Greek Letters

$\alpha_1,\alpha_2,\alpha_3,\alpha_4,$
α_5,α_6 = constants
ω = acentric factor
σ = standard deviation $[(G_{\text{calcd}} - G_{\text{obsd}})^2/(\text{No. of Points} - 1)]^{1/2}$

Subscripts

i = isomer
n = normal

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Vapor-Liquid Equilibria of Binary Systems of Methanol with Anisole, Chlorobenzene, Nitromethane, and Pyridine

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Vapor-liquid equilibrium data are reported for binary systems of methanol with anisole (PhOMe), chlorobenzene (PhCl), nitromethane ($MeNO_2$), and pyridine at 730 mm. of Hg. Of the four systems studied, only methanol–$MeNO_2$ forms a minimum azeotrope—at 64.4° C., near 95.0 mole % of methanol. The other three systems are nonazeotropic. Limiting values of the activity coefficients of each component in an excess of methanol have been evaluated.

AS PART of a continuing study of phase equilibria involving alcohols, vapor-liquid equilibrium data have been measured for four binary systems of methanol with anisole (PhOMe), chlorobenzene (PhCl), nitromethane ($MeNO_2$), and pyridine, at 730 mm. of Hg. These systems were chosen to obtain additional information on the azeotropic behavior of the solutions of various organic liquids with alcohols and to make a rough estimate of the limiting values of the activity coefficients of these liquids in excess methanol.

EXPERIMENTAL

The sample liquids used in this study were purified by repeated distillations through a 30-plate column. The final purified samples gave no trace of impurity peaks with gas chromatography with silicone DC 500 column and hydrogen carrier gas. Table I lists some physical properties of the final purified liquids as well as the Antoine constants used for vapor pressure calculation.

A modified Colburn still (*11, 12, 14*) was used for vapor-liquid equilibrium measurements. A thermistor was calibrated against a standard thermometer and used to measure equilibrium temperatures to within ± 0.05° C. The barometric pressure varied between 720 and 735 mm. of Hg during the measurements. The observed boiling points were corrected to 760 mm. of Hg.

Analysis of the equilibrium compositions was made by density measurement at 25.0° C. Densities were determined using a 10-ml. pycnometer and were reproducible to within ± 0.0001 gram per cc.

RESULTS AND DISCUSSION

Table II lists the experimental t-x-y data for the four binary systems studied. Temperature-composition and x-y

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Table I. Some Physical Properties of Purified Liquids and the Antoine Constants Used

		Methanol	PhOMe	PhCl	$MeNO_2$	Pyridine
Boiling point t, ° C.	obsd.	64.6	. . .	131.6	101.28	115.9
	lit.[a]	64.5	153.85	131.72	101.19	115.4
Density d_{25}^{4}	obsd.	0.78653	0.98937	1.10103	1.13117	0.97810
	lit.[a]	0.7866	0.98927	1.1013	1.1307	0.97824
Refractive index n_D^{25}	obsd.	1.3265	1.5147	1.5220	1.3798	1.5033
	lit.[a]	1.3267	1.5143	1.5219	1.3795	1.5075
Antoine constants						
A		8.07246[a]	7.3595[a]	6.94504[a]	7.26159[b]	7.05947[b]
B		1574.99	1718.7	1413.12	1436.38	1386.14
C		238.86	230	216.0	226.670	216.46

[a] Literature values are taken from references (*3, 7, 9, 15-17*). [b] Evaluated from the available data (*6, 10*).

Table II. Vapor-Liquid Equilibrium Data

Methanol Concentration, Mole %		Temp.,[a] ° C.	Activity Coefficients	
Liquid	Vapor		γ_1	γ_2
		METHANOL–ANISOLE		
2.1	54.3	128.7	3.477	0.939
3.0	58.2	121.7	3.128	1.076
4.3	70.2	112.2	3.401	1.054
11.9	86.8	84.9	3.523	1.359
31.6	93.4	72.0	2.241	1.478
39.4	93.7	71.4	1.848	1.636
44.9	94.3	70.6	1.677	1.683
53.1	95.1	69.7	1.483	1.773
65.0	95.9	68.6	1.274	2.084
74.7	96.1	68.1	1.133	2.805
84.5	97.2	66.7	1.065	3.481
90.1	97.8	66.1	1.028	4.402
92.9	98.0	65.6	1.020	5.711
96.1	98.8	65.2	1.009	6.346
		METHANOL–CHLOROBENZENE		
1.6	37.2	113.6	4.660	1.047
2.2	47.2	107.7	5.090	1.077
16.1	84.4	72.1	3.958	1.222
38.7	87.2	. . .	. . .	. . .
44.8	89.0	68.0	1.752	1.540
53.9	89.2	67.7	1.475	1.830
67.1	90.2	66.9	1.239	2.411
78.6	91.8	66.1	1.106	3.190
88.2	93.7	65.4	1.037	4.582
95.4	96.7	. . .	. . .	. . .

Methanol Concentration, Mole %		Temp.,[a] ° C.	Activity Coefficients	
Liquid	Vapor		γ_1	γ_2
		METHANOL–NITROMETHANE		
1.5	13.3	96.9	2.902	1.005
2.6	22.8	93.1	3.236	1.020
4.8	33.4	89.1	2.921	1.024
7.5	42.9	84.8	2.772	1.041
9.6	48.4	82.1	2.669	1.052
15.2	57.0	77.9	2.303	1.082
25.4	67.3	72.9	1.944	1.116
31.4	70.4	71.1	1.753	1.176
42.6	74.7	68.2	1.534	1.334
49.3	76.1	67.3	1.399	1.480
67.8	81.8	65.6	1.168	1.892
74.7	83.8	65.1	1.104	2.178
81.3	86.4	65.0	1.053	2.490
88.6	90.1	64.6	1.023	3.015
91.4	92.1	64.5	1.013	3.187
96.0	95.6	64.4	1.007	3.840
99.4	99.3	64.5	1.006	4.055
		METHANOL–PYRIDINE		
3.6	13.8	111.0	0.826	1.008
6.3	30.3	106.7	1.172	0.952
16.3	49.6	97.4	0.981	1.027
22.2	57.7	92.2	0.985	1.093
33.0	69.9	86.8	0.960	1.085
39.8	74.1	83.4	0.947	1.169
47.0	81.0	80.7	0.961	1.070
50.9	82.1	78.7	0.960	1.166
61.4	86.4	75.0	0.960	1.294
66.4	88.7	73.3	0.968	1.314
75.6	93.4	70.6	0.989	1.170
85.2	96.7	68.0	1.000	1.065
90.7	98.0	66.5	1.009	1.089
94.5	98.9	65.5	1.015	1.053

[a] Corrected to 760 mm. of Hg.

curves are shown in Figure 1, *A-D*. As Figure 1, *C* illustrates, the methanol-nitromethane system is azeotropic. The azeotropic mixture boils at 64.4° C. and contains 95.0 mole % of methanol. This is in good agreement with the results, 64.55° C. and 94.2 mole %, reported by Desseigne and Belliot (*2*). The other three systems are nonazeotropic.

The activity coefficients were calculated by the following relation:

$$\gamma = \frac{y\pi}{xP} \times \exp\left[(V-\beta) \times (P-\pi)/RT\right] \tag{1}$$

The temperature range extends from 64.4° C., a value slightly lower than the boiling point of methanol, to 154° C., the boiling point of anisole. The vapor pressure of methanol was greater than 10 atm. at the highest temperature. For the closest fit to the experimental data (*8, 15, 16*) in this region, it is necessary to use a set of the Antoine constants other than that given in Table I. However, the calculated values of vapor pressure using the present set of the constants are in good agreement with the smoothed values obtained by the Ambrose and Townsend equation (*1*) and recent experimental data (*8*); therefore they are used throughout the present calculation.

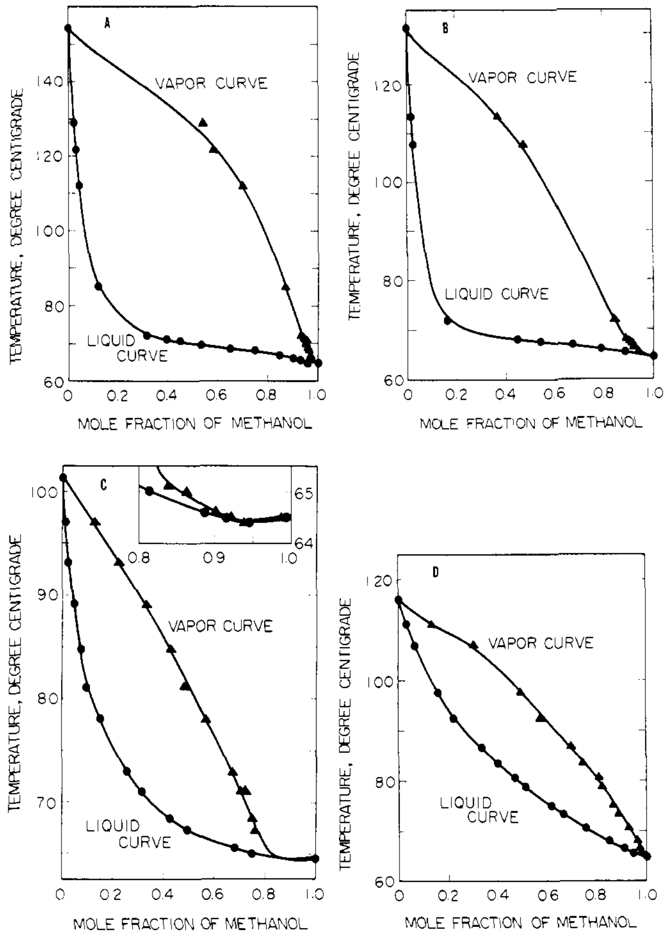

Figure 1. Vapor-liquid equilibrium diagrams for the binary systems

A. Methanol-anisole
B. Methanol-chlorobenzene
C. Methanol-nitromethane
D. Methanol-pyridine

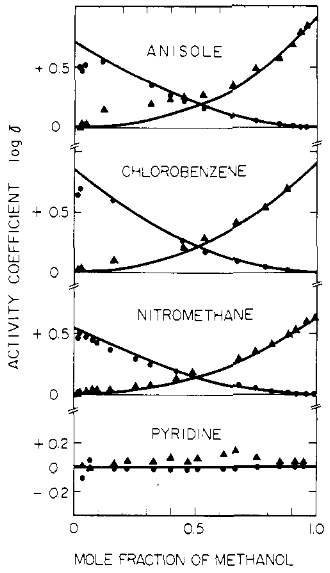

Figure 2. Activity coefficient vs. molar composition diagram

● $\log \gamma_1$
▲ $\log \gamma_2$
— γ calcd

Table III. Limiting Values of Activity Coefficients

System	$(\log \gamma_2)_{x_2 \to 0}$	$(\log \gamma_1)_{x_1 \to 0}$
MeOH(1)-MeOPh(2)	0.90 ± 0.02	0.70 ± 0.05
MeOH(1)-PhCl(2)	0.90 ± 0.04	0.85 ± 0.05
MeOH(1)-MeNO$_2$(2)	0.62 ± 0.02	0.55 ± 0.04
MeOH(1)-Pyridine(2)	0.03 ± 0.02	. . .

To evaluate the correction factor in Equation 1, the molar volume V and the second virial coefficient β must be determined. V was calculated by Fishtine's equation (*4*) and β was estimated by Wohl's generalized relation (*5*). The critical constants and other data necessary for these calculations are available in the literature (*4, 13*).

The calculated γ values are also given in Table II. It may be concluded that the methanol-pyridine system is nearly ideal and the other three systems show positive deviation from the ideal solution law, the degree of which increases in the order: nitromethane < anisole < chlorobenzene.

The present data for the solvent-rich portion were difficult to obtain, because boiling temperature changes sharply with mole fraction of methanol in this region. To test the thermodynamic consistency of the present data, the van Laar equation,

$$\log \gamma_1 = \frac{A}{\left[1 + \frac{Ax_1}{Bx_2}\right]^2} \quad \log \gamma_2 = \frac{B}{\left[1 + \frac{Bx_2}{Ax_1}\right]^2} \tag{2}$$

where $A = (\log \gamma_1)_{x_1 \to 0}$ and $B = (\log \gamma_2)_{x_2 \to 0}$, was used. Subscript 1 refers to methanol. Fitness of the isothermal log γ data to this equation indicates their consistency. As given in Figure 2, the experimental points for log γ_1 and log γ_2 agree with the calculated ones very well in the methanol-rich region, where boiling temperature change is not too large. But those at low methanol content deviate from the calculated line. The calculated values are based on Equation 2 and the estimated limiting activity coefficient values given in Table III. No calculated values were given for methanol-pyridine system, as the log γ data scattered along the ideal solution line and a complete evaluation of limiting value was impossible.

NOMENCLATURE

A, B = van Laar constants
P = vapor pressure of pure liquid, mm. of Hg
R = gas constant
T = temperature, ° K.
t = boiling temperature, ° C.
V = molar volume of liquid, cc./mole
$x,y,$ = composition of liquid and vapor molar fraction, respectively
β = second virial coefficient
γ = activity coefficient
π = total pressure, mm. of Hg

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Heat of Solution of Ammonium Bromide and the Entropies of the Aqueous NH_4^+ and Br^- Ions

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The heat of solution of NH_4Br has been determined as 4007 ± 15 cal. per mole. This datum has been combined with literature data to calculate the partial molal entropies of the aqueous ammonium and bromide ions as 26.6 ± 0.1 and 19.8 ± 0.1 cal. per (mole °K.), respectively. A thermochemical path has been devised to calculate $\Delta H^\circ = 45.18$ kcal. per mole for the reaction $NH_4Br(c) = NH_3(g) + HBr(g)$, in good agreement with a value derived from dissociation pressures.

THIS study was undertaken to provide a value for the heat of solution of NH_4Br—useful in the correlation of literature data concerning this material and related substances. Thermochemical paths were devised by which this heat of solution could be used to: confirm values for the partial molal entropies of the aqueous ammonium and bromide ions; confirm high temperature dissociation pressures of NH_4Br; calculate the heat of solution of $NH_3(g)$ in water; and determine an indirect value for the Br_2(liq)/Br (aq) electrode potential.

EXPERIMENTAL

The calorimeter and its adjuvant electrical circuitry closely follow the design of Wu, Birky, and Hepler (*48*). The reaction chamber is a silvered glass Dewar of ca. 950-ml. capacity, tapered at the open end to seal against O-ring gaskets about its aluminum cover. The aluminum cover is suspended from the top plate of a brass submarine that encloses the calorimeter. The submarine is, in turn, suspended from the top plate of a ca. 50-gallon water bath. Three brass chimneys pass from the bath top plate to the submarine and are aligned over corresponding holes through the aluminum calorimeter cover. The chimneys are of sufficient length to ensure that the submarine lies completely beneath the water level of the 50-gallon bath. One of the chimneys contains the calorimeter stirrer, another the electrical leads, and the third the sample holding device.

The calorimeter fluid is stirred by a glass spiral that terminates in a four-bladed propellor. The stirrer is held fixed by two ball-bearing seals and is driven through a belt and pulley system by a R.M.S. SCPVBK motor. Within the calorimeter the stirrer lies along the axis of a cylinder formed by a glass tubing spiral. The spiral contains the bifilarly wound calorimeter heater (250 ohms of No. 38 Manganin wire) and is filled with paraffin oil to facilitate heat exchange between the heater and the calorimeter fluid.

Samples that are not sensitive to air are contained in thin-walled glass bulbs of ca. 15-ml. capacity. The bulbs are fitted to the end of a spring-loaded glass rod by a wax seal. The rod passes through the aluminum calorimeter cover and through one of the chimneys to the outside. The reaction is initiated by depressing the rod to crush the bulb against a reinforced section of the calorimeter bottom.

Temperatures are sensed by a multijunction (5 or 10) copper-constantan thermocouple fabricated from No. 28 or No. 30 wire. The thermocouple is contained in an oil-filled well extending into the calorimeter fluid. The reference junctions are maintained in an external slurry of distilled-water ice.

The 50-gallon water bath is maintained at a preselected temperature (usually 1.5° C. above the calorimeter temperature) by the compensating actions of a Sargent water bath cooler and a 750-watt immersion heater controlled by a Fisher proportional temperature control. Temperature uniformity is maintained to ±0.02° C. by an additional circulating pump.

The heat capacity of the calorimeter and its contents is determined separately for each experiment from the temperature rise caused by the passage of current through the Manganin heater. Power is supplied to the heater by a Kepco regulated d.c. power supply. The heater current is determined by monitoring the potential drop across a Leeds and Northrup 4025-B standard 10-ohm resistor. Typically a current of 80 ma. is passed through the heater for 2 minutes. The resistance of the heater is determined