Isobaric Vapor-Liquid Equilibrium Data for the System 1-Propanol–*p*-Dioxane

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Vapor-liquid equilibrium data for the binary system 1-propanol–*p*-dioxane obtained at 760 mm. of mercury, using a vapor recirculatory equilibrium still, are reported.

DISTILLATION is used extensively for the separation of liquid mixtures. Accurate and complete vapor-liquid equilibrium data are necessary for the rational design of distillation towers. These data are obtainable under two fixed conditions, isothermal and isobaric. Most distillation processes are carried out at constant pressure rather than constant temperature, so that temperature-composition curves are more practical in engineering calculations, such as the number of plates, although from theoretical considerations pressure-composition curves are preferable. As part of a continuing equilibrium study of the important alcohol-ether systems, hitherto unreported vapor-liquid equilibrium data on the 1-propanol-*p*-dioxane system were determined at 760 mm. of mercury.

EXPERIMENTAL

Purity of Liquids. Analytical reagent grade liquids were used. 1-Propanol (Veb Labor Chemie Apolda, Germany) was further purified by refluxing over fresh quicklime for 6 hours and distilling in a 3 × 100 cm. glass column packed with McMahon packings. *p*-Dioxane (British Drug House, India) was refluxed over metallic sodium for 24 hours and distilled in the same column. The predistillate and residual liquids, each approximately one sixth of the original charge, were discarded and the heart cuts were used. Precautions were taken to minimize absorption of atmospheric moisture by the liquids. The physical properties of the liquids used are listed with literature data (*3*) in Table I.

Analytical Method. Refractive index measurements were adopted to analyze vapor and liquid samples from the still because of the wide difference between the refractive indices of the pure components of the binary system. An Abbe refractometer controlled at 30° ± 0.2° C. was used. The measurements were reproducible to within ±0.0002. Calibration data are shown in Table II.

Table I. Physical Properties of Pure Liquids

	Normal B.P., ° C.		Ref. Index, n_D^{25}	
Liquids	Exptl.	Lit.	Exptl.	Lit.
1-Propanol	97.1	97.15	1.3833	1.3835
p-Dioxane	101.30	101.40	1.4201	1.4202

Table II. Analytical Data for 1-Propanol-(1)–*p*-Dioxane (2) at 30° C.

x_1	n_D^{30}
0.0000	1.4184
0.1000	1.4150
0.2000	1.4120
0.3000	1.4076
0.4000	1.4039
0.5000	1.4002
0.6000	1.3966
0.7000	1.3929
0.8000	1.3892
0.9000	1.3856
1.0000	1.3820

Table III. Vapor-Liquid Equilibrium Data for 1-Propanol-(1)–*p*-Dioxane (2) System at 760 Mm. of Hg

(Experimental equilibrium data)

t, ° C.	x_1	y_1
98.40	0.100	0.162
96.90	0.200	0.270
95.80	0.300	0.372
95.40	0.400	0.480
95.21	0.500	0.520
95.30	0.600	0.590
95.40	0.700	0.665
95.60	0.800	0.757
96.30	0.900	0.865

Apparatus. Equilibrium data were obtained using a vapor recirculatory equilibrium still designed by Raju *et al.* (*2*). Mercury-in-glass fractional thermometers were used to measure temperatures to within ±0.1° C. Observed temperatures were corrected to 760 mm. of mercury by Equation 1 (*1*).

$$t_c = t_o + 0.00012\,(t_o + 273.2)\,(760 - \pi) \qquad (1)$$

Since atmospheric pressure recorded during experimental work showed only a small deviation from 760 mm. of mercury, pressure effects on the equilibrium data were negligible and no correction was made.

RESULTS

Experimental results are given in Table III.

NOMENCLATURE

n_D^{30} = refractive index at 30° C. in sodium light
x = mole fraction in liquid phase
y = mole fraction in vapor phase
π = total pressure, mm. of Hg

Subscripts

c = corrected
o = observed

LITERATURE CITED

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Vapor-Liquid Equilibrium of Water–Hydrogen Chloride System

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An experimental method for determining the vapor-liquid equilibrium of corrosive systems under moderate pressure is a static method with internal agitation and direct vapor phase sample injection to a gas chromatography unit. Experimental data were obtained for the water–hydrogen chloride system from −10.0° to 70.0° C. with pressure up to 222 p.s.i.a. The reproducibility of the liquid phase composition data was better than 0.4%, the vapor phase composition data about 5%. The interaction second virial coefficients for water and hydrogen chloride were calculated from the data.

THE thermodynamic properties of the H_2O-HCl binary system have been studied extensively in the past hundred years. Experimental vapor-liquid equilibrium measurements are normally limited to 1 atm. or less in pressure and to 30 mole % or less HCl in concentration. The most complete compilation of low pressure data is due to Zeisberg (*15*), who, in 1925, consolidated all reliable sources to tabulate the partial pressure of H_2O and HCl over aqueous HCl solution from 2 to 46 weight % HCl from 0° to 110° C. His work has been the basis of most engineering calculations and is quoted in Perry's handbook (*11*).

Based on thermodynamic deduction, the vapor-liquid equilibrium of the H_2O-HCl system can also be calculated from the e.m.f. measurement of a Pt.H_2/HCl (Aq.)/AgCl.-Ag cell. Fritz and Fuget (*3*) and Othmer and Naphtali (*10*) carried out such calculations from the e.m.f. data of Harned and Ehlers (*6*) and Åkerlöf and Teare (*1*) from 0° to 50° C. and composition from 0.01 to 15.8 molal HCl. The calculated partial pressures of HCl between 6 and 11 molal agreed within 5% with those compiled by Zeisberg (*15*) from manometric and calorimetric data. At lower concentration, because of experimental difficulties associated with other methods, the e.m.f. measurements give more consistent results. However, this method is normally limited to low pressure.

In 1960, Thumm (*5*) measured the solubility of HCl in water at and near the phase separation between 0° and 35° C. The concentrations of HCl in the aqueous phase with two liquid phases present agree reasonably (0.5 to 0.8% lower) with the values reported by Rupert (*13*).

The phase behavior of the water–hydrogen chloride system is normally classified as a type IV nonideal system, which has a maximum boiling azeotrope at low pressure and a phase separation at high pressure.

Most published vapor-liquid equilibrium data are around these two ends. There are practically no data in between for most applications. An experimental program to determine the equilibrium vapor-liquid compositions from −10° to 70° C. with pressure up to 222 p.s.i.a. was therefore initiated to fill this gap.

EXPERIMENTAL

Chemicals. Laboratory-distilled water was degassed for 10 minutes by boiling. Its purity was checked on a gas chromatograph normally used for vapor-liquid equilibrium composition analysis. No detectable organic and/or halogen compounds were found.

The HCl was purchased from the Matheson Co. Initially, technical grade was used; the impurities, mostly chlorinated hydrocarbons, interfered with the separation of water on the chromatographic column. An electronic grade with a minimum purity of 99.9% proved satisfactory.

Apparatus. The method used is generally known as the static method. The solution is charged into a closed cell, immersed in a thermostat. The contents are agitated until