(6) Bloomer, O. T., Rao, K. N., *Inst. Gas Technol., Chicago, Res. Bull.*, 18 (1952).
(7) Chueh, P. L., Prausnitz, J. M., *Ind. Eng. Chem., Fundam.*, **6**, 492 (1967).
(8) Hejmadi, A. V., Ph.D. Thesis, University of Michigan, 1970.
(9) Hejmadi, A. V., Katz, D. L., Powers, J. E., *J. Chem. Thermodyn.*, **3**, 483–496 (1971).
(10) Hilsenrath, J. T., "Tables of Thermodynamic and Transport Properties", Pergamon Press, London, 1960, pp 369–436.
(11) Hilsenrath, J. T. et al., "Tables of Thermal Properties of Gases", *Natl. Bur. Stand. (U.S.), Circ.*, 564 (1955).
(12) Klein, R. R., Ph.D. Thesis, Yale University, Hartford, Conn., 1969.
(13) Klein, R. R., Bennett, C. O., Dodge, B. F., *AIChE J.*, **17**, 958 (1971).
(14) Knoester, M., Taconis, K. W., Beenakker, J. J. M., *Physica (Utrecht)*, **33**, 389 (1967).
(15) Le B. Ba, D.Sc. Thesis, Laval University, to be published.
(16) Lee, J. I., Mather, A. E., *J. Chem. Thermodyn.*, **2**, 881 (1970).
(17) Lee, J. I., Mather, A. E., *J. Chem. Eng. Data*, **17**, 189 (1972).
(18) Lee, J. I., Mather, A. E., *Can. J. Chem. Eng.*, **50**, 95 (1972).
(19) Mickley, H. S., Sherwood, T. K., Reid, C. E., "Applied Mathematics in Chemical Engineering," McGraw-Hill, New York, N.Y., 1957.
(20) Montgomery, J. B., De Vries, J., *J. Am. Chem. Soc.*, **64**, 2372 (1942).
(21) Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibria," Prentice-Hall, Englewood Cliffs, N.J., 1969.
(22) Redlich, O., Kwong, J. N. S., *Chem. Rev.*, **44**, 233 (1949).
(23) Reid, R. C., Sherwood, T. K., "The Properties of Gases and Liquids", 2d ed, McGraw-Hill, New York, N.Y., 1966.
(24) Setaram Manual for Mass flowmeter U-70, "Société d'Etudes d'Automatisation de Régulation et d'Appareils de Mesures", Lyon, France.
(25) Van Eijnsbergen, B., Beenakker, J. J. M., *Physica (Utrecht)*, **39**, 499 (1968).

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Isobaric Vapor–Liquid Equilibria for Systems with Associating Vapor Phase Propionic Acid–Isopropylbenzene and Propionic Acid–*o*-Xylene Systems

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Vapor–liquid equilibria for the systems, propionic acid–isopropylbenzene and propionic acid–*o*-xylene, were obtained at 760 mmHg using a vapor recirculatory type of still. The activity coefficients were obtained by taking into consideration vapor phase association. Nothnagel's correlation based on chemical theory of vapor imperfections was used. The data satisfied the Herington criterion of thermodynamic consistency and were correlated by the Wilson equation.

This work forms part of an investigation concerning the use of organic acids as separating agents for separation of close boiling hydrocarbon mixtures by distillation. Vapor–liquid equilibrium data have been obtained experimentally for the systems propionic acid–isopropylbenzene and propionic acid–*o*-xylene. Both these systems formed minimum boiling azeotropes. The azeotropic conditions for propionic acid–isopropylbenzene and propionic acid–*o*-xylene systems are 139.00 °C, 72.68 mole % propionic acid, and 136.45 °C, 52.00 mole % propionic acid, respectively, whereas the corresponding values reported by Horsley (*4*) are 139.00 °C, 75.08 mole % propionic acid, and 135.4 °C, 51.94 mole % propionic acid, respectively.

Materials

Isopropylbenzene, *o*-xylene, and propionic acid, laboratory grade reagents from British Drug Houses Limited, were dried over anhydrous blue silica gel and further purified by distillation in a glass column described by Sood et al. (*10*). Table I lists the physical properties of the materials.

Procedure

A modified version of the equilibrium still with circulating vapor phase described by Raju et al. (*8*) was used for obtaining the *t–x–y* data. The temperature measurements were made by Anschutz type thermometers with an accuracy of ±0.05 °C. The pressure in the still was maintained at 760 ± 1 mmHg. The operation of the still was described elsewhere (*10*).

Equilibrium mixtures were analyzed by density and conductometric titration methods. A pycnometer of 4-mL capacity was used for density measurements. N/20 and N/50 sodium hydroxide solutions were used for finding acid-rich and acid-weak equilibrium mixtures, respectively, while carrying out conductometric titrations. The accuracy of both the methods is of the order of ±0.0002 g mL^{-1}.

Results

Figures 1 and 2 and Table II represent the vapor–liquid equilibrium data obtained in this investigation.

Liquid phase activity coefficients were calculated from the experimental data using the equation (*13*)

$$\gamma_i = \frac{\pi y_i}{P_i^0 x_i} Z_i \qquad (1)$$

where

$$Z_i = \exp\left[\frac{(\pi - P_i^0)(B_i - V_i) + \delta_{ij} y_j^2 \pi}{RT}\right] \qquad (2)$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \qquad (3)$$

The Antoine equation with constants given in literature (*5, 16*) was used for finding the vapor pressures of pure components as this equation closely represented the vapor pressure data given in literature (*11, 16*) over the temperature range involved. Liquid molal volumes were calculated by the surface tension

Table I. Physical Constants of Pure Compounds

Index	Compound	Density at 25 °C	Bp, °C
1	Isopropylbenzene	0.8576	152.40
		0.8575 (*11*)	152.392 (*16*)
2	*o*-Xylene	0.8758	144.45
		0.8759 (*11*)	144.411 (*16*)
3	Propionic acid	0.9880	140.95
		0.9879 (*11*)	140.99 (*14*)

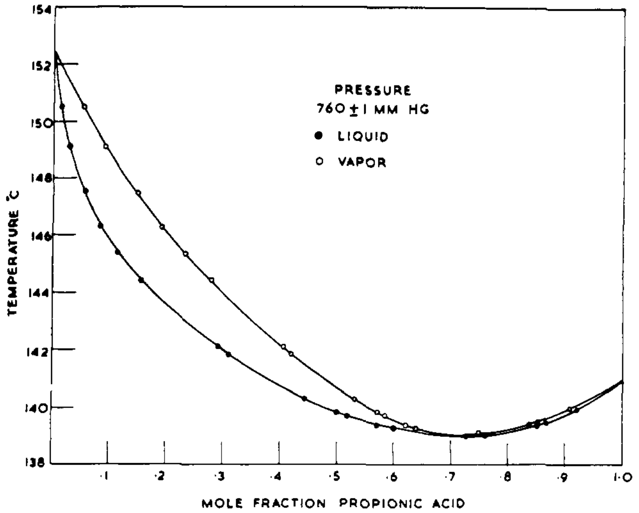

Figure 1. Boiling point-composition diagram for the propionic acid-isopropylbenzene system.

method (*2*). Second virial coefficients for propionic acid were estimated by Nothnagel's correlation (*6*) based on chemical theory of vapor imperfections and for isopropylbenzene and *o*-xylene by the Pitzer and Curl correlation (*7*).

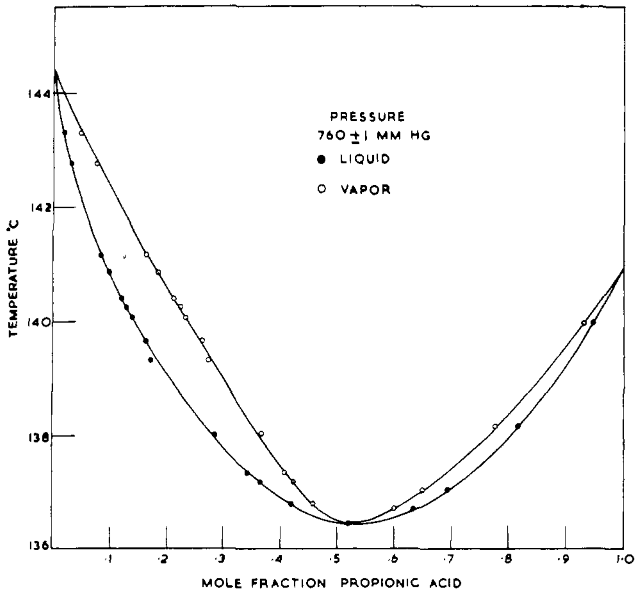

Figure 2. Boiling point-composition diagram for the propionic acid-*o*-xylene system.

Table II. Vapor-Liquid Equilibrium Data at 760 ± 1 mmHg Pressure

t, °C	x_i	y_i	Z_i	γ_i	Z_j	γ_j	$y_{i\,\text{calcd}}$[a]
			System Propionic Acid (i)–Isopropylbenzene (j)				
150.50	0.015	0.053	1.553	4.192	0.998	1.008	0.049
149.10	0.029	0.091	1.516	3.757	0.998	1.018	0.088
147.50	0.053	0.149	1.458	3.331	1.000	1.023	0.146
146.30	0.082	0.190	1.413	2.801	1.004	1.040	0.198
145.40	0.113	0.231	1.371	2.442	1.010	1.054	0.246
144.40	0.154	0.277	1.323	2.143	1.018	1.076	0.296
142.10	0.290	0.405	1.197	1.618	1.058	1.166	0.416
141.85	0.305	0.419	1.184	1.582	1.064	1.180	0.427
140.30	0.441	0.531	1.090	1.339	1.124	1.306	0.523
139.80	0.502	0.574	1.058	1.257	1.154	1.382	0.565
139.70	0.520	0.586	1.051	1.232	1.162	1.410	0.578
139.40	0.570	0.620	1.029	1.176	1.189	1.490	0.614
139.30	0.601	0.639	1.020	1.142	1.204	1.550	0.636
139.00	0.727	0.727	0.984	1.046	1.280	1.836	0.735
139.10	0.756	0.751	0.980	1.033	1.305	1.904	0.760
139.40	0.851	0.838	0.971	1.004	1.393	2.148	0.848
139.50	0.867	0.854	0.971	1.001	1.408	2.186	0.863
139.90	0.919	0.909	0.975	0.998	1.467	2.292	0.915
							$\text{rmsd}y_i = 0.009$
			System Propionic Acid (i)–*o*-Xylene (j)				
143.30	0.020	0.046	1.579	3.386	0.999	1.002	0.048
142.80	0.028	0.063	1.554	3.310	0.999	1.006	0.065
142.75	0.034	0.074	1.540	3.176	1.000	1.002	0.077
141.15	0.084	0.162	1.417	2.720	1.009	1.007	0.164
140.85	0.099	0.184	1.389	2.592	1.013	1.009	0.186
140.40	0.120	0.212	1.351	2.431	1.018	1.015	0.214
140.25	0.129	0.224	1.336	2.374	1.021	1.017	0.225
140.05	0.138	0.234	1.323	2.309	1.023	1.022	0.236
139.65	0.162	0.261	1.288	2.163	1.031	1.033	0.263
139.30	0.172	0.271	1.272	2.112	1.034	1.044	0.272
138.00	0.283	0.368	1.157	1.651	1.073	1.124	0.372
137.35	0.343	0.406	1.112	1.474	1.093	1.196	0.415
137.20	0.368	0.426	1.093	1.424	1.105	1.220	0.434
136.80	0.420	0.458	1.060	1.317	1.126	1.293	0.471
136.45	0.520	0.520	1.011	1.164	1.172	1.453	0.543
136.70	0.635	0.600	0.974	1.052	1.235	1.668	0.634
137.05	0.692	0.651	0.961	1.022	1.280	1.772	0.686
138.15	0.817	0.779	0.950	0.989	1.403	2.006	0.807
139.95	0.947	0.931	0.975	0.990	1.563	2.293	0.942
							$\text{rmsd}y_i = 0.015$

[a] *y* calculated from the Wilson equation.

Table III. Comparison of Data Fit in the Correlations

Correlation	rmsdy$_i$	Constants
System Propionic Acid (i)–Isopropylbenzene (j)		
van Laar	0.0107	$A = 1.4007$ $B = 0.8837$
Black	0.0105	$A = 1.3258$ $B = 0.9022$ $C = 0.1069$
Redlich–Kister	0.0109	$B = 1.0752$ $C = -0.2008$ $D = 0.1527$
Wilson	0.0091	$\Lambda_{ij} = 0.2831$ $\Lambda_{ji} = 0.8183$
System Propionic Acid (i)–*o*-Xylene (j)		
van Laar	0.0153	$A = 1.3198$ $B = 0.8718$
Black	0.0151	$A = 1.3766$ $B = 0.8592$ $C = -0.0816$
Redlich–Kister	0.0151	$B = 1.0564$ $C = -0.2501$ $D = -0.0180$
Wilson	0.0150	$\Lambda_{ij} = 0.3196$ $\Lambda_{ji} = 0.7950$

The vapor–liquid equilibrium data were tested for thermodynamic consistency by applying the Herington criterion (*3*). The data for both the systems satisfied this test. van Laar (*12*), Black (*1*), Redlich–Kister (*9*), and Wilson (*15*) equations were used to correlate the activity coefficient data with liquid composition using nonlinear least-squares method minimizing the function ln γ_i/γ_j. Values of rmsdy$_i$ along with constants for all the four equations are given in Table III. For both the systems, the data fitted well in the Wilson equation.

Glossary

B	gas phase second virial coefficient, cm^3 mol^{-1}
n	number of data points in each system
P^0	pure component vapor pressure, mmHg
R	gas constant
rmsdy	root-mean-square deviation in y, $[\Sigma(y_{\text{exptl}} - y_{\text{calcd}})^2/n]^{1/2}$
T	absolute temperature, °K
t	system temperature, °C
V	pure component liquid molal volume, cm^3 mol^{-1}
x	mole fraction in liquid phase
y	mole fraction in vapor phase
Z	vapor phase imperfection coefficient
γ	activity coefficient
π	system pressure, mmHg

Subscript

i	less volatile component
j	more volatile component
calcd	calculated
exptl	experimental

Literature Cited

(1) Black, C., *Ind. Eng. Chem.*, **50,** 403 (1958).
(2) Gold, P. I., Ogle, G. J., *Chem. Eng. (N.Y.)*, **75** (24), 170 (1968).
(3) Herington, E. F. G., *J. Inst. Pet., London*, **37,** 457 (1951).
(4) Horsley, L. H., *Adv. Chem. Ser.*, **No. 6,** 86 (1952).
(5) Lange, N. A., Ed., "Handbook of Chemistry", 10th ed, McGraw-Hill, New York, N.Y., 1967.
(6) Nothnagel, K. H., Abrams, D. S., Prausnitz, J. M., *Ind. Eng. Chem., Process Des. Dev.*, **12,** 25 (1973).
(7) Pitzer, K. S., Curl, R. F., *J. Am. Chem. Soc.*, **79,** 2369 (1957).
(8) Raju, B. N., Ranganathan, R., Rao, M. N., *Indian Chem. Eng.*, **7,** T33 (1965).
(9) Redlich, O., Kister, A. T., *Ind. Eng. Chem.*, **40,** 345 (1948).
(10) Sood, B. K., Bagga, O. P., Raju, K. S. N., *J. Chem. Eng. Data*, **17,** 435 (1972).
(11) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds", Vol. II, Elsevier, Amsterdam, 1965.
(12) van Laar, J., *J. Phys. Chem.*, **72,** 723 (1910).
(13) Van Ness, H. C., "Classical Thermodynamics of Non-Electrolyte Solutions", Pergamon Press, Oxford, 1964.
(14) Weast, R. C., Ed., "Handbook of Chemistry and Physics", 56th ed, The Chemical Rubber Co., Cleveland, Ohio, 1969.
(15) Wilson, G. M., *J. Am. Chem. Soc.*, **86,** 127 (1964).
(16) Zwolinski, B. J., Wilhoit, R. C., "Handbook of Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds", API 44-TRC Publications in Science and Engineering, Texas A&M University, College Station, Texas, 1971, pp 65, 287.

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