$$\log {}^{s}_{s}(\gamma) = \frac{E_m{}^\circ - E}{2k} - \log m \qquad (7)$$

using the respective values of $E_m{}^\circ$ evaluated above. The activity coefficients $\left({}^{s}_{S}\gamma\right)$ are referred to at a value of unity for infinitely dilute solutions in the respective solvents. The values of $\left({}^{s}_{S}\gamma\right)$ were plotted against molality on a large scale and from the plots the activity coefficients at round values of molalities were tabulated for HBr in ethylene glycol and HCl in propylene glycol (Table V). Values of relative partial molal heat content, $\bar{L}_2$, of HX were calculated from the temperature coefficients of $\left(\log {}^{S}_{S}\gamma\right)$ using the relation

$$\bar{L}_2 = -2 \times 2.303\, RT^2 \left[\frac{d \log({}^{s}_{s}\gamma)}{dT}\right]_P \qquad (8)$$

where T denotes temperature on the Kelvin scale.

Table V also includes $\bar{L}_2$ values for HX in the two solvents.

Since there is an average uncertainty of ±0.0005 volt in e.m.f. values, the activity coefficients $\left({}^{S}_{S}\gamma\right)$ in a logarithmic scale may involve an average error of nearly ±0.004 unit and, consequently, the average uncertainty in $\bar{L}_2$ is roughly ±90 cal. per mole.

LITERATURE CITED

(1) Akerlof, G., *J. Am. Chem. Soc.* **54**, 4125 (1932).

(2) Banerjee, S. K., Kundu, K. K., Das, M. N., *J. Chem. Soc.* **1967A**, 161.

(3) Curme, G. O., Johnston, F., "Glycols," Reinhold, New York, 1952.

(4) Harned, H. G., Owen, B. B., "The Physical Chemistry of Electrolyte Solutions," 3rd ed., Reinhold, New York, 1958.

(5) Kundu, K. K., Das, M. N., J. CHEM. ENG. DATA **9**, 82 (1964).

(6) *Ibid.*, p. 87.

(7) Palit, S. R., Das, M. N., Somayajulu, G. R., "Nonaqueous Titration," Indian Association for Cultivation of Science, Calcutta, 1954.

(8) Sen, U., Kundu, K. K., Das, M. N., *J. Phys. Chem.* **71**, 3665 (1967).

Received for review July 15, 1968. Accepted August 8, 1969. Work done under a project financed by the National Bureau of Standards.

Vapor-Liquid Equilibrium Data for the Ternary System: Methyl Acetate–Carbon Tetrachloride–Benzene

ISAMU NAGATA

Department of Chemical Engineering, Kanazawa University, Kanazawa, Japan

Equilibrium data for the title ternary system are reported at 1 atm. Experimental values are in good agreement with vapor compositions and temperatures calculated from the Wilson equation.

THREE related sets of isobaric binary data have been published: methyl acetate-carbon tetrachloride (*8*), methyl acetate–benzene (*6*), and carbon tetrachloride–benzene (*2*). This work presents vapor-liquid equilibrium data for the ternary methyl acetate-carbon tetrachloride–benzene system at 1 atm. The Wilson equation, expressing activity coefficients as a function of liquid compositions and temperature, is used to correlate the observed results.

EXPERIMENTAL

All C.P. chemicals were used after purification. Methyl acetate was purified in accordance with the method of Hurd and Strong (*4*). Carbon tetrachloride was refluxed with sodium hydrate, washed with water, dried with anhydrous potassium carbonate, and distilled. Repeated recrystallization gave benzene of good quality. Table I shows the properties of the chemicals used. A Jones vapor-recirculation equilibrium still, designed by Jones, Schoenborn, and Colburn (*3*), was used to obtain the vapor-liquid equilibrium data. Temperatures of boiling mixtures were measured using a Yokogawa P-7 potentiometer and a copper-constantan thermocouple, which was calibrated against a standard mercury thermometer. The temperature measurements are believed to be accurate within ±0.05° C. The atmospheric pressure variation was recorded for each experimental run with a mercury barometer. The appropriate corrections to barometric reading were added to the measured pressures (*3*). The maximum deviations of the observed pressures from 1 atm. were −13.2 and

Table I. Properties of Purified Chemicals

Chemical	B.P., ° C.	Density, 25° C.	Refractive Index, 25° C.
Methyl acetate	56.8	0.9273	1.3587
Carbon tetrachloride	76.8	1.5840	1.4572
Benzene	80.1	0.8737	1.4979

+1.9 mm. of Hg. The arithmetic mean deviation is −2.2 mm. for 31 data points and −0.9 mm. for 27 data points, excluding 4 points with more than −6 mm. deviation. Compositions of the ternary mixtures were determined at an intersection of isodensity and isorefractive index lines on a calibrated ternary analytical chart. A 10-cc. Ostwald pyconometer and an Atago Abbe refractometer were used at 25° ± 0.1° C. for this purpose. Maximum uncertainty in concentration determination is ±0.002 mole fraction for each component.

DATA REDUCTION

The fundamental equation for vapor-liquid equilibrium of component *i* is expressed by

$$\varphi_i y_i P = \gamma_i x_i f^{0L} \exp \frac{v_i^L P}{RT} \tag{1}$$

where, for the vapor phase, y_i is the mole fraction, P is the total pressure, and φ_i is the vapor phase fugacity coefficient; for the liquid phase, x_i is the mole fraction, γ_i is the activity coefficient, and f_i^{0L} is the reference fugacity, all at the temperature and pressure of the system. For low or moderate vapor densities, the virial equation of state, truncated after the second term, may be used to calculate the molar volume, v, and the fugacity coefficient, φ_i.

$$\frac{Pv}{RT} = 1 + \sum_{j=1}^{N} \sum_{i=1}^{N} y_i y_j B_{ij}/v \tag{2}$$

$$\ln \varphi_i = \frac{2}{v} \sum_{j=1}^{N} y_j B_{ij} - \ln \frac{Pv}{RT} \tag{3}$$

where B_{ii} and B_{jj} are the pure component second virial coefficients, and where B_{ij} $(i \neq j)$ is the interaction second virial coefficient. For pure nonpolar gases, the second virial coefficients are calculated from a correlation given by Pitzer and Curl (*10*) based on a three-parameter theory of corresponding states.

It is expressed by

$$\frac{P_{ci} B_{ii}}{RT_{ci}} = f_B^{(0)}(T_R) + \omega_i f_B^{(1)}(T_R) \tag{4}$$

where P_{ci} is the critical pressure of pure component i, T_{ci} is the critical temperature, T_R is the reduced temperature T/T_{ci}, and ω_i is the acentric factor defined by $\omega_i = -\log_{10}(P_i^s/P_{ci}) - 1.000$, where P_i^s is the saturation pressure of pure component i at $T_R = 0.7$. $f^{(0)}(T_R)$ and $f^{(1)}(T_R)$ are empirically determined (*10*). For pure polar gases, a correlation based on the extended corresponding states theory is given by O'Connell and Prausnitz (*9*).

$$\frac{P_{ci} B_{ii}}{RT_{ci}} = f_B^{(0)}(T_R) + \omega_{Hi} f_B^{(1)}(T_R) + f_\mu(\mu_R, T_R) - \eta_i f_a(T_R) \tag{5}$$

ω_{Hi} represents the acentric factor of the polar component's homomorph. $f_\mu(\mu_R, T_R)$ is a function of the reduced temperature and the reduced dipole moment

$$\mu_R = \frac{10^5 \mu_i^2 P_{ci}}{T_{ci}^2}$$

where μ_i is the dipole moment of pure component i in Debye. η_i is the association constant. $f_a(T_R)$ is the association function. Detailed numerical values of ω_H, μ, η, $f_\mu(\mu_R, T_R)$, $f_a(T_R)$ are available (*9*). The correlating equations presented for B_{ii} of the pure components are used to estimate the interaction coefficient $B_{ij}(i \neq j)$ with mixing rules for the various parameters (*9*).

The fugacity of the pure liquid corrected to the zero pressure is given by

$$f_i^{0L} = \varphi_i^s P_i^s \exp - \frac{v_i^L P_i^s}{RT} \tag{6}$$

where φ_i^s is the fugacity coefficient of pure vapor i at temperature T and saturation pressure P^s. φ^s may be calculated by the three-parameter corresponding states correlation of Lyckman *et al.* (*5*). For a multicomponent mixture, the activity coefficient can be calculated by the general Wilson equation (*11*).

$$\ln \gamma_i = 1 - \ln \left(\sum_{j=1}^{N} x_j \Lambda_{ij} \right) - \sum_{k=1}^{N} \left[\frac{x_k \Lambda_{ki}}{\sum_{j=1}^{N} x_j \Lambda_{kj}} \right] \tag{7}$$

Λ_{ij} is expressed by

$$\Lambda_{ij} = \frac{v_j^L}{v_i^L} \exp - (\lambda_{ij} - \lambda_{ii})/RT \tag{8}$$

To determine each set of the binary parameters with experimental data, a nonlinear least square fitting program was used. It is a method which minimizes the sum of squares of deviations in the vapor phase mole fraction plus the sum of squares of relative deviations in pressure for all data points. Table II shows numerical values of the parameters, the deviation of calculated results from experimental values in the vapor mole fraction, and the relative deviation in pressure. The magnitude of the deviations is comparable with the results obtained by Renon (*12*) for many binary systems. Saturation pressure data are obtained by an equation of the following general form with six empirical constants

$$\ln P^s\,(\text{atm.}) = C_1 + \frac{C_2}{C_3 + T} + C_4 T + C_5 T^2 + C_6 \ln T \tag{9}$$

where the constants are given below.

	C_1	C_2	C_3	C_4	C_5	C_6
Methyl acetate (*7*)	115.524640	−7240.8314	. . .	0.020397	. . .	−17.300005
Carbon tetrachloride (*11*)	43.731222	−5270.9369	. . .	0.001760	. . .	−5.000000
Benzene (*1*)	9.267536	−2788.5064	−52.36	. . .	. . .	. . .

Table II. Binary Parameters of Wilson Equation and Root-Mean-Square Deviations

System	Wilson Parameter, Cal./G. Mole		Deviation in Vapor Phase Mole Fraction × 1000	Relative^a Deviation in Pressure × 1000
	$\lambda_{12} - \lambda_{11}$	$\lambda_{12} - \lambda_{22}$		
Methyl acetate(1)-carbon tetrachloride(2)	540	−140	10	5
Methyl acetate(1)-benzene(2)	670	−320	8	9
Carbon tetrachloride(1)-benzene(2)	−250	400	4	5

$^a (P_{\text{exptl.}} - P_{\text{calcd.}})/P_{\text{exptl.}}$

Critical constants and liquid molar volume data are available elsewhere *(11)*. Experimental ternary equilibrium data are listed in Table III. The ternary equilibria are satisfactorily predicted with the Wilson equation, as shown in Table IV. Tables III and IV may be obtained from ASIS. The fugacity coefficients for each component range from 0.97 to 0.96. The root mean square deviations in the vapor mole fractions and in the boiling temperatures corrected to 1 atm. with the calculated results are given as follows: methyl acetate, 0.005; carbon tetrachloride, 0.004; benzene, 0.005; b.p., ° C., 0.35. Correction to 1 atm. was made using the Clausius Clapeyron equation.

ACKNOWLEDGMENT

The author is grateful to Takao Fukuda and Michiaki Nozawa, and to the Computer Center, Kyoto University, for the use of its facilities.

NOMENCLATURE

$C_1, C_2, C_3,$
C_4, C_5, C_6 = constants of vapor pressure equation
B_{ii}, B_{jj}, B_{ij} = second virial coefficients, ml. per gram mole
$f^{(0)}, f^{(1)}, f_a$ = functions of reduced temperature
f_μ = function of reduced dipole moment and reduced temperature
f^{0L} = reference state fugacity
P = total pressure, atm.
P_{ci} = critical pressure of pure component i, atm.
P_i^s = saturation pressure of pure component i, atm.
R = universal gas constant, cal. per gram mole, ° K.
T = absolute temperature, ° K.
T_{ci} = critical temperature of pure component i, ° K.
T_R = reduced temperature, T/T_{ci}
v = molar volume of vapor mixture, ml. per mole
v_i^L = liquid molar volume of pure component i, ml. per mole
x_i = liquid phase mole fraction of component i
y_i = vapor phase mole fraction of component i
γ_i = liquid phase activity coefficient of component i
η = association constant
Λ_{ij} = Wilson binary constant
λ_{ij} = energies of interaction between an i-j pair of molecules, cal. per gram mole
μ = dipole moment, Debye
μ_R = reduced dipole moment
φ_i = vapor phase fugacity coefficient of component i
φ_i^s = vapor phase fugacity coefficient of pure component i
ω_H = acentric factor of polar component's homomorph
ω_i = acentric factor of pure component i

LITERATURE CITED

(1) Am. Petrol. Inst. Research Project 44, Texas A&M University, College Station, Tex., 1964.
(2) Fowler, R.T., Lim, S.C., *J. Appl. Chem. (London)* **6**, 74 (1956).
(3) Hála, E., Pick, J., Fried, V., Vilim, O., "Vapour-Liquid Equilibrium," 2nd ed., pp. 201, 291, Pergamon, Oxford, 1967.
(4) Hurd, C.D., Strong, J.S., *Anal. Chem.* **23**, 542 (1951).
(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) *Ibid.*, **14**, 418 (1969).
(8) Nagata, I., *Kanazawa Daigaku Kogakubu Kiyo* **3**, 197 (1964).
(9) O'Connell, J.P., Prausnitz, J.M., *Ind. Eng. Chem. Process Design Develop.* **6**, 245 (1967).
(10) Pitzer, K.P., Curl, R.F., *J. Am. Chem. Soc.* **79**, 2369 (1957).
(11) Prausnitz, J.M., Eckert, C.A., Orye, R.V., O'Connell, J.P., "Computer Calculations for Multicomponent Vapor-Liquid Equilibria," pp. 29, 213-9, Prentice Hall, Englewood Cliffs, N. J., 1967.
(12) Renon, H., Ph.D. thesis, University of California, Berkeley, Calif., 1966.

RECEIVED for review August 7, 1968. Accepted August 2, 1969. For Tables III and IV, order NAPS Document NAPS-00642 from ASIS National Auxiliary Publications Service, % CCM Information Sciences, Inc., 22 West 34th St., New York, New York 10001; remit $1.00 for microfiche or $3.00 for photocopies.