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NOMENCLATURE

A = constant in Equation 6
B = constant in Equation 7
D = diffusion coefficient, cm^2/sec
ΔG = free energy of activation, cal/g-mol
He = Henry coefficient, cm^3 atm/g-mol
I = ionic strength, g-ion/l.
K = salting-out parameter, l./g-ion
x = mole fraction
y = variable defined in Equation 5

GREEK LETTERS

α = power in Equation 4
η = viscosity, g/cm sec

SUBSCRIPTS

o = pure water
i = species i

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Isothermal Vapor-Liquid Equilibria in Binary Mixtures Containing Alkanes and Ethers

VENKATACHALAPATI MARIPURI and GERALD A. RATCLIFF[1]
Department of Chemical Engineering, McGill University, Montreal, Que., Canada

Vapor-liquid equilibrium data were determined at 90°C for the binary systems di-*n*-propyl ether/*n*-octane, di-*n*-propyl ether/*n*-nonane, and di-*n*-butyl ether/*n*-heptane using a modified Gillespie still. These systems all exhibit nearly ideal behavior.

Experimental vapor-liquid equilibria were determined at 90°C for three binary mixtures containing ethers and alkanes using a modified Gillespie still. The still and experimental technique have been described elsewhere (*3*).

n-Heptane supplied by Eastman Organic Chemicals was further purified by redistilling in a packed column and collecting a fraction with physical properties reproducing literature values. Research-grade *n*-octane and *n*-nonane supplied by the Phillips Petroleum Co. and ethers from Aldrich Chemicals, were directly used without further purification. The physical properties of the chemicals used are listed in Table I.

Temperature was measured by a copper-constantan thermocouple and a Leeds and Northrup type K3 potentiometer and is believed accurate to ±0.05°C. Pressure was measured by a mercury manometer and cathetometer, and was controlled by a Cartesian manostat to within about 0.2% of the still pressure. Mixture compositions were determined by refractive index using a Carl Zeiss refractometer. The refractive index was measured against sodium light, and the temperature of the prisms was maintained at 25 ± 0.02°C by water circulated from a constant-temperature bath. A typical refractive index–composition plot is shown in Figure 1; the full calibration data are available elsewhere (*2*).

Table I. Physical Properties of Pure Compounds at 25°C

Compound	Refractive index		Density		Normal boiling point, °C	
	This work	Lit.	This work	Lit.	This work	Lit.
n-Heptane (*1*)	1.3850	1.3851	0.6792	0.6795	98.4	98.4
n-Octane (*1*)	1.3949	1.3950	0.6982	0.6982	125.4	125.6
n-Nonane (*1*)	1.4028	1.4030	0.7132	0.7138	151.0	150.8
Di-*n*-propyl ether (*4*)	1.3775	[a]	0.7375/30°C	0.7373/30°C	91.0	90.5
Di-*n*-butyl ether (*4*)	1.3960	[a]	0.7600/30°C	0.7597/30°C	141.5	142.4

Numbers in parentheses give references for literature values.
[a] Not available at a suitable temperature.

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[1] To whom correspondence should be addressed.

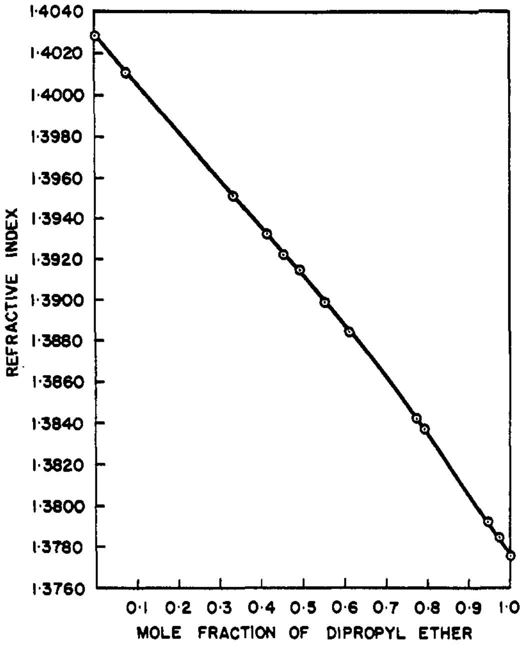

Figure 1. Refractive index-composition data for di-n-propyl ether/n-nonane mixtures at 25°C

Table II. Experimental Vapor-Liquid Equilibrium Data at 90°C

x_1	y_1	y_{ideal}	π, mm Hg	$\log \gamma_1$	$\log \gamma_2$
Di-*n*-propyl Ether(1)/*n*-Octane(2) Mixtures					
0.084	0.168	0.218	297.5	−0.0966	0.0292
0.214	0.388	0.453	363.2	−0.0544	0.0462
0.327	0.542	0.597	405.1	−0.0472	0.0334
0.393	0.621	0.664	475.7	−0.0001	0.0628
0.454	0.685	0.717	512.2	0.0109	0.0590
0.492	0.732	0.747	509.1	0.0023	0.0177
0.525	0.742	0.771	533.9	−0.0001	0.0499
0.633	0.819	0.840	612.9	0.0192	0.0646
0.750	0.902	0.901	682.0	0.0320	0.0084
0.867	0.948	0.952	735.2	0.0217	0.0376
0.895	0.965	0.963	759.5	0.0291	−0.0186
Di-*n*-propyl Ether(1)/*n*-Nonane(2) Mixtures					
0.106	0.415	0.452	166.8	−0.0525	−0.0068
0.155	0.525	0.561	178.3	−0.0868	−0.0444
0.200	0.620	0.635	207.4	−0.0604	−0.0535
0.250	0.658	0.699	253.2	−0.0461	0.0130
0.356	0.761	0.794	313.2	−0.0458	0.0127
0.391	0.799	0.817	348.5	−0.0200	0.0062
0.594	0.905	0.911	466.8	−0.0239	−0.0225
0.685	0.922	0.938	546.6	−0.0114	0.0663
0.843	0.968	0.974	646.7	−0.0102	0.0495
0.886	0.972	0.982	694.9	−0.0002	0.1591
0.973	0.992	0.996	747.2	−0.0020	0.2693
Di-*n*-butyl Ether(1)/*n*-Heptane(2) Mixtures					
0.075	0.020	0.021	580.6	−0.0253	0.0214
0.230	0.062	0.074	513.2	−0.0711	0.0306
0.345	0.105	0.124	471.8	−0.0530	0.0453
0.522	0.213	0.226	393.8	−0.0006	0.0504
0.566	0.250	0.259	364.0	0.0010	0.0382
0.645	0.327	0.324	323.6	0.0117	0.0286
0.672	0.337	0.354	324.4	0.0080	0.0575
0.795	0.513	0.509	260.1	0.0245	0.0338
0.930	0.760	0.781	198.4	0.0123	0.0776

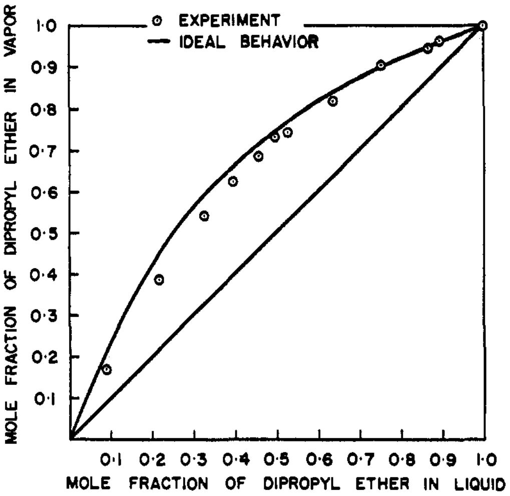

Figure 2. Vapor-liquid equilibrium of di-n-propyl ether/n-octane mixtures at 90°C

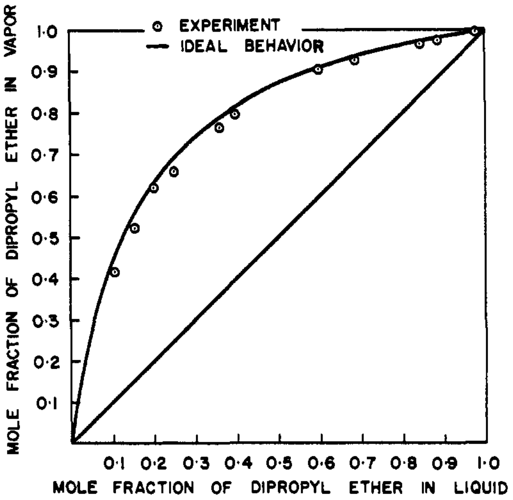

Figure 3. Vapor-liquid equilibrium of di-n-propyl ether/n nonane mixtures at 90°C

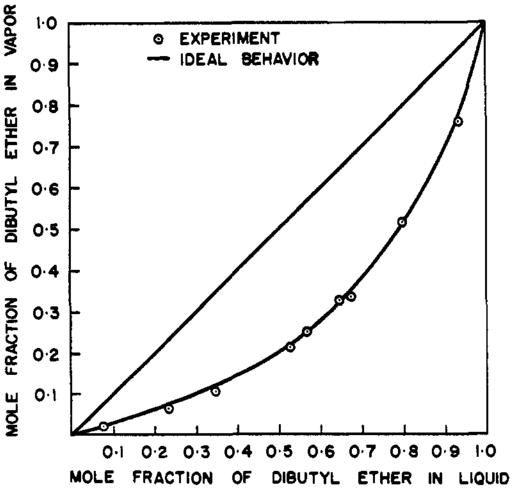

Figure 4. Vapor-liquid equilibrium of di-n-butyl ether/n-heptane mixtures at 90°C

RESULTS

The experimental vapor-liquid equilibrium data are presented in Table II. The liquid-phase activity coefficients were evaluated using the classical thermodynamic relationship:

$$\ln \gamma_i = \ln \left(\frac{\pi y_i}{x_i P_i^\circ}\right) + \frac{(\beta_i - v_2^L)(\pi - P_i^\circ)}{RT} \qquad i = 1,2 \tag{1}$$

Equation 1 allows for the effect of pressure on the liquid fugacity, and for the nonideality in the gas phase. For the latter, the virial equation was truncated to the second term. Wohl's (*5*) equation was employed to estimate the values of the second virial coefficients. Volumetric data were taken from the literature. For our systems, the contribution of the second term on the right-hand side of Equation 1 was very small.

During the experimental determinations, some difficulty was experienced in establishing the equilibrium pressure. Though pressures could be read accurately, pressure changes of 10–15 mm Hg showed no observable effect on the temperature. This was particularly true for the systems containing di-*n*-propyl ether. The following procedure was therefore adopted to determine the equilibrium pressure. The pressure was deliberately changed in small steps until the measured equilibrium temperature differed from 90°C. This gave pressures corresponding to temperatures of approximately 90 ± 0.05°C, and the mean pressure was taken to be the equilibrium pressure at 90°C.

The activity coefficients for these systems are close to unity. Considerable scatter was noted in the activity coefficient data, possibly due, at least in part, to the uncertainty in pressure. The equilibrium data were compared with ideal values calculated from

$$y_i = \frac{P_i^\circ x_i}{\Sigma P_i^\circ x_i} \qquad i = 1,2 \tag{2}$$

and are shown in Figures 2–4.

NOMENCLATURE

P° = pure component vapor pressure, mm Hg
R = gas constant, (mm Hg)(cc)/(g mol)(°K)
T = temp, °K
v = molal volume, cc/g mol
x = mole fraction in liquid
y = mole fraction in vapor

GREEK LETTERS

β = second virial coefficient
γ = activity coefficient
π = total pressure, mm Hg

SUBSCRIPTS

$1,2,i$ = component 1, 2, or i

SUPERSCRIPT

L = liquid

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Vapor-Liquid Equilibria of Methyl Propanoate–Methanol and Methyl Propanoate–Ethanol Systems at 25°C

JIŘÍ POLÁK and B. C.-Y. LU[1]
Department of Chemical Engineering, University of Ottawa, Ottawa, Canada

Vapor-liquid equilibria of the systems methyl propanoate–methanol and methyl propanoate–ethanol measured at 25°C are reported along with the results of the volumes of mixing at the same temperature.

Vapor-liquid equilibria at 25°C for the two binary systems, methyl propanoate–methanol and methyl propanoate–ethanol, were measured by a circulation method. The experimental equilibrium pressures and compositions, together with the liquid activity coefficients and excess Gibbs free energies, are presented. The excess volumes of the systems were calculated using the density values obtained by means of a pycnometer at 25°C.

EXPERIMENTAL

The method and equipment used in this study were described in earlier articles (*8*, *10*).

A circulation still with a total capacity of about 150 ml was used for the determination of vapor-liquid equilibrium compositions. When the temperature of 25°C was obtained in the still head, this temperature was maintained for 3 hr to ensure the establishment of equilibrium. Samples of the liquid and condensed vapor phases were taken immediately after boiling was discontinued, and analyses of both phases were made by measuring their densities in calibrated 5-ml capillary-stem pycnometers. The temperature of the still, as measured with a calibrated Beckmann thermometer, was maintained within ±0.005°C, and the pressure, as measured with a Texas Instrument Pressure gage, was read with a precision of ±0.04 mm Hg.

The concentrations of the samples were determined by mea-

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[1] To whom correspondence should be addressed.