H_2, NH_3, CO, etc. and diphenylmethane, bicyclohexyl, and 1-methylnaphthalene as the solvents (5). The temperature-solubility relationship may be represented by the following empirical equation:

$$\ln (H/(\text{Pa m}^3\text{ mol}^{-1})) = a + b/(T/\text{K}) \tag{2}$$

A linear least-squares analysis was performed to obtain the values of the constants a and b as shown in Table III. The values of ΔH (enthalpy of solution, kJ mol^{-1}) calculated from the constant b have also been included in Table III.

The solubility data for the binary mixtures were obtained at 303 K only. The solubility of CO in mixed solvents is characterized by a maximum for TCE + DMA and DMA + DBP systems and a minimum for the TCE + DBP system. The results could be well described by the expression

$$\ln H = x_1 \ln H_1 + x_2 \ln H_2 \tag{3}$$

which is the usual type of equation valid for ideal systems (8). The percent error between estimated (right-hand side of eq 3) and experimental values of H for the mixture was always less than ±3%.

Conclusion

The data presented in this paper are useful for the calculation of permeation parameters in the liquid membrane transport of CO and other design engineering calculations.

Glossary

a	empirical constant
b	empirical constant
H	Henry's constant
P_0	initial pressure
ΔP	pressure change due to absorption
P_v	vapor pressure of solvent
P_p	partial pressure of CO
R	gas constant
T	temperature
V_g	volume of gas
V_1	volume of liquid
x_1,x_2	mole fraction of components 1 and 2 in mixture

Registry No. CO, 630-08-0; TCE, 71-55-6; DMA, 127-19-5; DBP, 84-74-2.

Literature Cited

(1) Cargill, R. W., Ed. Carbon Monoxide. *Solubility Data Series*; Pergamon Press: Oxford, 1990; Vol. 43.
(2) Koval, C. A.; Noble, R. D.; Way, J. D.; Louie, B.; Reyes, Z. E.; Bateman, B. R.; Horn, G. M.; Reed, D. L. *Inorg. Chem.* **1985**, *24*, 1147.
(3) Nobel, R. D.; Way, J. D. In *Liquid Membranes, Theory and Applications*; Noble, R. D., Way, J. D., Eds.; ACS Symposium Series 347; American Chemical Society: Washington, DC, 1987; pp 1-26.
(4) Patil, G. S.; Baruah, S.; Dutta, N. N. *Gas Sep. Purif.* **1991**, *5*, 2.
(5) Tremper, K. K.; Prausnitz, J. M. *J. Chem. Eng. Data* **1976**, *21*, 295.
(6) Lyke, S. E.; Lilga, M. A.; Ozanich, R. M.; Nelson, D. A.; James, B. R.; Lee, C. L. *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, *25*, 517.
(7) Preston, G. T.; Funk, E. W.; Prausnitz, J. M. *Phys. Chem. Liq.* **1971**, *2*, 193.
(8) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977; p 359.

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Vapor–Liquid Equilibria at 760 mmHg for the System Vinyl Acetate–*n*-Decane

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Vapor–liquid equilibrium data for the vinyl acetate–*n*-decane system have been determined at 760 mmHg. The data were satisfactorily correlated by Wilson, UNIQUAC, and NRTL equations, and the appropriate parameters are reported.

Introduction

In the ethylene–vinyl acetate copolymer purification process, the liquid stream recycle is a mixture of vinyl acetate–*n*-decane which contains acetic acid as a major impurity.

Distillation is a good method to purify vinyl acetate. For the design and simulation of the distillation columns, phase equilibrium data are necessary. Binary vapor–liquid equilibrium (VLE) data were found in the literature for vinyl acetate–acetic acid (1–5) and acetic acid–*n*-decane (6). However, no VLE data were found for the vinyl acetate–*n*-decane.

In this work, we report experimental VLE measurements for vinyl acetate–*n*-decane. Among the different equations available in the literature for the correlation of binary equilibrium data, we have applied in this study the Wilson (7), UNIQUAC (8), and NRTL (9) liquid-phase activity coefficient models.

Table I. Refractive Indexes, n, and Normal Boiling Points, t_b, of the Pure Components

	n(20 °C)		t_b/°C	
component	this work	lit.	this work	lit.
vinyl acetate	1.3940	1.3941 (12)	72.9	72.84 (13)
n-decane	1.4115	1.4119 (12)	174.2	174.1 (13)

Experimental Section

Materials. Vinyl acetate (>99%), from Merck, was used without further purification. *n*-Decane (>95%), from FLUKA, was purified by distillation in a column (25-mm i.d. and 500 mm long) packed with 2.5 × 2.5 Dixon rings. Gas chromatography analysis after distillation showed less than 0.5% impurities. The properties of the components appear in Table I.

Apparatus and Procedure. The experimental apparatus is entirely made of glass and is schematically shown in Figure 1. In this apparatus, both the liquid and vapor phases are continuously recirculated in order to provide mixing of the phases and to ensure that equilibrium was established. The vapor

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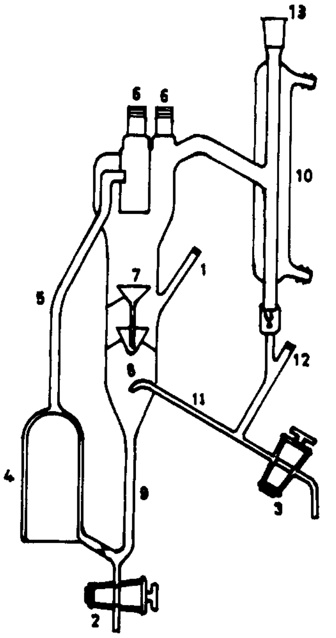

Figure 1. Experimental apparatus: (1) liquid-phase sampling system, (2, 3) cocks, (4) boiling flask, (5) Cottrell pump, (6) thermometer, (7) liquid-phase receiver, (8) liquid-phase reservoir, (9) recirculating liquid, (10) condenser, (11) vapor-phase condensate recycle, (12) vapor-phase condensate sampling system, (13) constant pressure system.

Table II. Experimental Vapor–Liquid Equilibrium Data for Vinyl Acetate (1)–*n*-Decane (2) at 760 mmHg: Boiling Temperature *t*, Liquid-Phase Mole Fraction x_1, and Vapor-Phase Mole Fraction y_1

t/°C	x_1	y_1	t/°C	x_1	y_1
72.9	0.9944	0.9997	84.5	0.4606	0.9756
75.0	0.9174	0.9916	91.2	0.3358	0.9578
75.3	0.9141	0.9930	102.1	0.2704	0.9348
76.6	0.8548	0.9876	104.5	0.2206	0.9173
77.7	0.8205	0.9842	105.3	0.2260	0.9217
77.8	0.7509	0.9876	123.8	0.1248	0.8383
78.7	0.7572	0.9839	154.5	0.0314	0.4053
79.8	0.6038	0.9814	159.6	0.0296	0.3715
82.1	0.4960	0.9780	166.0	0.0187	0.2547
82.6	0.5066	0.9735	166.9	0.0118	0.2174
82.7	0.4910	0.9741	171.7	0.0103	0.1327

condenser is connected to a constant-pressure system controlled by a Cartesian manostat. The accuracy in determination of pressure was $\Delta P = \pm 1$ mmHg. The equilibrium temperatures were measured with a certified mercury thermometer. The accuracy in determination of temperatures was ±0.1 °C.

The liquid and condensed vapor analyses were carried out by gas chromatography on a Hewlett-Packard 5880A with a flame ionization detector. The column was 300 cm long, had a $^1/_8$-in. o.d., and was packed with 10% UCW on Chromosorb PAW and operated isothermally at 160 °C. Injector and detector temperatures were 200 and 230 °C, respectively. A good separation was achieved with N_2 as the carrier gas, and calibration analyses were made, allowing concentration measurements with an accuracy to better than 2%.

Results

The experimental equilibrium data measurements at 760 mmHg are shown in Table II and Figure 2.

The data were correlated using the Wilson (*7*), UNIQUAC (*8*), and NRTL (*9*) equations for the liquid-phase activity coefficients. Vapor-phase nonidealities were calculated from the virial equation of state, truncated after the second term, with second virial coefficients obtained by the method of Hayden–O'Connell (*10*). The resulting vapor-phase fugacity coefficients were near unity. Standard-state fugacities for the liquid phase at zero pressure were calculated from the correlation of Prausnitz et al. (*8*).

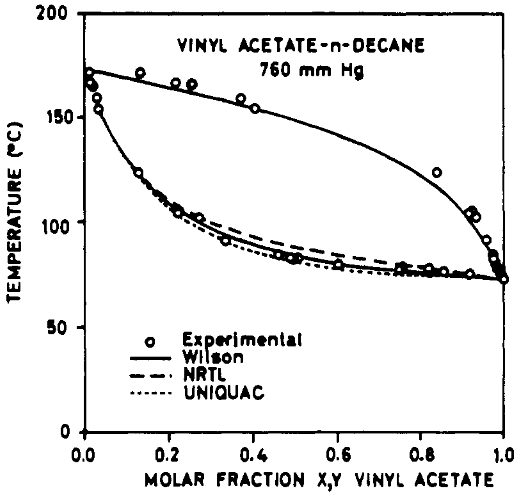

Figure 2. Vapor–liquid equilibrium diagram for vinyl acetate–*n*-decane at 760 mmHg of pressure.

Table III. Fitted Parameters from Data Correlation

model	parameters[a] A_{12}	A_{21}	α	$\lvert\Delta y_1\rvert_{av}$[b]	$\lvert\Delta t\rvert_{av}$[c]/°C
Wilson	1.3935	0.0940		0.0110	1.73
NRTL	213.5005	75.7204	0.3	0.0150	2.54
UNIQUAC	210.6756	−51.5387		0.0102	2.32

[a] Wilson, $A_{12} = \Lambda_{12}$, $A_{21} = \Lambda_{21}$; NRTL, $A_{12}/K = (g_{12} - g_{11})/R$, $A_{21}/K = (g_{21} - g_{22})/R$; UNIQUAC, $A_{12}/K = u_{12}/R$, $A_{21}/K = u_{21}/R$. [b] $|\Delta y_1|_{av} = (\sum|y_{1,\text{exptl}} - y_{1,\text{calcd}}|)/N$. [c] $|\Delta t|_{av} = (\sum|t_{\text{exptl}} - t_{\text{calcd}}|)/N$.

The binary parameters of each model were obtained by nonlinear regression based on Marquardt's algorithm (*11*) minimizing the objective function

$$\mathrm{OF} = \sum_{i=1}^{N}\left[\left(\frac{t_{\text{exptl}} - t_{\text{calcd}}}{\sigma_t}\right)_i^2 + \left(\frac{y_{1,\text{exptl}} - y_{1,\text{calcd}}}{\sigma_y}\right)_i^2\right] \qquad (1)$$

where σ_y and σ_t are the uncertainties for vapor-phase composition and boiling point, respectively. In this work, we have used $\sigma_y = 0.01$ and $\sigma_t = 0.1$ °C.

These parameters are reported in Table III with the average deviations in vapor-phase composition and boiling point between the experimental and the calculated values.

Glossary

g_{ij}	NRTL parameters, K
N	number of experimental points
t	temperature, °C
u_{ij}	UNIQUAC parameters, K
x_i	liquid mole fraction of component i
y_i	vapor mole fraction of component i

Greek Letters

α	NRTL nonrandomness parameter
Λ_{ij}	Wilson parameter

Subscripts

calcd	calculated
exptl	experimental
i,j	components i and j

Registry No. *n*-decane, 124-18-5; vinyl acetate, 108-05-4.

Literature Cited

(1) Capkova, A.; Fried, V. *Collect. Czech. Chem. Commun.* **1963**, *28*, 2235.
(2) Kato, M. *J. Chem. Eng. Data* **1988**, *33*, 499.

J. Chem. Eng. Data **1992**, *37*, 295-297

(3) Morrison, G. O.; Shaw, T. P. G. *Trans. Electrochem. Soc.* **1933**, *63*, 425.

(4) Pao, H. H. H. *Acta Chim. Sin.* (*Engl. Ed.*) **1976**, *34*, 79.

(5) Warazdin, W.; Surovy, J. *Chem. Zvesti* **1975**, *29*, 783.

(6) Zieborak, K.; Brzostowski, W. *Bull. Acad. Pol. Sci., Ser. Sci., Chim. Geol., Geogr.* **1957**, *5*, 309.

(7) Wilson, G. H. *J. Am. Chem. Soc.* **1964**, *86*, 127.

(8) Prausnitz, J. M.; Anderson, T. F.; Greus, E. A.; Eckert, C.; Hsieh, R.; O'Connell, J. *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1980.

(9) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135.

(10) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.

(11) Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431.

(12) *Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; Chemical Rubber Press: Boca Ratón, FL, 1990.

(13) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

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Solubility of Carbon Dioxide in Phenanthrene and in Pyrene

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The solubility of carbon dioxide in phenanthrene and pyrene has been measured in a semiflow vapor-liquid equilibrium apparatus over the temperature range from 423.15 to 523.15 K for phenanthrene and from 473.15 to 573.15 K for pyrene at pressures up to 50 atm. Henry constants, the partial molar volumes of carbon dioxide at infinite dilution, and the Margules parameters are determined from the solubility data.

Introduction

This work is a continuation of our studies on the phase behavior of carbon dioxide (CO_2) with hydrocarbon solvents that are of interest in the processing of petroleum products, production of coal liquids, and enhanced oil recovery operations. Previously reported data include the solubility of CO_2 in *n*-tetracosane or *n*-dotriacontane (*1*) and in naphthalene or biphenyl (*2*). Barrick et al. (*3*) reported the solubility of CO_2 in phenanthrene or pyrene at temperatures to 439.15 K. In the present study, the vapor-liquid equilibria of CO_2 in three-ring and four-ring aromatic solvents phenanthrene and pyrene have been measured at temperature ranges from 423.15 to 523.15 K and 473.15 to 573.15 K, respectively, and pressures from 10 to 50 atm. Henry constants, the partial molar volumes of CO_2 at infinite dilution, and the Margules parameters are obtained by fitting the Krichevsky-Ilinskaya equation (*4*) to the solubility data.

Experimental Section

The experimental apparatus used for the measurement of gas solubility was a semiflow vapor-liquid equilibrium apparatus. A detailed description of the experimental equipment and sampling procedure has been reported (*5*). Briefly, CO_2 passed continuously from a high-pressure cylinder through two cells in series while both were filled with a molten aromatic hydrocarbon. The first cell is the presaturator and the second the equilibrium cell. Upon saturation, the sample from the latter was withdrawn, released under pressure, and collected in a trap. The condensed aromatic hydrocarbon was weighed with an analytical balance, and the liberated gas from the trap was measured volumetrically in a buret for the liquid phase and in a wet test meter for the gas phase. The temperature of the equilibrium cell was measured to an accuracy of 0.2 K by a type J thermocouple inserted in the equilibrium cell. The pressure was measured by a Heise gauge to ±0.1 atm.

Table I. VLE Data for the Carbon Dioxide (2)-Phenanthrene (1) System for Temperature T, Pressure P, Liquid (x_2) and Vapor (y_2) Mole Fractions of Carbon Dioxide, and $K_2 = y_2/x_2$ Values

T/K	P/atm	x_2	y_2	K_2
423.15	10	0.0201	0.9994	49.62
	20	0.0402	0.9996	24.85
	30	0.0605	0.9996	16.51
	40	0.0796	0.9997	12.56
	50	0.0987	0.9997	10.13
473.15	10	0.0178	0.9966	55.96
	20	0.0348	0.9980	28.70
	30	0.0522	0.9982	19.13
	40	0.0699	0.9986	14.29
	50	0.0882	0.9987	11.32
523.15	10	0.0161	0.9856	61.26
	20	0.0332	0.9920	29.89
	30	0.0486	0.9940	20.44
	40	0.0658	0.9950	15.11
	50	0.0803	0.9955	12.40

Table II. VLE Data for the Carbon Dioxide (2)-Pyrene (1) System for Temperature T, Pressure P, Liquid (x_2) and Vapor (y_2) Mole Fractions of Carbon Dioxide, and $K_2 = y_2/x_2$ Values

T/K	P/atm	x_2	y_2	K_2
473.15	10	0.0145	0.9994	68.92
	20	0.0285	0.9997	35.10
	30	0.0433	0.9997	23.09
	40	0.0587	0.9998	17.05
	50	0.0737	0.9998	13.56
523.15	10	0.0127	0.9964	78.77
	20	0.0282	0.9982	35.37
	30	0.0421	0.9987	23.75
	40	0.0551	0.9988	18.14
	50	0.0684	0.9989	14.61
573.15	10	0.0128	0.9867	76.84
	20	0.0265	0.9927	37.43
	30	0.0409	0.9945	24.35
	40	0.0540	0.9968	18.45
	50	0.0686	0.9980	14.54

Materials. Carbon dioxide used in this work had a minimum purity of 99.5 mol %. The phenanthrene and pyrene were purchased from Tokyo Kasei Kogyo Co., Ltd., with a minimum purity of 98 mol %. No further purification of the chemicals was attempted.

Results

Tables I and II present the direct experimental vapor-liquid equilibrium data for liquid-phase mole fraction x_2 and vapor-phase mole fraction y_2, of CO_2, at temperature T and pressure P for CO_2 with phenanthrene and pyrene, respectively. Each

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