(4) M. Díaz Peña and M. L. McGlashan, *Trans. Faraday Soc.*, **57**, 1511 (1961).
(5) M. Díaz Peña and B. Cavero, *An. R. Soc. Esp. Fis. Quim.*, **5**, 357 (1964).
(6) M. Díaz Peña and G. Tardajos, *J. Chem. Thermodyn.*, **10**, 19 (1978).
(7) F. D. Rossini et al., "Selected Values of Physical Thermodynamic Properties of Hydrocarbons and Related Compounds", API Research Project 44, Carnegie Press, Pittsburgh, PA, 1953.
(8) J. Gomez and C. T. Liu, *J. Phys. Chem.*, **65**, 2148 (1961).
(9) I. Prigogine, "The Molecular Theory of Solutions", North-Holland Publishing Co., Amsterdam, 1957.
(10) R. A. Orwoll and P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1633 (1965).
(11) M. B. Ewing and K. N. Marsh, *J. Chem. Thermodyn.*, **9**, 371 (1977).

Received for review March 10, 1980. Accepted September 18, 1980.

Vapor–Liquid Equilibrium for the *p*-Dioxane–Acetonitrile System at 298.15 K

Franco Davolio, Graciela C. Pedrosa, and Miguel Katz*

Cátedra de Físico-Química, Instituto de Ingeniería Química, Facultad de Ciencias Exactas y Tecnología, Universidad Nacional de Tucumán, (4000) San Miguel de Tucumán, Argentina

Isothermal vapor–liquid equilibrium data were determined by using a Boublik–Benson still for the *p*-dioxane–acetonitrile system at 298.15 K. The results obtained were correlated in terms of the liquid activity coefficients of the two components by two-suffix Margules and van Laar equations.

Vapor–liquid data are necessary for interpretation of distillation processes. This paper reports the results of measurements on vapor–liquid equilibrium for the *p*-dioxane–acetonitrile system at 298.15 K. Experimental data for this system have not been reported in the literature, and this system was chosen because *p*-dioxane (component 1) is nonpolar and acetonitrile (component 2) is polar.

Experimental Section

Acetonitrile (Carlo Erba p.a.) was distilled over dried P_2O_5 at reduced pressure, and only the middle half of each distillation was recovered. *p*-Dioxane (Baker p.a.) was distilled over sodium at reduced pressure, and again only the middle half of each distillation was recovered.

Densities were determined with a Robertson specific gravity bottle. The refractive indexes for the sodium D line of the pure components were measured with a Jena dipping refractometer with an accuracy of ±0.000 02.

Equilibrium data were determined by using a modified version of the equilibrium still described by Boublik and Benson (*1*). The still and a water ebulloscope were attached to a large pressure vessel which could be maintained at any required pressure. The equilibrium value of the pressure was calculated from the boiling point of water in the ebulloscope. The latter could be determined with an accuracy of 0.01 °C by using a calibrated thermometer. The temperature in the still was also measured at 0.01 °C. Barometric pressure and room temperature were recorded for each experimental run, and necessary corrections were made on the observed pressure values. Compositions of the equilibrium liquid and condensed vapor phases were obtained from measurements of their refractive indexes at 298.15 K by using eq 1 (*2*), where x_1 is the molar fraction of *p*-dioxane.

$$n_D(x_1) = 0.93925x_1 + 0.76097(1 - x_1) + x_1(1 - x_1) \times [-0.21520 - 0.28471(2x_1 - 1) - 0.43586(2x_1 - 1)^2] \quad (1)$$

This equation correlates the results of a series of known composition mixtures of the two components. Table I gives densities, refractive indexes, and vapor pressures of the pure components and literature values for comparison.

Table I. Physical Properties of Pure Components at 298.15 K

	ρ		n_D		P^0	
compd	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.
p-dioxane	1027.1	1026.87	1.42021	1.42025	4.83	4.97[4]
acetonitrile	776.8	776.83	1.34135	1.34163	11.87	11.87[7]

[a] Reference 7.

Table II. Experimental and Calculated Isothermal Vapor–Liquid Equilibrium Results for *p*-Dioxane (1) plus Acetonitrile (2)

x_1	y_1	P	γ_1	γ_2
0.1125	0.0640	11.33	1.334	1.007
0.2000	0.1125	10.90	1.269	1.019
0.3070	0.1715	10.30	1.191	1.037
0.4005	0.2272	9.81	1.152	1.065
0.5170	0.3002	9.14	1.099	1.116
0.5506	0.3235	8.91	1.084	1.130
0.6470	0.4013	8.27	1.062	1.182
0.7465	0.4971	7.52	1.037	1.257
0.8130	0.5812	6.94	1.027	1.310
0.8988	0.7262	6.05	1.012	1.379
0.9300	0.7965	5.69	1.009	1.394

Results

The liquid-phase activity coefficients were estimated from the experimental data, taking into consideration the nonideality of the vapor phase by employing the following equation:

$$\ln \gamma_i = \ln \frac{y_i P}{x_1 P_i^0} + \frac{(B_{ii} - v_i^0)(P - P_i^0)}{RT} + (1 - y_i)^2 \frac{P\delta}{RT} \quad (2)$$

where

$$\delta = 2B_{12} - B_{11} - B_{22}$$

For *p*-dioxane at 298.15 K, $B_{11} = -1.948 \times 10^{-3}$ m^3 mol^{-1}; for acetonitrile at 298.15 K, $B_{22} = -3.722 \times 10^{-3}$ m^3 mol^{-1} and $B_{12} = -1.499 \times 10^{-3}$ m^3 mol^{-1}. These values were estimated from an empirical correlation (*6*).

Values of the molar fraction of *p*-dioxane in the liquid and vapor phases, the pressures, and the activity coefficients of both components are summarized in Table II.

Figure 1 shows the logarithm of the activity coefficients of both components vs. the molar fraction of *p*-dioxane.

A conventional thermodynamic consistency test was applied to the present system. It is a well-known area test that thermodynamically consistent isothermal test binary data should satisfy eq 3. However, some experimental error is inevitably

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2}\, dx_1 = 0 \quad (3)$$

0021-9568/81/1726-0026$01.00/0

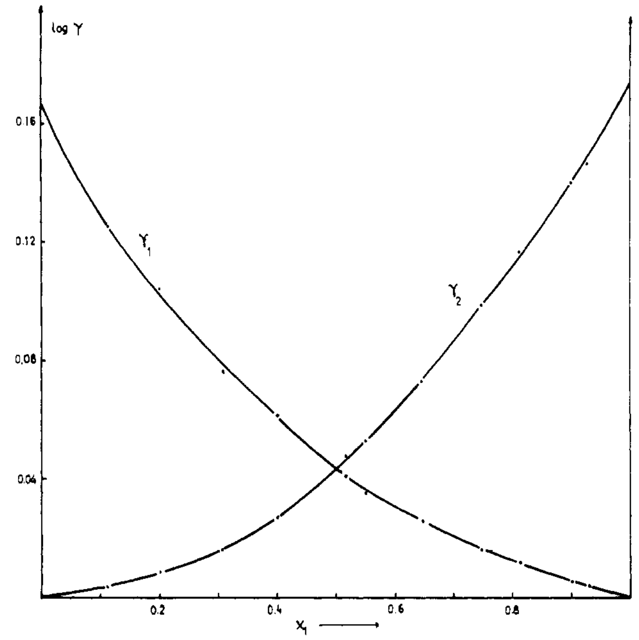

Figure 1. Logarithm of the activity coefficients vs. mole fraction of *p*-dioxane for the *p*-dioxane (1) plus acetonitrile (2) system at 298.15 K.

involved in the observed data. Practically, it may be acceptable to assume that a given set of data is consistent (*5*) if

$$0.02 > D = \frac{|\text{area above } x \text{ axis} - \text{area below } x \text{ axis}|}{|\text{area above } x \text{ axis} + \text{area below } x \text{ axis}|} \qquad (4)$$

For the present system, $D = 0.015$.

Experimental data are correlated with the following two-suffix Margules equation:

$$\begin{aligned} \log \gamma_1 &= x_2^2[A + 2x_1(B - A)] \\ \log \gamma_2 &= x_1^2[B + 2x_2(A - B)] \end{aligned} \qquad (5)$$

with $A = 0.1235$ and $B = 0.1881$ at 298.15 K.

In a similar way, the data are compared with the following two-suffix van Laar equation modified by Carlson and Colburn (*3*):

$$\log \gamma_1 = \frac{A}{\left(1 + \dfrac{x_1 A}{x_2 B}\right)^2} \qquad \log \gamma_2 = \frac{B}{\left(1 + \dfrac{x_2 B}{x_1 A}\right)^2} \qquad (6)$$

with $A = 0.1495$ and $B = 0.1955$.

The values of P and y_i were computed with the following equations:

$$P_{\text{cal}} = x_1\gamma_1 P_1^0 + x_2\gamma_2 P_2^0 \qquad (7)$$

$$y_1^{\text{cal}} = x_1\gamma_1 P_1^0 / P_{\text{cal}} \qquad (8)$$

over the complete concentration range. The calculated results are compared with the experimental values. The standard deviations are summarized as follows:

	σ_P	σ_y
eq 5	0.93	0.005
eq 6	0.50	0.004

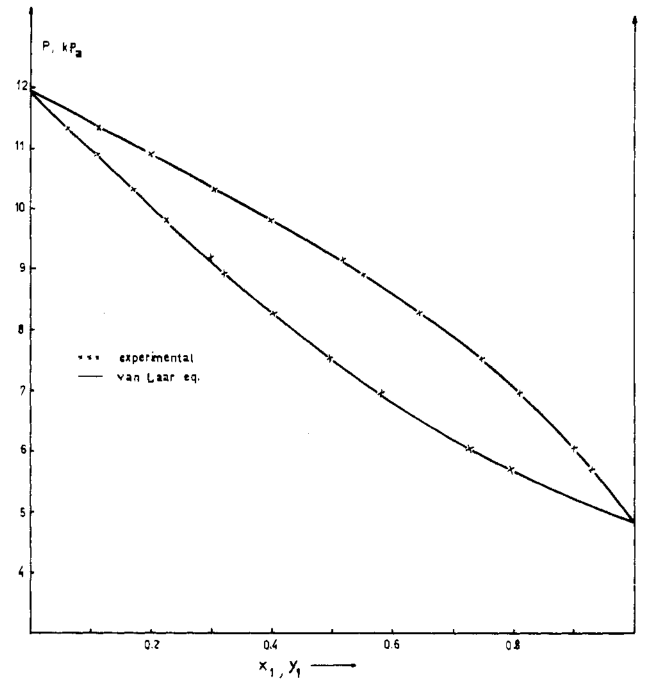

Figure 2. Comparison of experimental and calculated *P*–*x*–*y* values for the *p*-dioxane (1) plus acetonitrile (2) system at 298.15 K.

Figure 2 shows the experimental and calculated *P*–*x*–*y* values of this system, using only the van Laar equation which gives better agreement with the experimental values.

Glossary

A, B	coefficients of eq 5 and 6
B_{11}, B_{22}	gas-phase second virial coefficients, m^3 mol^{-1}
B_{12}	gas-phase second cross virial coefficients, m^3 mol^{-1}
D	area test constant
n_D	refractive index
P	total pressure, kPa
P_i^0	vapor pressure of pure component i, kPa
R	gas constant, 8.319 J mol^{-1} K^{-1}
v_i^0	molar volume of pure component i, m^3 mol^{-1}
x_i	liquid-phase molar fraction of component i
y_i	vapor-phase molar fraction of component i

Greek Letters

γ_i	activity coefficient of component i
ρ	density of the liquid component, kg m^{-3}
σ	standard deviation

Literature Cited

(1) Boublik, T.; Benson, G. C. *Can. J. Chem.* **1969**, *47*, 539.
(2) Boublik, T.; Lu, B. C. Y. *J. Chem. Eng. Data* **1977**, *22*, 333.
(3) Carlson, H. C.; Colburn, A. P. *Ind. Eng. Chem.* **1942**, *34*, 581.
(4) Crenshaw, J. L.; Cope, A. C.; Finkelstein, N.; Rogan, R. *J. Am. Chem. Soc.* **1938**, *60*, 2308.
(5) Herington, E. F. G. *J. Inst. Pet.* **1951**, *37*, 457.
(6) O'Connell, J. P.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1967**, *6*, 245.
(7) Weissberger, A. "Technique of Organic Chemistry", 2nd ed.; Interscience: New York, 1955; Vol. VII, Chapter III, p 224.

Received for review March 20, 1980. Accepted September 2, 1980. This work was supported by a SECYT research grant.