Literature Cited

(1) Acree, W. E., Jr.; Bertrand, G. L. *J. Solution Chem.* **1983**, *12*, 101-13.
(2) Acree, W. E., Jr.; Rytting, J. H. *J. Pharm. Sci.* **1982**, *71*, 201-5.
(3) Acree, W. E., Jr.; Rytting, J. H. *Int. J. Pharm.* **1982**, *10*, 231-8.
(4) Acree, W. E., Jr.; Rytting, J. H. *J. Pharm. Sci.* **1983**, *72*, 292-6.
(5) Acree, W. E., Jr.; Bertrand, G. L. *J. Pharm. Sci.* **1981**, *70*, 1033-6.
(6) Judy, C. L.; Acree, W. E., Jr. *Int. J. Pharm.* **1985**, *27*, 39-44.
(7) Judy, C. L.; Pontikos, N. M.; Acree, W. E., Jr. *Phys. Chem. Liq.* **1987**, *16*, 179-87.
(8) McCargar, J. W.; Acree, W. E., Jr. *Phys. Chem. Liq.* **1987**, *17*, 123-38.
(9) McCargar, J. W.; Acree, W. E., Jr. *J. Pharm. Sci.* **1987**, *76*, 572-4.
(10) Acree, W. E., Jr.; McCargar, J. W. *J. Pharm. Sci.* **1987**, *76*, 575-9.
(11) Acree, W. E., Jr.; McHan, D. R.; Rytting, J. H. *J. Pharm. Sci.* **1983**, *72*, 929-34.
(12) McCargar, J. W.; Acree, W. E., Jr. *J. Solution Chem.*, in press.
(13) Casellato, F.; Vecchi, C.; Girelli, A.; Casu, B. *Thermochim. Acta* **1973**, *6*, 361-8.
(14) Buckingham, J. *Dictionary of Organic Compounds*, 5th ed.; Chapman and Hall: New York, 1982; p 4840.
(15) Acree, W. E., Jr.; Bertrand, G. L. *J. Phys. Chem.* **1977**, *81*, 1170-3.
(16) Acree, W. E., Jr. *Thermodynamic Properties of Nonelectrolyte Solutions*; Academic Press: Orlando, FL, 1984.
(17) Prausnitz, J. M.; Lichtenthaler, R. N.; Gomez de Azevedo, E. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1986.
(18) Shahidi, F.; Farrell, P. G.; Edward, J. T.; Canonne, P. *J. Org. Chem.* **1979**, *44*, 950-3.
(19) McLure, I. A.; Swinton, F. L. *Trans. Faraday Soc.* **1965**, *61*, 421-428.
(20) Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds*; IUPAC Chemical Data Series No. 32; Blackwell Scientific Publications: Oxford, 1985.

Received for review February 22, 1988. Accepted August 1, 1988. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Thermodynamics of Binary Mixtures Containing Organic Carbonates. 2. Isothermal Vapor–Liquid Equilibria for Dimethyl Carbonate + Cyclohexane, + Benzene, or + Tetrachloromethane†

María J. Cocero and Fidel Mato*

Departamento de Ingeniería Química, Universidad de Valladolid, 47011 Valladolid, Spain

Isaías García and José C. Cobos

Departamento de Física Aplicada II, Universidad de Valladolid, 47011 Valladolid, Spain

Henry V. Kehiaian

Institut de Topologie et de Dynamique des Systèmes, Université Paris VII—CNRS, 1, Rue Guy de la Brosse, 75005 Paris, France

Vapor and liquid equilibrium phase compositions were determined at 298.15 K for binary systems containing dimethyl carbonate and cyclohexane, benzene, or tetrachloromethane. The data reported satisfy the Redlich–Kister thermodynamic consistency test. The results were correlated with five activity coefficient models.

Introduction

In part 1 of this series (*2*) we reported excess enthalpies for dimethyl carbonate + some *n*-alkanes, + cyclohexane, + methylcyclohexane, + benzene, + toluene, and + tetrachloromethane. In this paper isothermal vapor–liquid equilibrium (VLE) data are presented for the binary systems dimethyl carbonate (1) + cyclohexane (2), + benzene (2), or + tetrachloromethane (2) at 298.15 K. The data will serve for estimating interaction parameters for group contribution activity coefficient models. A literature search revealed indeed that no VLE data are available for dialkyl carbonates with any of the above-mentioned solvents.

Experimental Section

Materials. All the chemicals used were from Fluka. Dimethyl carbonate (purum, >99%), cyclohexane (puriss p.a., >99.5%), benzene (puriss p.a., >99.5%), and tetrachloromethane (puriss p.a., >99.5%) were used without further purification. Gas chromatographic analysis failed to show any significant impurities.

Prior to the actual measurements, the liquids were dried over a molecular sieve (Union Carbide Type 4A from Fluka). The densities and refractive indices were found to be the same as in our previous paper (*2*) and were in good agreement with literature values.

Apparatus and Procedure. Vapor–liquid equilibria were obtained by a saturation method. This method is based on the isothermal saturation of a flow of dry nitrogen passing through the liquid phase embedded in a packed column. The vapor phase is condensed in a liquid air trap, the condensate dissolved in a solvent adequate for gas chromatographic analysis (diethyl ether in this work). A more detailed description of the experimental equipment and operating procedure can be found in a previous paper (*3*).

The equilibrium temperature, T, was measured accurate to 0.05 K with a certified PROTON mercury thermometer (Model BER-MAN) previously calibrated with a Hewlett-Packard, Model 2804A, quartz thermometer.

The vaporized fraction of the liquid phase being very small (<0.5%), it was not necessary to make corrections for the liquid composition calculated directly from the weighed amounts charged to the column. The mole fraction of the liquid phase is accurate to within 0.0002. The composition of the vapor phase was determined by use of a Hewlett-Packard, Model 5890, gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard, Model 3390, electronic integrator. The column, 200 cm long and $^1/_4$ in. in diameter, was

---

† This paper is a contribution to the TOM Project (*1*).

Table I. Experimental x-y Data and Calculated Values of P, γ_i, and ϕ_i for the System Dimethyl Carbonate (1) + Cyclohexane (2) at 298.15 K

x_1	y_1	P/kPa	γ_1	γ_2	ϕ_1	ϕ_2
0.056	0.193	15.30	7.299	1.002	0.9926	0.9923
0.115	0.255	16.24	4.983	1.048	0.9921	0.9918
0.203	0.305	16.70	3.471	1.116	0.9919	0.9915
0.302	0.333	16.82	2.565	1.231	0.9919	0.9915
0.406	0.348	16.79	1.991	1.412	0.9919	0.9915
0.507	0.361	16.67	1.642	1.656	0.9919	0.9916
0.614	0.372	16.45	1.378	2.051	0.9920	0.9917
0.701	0.390	16.16	1.244	2.527	0.9922	0.9918
0.807	0.420	15.45	1.113	3.560	0.9925	0.9922
0.900	0.500	13.65	1.051	5.240	0.9934	0.9931

Table II. Experimental x-y Data and Calculated Values of P, γ_i, and ϕ_i for the System Dimethyl Carbonate (1) + Benzene (2) at 298.15 K

x_1	y_1	P/kPa	γ_1	γ_2	ϕ_1	ϕ_2
0.058	0.050	12.59	1.504	1.001	0.9939	0.9945
0.096	0.081	12.52	1.464	1.003	0.9939	0.9945
0.221	0.173	12.20	1.324	1.021	0.9941	0.9947
0.301	0.228	11.95	1.255	1.041	0.9942	0.9948
0.412	0.302	11.53	1.172	1.080	0.9944	0.9950
0.519	0.381	11.05	1.124	1.121	0.9947	0.9952
0.615	0.450	10.53	1.069	1.187	0.9949	0.9954
0.710	0.541	9.93	1.050	1.240	0.9952	0.9957
0.807	0.642	9.20	1.016	1.347	0.9955	0.9960
0.901	0.785	8.34	1.009	1.431	0.9960	0.9964

Table III. Experimental x-y Data and Calculated Values of P, γ_i, and ϕ_i for the System Dimethyl Carbonate (1) + Tetrachloromethane (2) at 298.15 K

x_1	y_1	P/kPa	γ_1	γ_2	ϕ_1	ϕ_2
0.036	0.043	15.36	2.540	1.002	0.9926	0.9931
0.114	0.105	15.40	1.964	1.022	0.9925	0.9930
0.223	0.170	15.18	1.602	1.065	0.9926	0.9931
0.315	0.219	14.83	1.428	1.111	0.9928	0.9933
0.398	0.264	14.42	1.324	1.159	0.9930	0.9935
0.491	0.312	13.86	1.220	1.232	0.9933	0.9937
0.598	0.372	13.08	1.128	1.344	0.9937	0.9941
0.695	0.439	12.23	1.071	1.480	0.9941	0.9945
0.801	0.548	11.01	1.045	1.647	0.9947	0.9950
0.910	0.713	9.25	1.006	1.943	0.9955	0.9958

packed with Carbowax 1500 and was operated isothermally within the range from 80 to 130 °C depending on the nature of the analyzed materials. The chromatograph was calibrated with synthetic mixtures. The mole fraction of the vapor phase, y, accurate to within 0.001, was calculated from the peak ratio of the samples. The validity of the method has been proved on several other binary systems (*3–5*).

Results and Discussion

Tables I–III present the experimental x–y VLE data for the systems dimethyl carbonate (1) + cyclohexane (2), + benzene (2), or + tetrachloromethane (2) at 298.15 K, together with the calculated values of total vapor pressures, P, liquid-phase activity coefficients, γ_1 and γ_2, and vapor-phase fugacity coefficients, ϕ_1 and ϕ_2.

Inasmuch as the method does not provide experimental data for the total vapor pressures, these values of P, as well as the activity coefficients, γ_i, and the fugacity coefficients, ϕ_i, were derived from the x–y–T data and from the vapor pressures of the pure components, P_i°, by means of an iterative procedure described elsewhere (*5*). The application of the procedure requires likewise an algebraic expression for the dimensionless excess Gibbs energy, $Q \equiv G^E/RT$, and for this purpose the four-parameter Margules equation has been used.

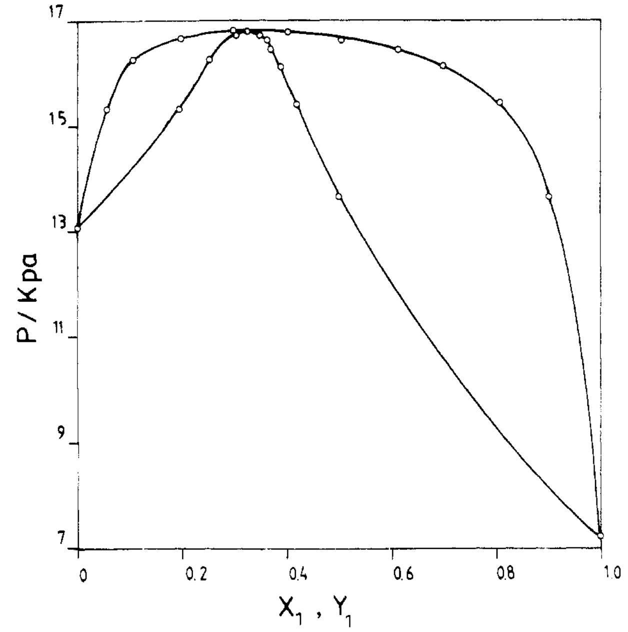

Figure 1. P–x–y phase equilibrium diagram for dimethyl carbonate (1) + cyclohexane (2) at 298.15 K: (O) experimental; (—) fit of the Wilson equation.

The vapor pressures of the pure components at 298.15 K (Table IV) were calculated from the Antoine coefficients reported in the literature (*6–8*).

Similar results were obtained when vapor-phase nonidealities were calculated from the Peng–Robinson (*9*) equation of state or from the virial equation of state truncated after the second term, with the second virial coefficients obtained by the method of Hayden and O'Connell (*10*). The values used for the critical constants, T_i^c and P_i^c, the acentric factors, ω_i, the dipole moments, μ_i, the coefficients a_{ii} and b_{ii} for Peng–Robinson equation, and the second molar virial coefficients, B_{ii}, are given in Table IV. The binary interaction coefficient δ_{12}, in the Peng–Robinson equation was set as zero for all the systems. The vapor-phase fugacity coefficients in Tables I–III were calculated by the Peng–Robinson equation.

The experimental data of the three systems were found to be thermodynamically consistent, as checked by using the Redlich–Kister area test (*11*).

The data were used to fit the adjustable parameters in the van Laar (*12*), Mato (*13*), Wilson (*14*), NRTL (*15*), and LEMF (*16*) equations by a nonlinear regression method. The following objective function, OF, was minimized

$$\mathrm{OF} = \sum_{i=1}^{N}\left[\left(\frac{\gamma_{1,\mathrm{exptl}} - \gamma_{1,\mathrm{calcd}}}{\gamma_{1,\mathrm{exptl}}}\right)^2 + \left(\frac{\gamma_{2,\mathrm{exptl}} - \gamma_{2,\mathrm{calcd}}}{\gamma_{2,\mathrm{exptl}}}\right)^2\right] \qquad (1)$$

Table IV. Pure Component Vapor Pressures, P_i° (*6–8*) at 298.15 K, Critical Temperatures, T_i^c (*22*), Critical Pressures, P_i^c (*22*), Acentric Factors, ω_i (*22*), Coefficients a_{ii} and b_{ii} for Peng-Robinson Equation, Molecular Dipole Moments, μ_i (*23, 24*), and Second Molar Virial Coefficients, B_{ii}

component	P_i°/kPa	T_i^c/K	P_i^c/kPa	ω_i	a_{ii}/J m^3 mol^{-2}	$b_{ii}/10^{-5}$ m^3 mol^{-1}	μ_i/D	$B_{ii}/10^{-6}$ m^3 mol^{-1}
dimethyl carbonate (1)	7.190	539.0	4630	0.462	3.168	7.52	0.90	2000
cyclohexane (2)	13.014	553.4	4070	0.212	3.329	8.80	0	1900
benzene (2)	12.690	562.2	4890	0.212	2.877	7.43	0	1500
tetrachloromethane (2)	15.228	556.4	4560	0.193	2.976	7.89	0	1700

Table V. Parameters A_{12} and A_{21} in the Activity Coefficient Models at 298.15 K for Dimethyl Carbonate (1) + Solvent (2) Mixtures and Average Absolute Deviations in Vapor-Phase Mole Fractions $\Delta(y_1)$

	A_{12}	A_{21}	$\Delta(y_1)$
van Laar (*12*)			
cyclohexane	2.1076	1.9390	0.014
benzene	0.4588	0.4528	0.002
tetrachloromethane	0.9688	0.7218	0.006
Mato (*13*)			
cyclohexane	2.1049	1.9396	0.014
benzene	0.4588	0.4528	0.002
tetrachloromethane	0.9624	0.7206	0.006
Wilson (*14*)[a]			
cyclohexane	3012	4688	0.005
benzene	1013	190	0.002
tetrachloromethane	955	1530	0.005
NRTL (*15*) (α_{12} = 0.47)[a]			
cyclohexane	3665	3922	0.006
benzene	567	631	0.002
tetrachloromethane	456	1995	0.005
LEMF (*16*)[a]			
cyclohexane	1870	1795	0.006
benzene	522	501	0.002
tetrachloromethane	1175	551	0.005

[a] Parameters A_{12} and A_{21} in J mol^{-1}.

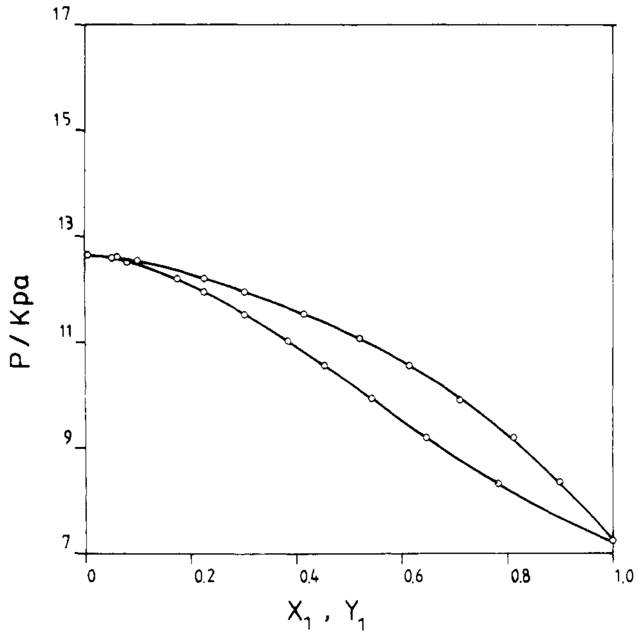

Figure 2. *P-x-y* phase equilibrium diagram for dimethyl carbonate (1) - benzene (2) at 298.15 K: (O) experimental; (—) fit of the Wilson equation.

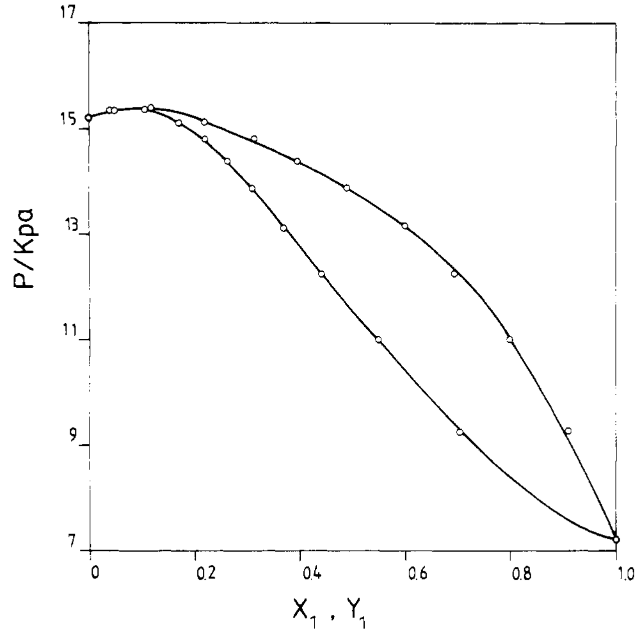

Figure 3. *P-x-y* phase equilibrium diagram for dimethyl carbonate (1) + tetrachloromethane (2) at 298.15 K: (O) experimental; (—) fit of the Wilson equation.

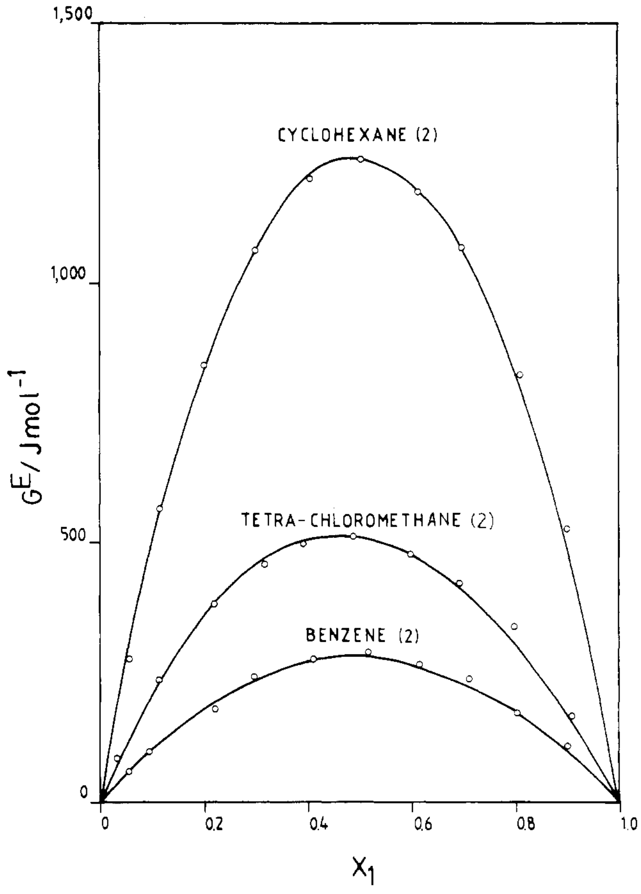

Figure 4. Molar excess Gibbs energy of dimethyl carbonate (1) + cyclohexane (2), + benzene (2), and + tetrachloromethane (2) at 298.15 K: (O) experimental; (—) calculated from the Wilson parameters.

where *N* is the number of experimental points. The model parameters are shown in Table V along with the average absolute deviations in vapor-phase composition:

$$\Delta(y_i) = \sum |y_{i,\text{calcd}} - y_{i,\text{exptl}}|/N \qquad (2)$$

The different correlating equations yield nearly the same deviations in vapor-phase composition for dimethyl carbonate + benzene or + tetrachloromethane. However, the equations of van Laar and Mato give larger deviations for the strongly nonideal dimethyl carbonate + cyclohexane system.

The *P-x-y* phase equilibrium diagrams of the three systems are shown in Figures 1-3. The molar excess Gibbs energies

$$G^E = RT[x_1 \ln \gamma_1 + x_2 \ln \gamma_2] \qquad (3)$$

are graphed in Figure 4. Comparing G^E of dimethyl carbonate with G^E of the structurally related compounds methyl acetate and acetone, we find that the general features of G^E are in accord with what has been reported for the excess molar enthalpies H^E (*2*). With the saturated alkane, cyclohexane, G^E-

(298.15 K,x_1 = 0.5) J mol^{-1} is relatively large, 1242 for dimethyl carbonate (this work), 983 for methyl acetate (*17*), and 1122 for acetone (*18*). With the two polarizable solvents, benzene and tetrachloromethane, G^E is much smaller, 282 and 514 J mol^{-1}, respectively, for dimethyl carbonate (this work); 238 (*19*) and ca. 365 J mol^{-1} (*20*), respectively, for methyl acetate; and 284 (*21*) and 523 J mol^{-1} (*22*), respectively, for acetone.

A quantitative treatment in terms of DISQUAC (*1*), an extended quasi-chemical group contribution method, of these vapor–liquid equilibria and H^E results and of additional measurements on dimethyl carbonate and diethyl carbonate + *n*-alkanes will be presented in a forthcoming paper.

Acknowledgment

We thank Prof. Rafael B. Mato for his helpful assistance in computer programming.

Glossary

a, b	parameters in the Peng–Robinson equation
A	parameter in the excess Gibbs energy, J mol^{-1}, for Wilson, NRTL, and LEMF equations
B	second molar virial coefficient, m^3 mol^{-1}
G	molar Gibbs energy, J mol^{-1}
N	number of experimental points on an isotherm
P	total vapor pressure, kPa
T	temperature, K
Q	dimensionless excess Gibbs energy (G^E/RT)
x	liquid mole fraction
y	vapor mole fraction
δ	binary interaction coefficient
γ	activity coefficient in the liquid
ϕ	fugacity coefficient in the vapor
μ	dipole moment, D
ω	acentric factor

Subscripts

i	property of component i (i = 1, 2)
12	interaction parameter

Superscripts

c	critical-point property
E	excess property
o	pure component property

Literature Cited

(1) Kehiaian, H. V. *Pure Appl. Chem.* **1985**, *57*, 15.

(2) Garcia, I.; Cobos, J. C.; Gonzalez, J. A.; Casanova, C.; Cocero, M. J. *J. Chem. Eng. Data* **1988**, *33*, 423.

(3) Mato, F.; Fernandez-Polanco, F.; Urueña, M. A. *An. Quim.* **1980**, *76*, 114.

(4) Mato, F.; Fernandez-Polanco, F.; Urueña, M. A. *An. Quim.* **1986**, *82*, 419.

(5) Mato, F.; Cocero, M. J. *An. Quim.* **1988**, *84*, 93.

(6) Gmehling, J.; Onken, U.; Grenzheuser, P. *Vapor–Liquid Equilibrium Data Collection*; Chemistry Data Series; DECHEMA: Frankfurt/Main, 1982; Vol. I, Part 5.

(7) *TRC Thermodynamic Tables—Hydrocarbons*; Thermodynamics Research Center, The Texas A&M University System: College Station, TX (loose-leaf data sheets, extant 1970, p k-2050, and 1954, p k-3200).

(8) *TRC Thermodynamic Tables—Non-Hydrocarbons*; Thermodynamics Research Center, The Texas A&M University System: College Station, TX (loose-leaf data sheets, extant 1973, p k-7240).

(9) Peng, D.-Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.

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

(11) Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 345.

(12) Van Laar, J. J. *Z. Phys. Chem.* **1910**, *72*, 723.

(13) Mato, F.; Mato, F. A. *Fluid Phase Equilib.* **1985**, *20*, 183.

(14) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.

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

(16) Marina, J. M.; Tassios, D. P. *Ind. Eng. Chem. Process Des. Dev.* **1973**, *12*, 67.

(17) Nagata, I. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1975**, 4.

(18) Tasic, A.; Djordjevic, B.; Grozdanic, D.; Afgan, N.; Malic, D. *Chem. Eng. Sci.* **1978**, *33*, 189.

(19) Nagata, I. *Int. DATA Ser., Sel. Data Mixtures Ser. A* **1975**, 7.

(20) Nagata, I. *Mem. Fac. Technol. Kanazawa Univ.* **1984**, *3*, 14.

(21) Brown, I.; Smith, F. *Aust. J. Chem.* **1957**, *10*, 423.

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

(23) Nelson, R. D., Jr.; Lide, D. R., Jr.; Maryott, A. A. *Selected Values of Electric Dipole Moments for Molecules in the Gas Phase*; National Standard Reference Data Series 10; National Bureau of Standards: Washington, DC, issued September 1, 1967; 25 pp.

(24) McClellan, A. L. *Tables of Dipole Moments*; Freeman: San Francisco, 1963.

Received for review March 23, 1988. Accepted August 9, 1988.