Isobaric Binary Vapor-Liquid Equilibria

Systems Acetic Acid–Ethylbenzene and Acetic Acid–*p*-Xylene

O. P. BAGGA and K. S. N. RAJU
Department of Chemical Engineering and Technology, Panjab University, Chandigarh, India

Vapor-liquid equilibrium data are reported for the two binary systems acetic acid–ethylbenzene and acetic acid–*p*-xylene at 725 mm of Hg pressure. Both systems formed minimum boiling azeotropes. The activity coefficient–composition data were tested for thermodynamic consistency and correlated by the Wilson equation for the acetic acid–ethylbenzene system and the van Laar equation for the acetic acid–*p*-xylene system.

The present investigation forms part of a research program to study the separation of close boiling hydrocarbon mixtures. Vapor-liquid equilibria for the systems acetic acid–ethylbenzene and acetic acid–*p*-xylene were determined at 725 mm of Hg pressure.

Data on the acetic acid–ethylbenzene system have been reported by Vilim and coworkers at 60° C (*21*). Othmer (*15*) has reported isobaric data for the acetic acid–xylene system at atmospheric pressure. Azeotropic data for these systems have been compiled by Horsley (*5*).

EXPERIMENTAL

Purity of Compounds. Acetic acid and ethylbenzene used in the present investigation were of laboratory reagent grade from British Drug Houses, Ltd., whereas *p*-xylene was of pure grade from Riedel. These were dried and further purified, in a 30-mm glass column packed with 3-mm ceramic insulation beads to a height of 1 meter. The column was run at total reflux for 30 minutes and the low boiling impurities were drawn off as rejects at low rate. When the desired boiling temperature was attained and remained constant for 15 minutes, the fraction was collected, the column being operated at nearly total reflux. The physical properties of pure compounds are listed in Table I.

Analytical Method. The mixtures were analyzed by the refractive index method, using a Bausch & Lomb Abbe-3L refractometer. The temperature of the prism assembly was kept constant at 35° ± 0.1° C, using a circulating type constant temperature bath with a merc-to-merc thermoregulator made by the Precision Scientific Co. A rectangular standard glass test piece having a nominal refractive index of 1.5126 supplied with the refractometer, with 1-bromonaphthalene as contacting liquid, was used to calibrate the refractometer. The compositions were measured with an accuracy of 0.5 mole % or better.

Apparatus. A modified recirculating type equilibrium still developed by Rao and coworkers (*17*) was used to obtain equilibrium vapor and liquid samples. A precision thermometer with a range of 100° to 150° C, calibrated in 0.02° C intervals, was used to measure temperature. The barometric pressure during the runs was 725 ± 3 mm of Hg. The variation of pressure inside the apparatus was mainly due to the fluctuations in atmospheric pressure, which were very small. The pressure drop inside the apparatus is considered negligible. The errors introduced were within the accuracy of the experimental measurements. Eighty- to 90-ml samples were charged to the still, which was operated for 3 hours after the recirculation was stabilized.

RESULTS

Acetic acid has a strong tendency for association in the vapor phase and is known to form dimers. The usual methods for calculating activity coefficients are not applicable for systems containing an associating component like acetic acid. The equations developed by Marek (*9, 10*) for binary mixtures containing an associating component were used to calculate the activity coefficients. The vapor

Table I. Physical Properties of Materials

	Acetic Acid	Ethylbenzene	*p*-Xylene
Molecular weight	60.05	106.16	106.16
Normal b.p., ° C (*7*)	118.1	136.2	138.4
Refractive index at 35° C			
Experimental	1.3660	1.4875	1.4885
Literature (*20*)[a]	1.3666	1.4878	1.4879
Density at 35° C			
Experimental	1.0274	0.8497	0.8433
Literature (*20*)[a]	1.0322	0.8538	0.8480
Critical temperature, ° K (*19*)	594.80	617.10	618.80
Critical pressure, atm (*19*)	57.10	36.90	33.90
Critical volume, ml/gmole (*19*)	171.0	374.0	378.0
Heat of vaporization at normal boiling point, g cal/gmole (*7*)	5813.89	8499.77	8620.19

[a] Literature values corrected to 35° C.

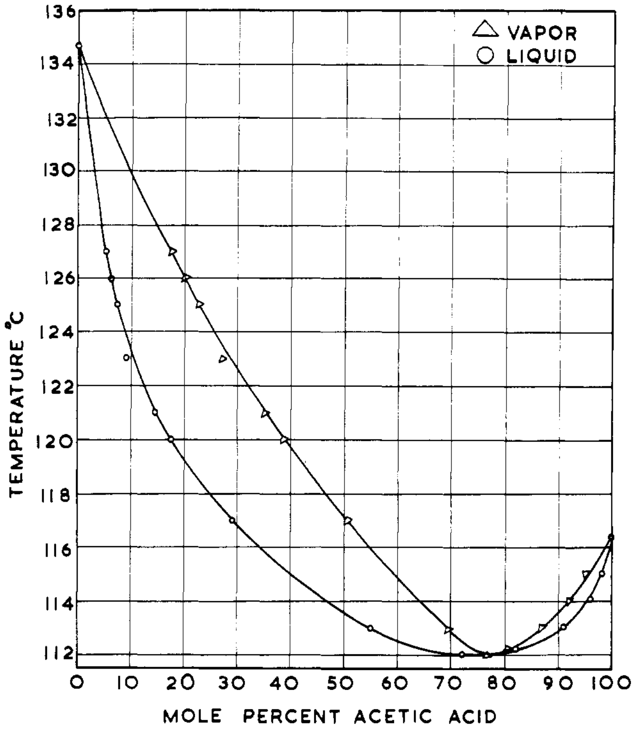

Figure 1. Boiling point–composition diagram for acetic acid–ethylbenzene system

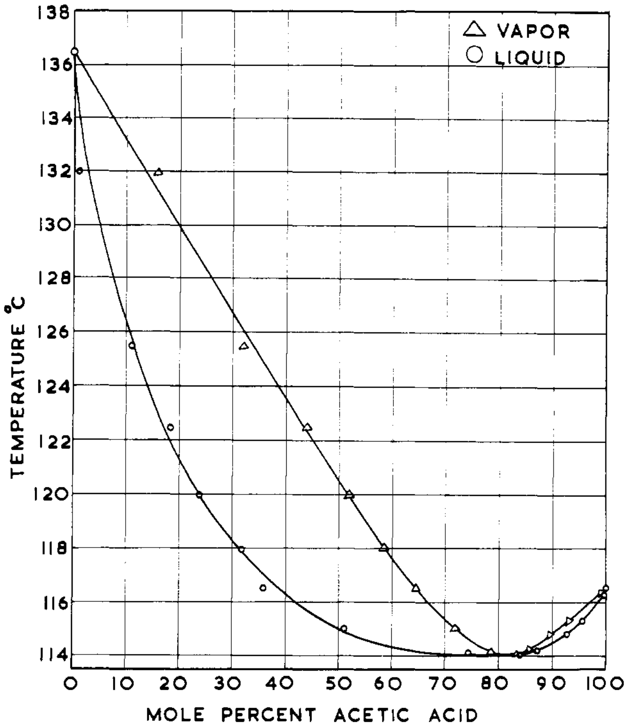

Figure 2. Boiling point–composition diagram for acetic acid–*p*-xylene system

phase nonideality correction factor for the nonassociating components, ethylbenzene and *p*-xylene, was calculated using the relationship

$$\theta = \exp\left[(P_i^0 - \bar{\Lambda})(V_i - \beta_i)/RT\right]$$

Antoine (*1*), Miller (semireduced) (*11*), Miller-Erpenbeck (*11*), Riedel-Plank-Miller (*11, 12*), and Frost-Kalkwarf-Thodos (*19*) vapor pressure equations were compared to represent the vapor pressure data for pure components from the literature (*6, 20*) over the temperature ranges of the binaries. Miller-Erpenbeck, Antoine, and Riedel-Plank-Miller (*12*) equations represented the literature data well for ethylbenzene, *p*-xylene, and acetic acid, respectively, and therefore were used to calculate the vapor pressures at system temperatures. The values of the constants in these equations are:

Compound	Constants	Equation
Acetic acid	$G = 2.40888,^a K = 0.93041^a$	Riedel-Plank-Miller (*12*)
Ethylbenzene	$C_b = 0.68801,^a B' = 5.69187,^a A = 5.18605^a$	Miller-Erpenbeck (*11*)
p-Xylene	$A = 6.99052$ (*7*), $B = 1493.43$ (*7*), $C = 215.307$ (*7*)	Antoine (*1*)

[a] Estimated.

The Pitzer and Curl correlation (*16*) was used to estimate the gas-phase second virial coefficients and the Yen and Woods correlation (*23*) to estimate liquid molal volumes for ethylbenzene and *p*-xylene.

Figures 1, 2, 3, and 4 and Table II represent the data obtained in this work. Activity coefficients calculated using Othmer's apparently smoothed data were compared with those calculated from the experimental data in Figure 4. The xylene isomer used in Othmer's work, not mentioned in his paper, might be *p*- or *m*-xylene or a mixture. The disagreement in the activity coefficient data at high xylene concentrations suggests that the xylene used might not be pure *p*-xylene.

Table II. Experimental and Estimated Vapor-Liquid Equilibrium Data at 725 ± 3 mm of Hg total pressure

t° C	x	y	γ_1	γ_{1c}	γ_2	γ_{2c}
			Acetic Acid(1)–Ethylbenzene(2)			
127.00	0.050	0.175	4.342	4.025	1.095	1.004
126.00	0.060	0.200	4.077	3.905	1.113	1.006
125.00	0.075	0.225	3.626	3.735	1.137	1.009
123.00	0.090	0.270	3.578	3.578	1.172	1.013
121.00	0.145	0.355	2.803	3.084	1.210	1.033
120.00	0.175	0.385	2.504	2.861	1.249	1.048
117.00	0.290	0.505	1.934	2.218	1.399	1.132
113.00	0.550	0.695	1.387	1.440	1.670	1.550
112.00	0.720	0.765	1.164	1.180	2.236	2.199
112.20	0.820	0.805	1.064	1.081	2.944	2.953
113.00	0.907	0.870	1.019	1.025	3.869	4.175
114.00	0.960	0.920	1.000	1.005	5.549	5.489
115.00	0.980	0.950	0.995	1.001	6.857	6.192
			Acetic Acid(1)–*p*-Xylene(2)			
132.00	0.010	0.160	18.323	3.522	0.983	1.000
125.50	0.110	0.320	3.176	2.872	1.121	1.013
122.50	0.185	0.440	2.511	2.483	1.160	1.039
120.00	0.240	0.520	2.282	2.242	1.196	1.068
118.00	0.320	0.585	2.015	1.947	1.273	1.129
116.50	0.360	0.645	1.896	1.821	1.255	1.168
115.00	0.510	0.720	1.495	1.451	1.419	1.392
114.10	0.745	0.785	1.115	1.117	2.249	2.174
114.00	0.837	0.834	1.048	1.048	2.816	2.770
114.20	0.870	0.855	1.028	1.031	3.109	3.054
114.80	0.925	0.895	0.999	1.010	3.935	3.640
115.30	0.955	0.930	0.996	1.004	4.411	4.036
116.30	0.996	0.992	1.002	1.000	5.748	4.687

Activity coefficients for acetic acid in the two binaries were also estimated from the activity coefficients for the nonassociating components by the method of Lodl and Scheller (*8*) and compared with those estimated by Marek's method (Figures 3 and 4).

Both the systems formed minimum boiling azeotropes. Table III lists the azeotropic data for these systems. The

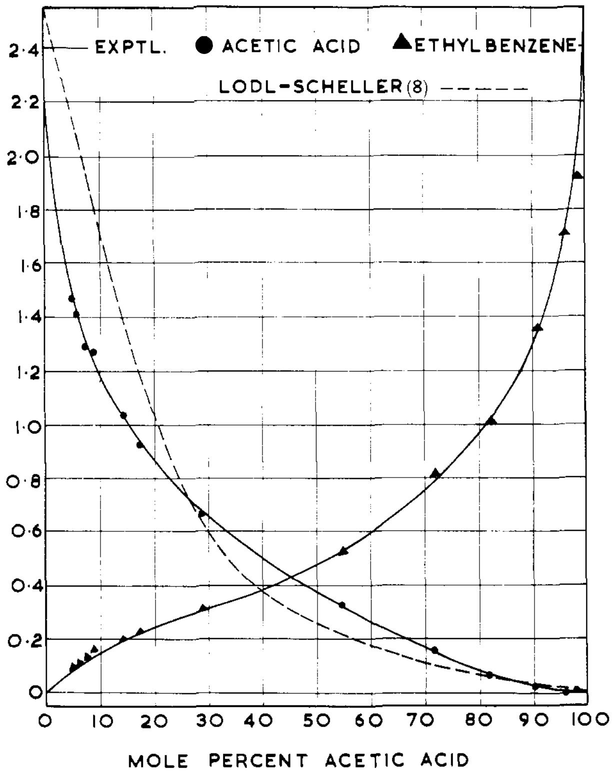

Figure 3. Activity coefficient–composition diagram for acetic acid–ethylbenzene system

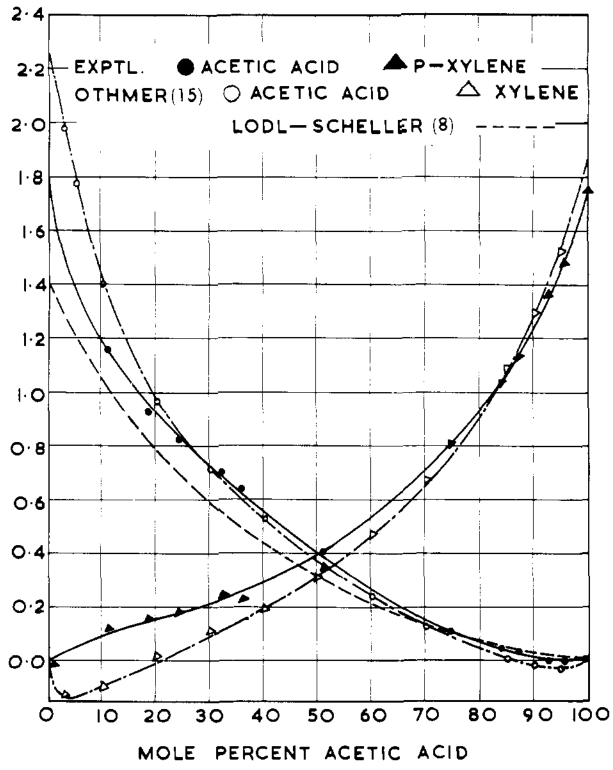

Figure 4. Activity coefficient–composition diagram for acetic acid–*p*-xylene system

Table III. Azeotropic Data

System	Composition, Mole % Acetic Acid		Temperature, ° C		
	Lit.	Exptl.	Lit. (*5*) (760 Mm Hg)	Lit. (adjusted) (725 mm Hg)	Exptl. (725 mm Hg)
Acetic acid–ethylbenzene	77.4	77.5	114.65	112.50	112.00
Acetic acid–*p*-xylene	81.9	81.5	115.25	113.41	114.00
Acetic acid–xylene[a]	81.0	. . .	115.30	113.45	. . .

[a] From plot of Othmer's data.

literature data (*5*, *15*) have been included for comparison with the experimental data in the table. The azeotropic temperatures from the literature at 760 mm of Hg were adjusted to 725 mm of Hg using the temperature-vapor pressure relationships, assuming the compositions essentially unaltered.

The data were assessed for thermodynamic consistency by applying the Redlich-Kister area test (*18*), Herington criterion (*4*), and Norrish and Twigg test (*13*). The data for both the binaries satisfied the Redlich-Kister and Herington tests. Values of Z as defined by Norrish and Twigg were calculated for both the systems at strategic compositions. The relationship between Z and x was approximately linear in both cases, especially in the middle concentration regions, with some deviations from linearity near the dilute and concentrated ends. Latent heats of vaporization for the pure components at the system temperatures were calculated by the Watson correlation (*22*) from latent heats of vaporization at normal boiling points taken from the literature (*7*).

The constants in the van Laar, Wilson, Redlich-Kister, and Chao binary correlations (*2*, *3*, *14*, *18*) were evaluated by least-squares fit of the experimental data for both the systems. The Wilson correlation gave a good fit of the experimental data for the acetic acid-ethylbenzene system, whereas the van Laar equation represented the acetic acid-*p*-xylene system well. The values of the constants in these equations are:

	A	B	Λ_{12}	Λ_{21}
Acetic acid–ethylbenzene	. . .	. . .	0.4499	0.2452
Acetic acid–*p*-xylene	1.28	1.56	. . .	. . .

ACKNOWLEDGMENT

The authors gratefully acknowledge the encouragement of Bimalendu Ghosh.

NOMENCLATURE

A, B = van Laar constants
k = ratio of molal latent heat of vaporization of lower to that of higher boiling component at the system temperatures
P^0 = vapor pressure of pure component, mm of Hg
R = universal gas law constant
T = absolute temperature, ° K
t = temperature, ° C
V = liquid molal volume of pure component, ml/gmole
x = mole fraction in liquid phase
y = mole fraction in vapor phase
Z = $\ln\left[(y_i/y_2^k)\cdot(x_2^k/x_1)\right]$

θ = vapor phase nonideality correction factor
β = gas-phase second virial coefficient
γ = activity coefficient
Λ = total pressure of system, mm. of Hg
Λ_{12}, Λ_{21} = Wilson constants

Subscripts

1 = more volatile component
2 = less volatile component
c = calculated value
i = component i

LITERATURE CITED

(1) Antoine, C., *Compt. Rend.* **107**, 681 (1888).
(2) Carlson, H.C., Colburn, A.P., *Ind. Eng. Chem.* **50**, 403 (1958).
(3) Chao, K.C., Hougen, O.A., *Chem. Eng. Sci.* **7**, 246 (1958).
(4) Herington, E.F.G., *J. Inst. Petrol.* **37**, 457 (1951).
(5) Horsley, L.H., *Advan. Chem. Ser.* No. **6**, 48–9 (1952).
(6) Jordan, T.E., "Vapor Pressure of Organic Compounds," p. 128, Interscience, New York, 1954.
(7) Lange, N.A., Ed., "Handbook of Chemistry," 9th ed., pp. 384, 1424, 1550, McGraw-Hill, New York, 1956.
(8) Lodl, S.J., Scheller, W.A., J. CHEM. ENG. DATA **12**, 485 (1967).
(9) Marek, J., *Collect. Czech. Chem. Commun.* **20**, 1490 (1955).
(10) Marek, J., Standart, G., *Ibid.*, **19**, 1074 (1954).
(11) Miller, D.G., *Ind. Eng. Chem.* **56**(3), 46 (1964).
(12) Miller, D.G., *J. Phys. Chem.* **69**, 3209 (1965).
(13) Norrish, R.S., Twigg, G.H., *Ind. Eng. Chem.* **46**, 201 (1954).
(14) Orye, R.V., Prausnitz, J.M., *Ibid.*, **57** 18 (1965).
(15) Othmer, D.F., *Ibid.*, **35**, 614 (1943).
(16) Pitzer, K.S., Curl, R.F., *J. Amer. Chem. Soc.* **79**, 2369 (1957).
(17) Raju, B.N., Ranganathan, R., Rao, M.N., *Indian Chem. Eng.* (2), T33 (1965).
(18) Redlich, O., Kister, A.T., *Ind. Eng. Chem.* **40**, 345 (1948).
(19) Reid, R.C., Sherwood, T.K., "Properties of Gases and Liquids," 2nd ed., pp. 124, 574, McGraw-Hill, New York, 1966.
(20) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Vol. II, pp. 101, 113, 277, Elsevier, Amsterdam, 1965.
(21) Vilim, O., Hala, E., Pick, J., Fried, V., *Chem. Listy* **48**, 989 (1954).
(22) Watson, K.M., *Ind. Eng. Chem.* **35**, 398 (1943).
(23) Yen, L.C., Woods, S.S., *A.I.Ch.E. J.* **12**(1), 95 (1966).

RECEIVED for review May 10, 1969. Accepted June 3, 1970.

Thermodynamic Properties of Acetone, Dimethyl Sulfoxide, and Their Solutions by Rayleigh Light Scattering

LINDA L. HAYNES, RAYMOND L. SCHMIDT, and H. LAWRENCE CLEVER
Department of Chemistry, Emory University, Atlanta, Ga. 30322

The Rayleigh light-scattering technique was applied to acetone, dimethyl sulfoxide, and their solutions to obtain isothermal compressibilities of the pure liquids and activity coefficients and excess Gibbs free energy of mixing of the solutions. The acetone–dimethyl sulfoxide solutions show an unsymmetrical excess free energy with a maximum of about 150 cal. per mole at 0.6 mole fraction acetone at 30° C. The light scattering of the pure liquids gives evidence that dimethyl sulfoxide has a temperature-dependent structuring while acetone does not. Solution densities were measured and excess volumes of mixing were found to be unsymmetrical and negative with a minimum of –0.47 ml. per mole at 0.65 mole fraction acetone.

Acetone, $(CH_3)_2CO$, and dimethyl sulfoxide $(CH_3)_2SO$, although showing superficial similarities, are different in structure, physical properties, and intermolecular forces. Acetone is a planar molecule; dimethyl sulfoxide is a pyrimidal molecule with a pair of unshared electrons on the sulfur. Some of their physical properties are compared in Table I, which leads to the expectation that their solutions will be nonideal.

Acetone–dimethyl sulfoxide solutions appear well suited for study by Rayleigh light scattering, which can be analyzed to obtain activity coefficients and excess Gibbs free energy of mixing (*5, 18*) when solution components differ in refractive index by 0.1 unit or more and the solutions show positive excess free energy of mixing. In addition, the Rayleigh scattering from pure liquids can be analyzed to obtain approximate isothermal compressibilities of the liquid (*17*) and evidence of temperature-dependent liquid structuring (*19, 20*). A recent book (*11*) gives the background and more detail about the light scattering technique.

Table I. Some Physical Properties of Acetone and Dimethyl Sulfoxide

Property	Acetone		Dimethyl Sulfoxide	
Melting point, ° C.	–95.35	(*8*)	18.52	(*3*)
Normal boiling point, ° C.	56.2	(*8*)	189	(*8*)
Molar volume, ml. $mole^{-1}$, 30°	74.53		71.61	
Dipole moment, D	2.88	(*14*)	3.9	(*4*)
Refractive index, n_D^{20}	1.3588	(*8*)	1.4783	(*16*)
Heat of fusion, cal. $mole^{-1}$	1366	(*10*)	3434	(*3*)
Heat capacity, liquid, cal. $deg.^{-1}$ $mole^{-1}$, 25°	29.8	(*10*)	36.6	(*3*)
Solubility parameter	9.9	(*9*)	12.9	(*7*)[a]
Isothermal compressibility, cm^2. $dyne^{-1} \times 10^{12}$, 30°	152		68	
Surface tension, dyne $cm.^{-1}$, 30°	22.42	(*2*)	42.41	(*2*)

[a] Calculated from heat of vaporization calculated from vapor pressure equation of (*7*).