$$\chi^* = [24.1 \ln M^* + 112] \times 10^{-6}$$

and

$$\ln M^* = 0.0378\ T - 11.67 \tag{3}$$

or by a direct fit independent of Equations 1 and 2, as

$$\chi^* = \left[\frac{20}{(M^*)^{0.45}} + 130 \right] \times 10^{-6} \tag{4}$$

These correlations were made to provide empirical relations of the susceptibility as a function of concentration and temperature. The theoretical expressions (*6*) do not, for the most part, fit the experimental data within one to two orders of magnitude.

LITERATURE CITED

(1) Freed, S., Thode, H.G., *Nature* **134**, 774 (1934).
(2) Huster, E., *Ann. Physik* **33**, 477 (1938).
(3) Hutchinson, C.A., Jr., Pastor, K.D., *J. Chem. Phys.* **21**, 1959 (1953).
(4) Levens, A.S., "Graphics," Wiley, New York, 1962.
(5) Suchannek, R.G., Naiditch, S., Klejnot, O.J., *J. Appl. Phys.* **38**, 690 (1967).
(6) Yost, D.M., Russell, H.R., Jr., "Systematic Inorganic Chemistry," p. 141, Prentice-Hall, New York, 1944.

RECEIVED for review October 23, 1967. Resubmitted March 21, 1969. Accepted June 23, 1969. This work was supported by the Advanced Research Projects Agency and the Office of Naval Research under Contract No. NONR 3437(00).

Vapor-Liquid Equilibrium Data for the Binary Systems Methanol-Benzene and Methyl Acetate–Methanol

ISAMU NAGATA
Department of Chemical Engineering, Kanazawa University, Kanazawa, Japan

Isobaric vapor-liquid equilibrium data are presented for the binary systems methanol-benzene and methyl acetate–methanol at 1 atm. The experimental data were well correlated with the van Laar equation.

BINARY vapor-liquid equilibrium data are presented for two combinations involving methanol as one component at 1 atm. A Colburn still was used to obtain experimental data. Each set of binary data shows a positive azeotrope. The data are compared with the existing literature values.

EXPERIMENTAL

Methanol, C.P. grade, was fractionated through a laboratory glass column with McMahon packings. Benzene, C.P. grade, was purified by repeated recrystallization. Methyl acetate, C.P. grade, was refluxed with acetic anhydride and then distilled through a packed column. The distillate was shaken with anhydrous potassium carbonate and redistilled. Table I shows the experimental properties of the purified chemicals compared with literature values.

A Colburn equilibrium still was used. Boiling temperatures of mixtures were measured by a calibrated copper-constantan thermocouple and a Yokogawa P-7 potentiometer. The accuracy of temperature measurement was within ±0.05° C. Since the atmospheric pressure changed during experimental runs within a range of +1.8 and −8.2 mm. of Hg from 1 atm., observed temperatures were corrected to 1 atm. by applying the Clausius-Clapeyron equation. Compositions of binary mixtures were determined using an Atago Abbe refractometer. Refractive index reading could be done with an accuracy of ±0.0002 at 25° C.

Table I. Properties of Materials

	Boiling Point, ° C.		Refractive Index, 25° C.	
Material	Exptl.	Lit.	Exptl.	Lit.
Methyl acetate	56.8	56.8(*6*) 56.9(*13*)	1.3587	1.3589(*6*)
Methanol	64.7	64.65(*13*)	1.3263	1.3266(*14*)
Benzene	80.1	80.1(*13*)	1.4979	1.4979(*1*)

RESULTS

The liquid phase activity coefficients were calculated from the following equation of equilibrium for *i*th component

$$\varphi_i y_i P = \gamma_i x_i f_i^{0L} \tag{1}$$

The fugacity coefficient φ_i is given by

$$\ln \varphi_i = \frac{2}{v} \sum_{j=1}^{N} y_j B_{ij} - \ln z \tag{2}$$

The virial equation of state truncated after the second term is used to evaluate the compressibility factor z

$$z = \frac{Pv}{RT} = 1 + \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j B_{ij}/v \tag{3}$$

The second virial coefficients B_{ii} and B_{jj} and the second virial cross coefficient $B_{ij} (i \neq j)$ were calculated from correlations based on a theory of corresponding states (*7, 8, 9*).

The liquid phase fugacity in the reference state f_i^{0L} is

$$f_i^{0L} = f_i^0 \exp\left(\frac{v_i^L P}{RT}\right) \tag{4}$$

The reference fugacity for pure components are calculated by

$$f_i^0 = \varphi_i^s P_i^s \exp\left(-\frac{v_i^L P_i^s}{RT}\right) \tag{5}$$

where φ_i^s is the fugacity coefficient of pure vapor i at temperature T and saturation pressure P_i^s. The three-parameter corresponding state correlation of Lyckman *et al.* (*5*) allows calculation of φ_i^s

$$\log \varphi_i^s = (\log \varphi_i^s)^{0} + \omega_i (\log \varphi_i^s)^{1} \tag{6}$$

where ω_i is the acentric factor and $(\log \varphi_i^s)^{0}$ and $(\log \varphi_i^s)^{1}$ are generalized functions of reduced temperature.

Table II shows vapor pressure data for methyl acetate. The present data and those at pressures greater than 1 atm. (*12*) were used to evaluate constants of the following equation (Table III).

$$\ln P^s\,(\text{atm.}) = C_1 + \frac{C_2}{C_3 + T} + C_4T + C_5T^2 + C_6 \ln T \tag{7}$$

Vapor pressure data for benzene and methanol were taken from the literature (*1*, *10*). Table IV presents binary equilibrium data. The experimental data of Williams *et al.* (*15*) for methanol-benzene are probably not so accurate as the current measurements. Black (*2*) has correlated binary equilibrium data of alcohols and hydrocarbons with the aid of the modified van Laar equation given by

$$\log \gamma_1 = A/\left(1 + \frac{Ax_1}{Bx_2}\right)^2 + E_1$$

$$\log \gamma_2 = B/\left(1 + \frac{Bx_2}{Ax_1}\right)^2 + E_2 \tag{8}$$

$$E_i = c_{ij}x_j(x_i - x_j)\,[3(x_i - x_j)(1 - x_i) + 2x_j]$$

His analysis is considerably extensive, so that his calculated results for methanol-benzene at 1 atm. may provide a sound criterion as to whether the present data are thermodynamically consistent or not. Figure 1,A shows a compari-

Table II. Vapor Pressure of Methyl Acetate

t, ° C.	Mm. of Hg
35	329.8
40	404.2
45	491.5
50	591.5
55	712.8
56.8	760.0

Table III. Constants of the Vapor Pressure Equation

Constants	Methyl Acetate	Methanol (*10*)	Benzene (*1*)
C_1	115.524640	49.951322	9.267536
C_2	−7240.831400	−5970.8229	−2788.5064
C_3	0.0	0.0	−52.36
C_4	0.020397	0.004250	0.0
C_5	0.0	0.0	0.0
C_6	−17.300005	−5.792000	0.0

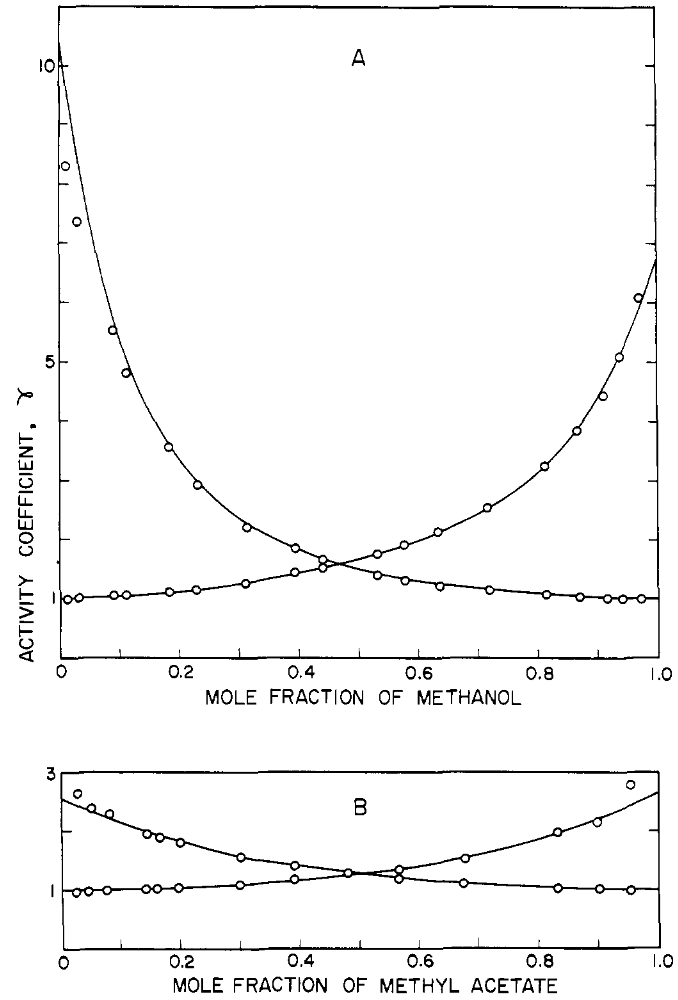

Figure 1. Activity coefficient *vs.* composition diagrams

A. Methanol-benzene, $A = 0.9176$, $B = 0.7225$, $c_{12} = 0.1050$ (2)

B. Methyl acetate–methanol, $A = 0.412$, $B = 0.422$, $c_{12} = 0$

○ Experimental

— Calculated

Table IV. Equilibrium Data at 1 Atm.

Methanol(1)-Benzene(2)							Methyl Acetate(1)–Methanol(2)						
t, ° C.	x_1	y_1	γ_1	γ_2	φ_1	φ_2	*t*, ° C.	x_1	y_1	γ_1	γ_2	φ_1	φ_2
76.5	0.010	0.128	8.347	0.987	0.984	0.966	63.3	0.026	0.086	2.683	0.973	0.956	0.957
71.1	0.028	0.263	7.395	1.006	0.976	0.965	62.1	0.045	0.129	2.415	0.991	0.955	0.956
62.7	0.088	0.455	5.544	1.049	0.966	0.967	60.6	0.076	0.200	2.326	0.997	0.955	0.955
62.0	0.109	0.475	4.798	1.060	0.965	0.967	58.9	0.140	0.292	1.948	1.014	0.954	0.954
59.9	0.179	0.530	3.533	1.109	0.962	0.968	58.3	0.160	0.319	1.898	1.022	0.954	0.953
59.3	0.226	0.538	2.908	1.181	0.961	0.969	57.3	0.196	0.362	1.817	1.041	0.953	0.952
59.1	0.311	0.554	2.192	1.290	0.960	0.969	56.0	0.297	0.452	1.563	1.078	0.953	0.951
58.6	0.399	0.566	1.821	1.444	0.960	0.969	54.9	0.388	0.507	1.393	1.164	0.952	0.950
58.4	0.438	0.573	1.655	1.553	0.959	0.970	54.4	0.476	0.560	1.275	1.239	0.952	0.950
58.4	0.529	0.597	1.426	1.751	0.958	0.971	54.0	0.564	0.607	1.182	1.351	0.952	0.949
58.3	0.575	0.603	1.330	1.919	0.959	0.971	53.8	0.672	0.672	1.106	1.511	0.952	0.949
58.4	0.634	0.615	1.225	2.154	0.958	0.971	53.3	0.830	0.776	1.052	2.032	0.951	0.948
58.4	0.715	0.643	1.135	2.569	0.957	0.973	55.0	0.899	0.847	1.001	2.178	0.953	0.949
58.9	0.811	0.694	1.058	3.271	0.957	0.975	55.9	0.953	0.905	0.980	2.801	0.953	0.949
59.7	0.866	0.737	1.018	3.864	0.956	0.977							
60.7	0.912	0.795	1.002	4.444	0.956	0.981							
61.7	0.939	0.831	0.978	5.117	0.957	0.983							
62.9	0.970	0.896	0.973	6.168	0.957	0.987							

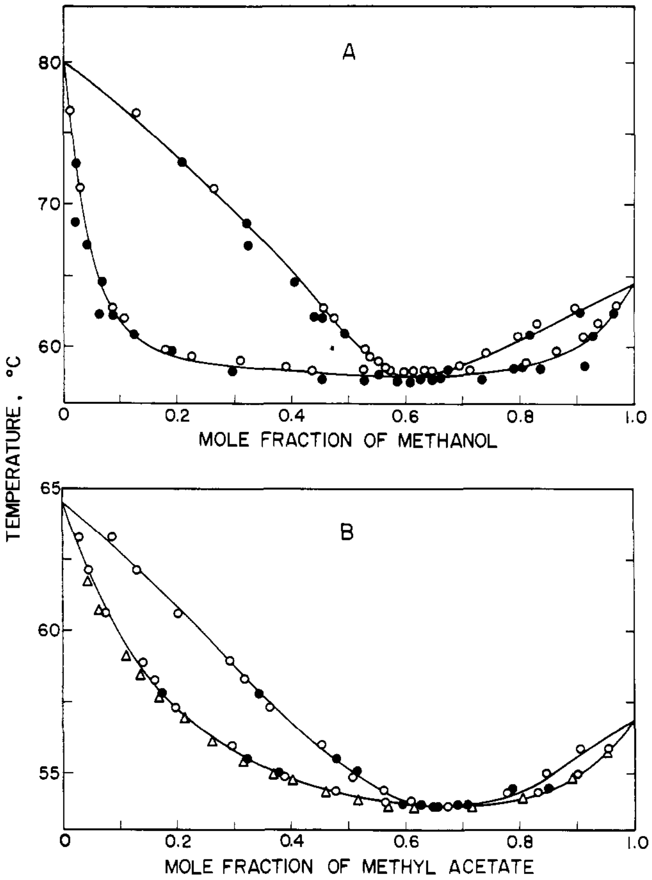

Figure 2. Temperature vs. composition diagrams

A. Methanol-benzene
Experimental
○ Nagata
● Shirai and Nakanishi
Calculated
— Black

B. Methyl acetate–methanol
Experimental
○ Nagata
● Dobroserdov and Bagrov
△ Bushmakin and Kish
Calculated
— Nagata

son of experimental and calculated activity coefficients. The calculated values were obtained from the constants estimated by Black at 1 atm. Figure 2,A shows that observed equilibrium data are in closer agreement with the calculated data of Black (*2*) than are the data of Shirai and Nakanishi (*11*). Equilibrium data for methyl acetate–methanol at 1 atm. have been published in the literature (*3, 4*). A diagram showing activity coefficient *vs.* composition is given in Figure 1,B. The present experimental data agree well with the data of Dobroserdov and Bagrov (*4*), as shown in Figure 2,B. The following are azeotropic data, interpolated from smoothed equilibrium results.

System	x_1	t, ° C.
Methanol(1)-benzene (2)	0.610	58.3
Methyl acetate(1)–methanol (2)	0.672	53.8

ACKNOWLEDGMENT

The author is grateful to Tatsuhiko Ohta and Takanori Tsurugi for their assistance in experimental work and to the Computer Center, Kyoto University, for the use of its facilities.

NOMENCLATURE

A, B, c_{ij} = van Laar constants
B_{ii}, B_{ij} = second virial coefficients
$C_1, C_2, C_3,$
C_4, C_5, C_6 = constants of vapor pressure equation
E_i = additive function of van Laar equation
f_i^0 = fugacity of component i in the reference state
f_i^{0L} = reference fugacity for pure liquid component i
P_i^s = saturation pressure of pure component i, atm.
P = total pressure, atm.
R = gas constant
t = temperature, ° C.
T = absolute temperature, ° K.
v = molar volume of vapor mixture, cc.
v_i^L = liquid molar volume of pure component i, cc.
x_i = liquid phase mole fraction of component i
y_i = vapor phase mole fraction of component i
z = compressibility factor
γ_i = liquid phase activity coefficient of component i
φ_i^s = fugacity coefficient of pure component i
$\left.\begin{matrix}(\log \varphi_i^s)^{(0)} \\ (\log \varphi_i^s)^{(1)}\end{matrix}\right\}$ = generalized functions of reduced temperature
φ_i = fugacity coefficient of component i
ω_i = acentric factor of pure component i

LITERATURE CITED

(1) American Petroleum Institute, Project **44**, "Selected Values of Properties of Hydrocarbons and Related Compounds," Texas A&M University, College Station, Tex., 1964.
(2) Black, C., *A.I.Ch.E. J.* **5**, 249 (1959).
(3) Bushmakin, I.N., Kish, I.N., *Zh. Priklad. Khim.* **30**, 200 (1957).
(4) Dobroserdov, L.L., Bagrov, I.V., *Ibid.*, **40**, 875 (1967).
(5) Lyckman, E., Eckert, C.A., Prausnitz, J.M., *Chem. Eng. Sci.* **20**, 685 (1965).
(6) Nagata, I., J. Chem. Eng. Data **7**, 360 (1962).
(7) O'Connell, J.P., Prausnitz, J.M., *Ind. Eng. Chem. Process Design Develop.* **6**, 245 (1967).
(8) Pitzer, K.S., *J. Am. Chem. Soc.* **77**, 3427, 3433 (1955).
(9) Pitzer, K.S., Curl, R.F., Jr., *Ibid.*, **79**, 2369 (1957).
(10) Prausnitz, J.M., Eckert, C.A., Orye, R.V., O'Connell, J.P., "Computer Calculations for Multicomponent Vapor-Liquid Equilibria," p. 214, Prentice Hall, Englewood Cliffs, N. J., 1967.
(11) Shirai, H., Nakanishi, K., *Kagaku Kogaku* **29**, 180 (1965).
(12) Stull, D.R., *Ind. Eng. Chem.* **39**, 515 (1949).
(13) Timmermans, J., "Physico-chemical Constants of Pure Organic Compounds," Vol. **II**, pp. 96, 251, 285, Elsevier, Amsterdam, 1965.
(14) Weissberger, A., Proskauer, E.S., Riddick, J.A., Toops, E.E., Jr., "Organic Solvents," 2nd ed., p. 90, Interscience, New York, 1955.
(15) Williams, G.C., Rosenberg, S., Rothenberg, H.A., *Ind. Eng. Chem.* **40**, 1273 (1948).

Received for review July 5, 1968. Accepted May 19, 1969.