Vapor-Liquid Equilibria of Binary Systems Containing Alcohols

Methanol–Ethyl Acetate and Methanol–Isopropyl Ether

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Vapor-liquid equilibrium data are reported for binary systems methanol–ethyl acetate (EA) and methanol–isopropyl ether (IPE) at 730 mm. of Hg. *t-x-y* relation and activity coefficients for the methanol-EA system obtained in the present work agreed very well with the previous results reported by Akita, Nagata, and Murti. IPE forms a positive azeotrope with methanol at 57.0° C. near 53.0 mole % of methanol.

THE INCREASING use of the alcohols in many industrial processes, as well as the theoretical interest in the nature of the associated solutions, has greatly stimulated the need for accurate and extensive information on the vapor-liquid equilibrium relations and the azeotropic behavior of their mixtures. Data are therefore available for more than several binary systems containing methanol or ethanol as one component (*11*). Because of a moderate hydrophilic-to-hydrophobic balance, the alcohol molecules can dissolve both water and various organic liquids very well and their mixtures show a wide variety of solution properties. Mixtures with hydrocarbons, for example, show a large positive deviation from Raoult's law, while the solutions of two alcohols are almost ideal.

A series of studies was undertaken for the purpose of investigating systematically the effect of various functional groups on the equilibrium relation of binary systems containing alcohols. This paper deals with the barometric vapor-liquid equilibrium data of methanol with ethyl acetate (EA) and with isopropyl ether (IPE). An earlier report (*8*) deals with the correlation of vapor-liquid equilibrium relationship in binary systems.

MATERIALS

The samples used in this study were of the highest purity available and purified further by repeated distillations through a 30-plate column. The criterion for the purified samples was the disappearance of a trace of impurity peak on their gas chromatogram. Silicone DC 550 was used as column and H_2 as carrier gas. Because the samples are hygroscopic, only freshly distilled liquids were mixed and used for equilibrium measurements.

Table I lists some physical properties of the final purified samples as well as the Antoine constants used for vapor pressure calculation.

EXPERIMENTAL PROCEDURE

The vapor-liquid equilibrium data were determined on a modified Colburn equilibrium still (*3*). Glass ring-like packings in the flash tube of the still make the flow of superheated vapor smooth and the boiling in the equilibrium chamber steady (*10*). Temperatures were measured by a Chromel-Alumel thermocouple or thermistor, which was calibrated against a standard thermometer (made by Toshiba Co. and guaranteed by the Japan Bureau of Standards).

The compositions of the vapor and liquid equilibrium samples were determined by density measurement at 25° C. using a bicapillary-type pycnometer and the mixture composition-density calibration curve (*7*) determined in this laboratory. Total experimental errors were estimated to be less than ±0.1 mole % of methanol.

RESULTS AND DISCUSSION

Tables II and III list the data obtained in this work. Since the mean pressure at which measurements were performed was 730 mm. of Hg, temperature was corrected to the normal boiling point.

The activity coefficients γ are calculated by

$$\gamma = \frac{\pi y}{p x} \tag{1}$$

The maximum boiling point difference between pure liquid and an azeotrope is less than 15° C., and the reduced temperature t_R ($t_R = t/t_C$, where t_C is the critical temperature) for both components falls between 0.32 and 0.23, and the vapor pressure of methanol (lower boiling point component)

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

	Methanol	EA	IPE
Boiling point, t, ° C.			
Obsd.	64.6	76.9	68.0
Lit.[a]	64.5	77.1	68.3
Density, d^{4}_{25}			
Obsd.	0.78653	0.89430	0.71838
Lit.[a]	0.7866	0.8946	0.7200
Refractive index, $n_{D_{25}}$			
Obsd.	1.3265	1.3702	1.3655
Lit.[a]	1.3267	1.3698	
Antoine constants[a]			
A	8.07246	7.30588	7.09712
B	1574.99	1357.7	1257.6
C	238.86	230.0	230.0

[a] Literature values are taken from (*4, 12, 13*).

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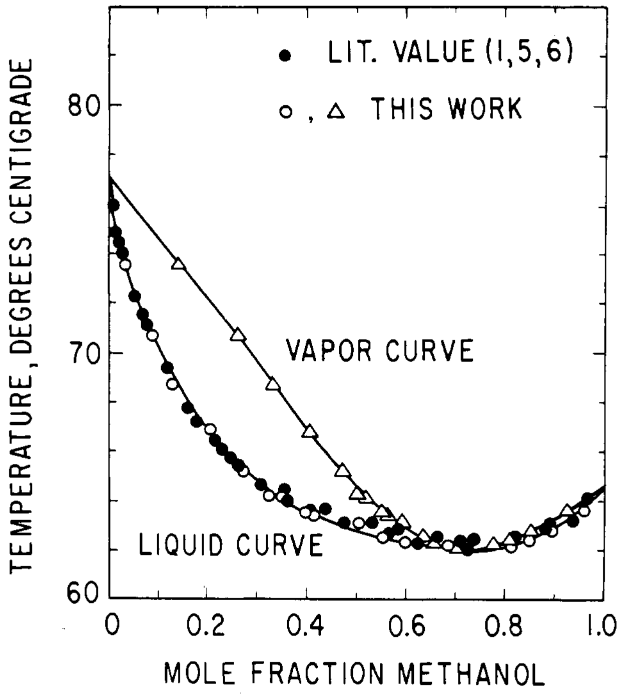

Figure 1. Boiling point diagram for methanol–ethyl acetate system

Table II. Vapor-Liquid Equilibria of the System Methanol–Ethyl Acetate at 730 Mm. of Hg

Methanol Concn., Mole %		Temp.,[a]	Activity Coefficients, γ	
Liquid	Vapor	° C.	Methanol	EA
3.4	14.2	73.5	2.976	1.002
8.9	26.0	70.6	2.327	1.014
12.7	33.5	68.7	2.254	1.013
20.6	40.7	66.8	1.823	1.065
27.3	47.6	65.2	1.713	1.089
32.5	50.0	64.2	1.570	1.151
34.8	52.1	64.1	1.534	1.153
39.8	54.7	63.5	1.444	1.201
41.4	55.9	63.4	1.423	1.212
50.5	59.4	63.1	1.252	1.325
55.2	63.6	62.5	1.258	1.351
59.8	65.2	62.3	1.200	1.451
60.2	64.3	62.6	1.161	1.477
61.7	64.5	62.3	1.151	1.554
67.0	69.0	62.2	1.138	1.571
81.2	77.9	62.2	1.059	1.976
85.2	81.0	62.4	1.041	2.140
89.4	85.6	62.8	1.032	2.234
93.7	90.3	63.5	1.011	2.454
95.8	92.8	63.6	1.013	2.741

[a] Corrected to 760 mm. of Hg.

Table III. Vapor-Liquid Equilibria of the System Methanol–Isopropyl Ether at 730 Mm. of Hg

Methanol Concn., Mole %		Temp.,[a]	Activity Coefficients, γ	
Liquid	Vapor	° C.	Methanol	IPE
7.0	19.8	62.4	3.103	1.049
12.4	29.0	60.7	2.750	1.046
28.5	41.8	58.0	1.921	1.151
42.0	48.0	57.4	1.538	1.297
55.1	53.4	57.0	1.320	1.517
65.0	57.7	57.2	1.202	1.758
72.7	61.3	57.8	1.113	2.018
76.2	63.3	58.1	1.084	2.175
82.0	67.9	58.5	1.064	2.482
83.9	69.5	58.9	1.046	2.598
88.8	75.0	60.0	1.021	2.949
90.1	76.2	60.1	1.017	3.164
92.7	79.6	60.9	1.000	3.576
96.8	88.1	62.8	0.982	4.464

[a] Corrected to 760 mm. of Hg.

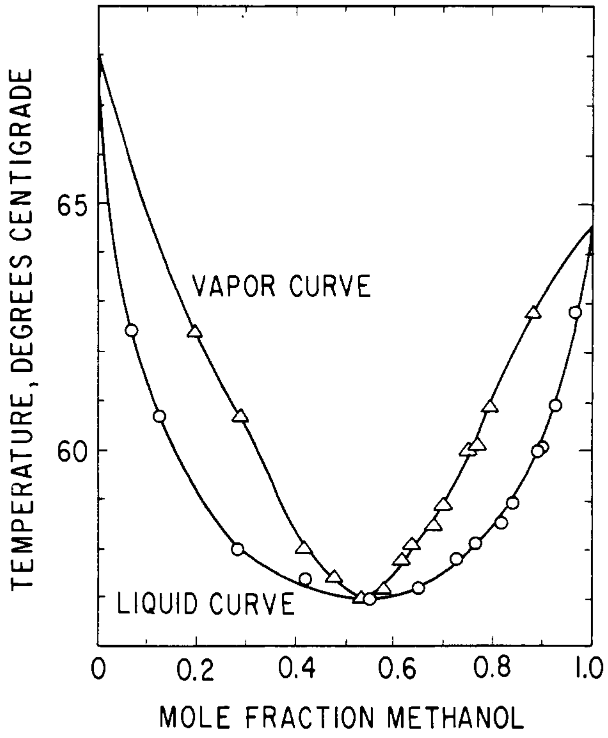

Figure 2. Boiling point diagram for methanol–isopropyl ether system

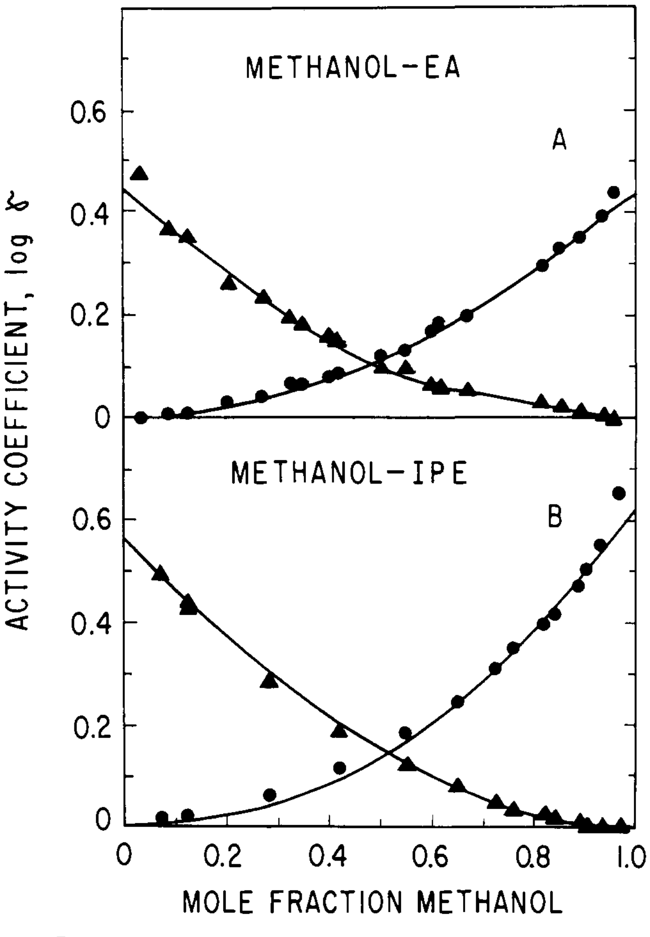

Figure 3. Activity coefficient *vs.* composition diagram

A. Methanol-EA ▲ = log γ_1
● = log γ_2
B. Methanol-IPE ▲ = log γ_1
● = log γ_2

Table IV. Limiting Activity Coefficients and Azeotropic Data

	Margules Constants		Azeotropic Data	
	MA	*MB*	x_1	t_A[a]
Methanol-EA				
Murti (*5*)			0.705	62.4
Nagata (*6*)	0.43	0.45	0.712	62.4
Akita (*1*)	0.430	0.430	0.710	62.3
This work	0.45	0.43	0.715	62.2
Methanol-IPE				
This work	0.56	0.62	0.530	57.0

[a] Boiling temperature of azeotrope, ° C.

is always less than 1200 mm. of Hg in the temperature range studied. At these conditions, the correction factor due to the vapor phase imperfection was negligible. As the *t-x-y* diagram in Figures 1 and 2 illustrates, the maximum boiling azeotrope in methanol-EA system occurs at 62.2° C. and consists of 71.5 mole % of methanol. Methanol-IPE is also shown to form an azeotropic mixture at 57.0° C. where mole % of methanol is 53.0.

The Redlich-Kister thermodynamic consistency test (*9*), modified by Herington (*2*) for isobaric data, showed that the present data are thermodynamically consistent.

The data can well be correlated with the 2-constant Margules equation:

$$\left.\begin{aligned}\log \gamma_1 &= x_2^2[MA + 2(MB - MA)x_1] \\ \log \gamma_2 &= x_1^2[MB + 2(MA - MB)x_2]\end{aligned}\right\} \qquad (2)$$

where the subscript 1 refers to methanol. A set of the Margules constants were evaluated from the data and tabulated in Table IV, and the experimental and calculated γ values are plotted in Figure 3.

The vapor-liquid equilibrium data for methanol-EA system were reported by Murti (*5*), Nagata (*6*), and Akita (*1*) and are also incorporated in Figure 1. This comparison shows that the four independent measurements agree with each other, and the still used in this study produces consistent data. A comparison of azeotropic data is also given in Table IV.

NOMENCLATURE

MA, MB = Margules constants
p = vapor pressure of pure liquid, mm. Hg
t = boiling temperature, ° C.
x, y = composition of liquid and vapor mole fraction, respectively
γ = activity coefficient
π = total pressure, mm. Hg

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Properties of 1,1,3,3-Tetramethylguanidine as a Nonaqueous Solvent

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A number of physical constants of 1,1,3,3-tetramethylguanidine (TMG) have been determined and indicate self-association in the liquid presumably through hydrogen bonding. The solvent has a dielectric constant of 11.5. Solubilities of alkali metal salts parallel those in liquid ammonia, but TMG has somewhat weaker dissolving power. In the presence of water, TMG is hydrolyzed to 1,1-dimethylurea; moist TMG reacts with carbon dioxide to form tetramethylguanidinium bicarbonate. The solvent titrates as a strong monoprotonic base in aqueous or nonaqueous media. Infrared spectra give evidence for protonation of TMG at the imine nitrogen.

THIS investigation was undertaken to evaluate 1,1,3,3-tetramethylguanidine, $(H_3C)_2NC(:NH)N(CH_3)_2$, as a solvent for inorganic reactions. Recently Longhi and Drago (*11*) prepared some transition metal complexes of tetramethylguanidine, and Williams *et al.* (*24, 25*) titrated several acids in the solvent. Little else has been published.

The authors report here certain physical properties of tetramethylguanidine and some solubilities and reactions in this solvent medium.

EXPERIMENTAL

Stock 1,1,3,3-tetramethylguanidine (TMG) was obtained from the American Cyanamid Co., Wayne, N. J. It was purified by vacuum distillation from BaO, and the fraction

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