J. Chem. Eng. Data 1986, 31, 43-45

Vapor–Liquid Equilibrium for 2-Propanol and Carbon Dioxide

Maciej Radosz

Exxon Research and Engineering Company, Annandale, New Jersey 08801

Vapor and liquid equilibrium compositions have been measured for 2-propanol and carbon dioxide at 44, 62, 81, and 121 °C (317, 335, 354, and 394 K) and at pressures from 1.4 to 12 MPa. Phase equilibrium *K* ratios are correlated with equations of state.

Introduction

Pure component properties for aliphatic alcohols are relatively well established (*1–3*), as are phase equilibria at low pressures (*4*, *5*). However, phase equilibria at elevated pressures are scarce. For example, *TPXY* data, experimentally measured phase equilibrium compositions of coexisting liquid (*X*) and vapor (*Y*) phases at constant temperature (*T*) and pressure (*P*), are virtually nonexistent. One category of binaries where *TPXY* data are needed is that of aliphatic alcohols and compressed gases. These are important binaries because aliphatic alcohols can be not only manufactured in the presence of but also separated with compressed gases. In particular, separating alcohols from water with compressed supercritical gases attracts attention (*6*, *7*) because the conventional distillative separations are very energy intensive.

2-Propanol and carbon dioxide are selected for this investigation to back up thermodynamic models needed to correlate and predict phase equilibria in multicomponent polar mixtures at elevated pressures. For example, ternary data for 2-propanol, carbon dioxide, and water (*7*, *8*) are being used to develop an equation of state with density-dependent mixing rules (*9*) and a group-contribution equation of state (*10*). Regardless of the approach taken, the binary interaction parameters should be based on binary *TPXY* data which, for 2-propanol and carbon dioxide, have not been available.

Experimental Section

These binary *TPXY* data for 2-propanol and carbon dioxide are measured with a variable-volume circulation apparatus shown in Figure 1. In general, this apparatus is applicable to vapor–liquid, vapor–liquid–liquid, and liquid–liquid equilibria at temperatures from 10 to 260 °C and at pressures up to 35 MPa. The concept of circulating phases in batch cells has been rather common in phase equilibrium measurements. The sampling method is similar to that proposed by Tsang and Streett (*11*) who evaporated and homogenized the condensed-phase samples prior to on-line GC analysis.

The keystone of the apparatus is a batch windowed cell which serves as a mixing and separating vessel and makes it possible to observe phase separation visually. Two circulation pumps provide the mixing energy needed to promote mass transfer. A variable-volume cylinder, which is part of the top phase recirculating loop, is used to maintain constant pressure while sampling. An on-line gas chromatograph allows rapid composition measurements. All parts of the apparatus which are in contact with phases, as shown in Figure 1, are enclosed in an air bath to ensure temperature uniformity. The experimental equipment and procedure are described in greater detail elsewhere (*8*).

2-Propanol used in this work was supplied by Fisher Scientific Co. (A-417 of 99+% purity) and carbon dioxide was supplied by Matheson (Coleman Instrument of 99.99+% purity). Both compounds were used for measurements without further purification.

Table I. Vapor–Liquid Equilibrium for 2-Propanol and Carbon Dioxide

		CO_2 mole fraction	
T, °C	*P*, psia (MPa)	liquid	vapor
43.5	850 (5.86)	0.4520	0.9915
43.6	1000 (6.90)	0.6038	0.9894
43.6	1150 (7.93)	0.8440	0.9855
61.8	200 (1.38)	0.0785	0.9664
61.7	400 (2.76)	0.1529	0.9791
61.7	600 (4.14)	0.2370	0.9818
61.8	850 (5.86)	0.3538	0.9830
61.3	1000 (6.90)	0.4368	0.9813
61.7	1150 (7.93)	0.5297	0.9794
62.0	1250 (8.62)	0.5950	0.9764
61.8	1350 (9.31)	0.6908	0.9713
81.6	850 (5.86)	0.2962	0.9672
81.3	1000 (6.90)	0.3603	0.9665
81.2	1250 (8.62)	0.4739	0.9629
81.3	1500 (10.34)	0.6114	0.9515
81.3	1650 (11.38)	0.7133	0.9335
121.5	1000 (6.90)	0.2831	0.8946
121.4	1250 (8.62)	0.3675	0.8959
121.4	1500 (10.34)	0.4583	0.8875
121.4	1750 (12.07)	0.5586	0.8652
121.0	1800 (12.41)	0.5889	0.8532

Experimental Results

Experimental mole fractions of carbon dioxide are reported in Table I and plotted vs. pressure in Figures 2 and 3 for coexisting liquid and vapor phases. The four isotherms, 44, 62, 81, and 121 °C, have been measured in the high-pressure and, therefore, high-density region, as expected in supercritical extraction. In addition, the 62 °C isotherm have been measured at lower pressures, down to 200 psia, to provide also the low-density phase compositions. This isotherm smoothly extrapolates to the 2-propanol vapor pressure at the carbon dioxide mole fraction equal to zero (Figure 3).

The mole fractions in Table I are averages of two to three GC analyses of each phase. Reproducibility of the results from one series of analyses, as well as from the repeated measurements, is typically 0.001, and always less than 0.003, in mole fractions. Based on this and other tests carried out on the systems of known phase equilibrium, *n*-decane/*n*-butane and water/2-butanol (*8*), the overall accuracy is believed to be better than 0.005 in mole fractions. The temperature and pressure measurements are accurate to 0.1 °C and 3.5 psi, respectively.

Correlation

The experimental *TPXY* data from Table I are correlated with three cubic equations of state, the Redlich–Kwong versions proposed by Soave (*12*), by Peng and Robinson (*13*), and by Zudkevitch and Joffe (*14*). These equations differ in the attractive part of the compressibility factor and in the way the pure component parameters are determined.

The Soave and Peng–Robinson energy parameters *a* are temperature-dependent while the molecular size parameters *b* are temperature-independent. Both *a* and *b* are calculated from generalized equations, originally fitted to vapor pressure, utilizing critical temperature, critical pressure, and Pitzer's acentric factor. On the other hand, the Joffe–Zudkevitch (RKJZ) parameters *a* and *b* are both temperature-dependent (*15*).

0021-9568/86/1731-0043$01.50/0

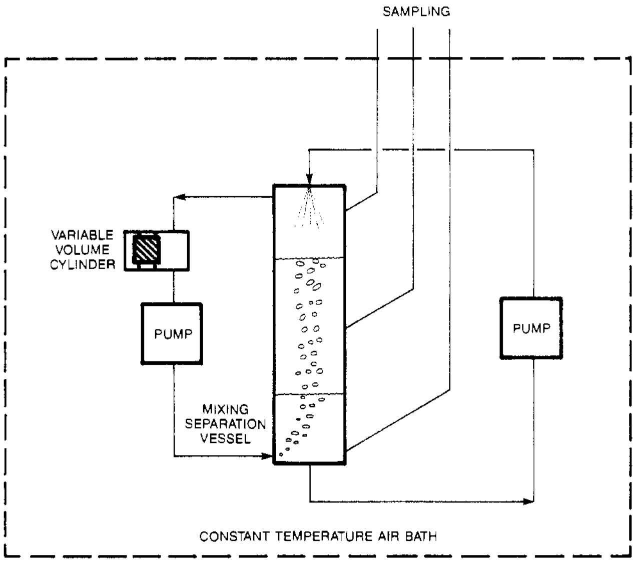

Figure 1. Simplified diagram of variable-volume circulation apparatus.

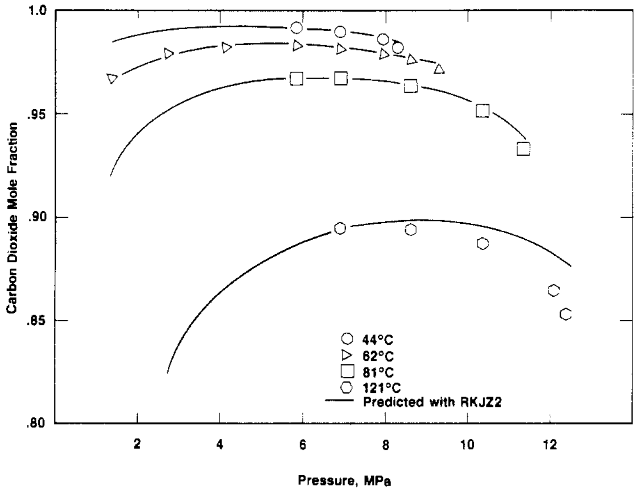

Figure 2. Experimental vapor-phase composition.

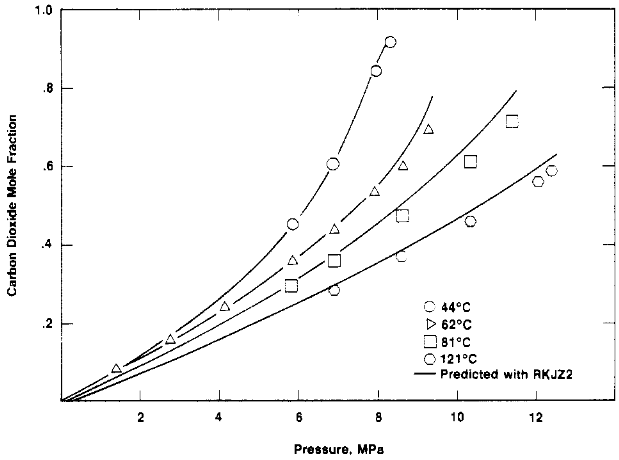

Figure 3. Experimental liquid-phase composition.

Moreover, they are adjusted to vapor pressure and liquid density, when used, rather than calculated from the criticals.

For mixtures, the common averaging equations are used

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \qquad b_m = \sum_i \sum_j x_i x_j b_{ij} \qquad (1)$$

$$a_{ij} = (1 - C_{ij})(a_i a_j)^{0.5} \qquad b_{ij} = 0.5(1 + D_{ij})(b_i + b_j) \qquad (2)$$

which are quadratic in mole fractions and are referred to as vdW1 (van der Waals one-fluid) mixing rules.

Table II. Binary Interaction Parameters for Equations of State

			absolute av devn in K ratio, %	
	C	D	carbon dioxide	2-propanol
Soave	0.098	0.000	2.8	6.6
Peng–Robinson	0.107	0.000	3.0	7.2
RKJZ1	0.095	0.000	1.7	6.6
RKJZ2	0.077	0.028	2.1	2.5

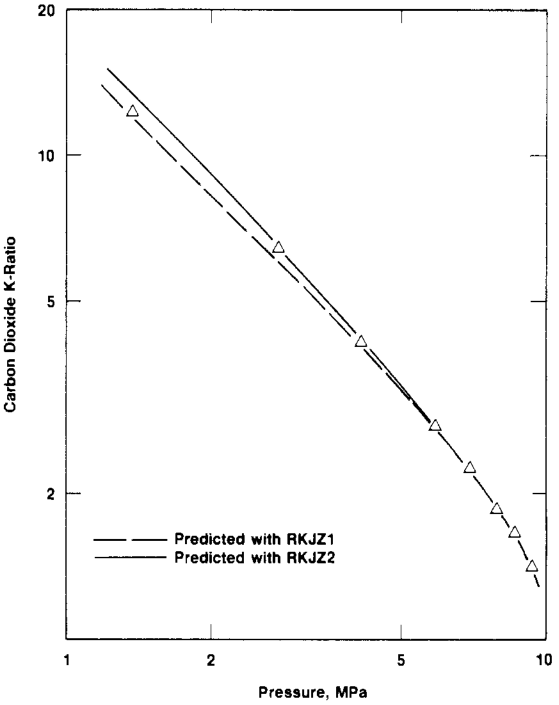

Figure 4. Experimental vapor–liquid ratio of mole fractions for carbon dioxide (K ratio) at 62 °C.

Four series of calculations were made, with RKJZ adjusting both binary parameters C and D (RKJZ2), and with Soave, Peng-Robinson, and RKJZ (RKJZ1) adjusting only C and setting D equal to zero. In all the cases, a regression program (*16*) minimizing deviations in the equilibrium K ratios was used. Results of the first series (RKJZ2) are shown in Figure 2 for the vapor-phase composition and in Figure 3 for the liquid-phase composition. The binary parameters and average absolute deviations (percent AAD) are given in Table II.

In addition, the predictions from RKJZ2 and RKJZ1 are illustrated in Figure 4 for the carbon dioxide equilibrium K ratio and in Figure 5 for the 2-propanol equilibrium K ratio. Based on Figure 5, and Table II, the two-parameter predictions (RKJZ2) appear to be more accurate than the one-parameter predictions (RKJZ1, which is similar to Soave and Peng–Robinson) for the 2-propanol K ratio, especially, at higher pressures.

Conclusion

The vapor–liquid equilibrium data measured for 2-propanol and carbon dioxide have been correlated with cubic equations of state. These data should be useful in developing new thermodynamic models of high-pressure phase equilibria in polar mixtures, such as the equation of state with density-dependent mixing rules and the group-contribution equation of state.

Glossary

a	energy-related parameter
b	molecular size-related parameter
C	binary energy-related parameter

J. Chem. Eng. Data **1986**, *31*, 45-47

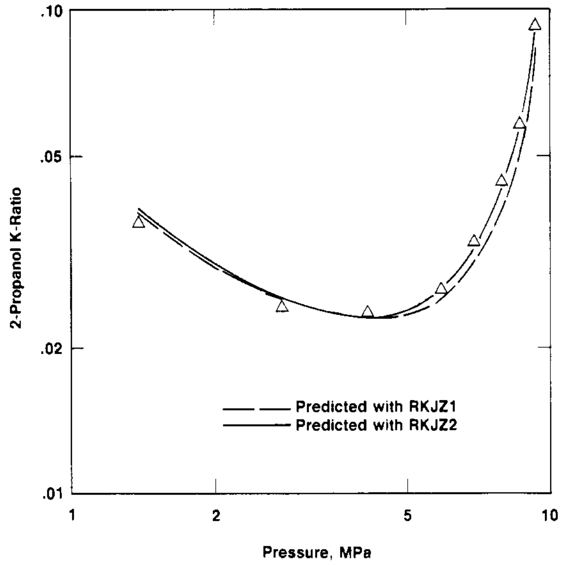

Figure 5. Experimental vapor-liquid ratio of mole fractions for 2-propanol (*K* ratio) at 62 °C.

D	binary molecular size-related parameter
i	*i*th component property
j	*j*th component property
K	equilibrium vapor/liquid ratio of mole fractions (*K* ratio)
m	mixture property
x	mole fraction

Acknowledgment

Acknowledgment is made to Mr. E. Niessen for his contribution in the measurements.

Registry No. 2-Propanol, 67-63-0; carbon dioxide, 124-38-9.

Literature Cited

(1) Wilhoit, R. C.; Zwolinski, B. J. *J. Chem. Phys. Ref. Data* **1973**, *2*, (Suppl. 1).
(2) Radosz, M. Postdoctoral Report, The Technical University of Norway, Trondheim, 1980.
(3) Radosz, M.; Lydersen, A. *Chem.-Ing.-Tech.* **1980**, *52*, 756 (Suppl.).
(4) Gmehling, J.; Onken, U.; Arlt, W. "Vapor-Liquid Equilibrium Data Collection"; DECHEMA: Frankfurt, 1977.
(5) Sorensen, J. M.; Arlt, W. "Liquid-Liquid Equilibrium Data Collection"; DECHEMA, Frankfurt, 1979.
(6) Paulaitis, M. E.; Kander, R. G.; DiAndreth, J. R. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 869.
(7) Kander, R. G.; Paulaitis, M. E. AIChE Annual Meeting, San Francisco, 1984; American Institute of Chemical Engineers: New York; 84b.
(8) Radosz, M. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 859.
(9) Prausnitz, J. M.; Hu, Y. AIChE Annual Meeting, San Francisco, 1984; American Institute of Chemical Engineers: New York; 102e.
(10) Brignole, E. A.; Skjold-Jorgensen, S.; Fredenslund, Aa. In "Supercritical Fluid Technology"; Penninger, J. M. L. et al., Eds.; Elsevier: Amsterdam, 1985.
(11) Tsang, C. Y.; Streett, W. B. *J. Chem. Eng. Data* **1981**, *26*, 155.
(12) Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 1197.
(13) Peng, D. Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.
(14) Zudkevitch, D.; Joffe, J. *AIChE J.* **1970**, *16*, 112.
(15) Gray, R. D. Jr.; Heidman, J. L. Jr.; Hwang, S. C.; Tsonopoulos, C. *Fluid Phase Equilib.* **1983**, *13*, 59.
(16) Heidman, J. L. Jr. "PHASER Regression Program"; Exxon Research and Engineering Co.: Florham Park, NJ, 1985.

Received for review January 28, 1985. Accepted May 15, 1985. Acknowledgment is made to Exxon Research and Engineering Company for permission to publish this paper.

Excess Enthalpies of Binary Mixtures of *n*-Decane with Hexane Isomers

Salah E. M. Hamam

Department of Chemical Engineering, Kuwait University, College of Engineering and Petroleum, Kuwait

George C. Benson*

Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4

Calorimetric measurements of excess enthalpies are reported for each of the five mixtures (*n*-decane–an isomeric hexane) at 298.15 K. The results for equimolar mixtures, together with previously published results for other (*n*-alkane–isomeric hexane) mixtures, are well correlated in terms of the acentric factors of the *n*-alkanes.

Currently we are studying the variations in the excess thermodynamic properties of binary mixtures which result from isomeric changes in one of the components. In this regard, we have been investigating systems formed by mixing an *n*-alkane with the five isomeric hexanes: *n*-hexane (*n*-C6), 2-methylpentane (2-MP), 3-methylpentane (3-MP), 2,2-dimethylbutane (2,2-DMB), and 2,3-dimethylbutane (2,3-DMB). Previous papers have reported excess enthalpies for mixtures of each of these isomers with *n*-heptane (*1*), *n*-octane (*2*), and *n*-dodecane (*3*). The present paper describes a similar study of (*n*-decane–isomeric hexane) mixtures.

Excess enthalpies of (*n*-decane–*n*-C6) mixtures have been studied several times in the past (*4*–*6*), but we are unaware of previous measurements on any of the other mixtures.

Experimental Section

Excess molar enthalpies H^{E}_{m} were determined at 298.15 K in an LKB flow microcalorimeter. Details of the equipment and its operation have already been described (*1*, *7*). For most of the measurements, the error in the determination of H^{E}_{m} is estimated to be less than 0.5%. However, it may be somewhat higher for small H^{E}_{m} (<10 J mol^{-1}).

The component liquids were obtained from the Phillips Petroleum Co. and were used without further purification. The *n*-decane was Pure Grade with a purity of at least 99 mol %. The isomeric hexanes were Research Grade with purities exceeding 99.9 mol %. At 298.15 K, the densities (in kg m^{-3}) of the samples used for the calorimetric measurements were as

0021-9568/86/1731-0045$01.50/0 © 1986 American Chemical Society