

positive. This may be attributed to the fact that the acid component tends to associate, especially at higher concentrations.

The characteristics of any two corresponding azeotropic mixtures formed by the acid isomers are very close and in no way would lead to the separation of the two acids. This conforms with the reported acid azeotropes formed by the six substances: *m*-xylene, ethylene bromide, chlorobenzene, benzyle chloride, anisole, and water (7). The reported acid compositions and boiling points of anisole azeotropes are slightly different from those obtained in our investigation. Our results have been repeatedly obtained several times.

Nomenclature

X = mole fraction of component in liquid phase

Y = mole fraction of component in vapor phase

t = temperature, °C

P = total vapor pressure (= 1 atm)

P^0 = vapor pressure of pure component

a, b, c = constants in Antoine equation

A, B = terms of Van Laar equation

γ = activity coefficient

Subscripts

1 = butyric acid component

2 = nonbutyric acid component

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Supplementary Material Available: boiling temperature-composition data and vapor-equilibrium data given in tables and figures (40 pages). Ordering information is given on any current masthead page.

Vapor-Liquid Equilibrium in the System Water/1,2-Propylenediamine

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Vapor-liquid equilibrium in the system water/1,2-propylenediamine was studied under atmospheric pressure (760 mmHg) using thoroughly purified propylenediamine (bp 120.9 °C, $d_4^{20} = 0.8640$, $n_D^{20} = 1.44672$), the refractometric method of analysis being the most reliable. The flow method and the equilibrium still of Villm, Hala, Pick, and Fried were used in the experiments. The peculiar trend of the equilibrium curve observed is presumably associated with the presence of a half-hydrate reported in the literature. A direct proof of the absence of an azeotrope under atmospheric pressure is the very pure propylenediamine obtained on rectification of the system, starting with dilute solutions, established during the purification of propylenediamine.

Propylenediamine, $C_3H_6(NH_2)_2$, is an important intermediate product in the synthesis of preparations belonging to the di-thiocarbamate series, used for pest control of plants. During the production process it must be isolated from an aqueous solution by rectification.

Data about the vapor-liquid equilibrium in the system water/propylenediamine are lacking and the data on its physicochemical properties are very scarce. The purpose of the present investigation was the study of the vapor-liquid equilibrium in the system water/propylenediamine under atmospheric pressure (760 mmHg).

In the experiments we used distilled water and propylenediamine (PDA, "Fluka", analytically pure, racemic mixture with

a certified 99 wt % purity grade, bp 119-120 °C, $d_4^{20} = 0.875$ and $n_D^{20} = 1.4460$), thoroughly purified according to the following method. It was first dried with solid KOH (analytically pure) for several days, as it had been found, by gas chromatography, to contain water. The dry propylenediamine was then purified by rectification in a heat-insulated bench-scale column (26 mm in diameter; glass-bead packing, mean diameter of beads 5.2 mm, layer depth 0.55 m). As column efficiency was relatively low, purification was carried out in two stages. The first stage involved alternating operation at total reflux (about 30 min) and a removal of the low-boiling fraction at the top of the column (3-5 min) at a reflux ratio of 2 to 3 (48 h of operation in all). The second stage starts when, in the course of the distillation, temperature of the vapor phase (measured at the top of the column) changed no more. This stage represented conventional rectification carried out at a reflux ratio of 40-45. For the experiments we used the middle fraction (about 300 ml from a total of 1500 ml) having the following physicochemical properties: boiling point 120.9 °C (120.5° (1) 120.9° (4)); density 0.8640 g/cm³ (0.8635 (4)); refraction coefficient 1.446 72.

The starting solutions employed were prepared by mixing propylenediamine with distilled water. They were left to stand for at least 24 h before use. The aim was to achieve chemical equilibrium in the solution, needed on account of the presence of a half-hydrate reported in the literature (1, 3-6, 9).

Considering the high accuracy required in the study of the vapor-liquid equilibrium of the system, gas chromatography proved inadequate as a method of analysis; it was employed (as mentioned above) only for a qualitative characterization of the

Table I. Refraction Coefficient for Liquid Mixtures of Water and Propylenediamine at 20 °C

No.	X, mass %	n^{20}_D	No.	X, mass %	n^{20}_D
1	0.0	1.33300	17	74.0	1.44190
2	5.0	1.34060	18	76.0	1.44308
3	10.0	1.34880	19	78.0	1.44425
4	15.0	1.35770	20	80.0	1.44519
5	20.0	1.36670	21	82.0	1.44584
6	25.0	1.37520	22	84.0	1.44642
7	30.0	1.38370	23	86.0	1.44693
8	35.0	1.39240	24	88.0	1.44738
9	40.0	1.40130	25	90.0	1.44779
10	45.0	1.40970	26	91.0	1.44798
11	50.0	1.41740	27	92.0	1.44792
12	55.0	1.42440	28	94.0	1.44768
13	60.0	1.43030	29	96.0	1.44742
14	65.0	1.43520	30	98.0	1.44712
15	70.0	1.43920	31	100.0	1.44672
16	72.0	1.44062			

Table II. Vapor-Liquid Equilibrium in the System Water/Propylenediamine at 1 atm

No.	X, mol %	Y, mol %	t, °C	γ_1	γ_2
1	0.00	0.00	120.90	—	—
2	0.80	6.60	120.70	4.1176	0.9432
3	4.50	9.20	120.15	1.0384	0.9699
4	6.65	9.75	119.70	0.7555	0.9976
5	12.35	13.65	119.15	0.5767	1.0331
6	12.55	14.55	119.05	0.6096	1.0296
7	17.05	19.20	118.65	0.6003	1.0356
8	20.10	20.95	118.35	0.5609	1.0647
9	31.60	32.15	117.80	0.5570	1.0830
10	33.10	37.45	117.75	0.6209	1.0224
11	39.70	46.85	115.95	0.6859	1.0148
12	41.10	49.25	116.15	0.6936	0.9864
13	41.10	51.45	115.80	0.7307	0.9529
14	52.65	64.80	114.30	0.7542	0.8980
15	57.10	68.80	113.75	0.7522	0.8928
16	59.65	71.25	113.35	0.7560	0.8849
17	65.75	79.40	111.70	0.8062	0.7842
18	70.80	85.30	110.50	0.8378	0.6800
19	80.30	92.85	107.05	0.9038	0.5441
20	90.55	98.05	102.35	0.9961	0.3576
21	94.35	99.15	101.00	1.0140	0.2719
22	97.60	99.00	100.30	1.0034	0.7700

initial solutions with respect to purification. Since the conventional acidimetric determination proved unreliable for our purpose and we found in the literature no chemical method elaborated to suit the present case, we chose the refractometric method as most relevant. Measurements were made with a "Pulfrich" immersible refractometer, having an accuracy of 1×10^{-5} . The purified propylenediamine was used for constructing a calibration curve which displayed a small but distinct maximum at a composition, close to the composition of the half-hydrate (Table I).

In the experiments we used the equilibrium still of Vilim, Hala, Pick, and Fried (7) and the flow method. Constant level in the tank, (ensuring stable operation) was maintained by feeding the initial mixture out of a separation funnel, under the same pressure as the apparatus itself, i.e., 760 ± 1 mmHg, kept with a sensitive manostat. Temperature was measured with an accuracy of ± 0.05 °C with a calibrated thermocouple (chromel-kopel).

The attaining of steady-state operation was judged by the constancy of temperature in the separation section of the ap-

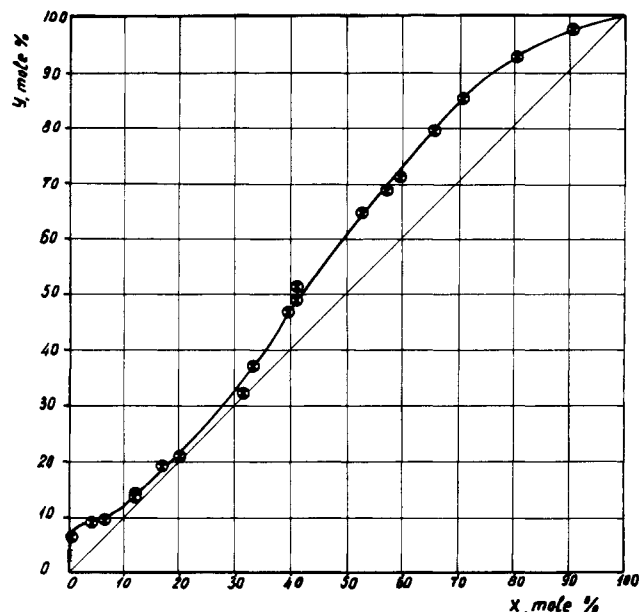


Figure 1. Vapor-liquid equilibrium in the system water/propylenediamine at 1 atm.

paratus. With the apparatus employed, reliable equilibrium data are obtained only when the throughputs of the vapor condensate and the liquid phase from which it is formed are kept at a ratio of about 1:10. This is achieved by varying the voltage applied on the heaters. Samples are taken without disturbing the operation regime. The experimental data are shown in Table II.

The activity coefficient, γ , was calculated from the relationship which reflects deviation from Raul's law for nonideal mixtures:

$$\nu_i y_i P_t = \gamma_i \chi_i P_i \quad (1)$$

wherein ν is the fugitivity of the i th component, assumed to be 1; y_i is the concentration of the i th component in the vapor phase, mole percent; P_t is the total pressure in the system, atmospheres; χ_i is the concentration of the i th component in the liquid phase, mole percent, and P_i is the vapor pressure of the i th component at the boiling temperature of the liquid mixture, atmospheres.

As we did not find in the literature data on the vapor pressure of propylenediamine, when calculating the activity coefficient (Table II), we had to use an empirical quantitative relationship to correlate the vapor pressure data of propylenediamine (P_2). It proved that our experimental data are described with an accuracy of $\pm 1.8\%$ by the equation of Calingert-Davis (2):

$$\log p = a - \frac{b}{230 + t} \quad (2)$$

with constants, $a = 7.1572$ and $b = 1500$.

The peculiar trend of the equilibrium line (Figure 1) may be explained by the presence of a stable half-hydrate (1, 3-6, 9) which binds part of the water and represents a third component in the system. This assumption appears to be favorable because the deviation of the equilibrium curve starts with the composition of the half-hydrate and disappears at higher concentrations of water.

A direct proof of the absence of an azeotrope under atmospheric pressure was the separation of the system by way of rectification, with a very pure propylenediamine obtained as a product when one starts with dilute solutions; this fact was established by us during the purification of propylenediamine.

A thermodynamic test of consistency of the data on vapor-liquid equilibrium was not carried out because in our case the equation of Gibbs–Duhem, on which most of these tests are based, is inapplicable (8).

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Isothermal Joule–Thomson Coefficients in Mixtures of Methane and Carbon Dioxide

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Experimental measurements of the isothermal effect of pressure on enthalpy, $\phi \equiv (\partial H/\partial P)_T$, have been made on two mixtures of CH₄ + CO₂ (14.5 and 42.3 mol % CH₄) in the temperature range 273–363 K at pressures up to 137 bar. Comparisons of the results with values calculated from equations of state and using the principle of corresponding states indicate that a modified Benedict–Webb–Rubin equation, utilizing interaction parameters, predicts the effect of pressure on enthalpy within $\pm 2\%$.

Accurate values of the enthalpy of mixtures over a range of pressures and temperatures are necessary for design of heat exchangers and separation processes. While the enthalpy of many mixtures at low pressures can be calculated from a knowledge of the ideal gas heat capacities, few experimental studies of the effect of pressure on enthalpy have been made. In the usual case, this effect is calculated from P-V-T data together with thermodynamic relations. Accurate direct measurements are desirable for improvements of methods of prediction of the effect of pressure and are useful directly.

In this investigation measurements of the isothermal Joule–Thomson coefficient, ϕ , were made. This property is a direct measure of the effect of pressure on enthalpy:

$$\phi \equiv \left(\frac{\partial H}{\partial P} \right)_T \quad (1)$$

It is related to the adiabatic Joule–Thomson coefficient, μ , by:

$$\phi = -\mu C_p \quad (2)$$

where C_p is the isobaric heat capacity.

Values of ϕ can be obtained from P-V-T data or an equation of state by means of the relation:

$$\phi = V - T \left(\frac{\partial V}{\partial T} \right)_P \quad (3)$$

The value of ϕ at zero pressure is finite and using the virial equation of state can be expressed as:

$$\phi^0 = B - T \left(\frac{dB}{dT} \right) \quad (4)$$

In the present experiments with a finite pressure drop, the values of the enthalpy change determined are converted to values of ϕ by the limiting process

$$\phi = \lim_{P_2 \rightarrow P_1} \left[\frac{H_{P_2} - H_{P_1}}{P_2 - P_1} \right]_{T,x} \quad (5)$$

For comparison with methods of prediction and other results, ϕ values can be integrated to obtain the enthalpy departure

$$(H^0 - H)_T = \Delta H_T = - \int_0^P \phi \, dP \quad (6)$$

Earlier work describing measurements of ϕ have been reviewed by Mather et al. (13). Since that time Alkasab et al. (1), and Alkasab and Budenholzer (2), have described a throttling apparatus utilizing a valve for determination of both ϕ and μ together with results for three mixtures of methane and ethane. Russian workers, Vukalovich et al. (21, 22, 23), have also used a throttling valve to measure ϕ for CO₂ and mixtures of CO₂ + N₂. Peterson and Wilson (17) have also employed a throttling valve for integral measurements of the effect of pressure on enthalpy of CO₂, equimolar CH₄ + CO₂ and CH₄ + C₂H₆ + CO₂ mixtures. Recently, Pocock and Wormald (18) used an adjustable throttle for the measurement of ϕ for N₂ at temperatures from 78 to 298 K at pressures below 6 bar. The results were used to derive second virial coefficients.

This work describes a modified capillary tube throttle, presents data for two mixtures CH₄ + CO₂, and compares the experimental results with various methods of prediction.

Experimental Section

A schematic diagram of the apparatus is shown in Figure 1. A Corblin A2CV250 diaphragm compressor is used to recycle the gas under investigation. This compressor operates at constant volumetric throughput and a by-pass under pressure control is used to vary the flow rate through the calorimeter section. A bank of four storage tanks provides additional material for operation up to pressures of 140 bar. The gas passes through buffer tanks to the calorimeter under pressure control. The fluid enters the calorimeter bath, a stainless steel Dewar vessel, and passes through 30 m of copper tubing before entering the throttling calorimeter. Cooling of the bath at the desired operating temperature is provided by water at elevated temperatures and liquid nitrogen at low temperatures. The effect of the coolant is balanced by a temperature controller (Hallikainen Thermotrol) which activates a 500-W heater. After passing through the calorimeter the fluid exits through a manually operated throttling valve which reduces the pressure to about 2 bar. The flow rate is then de-