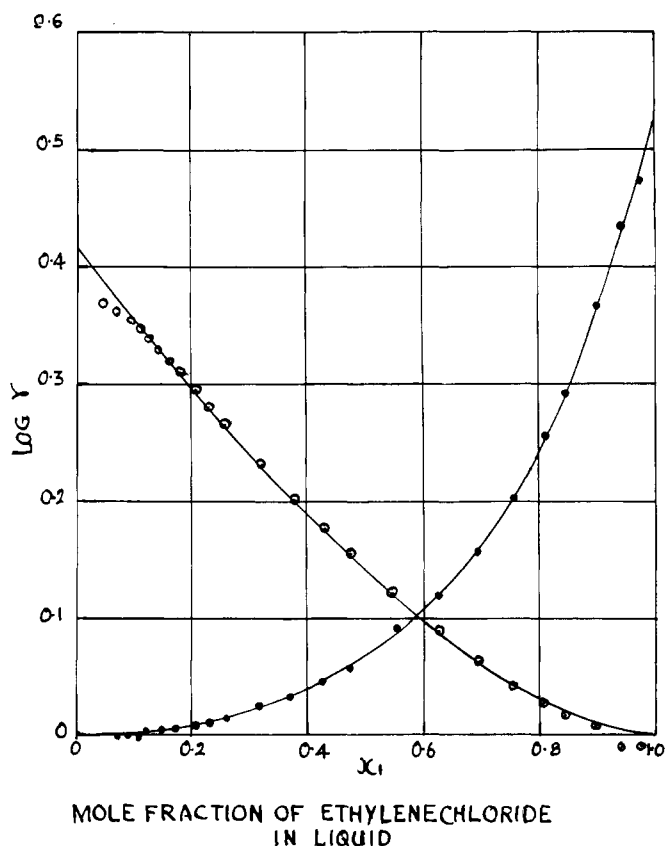


Figure 2. $\log \gamma$ vs. x_1 plot
 ○ $\log \gamma_1$ ● $\log \gamma_2$

RESULTS AND DISCUSSION

The experimental vapor-liquid equilibrium data are presented in Table III. Figures 1 and 2 show t - x - y and $\log \gamma$ vs. x_1 (mole fraction of ethylene dichloride in liquid) plots, respectively.

The ratios of the activity coefficients were correlated by Chao's (1) modified Redlich-Kister equation

$$\log \frac{\gamma_1}{\gamma_2} = a + b(x_2 - x_1) + c(6x_1x_2 - 1)$$

where $a = 0.0313$, $b = 0.434$, and $c = 0.06$.

The individual activity coefficients were calculated by the method suggested by Nagata (6). The root mean square deviation in the calculation of the vapor composition is 0.3%. The calculated values of γ_1 are shown in Table III.

The thermodynamic consistency was checked by Herington's (3) area test, showing $D < J$ ($D = 13.29$, $J = 14.62$).

LITERATURE CITED

- (1) Chao, K.C., *Ind. Eng. Chem.* **51**, 93 (1959).
- (2) "Chemical Engineers' Handbook" (Asian Edition), J.H. Perry, Ed., pp. 3-70, McGraw-Hill, 1963.
- (3) Herington, E.F.G., *J. Inst. Petrol.* **37**, 457 (1951), as cited by Hala, E., Pick, J., Fried, V., Vilim, O., "Vapour Liquid Equilibrium," p. 332, Pergamon, London, 1967.
- (4) Jordan, T.E., "Vapour Pressures of Organic Compounds," p. 66, Interscience, New York, 1954.
- (5) Mainkar, S.V., Mene, P.S., *Ind. Chem. Eng.* **9**, 120 (1967).
- (6) Nagata, I., *J. CHEM. ENG. DATA* **7**, 360 (1962).
- (7) Timmermans, J., "Physico Chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950.

RECEIVED for review October 14, 1968. Accepted May 11, 1969.

Isothermal Compressibility of Water at Various Temperatures

FRANK J. MILLERO, RICHARD W. CURRY, and WALTER DROST-HANSEN
 Institute of Marine Sciences, University of Miami, Miami, Fla. 33149

An apparatus is described for the measurement of the isothermal compressibility of liquids at pressures up to 50 atm. and temperatures to 60°C. The apparatus has been used to measure the isothermal compressibility of water from 2° to 55°C. The results are discussed briefly and compared to the values obtained by other workers.

COMPRESSIBILITY measurements have been made both isothermally and adiabatically on aqueous solutions (6) and on water (1, 3-5, 7, 9-14). Most prior studies of isothermal compressibility have been made over extended pressure ranges, and very few measurements are available at or near 1 atm. Furthermore, only a very limited number of studies have been made of the compressibility of aqueous

solutions as a function of temperature. To remedy this situation somewhat, the authors have initiated a study of the isothermal compressibility of aqueous solutions at low pressures and as a function of temperature.

The present report describes the compressibility apparatus and some isothermal compressibility measurements made on water between 2° and 55°C. Recently,