Vapor-Liquid Equilibrium for the Ternary System Tetrahydrofuran-Water-Dimethylformamide

CHETAN S. SHAH[1] and HOWARD L. GREENE
The University of Akron, Akron, Ohio 44304

Vapor-liquid equilibrium data for the ternary system tetrahydrofuran-water-dimethylformamide have been measured at 1-atm. total pressure. The resulting liquid phase activity coefficients are tabulated and correlated as a function of liquid phase composition using regression analysis. Extractive distillation of tetrahydrofuran-water mixtures using dimethylformamide as the solvent appears feasible.

BINARY vapor-liquid equilibrium data for the systems tetrahydrofuran-water and water-dimethylformamide have been available in the literature (*1, 2*) for some time, primarily because of commercial importance in the polymer industry.

Recently, however, it has been proposed (*8*) that recovery of THF from water can be more economically obtained using extractive distillation techniques with DMF as the third solvent. The resulting need for equilibrium data on the ternary system THF-water-DMF becomes evident.

This paper presents vapor-liquid equilibrium data for the THF-water-DMF system at 1-atm. total pressure, along with the resulting liquid phase activity coefficient correlations based on regression analysis. The method of separating THF-water mixtures (which form a binary azeotrope) by extractive distillation using DMF is also discussed.

EXPERIMENTAL

Solvents. Both the THF and DMF had purities greater than 99.8% by weight as analyzed by a gas chromatograph. Further purification prior to use was unnecessary, since the major impurity was water, the third component in the system.

Apparatus and Procedure. The experimental apparatus is shown schematically in Figure 1. The equilibrium still used was a modified version of the vapor recirculation type Braun still (*7*), designed by Hipkin and Myers (*3*). A more detailed description of the still and peripheral equipment may be found in the literature (*3, 7, 8*). The standardized procedures for obtaining equilibrium and for sampling the resultant vapor and liquid, as outlined by Nelson (*7*), were followed. The still pressure was maintained at 760 ± 1 mm. of Hg during all runs using the nitrogen bleed. Still temperature measurements were accurate to within 0.1° C.

Liquid and condensed vapor analyses were carried out by injecting 3 μl. of each collected sample into a Varian, Model 202B gas chromatograph with a Poropak Q column. Helium was the carrier gas. Output peaks for THF, DMF, and water were recorded on a Leeds & Northrup Speedomax W recorder equipped with a Model 224 disc integrator. Previous calibration of the chromatograph with THF-water-DMF mixtures of known composition indicated accurate determination of liquid and vapor samples to within ± (0.001 to 0.004) mole fraction, depending on composition level.

RESULTS AND DISCUSSION

Vapor-Liquid Equilibrium Data. Equilibrium values of x and y for ternary mixtures as obtained by gas chromatographic analyses are given in Table I. Calculated values of the respective liquid phase activity coefficients are tabulated in Table II.

Binary equilibrium data for THF-DMF were also obtained experimentally (Table III). Equilibrium data for the THF-water and DMF-water binary systems were obtained from the literature (*1, 2*), although several check runs—i.e., runs 34 to 37—were performed to verify the experimental methods further. The ternary x-y data are also shown graphically in Figure 2, which suggests the absence of any ternary azeotrope, except possibly at very high THF concentrations, out of the range of experimental determinations.

Liquid phase activity coefficient calculations are based on Raoult's and Dalton's laws

$$P_i = py_i = \gamma_i P_i^* x_i \tag{1}$$

along with the assumption of vapor phase ideality. This assumption was checked using the method of Mertes and Colburn (*6*) and found to be valid to within 0.4% over the entire range of compositions for 1-atm. total pressure.

Thermodynamic Consistency. Thermodynamic consistency of the vapor-liquid equilibrium data was checked using the method proposed by McDermott and Ellis (*5*) for multicomponent systems. The vapor-liquid data were classified into three groups (temperaturewise), such that each pair of points within a group was within a normal boiling point range of 3° C. On this basis, runs 3, 13, and 31 with deviations more than three times the average may be in error, and hence were not included in the subsequent regression analysis.

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[1] Present address, General Tire & Rubber Co., Akron, Ohio 44309

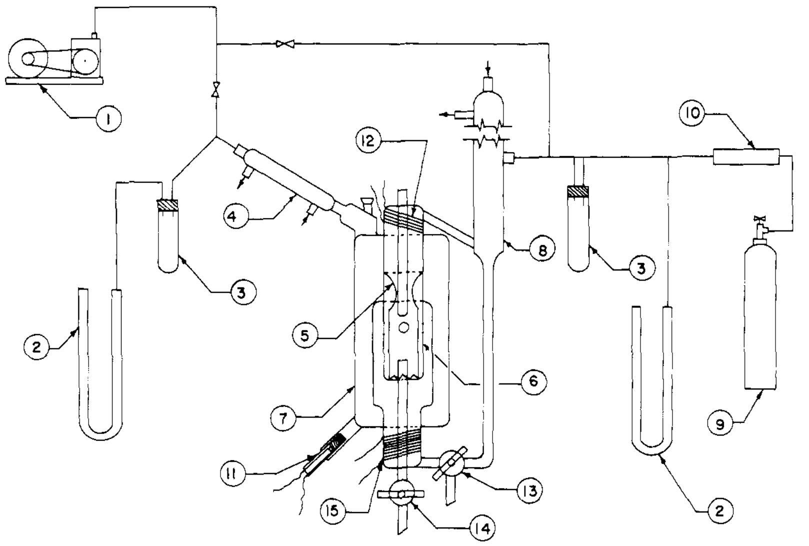

Figure 1. Schematic of experimental apparatus

1. Vacuum pump
2. Mercury manometer
3. Safety trap
4. Jacket condenser
5. Venturi
6. Contactor
7. Jacket
8. Still condenser
9. Nitrogen source
10. Drying tube
11. Jacket heater
12. Overhead heater
13. Condenser vapor-sampling stopcock
14. Liquid-sampling stopcock
15. Reboiler heater

Table I. Vapor-Liquid Equilibrium Data for THF-Water-DMF System

Run No.	Temp., °C.	Tetrahydrofuran (THF)		Water		Dimethylformamide (DMF)	
		x_1	y_1	x_2	y_2	x_3	y_3
1	69.4	0.065	0.890	0.879	0.105	0.055	0.004
2	72.0	0.092	0.926	0.810	0.064	0.096	0.008
3	69.2	0.256	0.958	0.519	0.022	0.220	0.020
4	74.1	0.472	0.901	0.116	0.076	0.410	0.021
5	82.9	0.079	0.694	0.610	0.281	0.311	0.024
6	81.6	0.109	0.742	0.434	0.222	0.458	0.034
7	93.1	0.123	0.730	0.253	0.196	0.623	0.074
8	111.0	0.006	0.035	0.413	0.826	0.582	0.138
9	120.6	0.058	0.426	0.066	0.210	0.875	0.359
10	136.3	0.005	0.097	0.023	0.179	0.974	0.723
11	67.0	0.129	0.880	0.777	0.077	0.092	0.043
12	69.2	0.041	0.848	0.930	0.152	0.020	~0
13	76.2	0.010	0.423	0.964	0.571	0.026	0.005
14	67.2	0.315	0.920	0.559	0.071	0.120	0.007
15	65.0	0.514	0.964	0.464	0.035	0.023	~0
16	65.1	0.884	0.964	0.022	0.030	0.092	0.005
17	66.5	0.957	0.994	0.002	~0	0.040	0.005
18	66.1	0.367	0.891	0.341	0.103	0.291	0.004
19	67.2	0.392	0.946	0.232	0.043	0.375	0.010
20	69.0	0.470	0.933	0.262	0.047	0.155	0.019
21	67.1	0.492	0.864	0.281	0.126	0.226	0.010
22	69.3	0.691	0.946	0.139	0.043	0.208	0.010
23	67.2	0.414	0.946	0.051	0.043	0.533	0.010
24	94.2	0.139	0.734	0.175	0.167	0.685	0.098
25	100.5	0.132	0.717	0.114	0.121	0.753	0.160
26	69.0	0.729	0.967	0.079	0.022	0.191	0.010
27	66.1	0.755	0.952	0.157	0.043	0.087	0.003
28	88.9	0.172	0.751	0.135	0.183	0.691	0.064
29	67.5	0.496	0.855	0.284	0.140	0.219	0.004
30	77.5	0.198	0.813	0.358	0.158	0.442	0.027
31	74.7	0.402	0.923	0.154	0.056	0.441	0.022
32	70.6	0.102	0.882	0.839	0.118	0.058	0.009
33	84.9	0.032	0.653	0.844	0.332	0.124	0.014
34	110.8	0	0	0.600	0.878	0.400	0.122
35	119.3	0	0	0.400	0.777	0.600	0.223
36	136.0	0	0	0.076	0.472	0.924	0.528
37	100.5	0	0	0.990	0.996	0.010	0.004

Table II. Liquid Phase Activity Coefficients for THF-Water-DMF

Run No.	Tetrahydrofuran (THF), γ_1	Water, γ_2	Dimethylformamide (DMF), γ_3
1	12.131	0.397	1.574
2	8.304	0.235	1.549
3	3.081	0.142	1.679
4	1.459	1.791	0.787
5	5.283	0.877	0.808
6	4.218	1.027	0.802
7	2.876	1.000	0.739
8	2.169	1.370	0.844
9	2.782	1.636	1.058
10	0.729	2.477	1.166
11	6.528	0.367	0.937
12	18.376	0.548	. . .
13	30.591	1.469	3.011
14	2.795	0.468	1.881
15	1.904	0.305	. . .
16	1.108	5.586	1.258
17	1.018	. . .	2.793
18	2.413	1.165	0.348
19	2.282	0.863	0.541
20	1.779	0.614	0.763
21	1.665	1.651	0.882
22	1.300	1.146	0.896
23	2.160	3.149	0.382
24	2.337	1.140	0.797
25	2.070	1.047	1.062
26	1.188	0.957	0.982
27	1.253	1.064	0.921
28	2.410	2.204	0.823
29	1.645	1.777	0.629
30	2.806	1.059	0.823
31	1.720	0.961	0.678
32	7.432	0.427	2.886
33	11.296	0.692	0.849
34	. . .	1.003	2.437
35	. . .	0.672	1.333
36	. . .	1.963	0.259
37	. . .	0.988	4.970

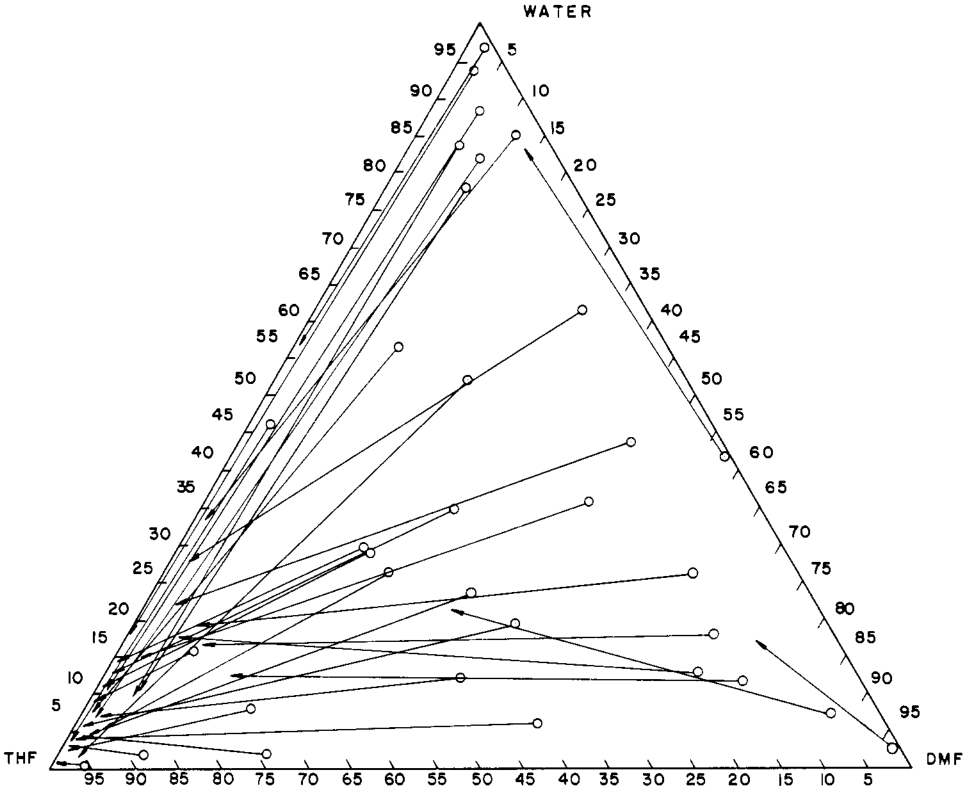

Figure 2. Vapor-liquid equilibrium diagram for THF-water-DMF system

Table III. Vapor-Liquid Equilibrium Data for Binary System THF-DMF at 1 Atm.

Run No.	Temp., °C.	THF Mole Fraction		Activity Coefficient	
		Liquid	Vapor	THF	DMF
1	114.3	0.087	0.690	2.945	1.076
2	109.0	0.134	0.754	2.094	1.053
3	96.0	0.212	0.810	1.711	1.263
4	84.0	0.489	0.906	1.066	1.747
5	77.6	0.679	0.939	0.938	2.407
6	74.0	0.885	0.958	0.839	5.551
7	70.2	0.960	0.974	0.876	11.761

Correlation of Liquid Phase Activity Coefficients. Empirical correlation of activity coefficients as a function of liquid or vapor phase composition was obtained by regression analysis techniques using an IBM 360 Model 44 computer. The resulting model equation in terms of x_i's for each component and for each stated range of composition are tabulated below, along with an estimate for goodness of fit. Extrapolation of these equations to compositions outside of the stated ranges is not recommended.

Correlation of γ_i with Liquid Phase Compositions

$0.006 < x_1 < 0.1$, $R = 0.9961$:

$$\gamma_1 = -8.37\,x_1^2 - 1.36\,x_2x_1 + 11.1\,x_3x_1 + 3.43\,x_2^2 + 0.594\,x_3^2 - 0.193\,x_2x_3$$

$0.1 < x_1 < 0.9$, $R = 0.9757$:

$$\ln \gamma_1 = 0.776 - 1.08\,x_1^2 + 2.13\,x_2^2$$

$0.9 < x_1 < 1.0$:

$$\gamma_1 = 1.0$$

$0.02 < x_2 < 0.12$:

$$\gamma_2 = 1.0$$

$0.12, < x_2 < 0.98$, $R = 0.9613$:

$$\ln \gamma_2 = 0.818 - 1.14\,x_1^2 + 1.71\,x_2^2$$

$0.98 < x_2 < 1.0$:

$$\gamma_2 = 1.0$$

$0.02 < x_3 < 0.98$, $R = 0.7857$:

$$\gamma_3 = 1.99 - 0.62\,x_1 - 4.27\,x_3 - 1.80\,x_2x_3 + 0.480\,x_2^2 + 4.24\,x_3^2$$

$0.98 < x_3 < 1.0$:

$$\gamma_3 = 1.0$$

Application to Multicomponent Distillation Problems. These activity coefficient correlations are conveniently computer-programmed for use with the available iterative methods used in distillation column design, such as the method of Lewis and Matheson (*4*). A block diagram and computer program listing using this method are available (*8*).

Separation by Extractive Distillation. The ternary vapor-liquid equilibrium results shown in Figure 2 indicate that the THF-water binary azeotrope which normally forms at 82 mole % THF (at 1 atm.) can be successfully bypassed by addition of DMF to the column several stages above the THF-water feed plate. The DMF addition enhances the volatility of THF with respect to water, making production of 99+ mole % THF feasible in a single atmospheric still. A second column for water-DMF separation would, however, be necessary. This technique is outlined in detail in the literature (*8*).

NOMENCLATURE

P = total pressure, mm. Hg
p_i = partial pressure of i, mm. Hg
p_i^* = vapor pressure of i, mm. Hg
R = correlation coefficient
T = temperature, °C.
x_i = liquid phase mole fraction of i
y_i = vapor phase mole fraction of i
γ_i = liquid phase activity coefficient

Subscripts

1 = tetrahydrofuran (THF)
2 = water
3 = dimethylformamide (DMF)
i = component

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Solubility of Ethylene in Aqueous Silver Nitrate and Potassium Nitrate Solutions

Silver Ion–Ethylene Association Constant

H. LAWRENCE CLEVER, EUGENE R. BAKER, and WILLIAM R. HALE
Department of Chemistry, Emory University, Atlanta, Ga. 30322

The solubility of ethylene gas in aqueous silver nitrate and potassium nitrate solution was determined at 0.945-atm. ethylene partial pressure and 30° C. The enhanced solubility in silver nitrate solution was assumed due to a 1 to 1 $CH_2{=}CH_2—Ag^+$ association. The zero ionic strength association constant for the reaction $Ag^+(aq.) + CH_2{=}CH_2(aq.) \rightleftarrows CH_2{=}CH_2—Ag^+(aq.)$ is 76, and for $Ag^+(aq.) + CH_2{=}CH_2(CCl_4) \rightleftarrows CH_2{=}CH_2—Ag^+(aq.)$ is 2.36.

EQUILIBRIUM constants for the silver ion-alkene association are reported (*2, 3, 6, 7, 10, 11, 12*) for various alkenes, cycloalkenes, and methylenecycloalkanes for the reaction

$$Ag^+(aq.) + \text{alkene}\ (aq.) \rightleftarrows \text{alkene}\cdot Ag^+(aq.) \qquad K_1$$

or

$$Ag^+(aq.) + \text{alkene}\ (CCl_4) \rightleftarrows \text{alkene}\cdot Ag^+(aq.) \qquad K_0$$

The two association constants are related through the distribution constant of the alkene between carbon tetrachloride and water (or salt solution)

$$\text{Alkene}\ (aq.) \rightleftarrows \text{alkene}\ (CCl_4) \qquad K_D$$

by $K_1 = K_D K_0$. Reported here is the association constant of the reaction

$$CH_2{=}CH_2(aq.) + Ag^+(aq.) \rightleftarrows CH_2{=}CH_2\cdot Ag^+(aq.)$$

calculated from ethylene gas solubilities in dilute aqueous solutions of silver nitrate and potassium nitrate.

EXPERIMENTAL

Chemicals. Ethylene, Matheson C.P. grade, 99.5% minimum. Reagent grade silver nitrate and potassium nitrate were used without further purification.

Gas solubility apparatus was similar to that described by Markham and Kobe (*9*). Solubilities were measured at an ethylene partial pressure of 0.945 atm. at 30° C. Aqueous solutions of silver nitrate and potassium nitrate were prepared, degassed by refluxing under vacuum, and transferred to the solubility apparatus without contact with atmospheric gases. The solubility of ethylene gas at a partial pressure of 0.945 atm. was measured by observing the volume of gas, saturated with water vapor from the solution, taken up by an 88.5-ml. sample of the degassed solution at 30° C. and a total pressure of 1 atm.

RESULTS AND DISCUSSION

Results are tabulated in Table I. The solubilities are reported as volume of ethylene, in milliliters, reduced to

Table I. Solubility of Ethylene in Aqueous Silver Nitrate and Potassium Nitrate Solutions at 30° C.

Solubility in Silver Nitrate		Solubility in Potassium Nitrate		
$AgNO_3$, m./l.	C_2H_4, ml. (STP)/ liter solution at 0.945 atm.	KNO_3, m./l.	C_2H_4, ml. (STP)/ liter solution at 1 atm.	$S°/S$
0.0	92.8 ± 0.5 (5)[a]	0.0	98.2 ± 0.5 (5)	1.000
0.0011	99.2 ± 0.2 (2)	0.0084	96.2 (1)	1.021
0.0028	104 ± 0.0 (2)	0.0173	92.7 ± 1.0 (2)	1.059
0.0056	119 ± 2.0 (2)	0.0280	89.6 ± 3.0 (2)	1.096
0.0113	149 ± 2.0 (2)	0.115	84.2 ± 2.5 (3)	1.166
0.0226	200 ± 2.0 (2)	0.525	73.0 ± 5.2 (4)	1.345
0.0338	242 (1)	1.08	71.0 ± 1.6 (3)	1.383

[a] Numbers in ( ) are number of determinations.