J. of Supercritical Fluids 55 (2010) 696–700

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Volumetric properties of carbon dioxide + 2-butanol mixtures at 313.15 K

Daisuke Kodama*, Masahiro Kato, Satoshi Hashimoto, Tomoo Kaneko

Department of Chemical Biology and Applied Chemistry, College of Engineering, Nihon University, 1 Nakagawara, Tokusada, Tamura-machi, Koriyama, Fukushima 963-8642, Japan

ARTICLE INFO

Article history:
Received 15 June 2010
Received in revised form 5 September 2010
Accepted 15 September 2010

Keywords:
pVT
Density
Data
Mixture
Carbon dioxide
2-Butanol

ABSTRACT

Volumetric properties were measured of carbon dioxide + 2-butanol mixtures at 313.15 K, using the vibrating tube Anton Paar DMA 512P density meter. In the present experiments, no analytical instrument was required. The saturated pressures were also measured of carbon dioxide + 2-butanol mixtures at 313.15 K by the synthetic method. The experimental data obtained were correlated with the density equation, Soave–Redlich–Kwong (SRK) equation of state, and the pseudocubic equation of state.

1. Introduction

The phase equilibrium properties of mixtures containing supercritical fluid (SCF) at elevated pressures continue to be of importance in process development and research. The growing motivation for studying equilibrium of several coexisting phases arises from the need to describe such phase behavior for fluid mixtures of interest in SCF extraction. A large number of applications of SCF technology have been proposed covering the food, pharmaceutical, chemical reaction, coal and oil processing, waste treatment, plastic recycling, and producing industries. Carbon dioxide is widely used in SCF applications because it has moderate critical temperature and it is nontoxic, nonflammable, and safe with a small impact on the environment. Supercritical carbon dioxide and alcohol are excellent candidates for industrial use because of their unique and suitable solvent properties. 2-Butanol is widely used as the release solvent of paint, the industrial cleaner, and the syntheses for other chemical compound. Recently, carbon dioxide expanded liquids [1] are tunable solvent media for conducting chemical reactions, separations, and materials processing. The application of supercritical carbon dioxide as benign medium in chemistry and chemical engineering satisfies green chemistry. The volumetric properties and vapor–liquid equilibria (VLE) for carbon dioxide + organic solvent mixtures are required to design processes utilizing carbon dioxide as supercritical solvent.

Previously, we have reported volumetric properties data of carbon dioxide + methanol [2], carbon dioxide + ethanol [3], carbon dioxide + 1-propanol [4], carbon dioxide + 2-propanol [5], carbon dioxide + methyl acetate [6], carbon dioxide + ethyl acetate [7], and carbon dioxide + isopropyl ethanoate [8]. For carbon dioxide + 2-butanol mixtures, VLE were reported by some researchers [9–12] without the volumetric properties data.

In the present study, the volumetric properties in the homogeneous region of carbon dioxide + 2-butanol mixtures were measured at 313.15 K. The saturated pressure was also measured by the synthetic method. The density behaviors of fluid mixtures at high pressures were correlated by the density equation [13]. The partial molar volumes of carbon dioxide and 2-butanol were calculated, based on the calculated results by density equation. Furthermore, the experimental saturated pressures obtained were correlated with Soave–Redlich–Kwong (SRK) equation of state [14] and the pseudocubic equation of state [15].

2. Experimental

2.1. Materials

Carbon dioxide was supplied by Showa Tansan Co. Ltd. with 99.999 mol%. 2-Butanol was supplied by Wako Pure Chemical Industries, Ltd. and used without further purification. The purity of 2-butanol was determined to be 99.9 mol% from gas chromatograph peak areas.

2.2. Apparatus and procedures

The apparatus and experimental procedure are those described in previous papers [2–8,16]. In the experiment, carbon dioxide filled to the cell after the evacuation. The pressure difference between

* Corresponding author. Tel.: +81 24 956 8813; fax: +81 24 956 8862.
E-mail address: dkodama@chem.ce.nihon-u.ac.jp (D. Kodama).

0896-8446/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.supflu.2010.09.019

Nomenclature

A, B	composition independent parameters in Eq. (1)
a, b	parameters in pseudocubic EOS (7)
k, l	binary interaction parameters
K_a	correlation factor
M	molar mass [kg kmol^{-1}]
p	pressure [kPa]
R	gas constant [kPa m^3 mol^{-1} K^{-1}]
S	parameter in pseudocubic EOS (11)
T	temperature [K]
v	molar volume [m^3 kmol^{-1}]
$\bar{v}$	partial molar volume [m^3 kmol^{-1}]
x	mole fraction
Z	compressibility factor

Greek symbols

α, β, κ, λ	composition independent parameters in Eq. (1)
ε, θ, σ, ξ	parameters in pseudocubic EOS (7) and (8)
ρ	density [kg m^{-3}]
σ	standard deviation on density [kg m^{-3}]
ω	acentric factor

Subscripts

c	critical property
ij	components
r	reduced property
1	carbon dioxide
2	2-butanol
calc	calculated
expl	experimental

Superscripts

0	pure component
*	reference state in Eq. (1)
#	apparent value
∞	infinite dilution

the upper and lower spaces was kept close to zero, to minimize the leakage between the upper and lower rooms in the cell. The amount of carbon dioxide was determined from the volume and experimental density at the experimental pressure and temperature. The volume of 2-butanol was charged into the cell with the syringe pump with an uncertainty ±0.01 cm^3. The amount of 2-butanol can be determined by the volume and density. The composition of the mixture was evaluated by the amount of carbon dioxide and the one of 2-butanol injected into the cell. As the volume of cell was changed, the volumetric properties of the mixture could be measured at a fixed and known composition. The discontinuity of the pressure as a function of cell volume was shown in Fig. 1, was used as the determinant of the saturated pressure. The saturated densities of the vapor and liquid were measured at the fixed pressure, while maintaining the vapor–liquid equilibrium separation in the cell. The experimental uncertainties of the pressure, density, temperature and composition, respectively, are 0.001 MPa, 0.1 kg m^{-3}, 0.01 K, and 0.001 mole fraction.

3. Correlation

3.1. Density equation

The experimental density data were correlated by the following equation [13].

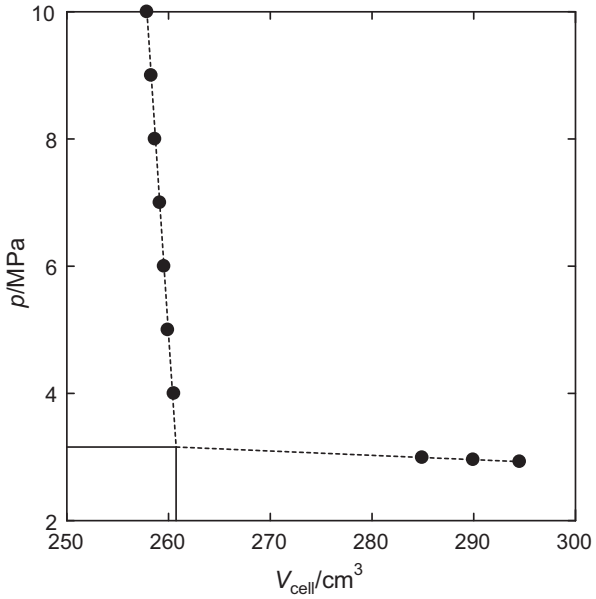

Fig. 1. Typical example of experimental results by synthetic method at 313.15 K, 0.200 CO_2 mole fraction: (●) experimental.

$$\rho = \frac{x_1\rho_1^{0*} + x_2\rho_2^{0*} + \alpha x_1 x_2\{x_1 + \beta x_2/x_1 - \kappa x_1 x_2 + \lambda x_2\}}{1 - \ln\{1 - (1 - (p/p^*)/1 + \exp[A - B/(x_1 + 6x_2)])\}} \quad (1)$$

where, ρ, x, and p, respectively, are density, mole fraction, and pressure. The superscripts, 0 and *, denote pure component and reference state, respectively. p^* means the reference pressure at high pressure. The subscripts, 1 and 2, denote carbon dioxide and 2-butanol, respectively. Eq. (1) has six parameters, α, β, κ, λ, A, and B. Those parameters are independent on composition.

The density data of carbon dioxide + 2-butanol mixtures at 313.15 K have been correlated by the present density Eq. (1). First, the four parameters in Eq. (1), α, β, κ, and λ, were obtained by the optimization of the Marquardt method to minimize the sum of the square of the difference between the calculated density and experimental density at the highest reference pressure p^*, giving the essential restriction to satisfy the experimental density of pure carbon dioxide. Eq. (1) becomes therefore applicable in the full composition range at the reference pressure p^*. Next, the remaining parameters in Eq. (1), A and B, were obtained by the optimization of the Marquardt method to minimize the sum of the square of the difference between the calculated density and experimental one in the composition range of the mole fraction of carbon dioxide from 0.0 to 0.95.

3.2. Partial molar volume

The partial molar volumes of carbon dioxide and 2-butanol were calculated as follows:

$$\bar{v}_1 = v + x_2\left(\frac{dv}{dx_1}\right) \quad (2)$$

$$\bar{v}_2 = v - x_1\left(\frac{dv}{dx_1}\right) \quad (3)$$

where

$$v = \frac{M}{\rho} \quad (4)$$

$$M = x_1M_1 + x_2M_2 \quad (5)$$

in which, v, $\bar{v}$, M, x, and ρ denote molar volume, partial molar volume, molar mass, mole fraction, and density, respectively. The