

equation of state. Since y_i enters into the calculation of φ_i , an initial estimate of φ_i must be made, here $\varphi_i = 1$.

(3) Solve eq 1 for g . Knowing g and g' gives the activity coefficients, and $y_i(\text{calcd})$ follows from $y_i = f_i^0 x_i \gamma_i / P \varphi_i$.

(4) Calculate new values of φ_i using $y_i(\text{calcd})$ from step 3. Repeat 2–4 until successive values of $y_i(\text{calcd})$ agree to within 10^{-6} . The end result is a set of values γ_i and $y_i(\text{calcd})$, which are thermodynamically consistent with the P - x data. Interpolation among $g(x_i)$ gives readily $y_i(\text{calcd})$ corresponding to the P - x data points. If $y_i(\text{exptl})$ agrees satisfactorily with $y_i(\text{calcd})$, the data are thermodynamically consistent.

Discussion

Equation 1 was solved using two internal collocation points. Using higher-order approximations does not alter the results significantly. The calculated activity coefficients and vapor phase mole fractions are given in Table II. The overall agreement between $y_i(\text{calcd})$ and $y_i(\text{exptl})$ is within 0.010 mol fraction. Considering the amount of impurities in the Freons and the uncertainties in the composition measurements and calculation of fugacity coefficients, the data set is thermodynamically consistent. The data may thus be included in the basis for correlating the thermodynamic properties of mixed refrigerants.

Acknowledgment

The authors are grateful to Statens teknisk-videnskabelige Forskningsrad for financial support and to Mr. Bent Johnsen for assistance with the experiments.

Nomenclature

A = coefficient in Legendre polynomial
 f = fugacity
 g = reduced excess Gibbs free energy, G^E/RT
 L = Legendre polynomial

P = pressure
 R = the gas constant
 T = temperature
 V = liquid molar volume
 x = liquid-phase mole fraction
 y = vapor-phase mole fraction
 γ = activity coefficient
 φ = fugacity coefficient

Superscripts

0 = standard state
sat = at saturation
E = excess property

Subscripts

1, 2, i = components
 k = order of Legendre polynomial
 n = maximum degree of Legendre polynomial
 σ = along saturation line

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Received for review July 15, 1975. Accepted December 11, 1975.

A copy of the computer program used and printout of the intermediate results can be obtained from the authors for a fee of \$10.

Vapor-Liquid Equilibrium Data for the Systems $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ and $\text{CO}_2 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$

Aage Fredenslund,* Jørgen Mollerup, and Kenneth R. Hall†

Instituttet for Kemiteknik, Danmarks tekniske Højskole, 2800 Lyngby, Denmark

Earlier work from this laboratory resulted in isothermal vapor-liquid equilibrium (VLE) data for the systems $\text{CO}_2 + \text{C}_2\text{H}_4$ and $\text{CO}_2 + \text{C}_2\text{H}_6$. We now report isothermal VLE data for the $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ system and isothermal-isobaric VLE data for the ternary system $\text{CO}_2 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ at 263.15 and 293.15 K. The pressures range from 20 to 60 atm.

Carbon dioxide, ethylene, and ethane are important compounds in the gas processing industry, and knowledge of the properties of the pure components and their mixtures is of practical importance for designing process equipment. The vapor-liquid equilibria among these compounds is complex; the

mixtures are nonideal with $\text{CO}_2 + \text{C}_2\text{H}_6$ and $\text{CO}_2 + \text{C}_2\text{H}_4$ forming minimum boiling azeotropes. In this work, we provide VLE data for the $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ system and for the $\text{CO}_2 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ system at two temperatures: 263.15 K, where all components are condensable, and 293.15 K, where CO_2 and C_2H_6 are condensable and C_2H_4 is noncondensable. Earlier work in this laboratory (4, 14) produced VLE data for the systems $\text{CO}_2 + \text{C}_2\text{H}_4$ and $\text{CO}_2 + \text{C}_2\text{H}_6$. This paper then completes a reliable and self-consistent description of mixtures of these compounds.

Other laboratories have studied the component binaries. References 7, 10, 11, 15, and 18 report VLE data for $\text{CO}_2 + \text{C}_2\text{H}_4$, while ref 3, 6, 7, 12, 13, 15, and 16 investigated $\text{CO}_2 + \text{C}_2\text{H}_6$. Reference 9 provides data for $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$, and ref 2 predicts the low pressure behavior of the ternary. These data do not form a complete description, which led to the current study.

* Chemical Engineering Department, Texas A&M University, College Station, Texas 77843.

Table I. Vapor-Liquid Equilibrium in the C₂H₄ + C₂H₆ System^a

T/K	Exptl values			Calcd values				
	P/atm	x _{C₂H₄}	y _{C₂H₄}	y _{C₂H₄}	φ _{C₂H₄}	φ _{C₂H₆}	γ _{C₂H₄}	γ _{C₂H₆}
263.15	18.34	0.0000	0.0000	0.0000	0.861	0.800	1.109	1.000
Symmetric convention	19.06	0.0462	0.0706	0.0703	0.854	0.793	1.097	1.000
	20.48	0.1446	0.2036	0.2043	0.840	0.777	1.074	1.003
	22.03	0.2561	0.3324	0.3366	0.825	0.761	1.051	1.008
	23.96	0.3982	0.4823	0.4847	0.807	0.742	1.029	1.019
	26.82	0.6138	0.6814	0.6832	0.781	0.714	1.008	1.039
	29.10	0.7894	0.8320	0.8322	0.760	0.693	1.001	1.055
	29.86	0.8476	0.8777	0.8798	0.754	0.686	1.000	1.059
	31.05	0.9392	0.9516	0.9529	0.743	0.675	1.000	1.061
	31.94	1.0000	1.0000	1.0000	0.736	0.667	1.000	1.061
			[y(exptl) - y(calcd)] _{av} = 0.0016					
293.15	37.14	0.0000	0.0000	0.0000	0.818	0.704	1.000	1.000
Unsymmetric convention	38.46	0.0539	0.0662	0.0667	0.809	0.693	1.005	1.000
	40.85	0.1537	0.1772	0.1817	0.791	0.672	0.988	1.002
	43.57	0.2663	0.2968	0.3005	0.772	0.648	0.970	1.007
	45.98	0.3664	0.3936	0.3971	0.758	0.626	0.952	1.015
	46.85	0.3988	0.4251	0.4266	0.753	0.619	0.945	1.019
	47.85	0.4532	0.4722	0.4757	0.746	0.608	0.936	1.027
		[y(exptl) - y(calcd)] _{av} = 0.0029				Henry's constant = 38.0 atm		

^a The mole fractions are given with four significant figures in order to avoid round-off errors; the mole fractions are only believed accurate to within 0.003.

Table II. Vapor-Liquid Equilibrium in the CO₂ + C₂H₄ + C₂H₆ System^a

P/atm	x _{CO₂}	y _{CO₂}	x _{C₂H₄}	y _{C₂H₄}	x _{C₂H₆}	y _{C₂H₆}
T = 293.15 K						
45.01	0.0512	0.0762	0.1956	0.2173	0.7531	0.7065
45.08	0.0839	0.1243	0.1166	0.1318	0.7995	0.7439
45.00	0.1056	0.1526	0.0632	0.0697	0.8312	0.7777
60.09	0.9006	0.8863	0.0354	0.0419	0.0640	0.0718
T = 263.15 K						
23.05	0.0452	0.0819	0.2190	0.2763	0.7358	0.6418
23.10	0.0718	0.1311	0.1584	0.1973	0.7699	0.6716
23.11	0.1005	0.1813	0.0939	0.1145	0.8056	0.7042
28.01	0.0200	0.0304	0.6499	0.7165	0.3301	0.2532
28.11	0.1055	0.1437	0.4879	0.5286	0.4065	0.3275
28.01	0.1655	0.2245	0.3596	0.3913	0.4747	0.3841
28.03	0.2668	0.3530	0.1856	0.1968	0.5476	0.4501
28.06	0.3522	0.4476	0.0407	0.0348	0.6070	0.5085
28.04	0.9309	0.8892	0.0267	0.0411	0.0423	0.0695
28.04	0.9294	0.8882	0.0568	0.0887	0.0136	0.0230
29.98	0.0587	0.0731	0.7295	0.7692	0.2116	0.1577
30.03	0.1251	0.1583	0.6103	0.6417	0.2645	0.1998
29.97	0.2165	0.2625	0.4502	0.4666	0.3331	0.2708
30.01	0.3207	0.3779	0.2920	0.3036	0.3872	0.3184
30.05	0.4768	0.5312	0.1045	0.1093	0.4184	0.3595
30.00	0.5750	0.6111	0.0000	0.0000	0.4250	0.3889
29.83	0.7848	0.7588	0.0000	0.0000	0.2151	0.2412
29.99	0.7927	0.7572	0.0446	0.0551	0.1625	0.1875
30.09	0.7918	0.7494	0.0793	0.0982	0.1288	0.1522
30.09	0.8025	0.7509	0.1093	0.1398	0.0881	0.1091
30.10	0.8135	0.7573	0.1444	0.1882	0.0419	0.0544
32.01	0.0451	0.0529	0.9186	0.9183	0.0364	0.0288
31.95	0.0943	0.1084	0.8281	0.8322	0.0776	0.0594
32.00	0.2436	0.2620	0.6309	0.6260	0.1255	0.1119
32.00	0.3562	0.3790	0.4682	0.4744	0.1757	0.1466
31.96	0.4632	0.4739	0.3612	0.3746	0.1756	0.1514
32.00	0.5860	0.5660	0.3055	0.3307	0.1083	0.1033
32.01	0.6430	0.6041	0.3156	0.3569	0.0412	0.0388

^a The mole fractions are given with four significant figures to avoid round-off errors; the data are only believed accurate to within 0.005 mole fraction.

Experimental Section

The experimental apparatus, described in detail elsewhere (5), is of the vapor recirculation type. A diaphragm compressor

circulates the vapor through stationary liquid in the equilibrium cell. Upon equilibration, the temperature, pressure, vapor composition, and liquid composition are observed. Temperature observation and control are within 0.01 K, pressure measure-

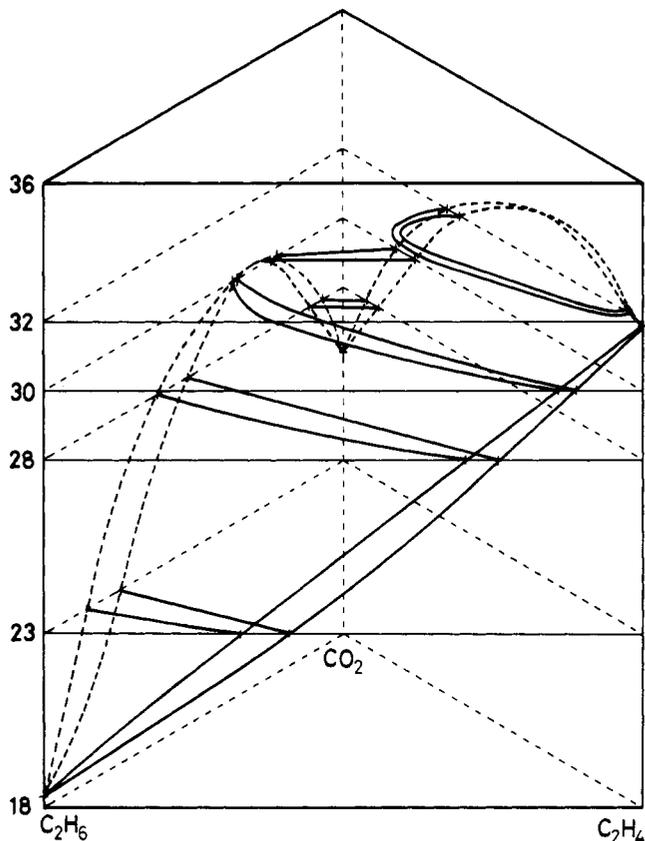


Figure 1. $\text{CO}_2 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ surface at 263.15 K. Curves are in the constant pressure planes: (—) corresponds to data of this work; (---) corresponds to data in (4, 14). The pressure is in atmospheres.

ment (with dead-weight gauges) is within 0.02%, and composition reproducibility on the gas chromatograph is within 0.005 in mol fraction (within 0.003 for binaries). The pressure change upon sampling (three vapor and three liquid samples for each point) was less than 0.05%.

All gases are research grade of 99.95% purity or better and received no additional purification. Alfa of Sweden is the supplier. The gas chromatograph columns were: for $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$, 5 Å molecular sieve (80–100 mesh) 3 ft \times 1/8 in. diameter; for $\text{CO}_2 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$, Porapak Q (80–100 mesh) 10 ft \times 1/8 in. diameter.

Consistency Test

We have chosen to compare y_i (exptl) with y_i (calcd) for the consistency test (19). To employ this test requires solution of

$$P = y_1 P + y_2 P = \frac{x_1 f_1^0 \gamma_1}{\varphi_1} + \frac{x_2 f_2^0 \gamma_2}{\varphi_2} \quad (1)$$

where, for a binary mixture

$$\gamma_i = \exp \left\{ g + (-1)^{i+1} (1 - x_i) \times \left[\left(\frac{dg}{dx_1} \right)_\sigma - \frac{V^E}{RT} \left(\frac{dP}{dx_1} \right)_\sigma \right] \right\} \quad i = 1 \text{ or } 2 \quad (2)$$

subject to the constraining condition that

$$g = x_1 x_2 \sum_{k=1}^n A_k L_k(x_1) \quad (3)$$

if the symmetric convention applies to the activity coefficients (263.15 K), or

$$g = \left(\frac{x_1}{x_{1,\max}} \right)^2 \sum_{k=1}^n A_k L_k \left[\left(\frac{x_1}{x_{1,\max}} \right)^2 \right] \quad (4)$$

if the unsymmetric convention applies to the activity coefficients (293.15 K). These expressions derive from the conditions for vapor–liquid phase equilibrium and the isothermal, nonisobaric Gibbs–Duhem equation. Equation 4 is chosen from the point of view of numerical expediency, and eq 2 is readily derived from eq 1, 4, and 5 in ref 1.

The solution of eq 1–4 is iterative and proceeds as described in (7): (1) Obtain an analytical expression for the P – x data using either orthogonal polynomials or a spline fit. (2) Evaluate V^E , f_i^0 , and φ_i using the Redlich–Kwong equation. Initially assume $\varphi_i = 1$ lacking an estimate for y_i . Evaluate $(dP/dx_1)_\sigma$. (3) Solve eq 1 for g , use eq 3 or 4 to obtain dg/dx_1 . Use orthogonal collocation for the solution. (4) Calculate y_i from y_i (calcd) = $x_i f_i^0 \gamma_i / P \varphi_i$. (5) Iterate steps 2–4 until successive values of y_i (calcd) agree within 10^{-6} . The necessary thermodynamic properties, φ_i and V^E , are calculated following very closely the methods of ref 17 (pp 18–22, 44, 56–57, and 66). For the deviation from the geometric mean, k_{12} , we use 0.01.

The end result is a set of γ_i and y_i (calcd) which are thermodynamically consistent with the P – x data. If y_i (calcd) agree satisfactorily with y_i (exptl), the data are thermodynamically consistent. We apply this consistency test only to binary systems.

Results

Table I contains the data for the $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ binary. Table II contains the $\text{CO}_2 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ ternary data. These are raw data and have not been smoothed in any way. The binary data, when subjected to the consistency test, display consistency within 0.002 in mol fraction. Figure 1 presents a visualization of the ternary surface at 263.15 K.

Acknowledgments

The authors appreciate the assistance of Mr. Bent Johnsen.

Nomenclature

- A_k = coefficient for Legendre polynomial
- L_k = Legendre polynomial
- P = pressure
- R = gas constant
- T = temperature
- V^E = excess volume
- f_i^0 = standard state fugacity of component i
- g = reduced excess Gibbs function: G^E/RT
- n = degree of Legendre polynomial
- x_i = mole fraction of component i in liquid
- $x_{i,\max}$ = largest experimental value of x_i
- y_i = mole fraction of component i in vapor
- γ_i = activity coefficient of component i in liquid
- φ_i = fugacity coefficient of component i in vapor

Subscripts

- i = denotes component
- σ = denotes along saturation line

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Received for review August 19, 1975. Accepted December 11, 1975. Aa. Fredenslund and J. Mollerup acknowledge financial support from Statens tekniskvidenskabelige Forskningsraad; K. R. Hall acknowledges financial support from NSF Grant ENG 74-23411, The American Gas Association, and PRF Grant 7594-AC 7.

The Density and Enthalpy of Mixing of Solutions of Acetonitrile and of Dimethyl Sulfoxide with Several Aromatic Hydrocarbons

Afaf H. Absood, Maha S. Tutunji, Kuei-Yen Hsu, and H. Lawrence Clever*

Department of Chemistry, Emory University, Atlanta, Georgia 30322

The density at 30.0 °C was measured for solutions of acetonitrile and of dimethyl sulfoxide with benzene, 1,4-dimethylbenzene, and 1,3,5-trimethylbenzene. The excess enthalpy of mixing was measured by flow microcalorimetry at 25.0 °C for the same systems plus solutions with 1,2,4-trimethylbenzene. All of the enthalpies of mixing are endothermic. With both acetonitrile and dimethyl sulfoxide the enthalpies of mixing at one-half mole fraction become more positive in the order benzene < 1,4-dimethylbenzene < 1,2,4-trimethylbenzene < 1,3,5-trimethylbenzene. Excess volumes were calculated from the solution densities. The excess volumes are negative in the benzene solutions, but they are positive for the 1,3,5-trimethylbenzene solutions. The trends in excess enthalpy and excess volume are consistent with the observed liquid-liquid immiscibility below 21.6 °C in 1,3,5-trimethylbenzene-dimethyl sulfoxide solutions.

This paper is part of a continuing series of a study of the properties of binary mixtures of aromatic hydrocarbons with polar molecules. Previous reports have been made on hydrocarbon-nitroalkane mixtures (6, 7, 8, 12). The present paper reports the density at 30 °C and the enthalpy of mixing at 25

°C of aromatic hydrocarbon solutions of acetonitrile and of dimethyl sulfoxide. Several of these solutions have been studied by others. There are reports of the density, excess volume, excess Gibbs energy, and enthalpy of mixing of benzene-acetonitrile mixtures (3, 4, 5) and of excess volume, enthalpy of mixing, and excess Gibbs energy of mixing of benzene-dimethyl sulfoxide mixtures (1, 9, 16, 18).

Experimental Section

Solution Components. Summarized in Table I are the source, purification, density, and refractive index of the solution component compounds acetonitrile, dimethyl sulfoxide, benzene, 1,4-dimethylbenzene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene. The method of acetonitrile purification was that of O'Donnell, Ayres, and Mann (22). The physical properties agree satisfactorily with accepted literature values.

Experimental Methods. Density. Densities were determined in a 16-cm³ density bottle with a constant bore capillary neck of (1.00 ± 0.08) mm which was graduated in 1-mm intervals for a length of 2 cm. The bottle was calibrated with freshly boiled distilled water. The density measurements were made at (30.00 ± 0.01) °C.

Solutions for the measurement of density were prepared

Table I. Source, Purification, and Physical Properties of Solution Components

Compound	Source	Purification	Bp, °C (mmHg)	d_{30} , g cm ⁻³	n_{25}^D
Acetonitrile	Fisher certified 99 mol %	Refluxed with Na ₂ CO ₃ and KMnO ₄ , distilled, acidified, filtered, distilled thru 24-in. helice packed column	80 (742)	0.77145	1.34140
Dimethyl sulfoxide	Fisher certified ACS grade	Dried over 4A molecular sieve, fractionally crystallized, distilled from CaH ₂ thru 24-in. helice packed column	80 (20)	1.0913	1.4770 (20°)
Benzene	Phillips pure grade, 99 mol %	Shaken with successive portion of H ₂ SO ₄ , water washed until neutral to litmus, dried over CaSO ₄ , distilled from CaH ₂ thru 24-in. helice packed column	79.3 (742)	0.86838	1.49800
1,4-Dimethylbenzene (<i>p</i> -xylene)	Eastman practical grade	Dried over CaSO ₄ , distilled from CaH ₂ thru 24-in. helice packed column	137.5 (742)	0.85230	1.49320
1,2,4-Trimethylbenzene (pseudocumene)	Phillips research grade	Lot no. 1345, 99.89 mol %, used without purification		0.86796	1.50250
1,3,5-Trimethylbenzene (mesitylene)	Eastman practical grade	Dried over CaSO ₄ , distilled from sodium thru 24-in. helice packed column	162.5 (740)	0.85572	1.49610