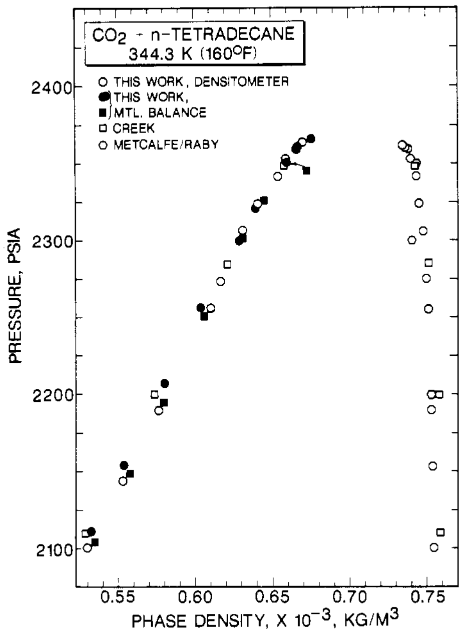

Figure 4. Comparison of phase density measurements.

ment with Metcalfe and Raby at 2200 psia.

For vapor densities, the present results agree very well with Creek's data at 2285 psia and above (differences less than 0.002 g/cm^3), with larger differences at lower pressures. The estimated uncertainty in our material balance densities is 0.005 g/cm^3 (~0.8%). Two separate runs were made, which generally deviate in opposite directions from our densitometer results. The average of the two material balance runs differs by no more than 0.002 g/cm^3 from the densitometer results.

Probably the major conclusion to be drawn from the above analyses is that various investigators are likely to produce saturated-phase densities that are consistent to no better than about 1%.

Glossary

A_i, B_i, G_i	parameters in eq A1–A4
f^L	volume fraction liquid in equilibrium cell
m	total mass in equilibrium cell
m^L	mass of liquid in equilibrium cell
m^V	mass of vapor in equilibrium cell
P	pressure
P_c	critical pressure
P^*	scaled pressure, $(P_c - P)/P_c$
V	total volume of equilibrium cell
x	liquid-phase mole fraction
y	vapor-phase mole fraction
Y	general experimental variable
z_c	critical composition (mole fraction)

Greek Letters

α, β, ν	scaling-law parameters (critical indices)
γ	interfacial tension
ϵ_Y	uncertainty in measured variable Y
ρ^L	liquid-phase density
ρ^V	vapor-phase density
ρ_c	critical density
$\Delta\rho$	liquid-phase density minus vapor-phase density
ϕ	general "order parameter"

Registry No. CO_2, 124-38-9; tetradecane, 629-59-4.

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Vapor–Liquid Equilibria in Binary Systems Containing Ethanol with Hexamethyldisiloxane and Dimethyl Sulfoxide

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Results of the experimental determination of isobaric vapor–liquid equilibrium data for the binary systems hexamethyldisiloxane (HMDS) with ethanol and ethanol with dimethyl sulfoxide (DMSO) are reported. This work is a continuation of studies on phase equilibria in binary systems (*1–6*).

Reagents

Hexamethyldisiloxane (HMDS) was supplied by CIECH, Gliwice. After purification it had bp 100.8–101 °C, $d^{20}_4 = 0.7634$ g cm^{-3}, and $n^{20}_D = 1.3777$.

Dimethyl sulfoxide had bp 189.0 °C, $d^{20}_4 = 1.008$ g cm^{-3}, and $n^{20}_D = 1.4779$. Ethanol boiled at 78.3 °C and had $d^{20}_4 =$

Table I. Experimental Liquid-Vapor Equilibria under a Pressure of 14.665 kPa and Values of HMDS and DMSO Mole Fraction in Vapor Calculated from the Redlich-Kister Equation in the Systems HMDS + Ethanol and DMSO + Ethanol

HMDS + Ethanol

	HMDS mole fraction		
	vapor		
temp, K	calcd	exptl	liquid
306.65	0.2026	0.210	0.080
305.65	0.2492	0.260	0.100
305.15	0.2830	0.300	0.115
304.65	0.3250	0.340	0.135
304.15	0.3602	0.375	0.155
303.65	0.3869	0.385	0.190
303.40	0.3980	0.395	0.205
303.15	0.4050	0.400	0.235
303.05	0.4100	0.407	0.350
302.65	0.4116	0.410	0.410
302.90	0.4119	0.415	0.465
303.05	0.4178	0.420	0.545
303.65	0.4186	0.435	0.660
304.15	0.4401	0.450	0.775
306.90	0.5368	0.550	0.900
308.65	0.5950	0.590	0.930
311.90	0.7063	0.700	0.960

DMSO + Ethanol

	DMSO mole fraction		
	vapor		
temp, K	calcd	exptl	liquid
328.95	0.0018	0.010	0.4875
337.65	0.0145	0.016	0.5975
339.90	0.0222	0.025	0.6400
343.95	0.0342	0.036	0.7100
349.65	0.0489	0.050	0.7625
354.65	0.0672	0.060	0.8050
364.65	0.1225	0.130	0.8500
373.89	0.2321	0.210	0.9000

0.7894 g cm^{-3} and $n^{20}{}_{D}$ = 1.3614.

Measurements

A relationship between the boiling point and composition of a system was determined by using a modified Świętoslawski ebulliometer (*7*, *8*). Under isobaric conditions the temperature was held constant to within ±0.05 K. The composition of the liquid and condensate was determined on the basis of the refractive index measurements by using previously prepared calibration graphs.

Results and Conclusions

Results of the measurements are listed in Table I. They were used to construct liquid-vapor plots shown in Figures 1 and 2. The system ethanol + HMDS exhibited strong positive deviations from ideal behavior. Under the pressure of 14.67 kPa an azeotrope is formed; it boils at 302.12 K with mole fraction of ethanol = 0.590.

The DMSO + ethanol system turned out to be a zeotropic one; for classification and terminology of vapor-liquid diagrams see Brostow (*9*). The boiling point range is 309.25-399.35 K. There are large differences in the composition of the liquid and vapor phases.

Thermodynamic verification of the experimental data was performed by using bi-, tri-, and tetraparametric Redlich-Kister equations (*10*):

$$Q = \frac{G^E}{RT} = x_1x_2;\quad \sum_{i=1}^{n} A_i(x_1 - x_2)^{i-1} \qquad (1)$$

where Q is often called the thermodynamic potential, G^E is the excess Gibbs function, x_i is the mole fraction of the ith component, A_i's are constants, R is the gas constant, and T is the absolute temperature in K.

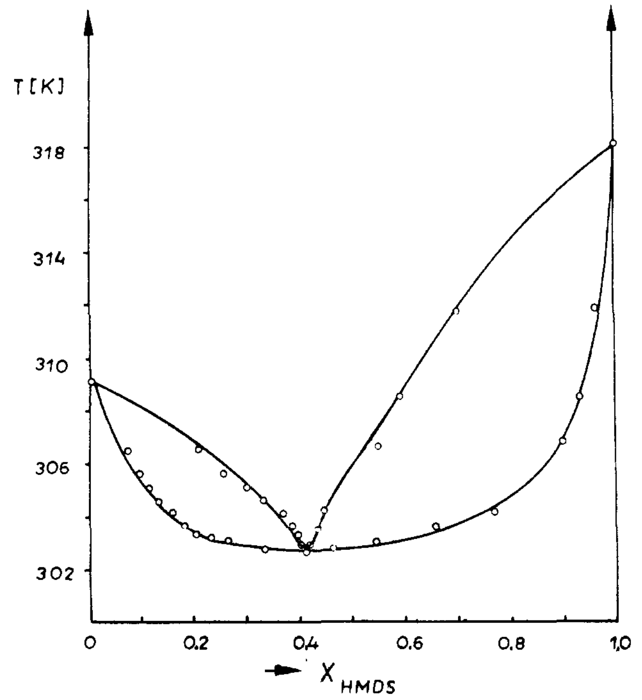

Figure 1. Isobaric vapor-liquid equilibrium diagram at 14.67 kPa for the system HMDS + ethanol.

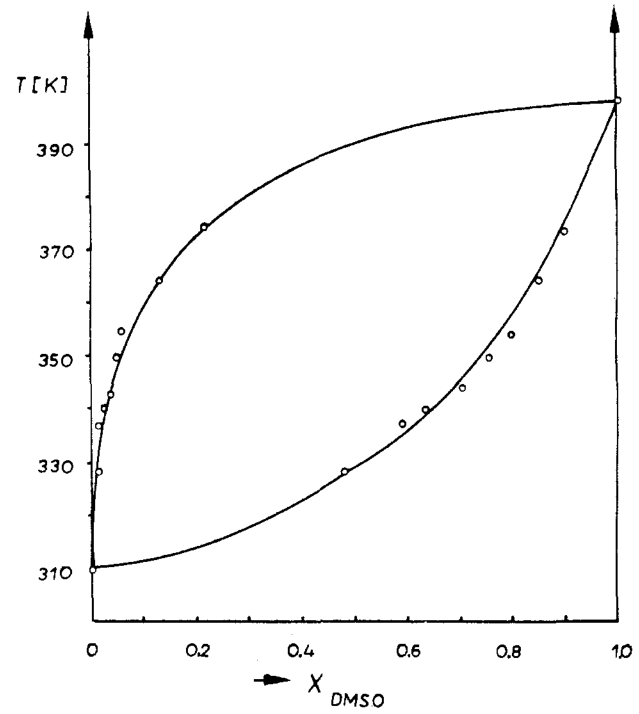

Figure 2. Isobaric vapor-liquid equilibrium diagram at 14.67 kPa for the system dimethyl sulfoxide + ethanol.

Activity coefficients, γ_1 and γ_2, of components 1 and 2 of the liquid phase were calculated from experimental data as

$$Q = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \qquad (2)$$

where

$$\ln \gamma_1 = \frac{Py_1\varphi_1}{P_1{}^{\circ}x_1} \quad \text{and} \quad \ln \gamma_2 = \frac{Py_2\varphi_2}{P_2{}^{\circ}x_2} \qquad (3)$$

The vapor pressure of the pure component, P°, was calculated from the Antoine equation (*11*):

$$\log P^\circ = A - B/(C + T)$$

where A, B, and C are constants. As the A, B, and C constants for DMSO are not known, they were calculated from the values of critical temperatures (*12*). Fugacities φ_1 and φ_2 of the components were calculated under consideration of the second virial coefficient

$$\ln \varphi_1 = \frac{(B_1 - V_1)(P - P^\circ)}{RT} + \frac{(2B_{1,2} - B_1 - B_2)}{RT} P y_2^{\,2} \qquad \text{(4a)}$$

$$\ln \varphi_2 = \frac{(B_2 - V_2)(P - P^\circ)}{RT} + \frac{(2B_{1,2} - B_1 - B_2)}{RT} P y_1^{\,2} \qquad \text{(4b)}$$

where y_1 and y_2 are mole fractions of the components in the vapor phase, V_1 and V_2 are molar volumes of the components, and P is the total pressure. The second virial coefficients, B_1 and B_2, of components 1 and 2 as well as $B_{1,2}$ for the mixture were calculated by the Pitzer–Curl method (*13*) from

$$B_1 = (RT_c/P_c)(F_1 + \omega F_2) \qquad (5)$$

where

$$F_1 = 0.1445 - 0.33T_r^{-1} - 0.1385T_r^{-2} - 0.0121T_r^{-3} \qquad (6)$$

$$F_2 = 0.073 + 0.46T_r^{-1} + 0.5T_r^{-2} - 0.097T_r^{-3} - 0.0073T_r^{-8} \qquad (7)$$

$$T_r = T/T_c \quad \text{and} \quad \omega = \log (P^\circ/P_c) - 1 \qquad (8)$$

Partial pressure, P°, which occurs in the evaluation of the acentric coefficient ω, was calculated for $T = 0.7T_c$. The value of $B_{1,2}$ was calculated from the following combining rules (*14*):

$$T_{c_{1,2}} = (T_{c_1}T_{c_2})^{1/2} \quad \text{and} \quad \omega_{1,2} = \frac{\omega_1 + \omega_2}{2} \qquad (9)$$

$$P_{c_{1,2}} = \frac{4T_{c_{1,2}}\left(\dfrac{P_{c_1}V_{c_1}}{T_{c_1}} + \dfrac{P_{c_2}V_{c_2}}{T_{c_2}}\right)}{(V_{c_1}^{\,1/3} + V_{c_2}^{\,1/3})^3} \qquad (10)$$

Critical values V_c, T_c and P_c (volume, temperature, and pressure, respectively) for HMDS were taken from the article by Dickinson (*15*) whereas the T_c value for the alcohol from Timmermans (*16*). The remaining critical values were calculated as described by Reid (*17*).

The activity coefficients calculated from the experimental data enable one to find constants A_i in the Redlich–Kister equation. To find these constants, a program was developed that utilized orthogonal polynomials.

Having found the constants in the Redlich–Kister equation, the theoretical composition of the vapor phase, y_1 and y_2, was determined as

$$y_{1_{\text{calcd}}} = \frac{P_1^\circ x_1 \gamma_1}{P\varphi_1} \quad \text{and} \quad y_{2_{\text{calcd}}} = \frac{P_2^\circ x_2 \gamma_2}{P\varphi_2} \qquad (11)$$

and listed in Table I.

Table II. Constants A_i in the Redlich-Kister Equation and Mean Quadratic Error (RM(y))

no. param	numerical values	RM(y)
	HMDS + Ethanol	
2	$A_1 = 1.9634$	0.0302
	$A_2 = 0.1929$	
3	$A_1 = 2.1505$	0.0348
	$A_2 = 0.2140$	
	$A_3 = -0.4736$	
4	$A_1 = 2.1401$	0.02991
	$A_2 = 0.1247$	
	$A_3 = -0.4973$	
	$A_4 = 0.3908$	
	DMSO + Ethanol	
4	$A_1 = -0.0657$	0.0089
	$A_2 = -8.6288$	
	$A_3 = 17.2393$	
	$A_4 = -18.1993$	

Theoretical values of γ_1 and γ_2 in these expressions were follow from differention of eq 1 as

$$\ln \gamma_1 = x_2^{\,2}\,(A_1 + A_2(3x_1 - x_2) + A_3(x_1 - x_2) \times (5x_1 - x_2) + A_4(x_1 - x_2)^2(7x_1 - x_2) + \ldots) \qquad \text{(12a)}$$

$$\ln \gamma_2 = x_1^{\,2}\,(A_1 - A_2(3x_2 - x_1) - A_3(x_1 - x_2) \times (5x_2 - x_1) - A_4(x_1 - x_2)^2(7x_2 - x_1) + \ldots) \qquad \text{(12b)}$$

The mean quadratic error was assumed as a measure of the agreement between the theoretical and experimental results:

$$\text{RM}(y) = \left[\left(\sum_{i=1} (y - y_{\text{calcd}})^2\right)/n\right]^{1/2} \qquad (13)$$

RM(y) values in the bi-, tri-, and tetraparametric equations were juxtaposed with the values of the constants in these equations in Table II. As can be seen in the tables, the agreement between the calculated and experimental mole fractions in the vapor phase is entirely satisfactory. This is both for the HMDS-containing azeotropic system and for the DMSO-containing zeotropic system.

Registry No. HMDS, 107-46-0; DMSO, 67-68-5; EtOH, 64-17-5.

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