Enthalpy Data for the Benzene-1-Propanol System

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Enthalpy data were measured for mixtures of benzene and 1-propanol containing 0.250 and 0.480 mole fraction benzene. Data covered the range from 40 to 440 p.s.i.a. and 250° to 429° F. and included the critical region.

IN ORDER TO TEST and develop methods for predicting thermodynamic properties of polar systems experimental data are needed for both pure components and mixtures. A flow calorimeter developed earlier has been used to measure enthalpies of alcohols, ethers, and ketones (*1*) and binary mixtures of benzene with methanol (*3*), and with ethanol (*5*). In continuation of this work, the present paper presents *p-H* data for the benzene-1-propanol system.

EXPERIMENTAL

Range of Measurements. Measurements were carried out for two mixtures, containing 0.250 and 0.480 mole fraction benzene. Data were taken from 40 to 440 p.s.i.a. and 250° to 429° F. and included the critical region.

Purity of Chemicals. BENZENE. The benzene used (Fisher Scientific Co.) was stated to be thiophene free and conformed with ACS specifications. The boiling range was 80.0–80.3° C.

1-PROPANOL. The 1-propanol was also obtained from Fisher Scientific Co. and had a boiling range of 96.9–97.2° C.

FREON-11 (calorimeter fluid). The Freon, obtained from Du Pont, was reported to be 99.99% pure.

Method and Calculations. The enthalpy is determined by measuring the energy transferred from the test fluid to boiling Freon-11 in a flow calorimeter. The fluid flows through a coiled tube immersed in boiling Freon-11 at atmospheric pressure. The enthalpy transferred from the fluid to the Freon-11 is evaluated from the heat of vaporization of the Freon and the mass flow rate W_s of the fluid according to the equation

$$\Delta H_c = -\frac{L_f\, W_f}{W_s} \qquad (1)$$

The experimental apparatus is described fully in the earlier papers (*1, 3*). Four corrections must be applied to the enthalpy change in the calorimeter, ΔH_c, in order to establish the enthalpy H of the fluid at calorimeter entrance conditions and with respect to $H = O$ for the pure components at 77° F. (saturated liquid state). The first, Δh_1, is due to the deviation of the actual entrance temperature to the calorimeter from the desired isotherm value. This correction was evaluated from the specific heat of the fluid, as estimated from the uncorrected data, according to the equation

$$\Delta h_1 = C_p\, \Delta t_1 \qquad (2)$$

The value of Δh_1 was of the order of 2.0 B.t.u./lb. The second correction, Δh_2, took into account the deviation of the actual outlet temperature from the datum temperature of 77° F. The average value of Δh_2 was 0.6 B.t.u./lb. The pressure of the fluid leaving the calorimeter was only a small amount less than the pressure at the inlet. Hence, a third correction Δh_3 is necessary, if the enthalpy data are to refer to a base state of saturated liquid (the vapor pressure of the mixtures at 77° F. was always subatmospheric). The maximum pressure at the outlet in this study was only slightly above 400 p.s.i.a. Hence this correction is small (0 to 1.0 B.t.u./lb. at 400 p.s.i.a.) and was approximated from the correlation of Watson (6) for hydrocarbons. Finally, ΔH_c must be corrected for the heat of mixing at 77° F. to use the reference state of pure liquid components. Heat of mixing data are available (*2*) at 15° C. and are as large as 5.8 B.t.u./lb. at a mole fraction benzene of 0.64. These results were used at 77° F. (25° C.) without change since estimates of the effect of temperature on the heat of mixing indicate a negligible change between 15° and 25° C. The corrected value of H above the chosen reference state thus is given by the expression

$$H = \frac{L_f\, W_f}{W_s} + \Delta h_1 + \Delta h_2 + \Delta h_3 + \Delta H_m \qquad (3)$$

The composition of the mixture in the equipment was determined periodically by measuring the index of refraction of the liquid sample collected for each run. A calibration curve, prepared from carefully weighed, synthetic samples, was used to convert the index of refraction to composition.

RESULTS

Accuracy and Precision of Data. The accuracy of the apparatus was checked by measuring enthalpy values for pure benzene in the liquid phase at 250° F. and 100 p.s.i.a. and in the vapor phase at 350° F. and 95 p.s.i.a. The liquid phase measurement gave 74.9 B.t.u./lb. and compared with 77.8 B.t.u./lb. from Organick and Studhalter (*4*), 74.0 B.t.u./lb. from Storvick (*5*), and 77.7 B.t.u./lb. from Eubank (*1*). The measured value for the vapor phase was 265.9 B.t.u./lb. in comparison with 266.1 B.t.u./lb. from Organick and Studhalter and 269.7 B.t.u./lb. as determined by Eubank.

Multiple runs at the same conditions indicated an experimental precision of about 1.0%. From the measurements and comparisons it is estimated that the errors in the data are of the order of 3.0 B.t.u./lb.

Tables and Diagrams. The enthalpies calculated from Equation 3 were plotted on large-scale *p-H* diagrams and the final values read from the smoothed curves. These results are given in Tables I and II and the smoothed curves are shown in Figures 1 and 2, along with the experimental points. The critical point is estimated to be 400° F. and 306 p.s.i.a. for the 25.0 mole % benzene mixture and 399° F. and 290 p.s.i.a. for the 48.0 mole % system.

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Table I. Thermodynamic Properties of the Binary Mixture Containing 0.250 Mole Fraction Benzene and 0.750 Mole Fraction 1-Propanol

Datum: $H = 0$, pure, saturated liquid components at 77° F.

Saturated Mixture

	Liquid		Vapor	
Pressure, P.S.I.A.	Temp., ° F.	Enthalpy, B.t.u./lb.	Temp., ° F.	Enthalpy, B.t.u./lb.
50	251	104	259	347
100	296	139	298	344
150	332	171	337	341
200	368	200	364	336
250	380	227	380	329
300	399	262	399	304
306	400	283	400	283

Superheated Mixture

	Temperature, ° F.				
	251	350	380	404	429
Pressure, P.S.I.A.	Enthalpy, B.t.u./lb.				
0	357	416	435	453	470
50	...	402	424	442	460
100	...	377	404	426	447
150	...	350	380	407	431
200	...	...	355	388	414
250	...	...	330	366	395
300	...	...	...	330	377
350	...	...	...	212	357
400	...	...	...	212	239
450	...	...	...	212	227
500	...	...	...	212	227

Table II. Thermodynamic Properties of the Binary Mixture Containing 0.480 Mole Fraction Benzene and 0.520 Mole Fraction 1-Propanol

Datum: $H = 0$, pure, saturated liquid components at 77° F.

Saturated Mixture

	Liquid		Vapor	
Pressure, P.S.I.A.	Temp., ° F.	Enthalpy, B.t.u./lb.	Temp., ° F.	Enthalpy, B.t.u./lb.
50	243	92	252	293
100	286	128	291	307
150	329	163	331	317
200	361	198	361	322
250	384	235	383	320
286	398	271	398	302
290	399	290	399	290

Superheated Mixture

	Temperature, ° F.				
	250	348	380	401	409
Pressure, P.S.I.A.	Enthalpy, B.t.u./lb.				
0	303	370	398	428	450
50	...	366	394	426	447
100	...	355	385	420	442
150	...	336	368	409	432
200	...	...	345	393	420
250	...	...	...	372	400
300	...	...	...	271	368
350	...	...	...	221	250
400	...	...	...	215	227
450	...	...	...	215	227

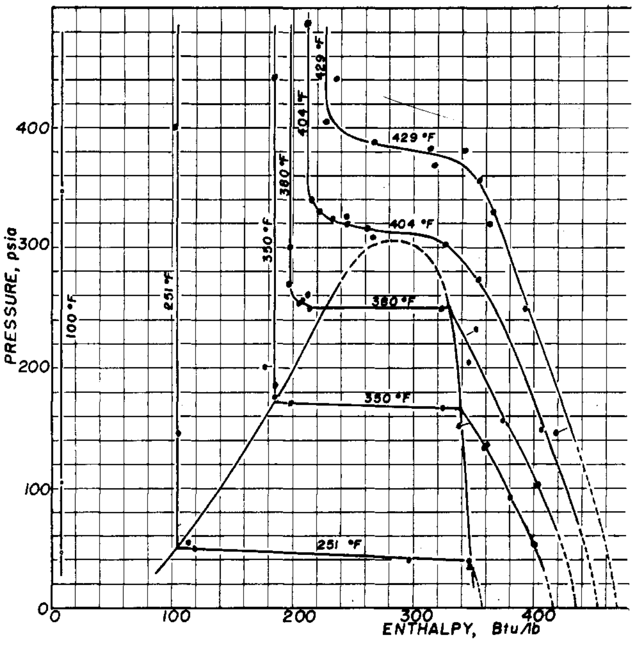

Figure 1. Pressure-enthalpy diagram, benzene-1-propanol system, 0.250 mole fraction benzene
Datum: $H = 0$, pure saturated liquid components at 77° F.

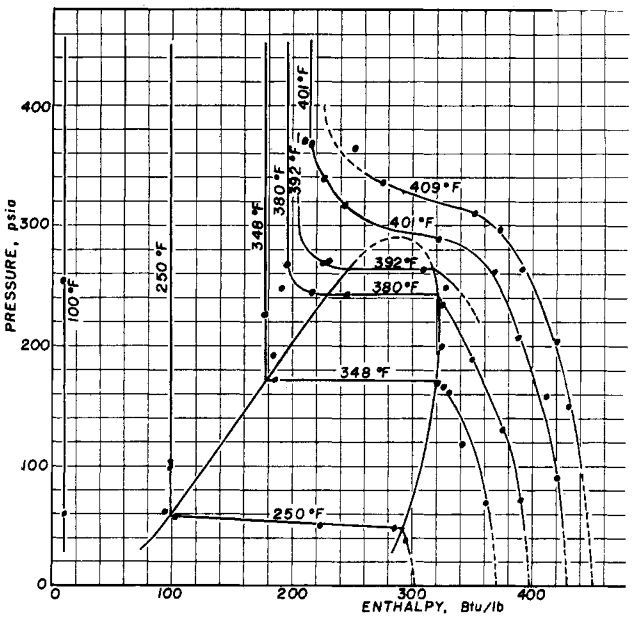

Figure 2. Pressure-enthalpy diagram, benzene-1-propanol system, 0.480 mole fraction benzene
Datum: $H = 0$, pure saturated liquid components at 77° F.

DISCUSSION

The critical temperatures of benzene and 1-propanol, 552° F. and 507° F. (*1*) are close to each other. Similarly the critical pressures, 737 and 714 p.s.i.a., do not differ greatly. In the benzene-methanol and benzene-ethanol systems (*3*, *5*) the critical values for the pure components are significantly different, and the critical temperatures of binary mixtures in these systems were between the values for the pure components. However, for benzene-1-propanol the critical temperatures of both mixtures are well below the pure component values.

Figure 3 shows the vapor pressure curves for benzene and 1-propanol and also the bubble and dew point curves for the two mixtures. Two items are significant on this plot. First, the vapor pressure curves for both the pure components and the mixtures are close together, although

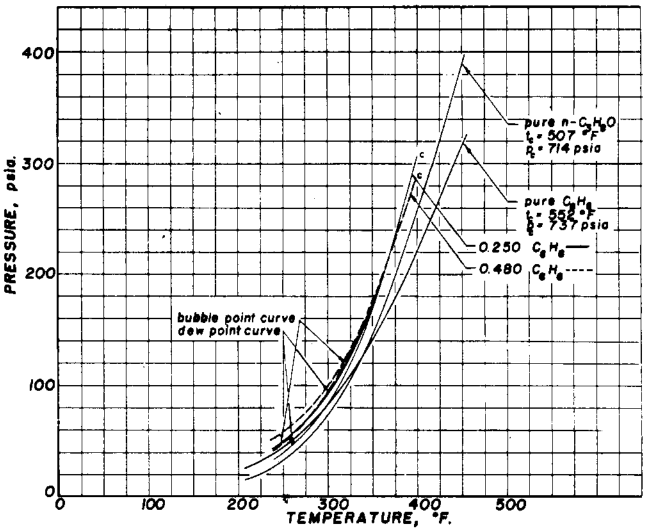

Figure 3. Pressure-temperature diagram, benzene–1-propanol system

the mixture curves end at lower temperatures because of the lower critical points. The solid lines in Figure 3 represent the bubble and dew point curves for the 25.0 mole % benzene system. These curves coincide from about 367° F. to the critical point. This indicates that azeotropic conditions exist over this temperature range. Similar azeotrope formation exists for the 48.0 mole % system (shown as dotted lines in Figure 3) starting approximately at the same temperature. This behavior is also evident from the flat isotherms in the two-phase region in Figures 1 and 2 above about 367° F.

ACKNOWLEDGMENT

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NOMENCLATURE

C = critical point
C_p = specific heat at constant pressure, B.t.u./(lb.)(° F.)
Δh = enthalpy correction, B.t.u./lb.
H = enthalpy of binary mixture referred to $H = 0$ for the pure components as saturated liquids at 77° F., B.t.u./(lb. of mixture)
L_f = heat of vaporization of Freon-11, B.t.u./lb.
ΔH_c = enthalpy difference between entrance and exit conditions of the calorimeter, B.t.u./lb.
ΔH_m = heat of mixing at 77° F., B.t.u./(lb. of mixture)
p = pressure, p.s.i.a.
p_c = critical pressure
t = temperature, ° F.
t_c = critical temperature
W_f = mass of Freon-11 sample, lb.
W_s = mass of mixture sample, lb.

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Thermodynamics of Liquid Surfaces

Surface Tension of *n*-Hexane–Cyclohexane Mixtures at 25°, 30°, and 35° C.

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A single parameter equation reproduces the experimental surface tensions of *n*-hexane–cyclohexane mixtures with an average deviation of 0.05 dyne/cm. at temperatures of 25°, 30°, and 35° C.

THE SURFACE TENSION of several *n*-hexane–cyclohexane mixtures has been measured at 25°, 30°, and 35° C. The single parameter equation:

$$\exp(-41.74\gamma/T) = X_1 \exp(41.74\,\gamma_1/T) + X_2 \exp(-41.74\,\gamma_2/T \quad (1)$$

reproduces the data at the three temperatures with a mean deviation of 0.05 dyne/cm. In the equation, γ is the mixture surface tension, γ_1 and γ_2 are the surface tensions of pure *n*-hexane and pure cyclohexane, respectively (Table I); X_1 and X_2 are the respective mole fractions, and T is the absolute temperature.

EXPERIMENTAL

Materials. Both the *n*-hexane and cyclohexane were Phillips Petroleum Pure Grade (99 mole %). Both were shaken with concentrated sulfuric acid, washed, dried over sodium, and distilled through a 20-plate packed column. The purified samples were stored over sodium until used. Density, refractive index (*8*), and surface tension (*5-7, 10*) checked well with accepted values.

Surface Tension. The surface tensions were measured by the maximum bubble pressure technique on apparatus built and described by Quayle (*5*). The bubble pressure air was