Vapor-Liquid Equilibrium of Isobutyl Alcohol–Dimethyl Sulfide System

TEREZIA BETANCOURT[1] and ALAN F. McMILLAN[2]
Department of Chemical Engineering, Nova Scotia Technical College, Halifax, Nova Scotia, Canada

Vapor-liquid equilibrium data have been measured for the isobutyl alcohol–dimethyl sulfoxide system at 80.0°, 92.5°, and 105.0°C. These equilibrium data were measured in a vapor recirculating still at pressures in the range from 20–662 mm of Hg, and the analyses were done by refractometry. The Redlich-Kister procedure was used to check the thermodynamic consistency of the data, and the data were correlated with three-constant Redlich-Kister equations.

Because of the many possible industrial applications of dimethyl sulfoxide (DMSO), there is continuing interest in this laboratory in its properties (*1*). In this study isothermal vapor-liquid equilibrium data for the binary system DMSO and isobutyl alcohol are presented.

EXPERIMENTAL

Materials. DMSO of 99.9% purity (J. T. Baker Chemical Co., Phillipsburg, NJ) and isobutyl alcohol also of 99.9% purity (Fisher Scientific Co., Fair Lawn, NJ) were further purified in a laboratory fractionating column with 21 sieve plates. The DMSO was distilled at 400 mm of Hg, and the middle fraction boiling at 162°C was collected. The isobutyl alcohol was fractionated at atmospheric pressure and the middle fraction boiling at 107°C at 754 mm of Hg was retained.

Apparatus and Procedure. The vapor recirculating still (Figure 1) was designed by Hipkin and Myers (*3*), modified by Myers and manufactured by the James F. Scanlon Co. of Whittier, CA. In this design, the contactor is self-lagged with its own vapors to ensure adiabatic, steady-state operation. All parts except for the Teflon sample valves were made of borosilicate glass. The power supplied to the immersion heater for the boiler was controlled by a variable autotransformer. For control of pressure a vacuum pump was connected in series with a Cartesian manostat (type C-2100, Robert Gilmont Instruments, Cole-Parmer Instrument Co., Chicago, IL) covering a full range of pressures, 0-760 mm of Hg. The pressures were measured by means of a mercury manometer of 10-mm diameter to an accuracy of 1 mm of Hg using a millimeter scale. These measurements were converted to standard conditions. Temperatures were measured to an accuracy of ±0.1°C by a Fisher immersion thermometer with 0.1°C divisions, standardized against a quartz thermometer calibrated at the freezing point and boiling point of water.

A sample of 50 ml of the binary mixture was charged into the vaporizer and 30 ml of the same solution into the contactor. The still was then connected to the vacuum line and the pressure set approximately to correspond to the desired temperature. At this stage, the liquid was brought to the boil and the pressure gradually adjusted to attain the desired equilibrium temperature accurately. When the equilibrium temperature was reached (after approximately 3 hr), the two phases were kept in contact for a period of 30 min, and then samples were removed from the contactor and condensate return line, were quickly cooled, and finally analyzed.

The weight fractions of DMSO in these samples were obtained to an accuracy of ±0.001 by measuring the refractive indices and using a calibration chart. This calibration chart was constructed from the data of Table I which gives the measured

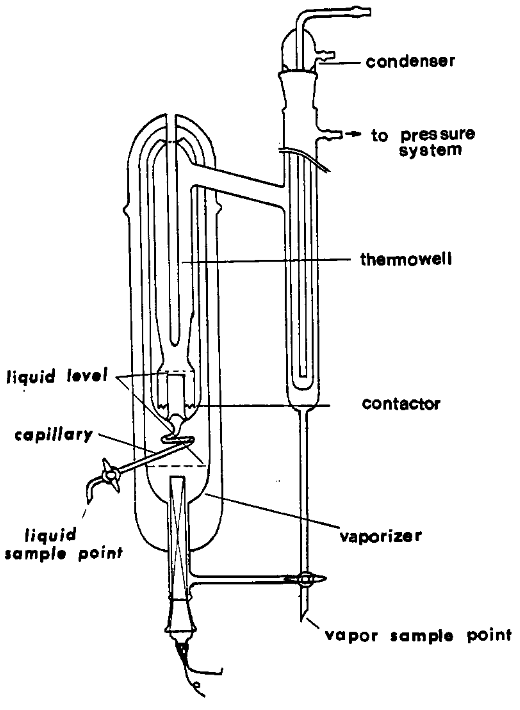

Figure 1. Vapor-liquid equilibrium still

Table I. Refractive Indices of Isobutyl Alcohol–DMSO System at 25°C

DMSO, wt %	Refractive index	DMSO, wt %	Refractive index
0.00	1.3932	51.57	1.4288
1.42	1.3940	59.53	1.4356
8.17	1.3981	65.89	1.4413
16.42	1.4033	67.23	1.4423
20.60	1.4058	67.71	1.4429
23.43	1.4080	72.06	1.4469
27.53	1.4107	72.25	1.4474
31.02	1.4130	77.00	1.4515
35.49	1.4163	82.40	1.4574
37.82	1.4180	84.82	1.4598
42.46	1.4215	87.99	1.4627
45.89	1.4242	89.18	1.4644
46.51	1.4246	93.20	1.4685
		100.00	1.4765

---

[1] Present address, Department of Mineral Engineering, Nova Scotia Technical College, Halifax, Nova Scotia, Canada.
[2] To whom correspondence should be addressed.

refractive indices of the isobutyl alcohol-DMSO system at 25°C, the samples of known composition being prepared by weight. The refractive indices were measured with a Spencer-Abbé refractometer thermostatically controlled at 25°C, using a sodium vapor lamp as a light source.

The maximum errors in temperature, pressure, and composition were estimated to be 0.1°C, 1 mm of Hg, and 0.1 wt %, respectively.

DATA AND ITS CONSISTENCY

The equilibrium data are reported in Table II for 80.0°, 92.5°, and 105.0°C. In this table are tabulated the equilibrium liquid and vapor phase compositions as mole fractions of isobutyl alcohol (x_1 and y_1), the total pressure π in mm of Hg, and the calculated activity coefficients of the alcohol and DMSO, γ_1 and γ_2. These activity coefficients were calculated using the relationship

$$\gamma_1 = \frac{\pi y_1}{P_1^\circ x_1} \tag{1}$$

where P_1° is the vapor pressure of the pure component i. The derivation of Equation 1 assumes ideal gas behavior, and the standard state is the pure liquid at the temperature and pressure of the system.

Table II. Experimental Vapor-Liquid Equilibrium Data for DMSO–Isobutyl Alcohol System

Mole fraction isobutyl alcohol		Total pressure, π, mm of Hg	Activity coefficients	
Liquid, x_1	Vapor, y_1		Isobutyl alcohol, γ_1	DMSO, γ_2
		80.0°C		
0.0275	0.2408	19.7	0.691	1.003
0.0462	0.3591	23.0	0.716	1.008
0.0735	0.4643	27.6	0.697	1.041
0.0964	0.5259	30.8	0.672	1.054
0.1386	0.6157	38.3	0.681	1.114
0.1848	0.6838	44.8	0.663	1.133
0.2489	0.7525	55.8	0.675	1.199
0.3555	0.8441	75.1	0.713	1.185
0.4162	0.8785	86.2	0.728	1.170
0.4982	0.9190	105.3	0.777	1.108
0.5799	0.9452	125.5	0.818	1.068
0.6528	0.9660	147.7	0.874	0.944
0.7228	0.9800	166.8	0.904	0.783
0.8180	0.9925	199.0	0.966	0.534
0.8808	0.9972	217.0	0.983	0.338
		92.5°C		
0.0350	0.2901	38.5	0.776	1.033
0.0442	0.3492	42.0	0.809	1.044
0.0555	0.3960	45.0	0.782	1.050
0.0955	0.5285	57.4	0.773	1.092
0.1371	0.6056	69.0	0.742	1.150
0.2013	0.7090	84.3	0.723	1.121
0.2500	0.7597	98.8	0.731	1.155
0.3605	0.8421	131.0	0.745	1.180
0.4156	0.8808	150.0	0.774	1.116
0.4631	0.8998	171.3	0.811	1.166
0.5908	0.9485	223.3	0.873	1.025
0.6874	0.9724	270.0	0.930	0.869
0.8063	0.9895	328.0	0.981	0.645
0.9273	0.9981	390.0	1.002	0.373
		105.0°C		
0.0551	0.4026	76.0	0.832	1.027
0.0826	0.4931	87.5	0.784	1.034
0.1131	0.5610	101.5	0.757	1.074
0.1397	0.6160	112.0	0.741	1.069
0.1587	0.6564	121.8	0.756	1.063
0.1912	0.6978	137.0	0.750	1.094
0.2245	0.7368	152.0	0.748	1.102
0.2574	0.7660	166.8	0.744	1.123
0.3193	0.8208	198.5	0.765	1.117
0.3483	0.8434	216.0	0.784	1.109
0.4034	0.8763	251.0	0.818	1.112
0.4207	0.8849	259.0	0.817	1.099
0.5071	0.9147	315.2	0.853	1.166
0.5729	0.9448	363.2	0.898	1.003
0.6510	0.9648	421.8	0.938	0.909
0.7060	0.9748	467.3	0.968	0.856
0.8005	0.9889	546.0	1.011	0.644
0.9400	0.9981	623.0	0.997	0.423

The vapor pressure data for DMSO were taken from the literature (*2*) while the constants of the Antoine equation (*5*) for the isobutyl alcohol were obtained through a least-square fit using the pressure data reported by Perry (*4*).

The variation of the activity coefficients with liquid phase composition at 80°C is shown in Figure 2. The curves at the other two temperatures had similar shapes and shifted slightly with temperature.

The plot of log γ_1/γ_2 vs. mole fraction of isobutyl alcohol in the liquid phase for the data at 80°C (Figure 3) gives the ratio of the positive areas to the negative areas of 0.97. The ratios at 92.5 and 105.0°C were 1.03 and 1.00 indicating thermodynamic consistency by the Redlich-Kister procedure (*6*).

The excess free energies were also calculated using the equation

$$g^E = RT \sum_{i=1}^{2} x_i \log \gamma_i \tag{2}$$

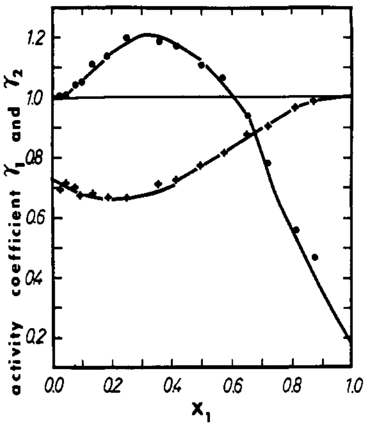

Figure 2. Activity coefficients for isobutyl alcohol–DMSO system at 80°C

+ Isobutyl alcohol
● DMSO

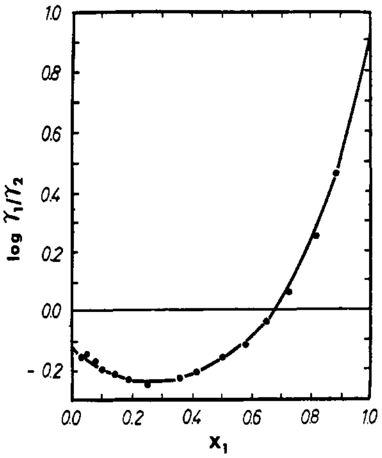

Figure 3. Redlich-Kister plot for isobutyl alcohol–DMSO system at 80°C

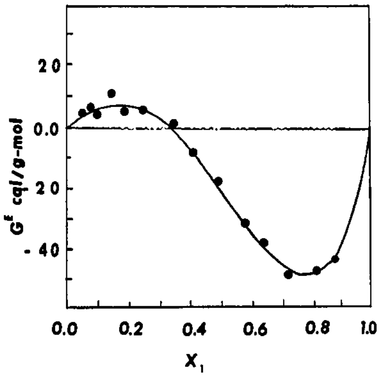

Figure 4. Excess Gibbs energy of system isobutyl alcohol–DMSO at 80°C

Table III. Constants of Redlich-Kister Equations for Isobutyl Alcohol–DMSO System

°C	*B*	*C*	*D*
80.0	−0.427	−0.352	−0.085
92.5	−0.343	−0.265	−0.029
105.0	−0.273	−0.184	+0.021

and are plotted as a function of the mole fraction of isobutyl alcohol in the liquid phase for 80°C in Figure 4.

The data were correlated with the three-constant Redlich-Kister equation (*7*),

$$\log \frac{\gamma_1}{\gamma_2} = B(1 - 2x_1) + C[6x_1(1 - x_1) - 1] + D(1 - 2x_1)[1 - 8x_1(1 - x_1)] \quad (3)$$

The values of the Redlich-Kister constants at the three temperatures are given in Table III.

The standard errors in mole percent when 2-constant Redlich-Kister equations were used were 2.35, 1.23, and 2.35 at 80.0°, 92.5°, and 105.0°C, respectively, while for the 3-constant equations, the standard errors were 0.55, 0.45, and 0.43. The *t*-test shows that there is a 99% confidence level for the three-constant equation, the variance σ^2 being 0.00003, 0.00002, and 0.000019 at 80.0°, 92.5°, and 105.0°C, respectively.

NOMENCLATURE

B, C, D = constants of Redlich-Kister equation
$P°$ = vapor pressure of pure component
x = mole fraction of component in liquid phase
y = mole fraction of component in vapor phase
γ = activity coefficient
π = total pressure
σ^2 = variance of fit
g^E = excess free energy

SUBSCRIPTS

1 = isobutyl alcohol component
2 = DMSO component

LITERATURE CITED

(1) Chandok, S. S., McMillan, A. F., *J. Chem. Eng. Data*, **14**, 286 (1969).
(2) Douglas, T. B., *J. Amer. Chem. Soc.*, **68**, 1072 (1946).
(3) Hipkin, H., Myers, H. S., *Ind. Eng. Chem.*, **46**, 2524 (1954).
(4) Perry, J. H., "Chemical Engineer's Handbook", pp 3–48, 4th ed., McGraw-Hill, New York, NY, 1963.
(5) Prausnitz, J. M., Eckert, C. A., Orye, R. V., O'Connell, J. P., "Computer Calculations for Multicomponent Vapor-Liquid Equilibria," p 73, Prentice-Hall, Englewood Cliffs, NJ, 1967.
(6) Redlich, O., Kister, A. T., *Ind. Eng. Chem.*, **40**, 345 (1948).
(7) Wohl, K., *Trans. Am. Inst. Chem. Eng.*, **42**, 215 (1946).

RECEIVED for review August 20, 1971. Accepted April 17, 1972. Work supported by the National Research Council of Canada.

Solubility and Hydrolysis in System NH_3–$H_6P_4O_{13}$–H_2O

THAD D. FARR, JOSEPH W. WILLIARD, and JOHN D. HATFIELD
Division of Chemical Development, Tennessee Valley Authority, Muscle Shoals, AL 35660

The 0°C solubility isotherm of the system NH_3–$H_6P_4O_{13}$–H_2O comprises three branches in the pH range 2.2–6.3; the saturating solids are $(NH_4)_4H_2P_4O_{13}$, $(NH_4)_5HP_4O_{13}\cdot H_2O$, and $(NH_4)_6P_4O_{13}\cdot 2H_2O$. The invariant solution in equilibrium with the tetra- and pentaammonium salts contains 10.8% N and 48.6% P_2O_5 and has a pH of 4. In dilute solutions at 25°C ammonium tetrapolyphosphate hydrolyzes in a series of consecutive first-order reactions that produce tripoly-, pyro-, and orthophosphate; the several rate constants were determined as functions of pH.

In the continuing study of the properties of ammonium polyphosphates (*3–5*), phase relationships in the system ammonia–tetrapolyphosphoric acid–water at 0°C were determined over the pH range 2.2 to 6.3, and the rates of hydrolysis of 0.2*M* solutions of ammonium tetrapolyphosphate at 25°C were determined as functions of pH.

Hexammonium tetrapolyphosphate of purity suitable for use in the solubility and hydrolysis studies was prepared by a modification of two published procedures (*8, 12*). Lead orthophosphate was heated for 32 hr at 570°C to produce lead tetrapolyphosphate which was dissolved and converted to the ammonium salt with ammonium sulfide; the last traces of lead were precipitated with hydrogen sulfide. The lead-free filtrate was treated with methyl alcohol, and the precipitated crystals were filtered off, dissolved in a minimum of water, and reprecipitated with alcohol. On air drying, the triclinic