High-Pressure Vapor−Liquid Equilibrium Data and Modeling of Propane + Methanol and Propane + Ethanol Systems

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Isothermal vapor−liquid equilibrium data for binary systems of propane with methanol and ethanol were measured from 313.55 K to 349.78 K and from 0.3 MPa to 2.8 MPa. A circulating-type apparatus with a view cell was used. The measured data show highly nonideal behavior due to their associating tendency of alcohols, and these make them difficult to correlate reliably with classical theories. The data were correlated with sufficient accuracy by using the equation of state proposed earlier by the authors.

Introduction

Alkane + alkanol mixtures are a class of mixtures that show remarkable deviations from ideal solution behavior; they have attracted particular attention in recent years. Vapor−liquid equilibrium (VLE) data for these mixtures are essential to develop new thermodynamic models and to design and operate new processes. Further, information on high-pressure behavior of fluids has been valuable in the design of new separation processes in various fields such as the food, pharmaceutical, and fine chemical industries.[1] Joung et al.[2] measured VLE data for the CO_2 system with methanol, ethanol, 2-methoxyethanol, and 2-ethoxyethanol binary systems with a circulation-type experimental apparatus. In this work, we measured the equilibrium pressure (P), temperature (T), liquid-phase composition (x), and vapor-phase composition (y) for the propane + methanol and propane + ethanol binary systems.

Experimental Section

Chemicals. Propane gas (>99.9% purity) was purchased from Seoul Special Gas Co. (Seoul, Korea) and used without further purification. Methanol (HPLC grade, >99.9% purity) was obtained from Mallinckrodt, Baker, Inc. (Paris, Kentucky, USA), and ethanol (HPLC grade, >99.9% purity) was purchased from J. T. Baker, Inc. (Phillipsburg, New Jersey, USA). They were used directly without further purification.

Apparatus. Details of this apparatus are described in our previous works.[2] The equipment consists of three major parts: a high-pressure equilibrium cell, pressure and temperature control parts, and sampling devices and analytic parts. The equilibrium cell was equipped with a sapphire window in order to view the contents of the cell. The cell volume is 50 mL, and it was designed to operate safely up to 30 MPa. Temperature was controlled within ±0.1 K by a PID controller, and temperature was measured with an accuracy of ±0.05 K by a RTD. The equilibrium pressure was measured by a Heise gauge (Heise Co., Newtown, Connecticut, USA) within ±0.01 MPa. A hand pump from HIP, Co. (Erie, Pennsylvania, USA), was used to control pressure precisely. By using a circulation pump from Thermo Separation Products, Inc. (Riviera Beach, Florida, USA), the vapor and liquid phases were circulated until the system reached equilibrium.

Propane was fed with an ISCO Syringe Pump from ISCO 260DM (Lincoln, Nebraska, USA). Alcohols were delivered with a liquid pump from Thermo Separation Products, Inc. (Riviera Beach, Florida, USA). The equilibrated samples of the vapor and liquid phases were taken with a sampling valve from Rheodyne L. P. (Rohnert Park, California, USA) and analyzed with an online gas chromatograph from GL Science, Inc. (Tokyo, Japan). The internal volume of the sampling loop for the vapor phase was 5 μL, and for the liquid phase, it was 1 μL.

Procedures. Experiments were carried out in the following manner. An important preliminary step is to thoroughly clean the equilibrium cell and its tubing. Thus, all internal volumes of the apparatus including the equilibrium cell were rinsed several times by both liquid propane and alcohols; the degree of cleanness was checked by analyzing the rinsed liquid propane with a gas chromatograph. Then, any residual solvents and the air occupying the equilibrium cell were evacuated with a vacuum pump from Sinku Kiko Co., Ltd. (Yokohama, Japan), and subsequently, the propane and alcohol samples were fed into the cell.

Circulation of the mixture for several hours brought the system to an equilibrium temperature and pressure. Then, both vapor- and liquid-phase samples were taken and analyzed. Sampling and analysis were repeated three or more times; the mean value was taken as the final measured composition. Also, equilibrium pressures were checked repeatedly and recorded. Measurements were done continuously by increasing the mole fraction of propane gas.

MF−NLF−HB Equation of State Model

The multifluid nonrandom lattice fluid hydrogen-bonding equation of state (MF−NLF−HB EOS) model is an extended version of the MF−NLF model previously formulated by Yoo et al.[3,4] It includes the addition of the theory of hydrogen bonding proposed by Veytsman.[5] Omitting the detail of the MF−NLF−HB derivation,[6] the general ex-

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pression of the model can be written as

$$P = \frac{1}{\beta V_{\mathrm{H}}}\left\{\frac{z}{2}\ln\left[1+\left(\frac{q_{\mathrm{M}}}{r_{\mathrm{M}}}-1\right)\rho\right] - \ln(1-\rho) - v^{\mathrm{HB}}\rho + \frac{z}{2}\sum_{i=1}^{c}\theta_i\left(\frac{\tau_{0i}}{\sum_{k=0}^{c}\theta_k\tau_{ki}} - 1\right)\right\} \quad (1)$$

where $q_{\mathrm{M}} = \sum x_i q_i$, $r_{\mathrm{M}} = \sum x_i r_i$, $\rho = \sum \rho_i$, $\rho_i = V_i^*/V$, $V_i^* = N_a r_i V_{\mathrm{H}}$, and x_i is the mole fraction of species i in a mixture. The fraction of hydrogen bonds in the system, v^{HB}, is given by the summed fraction of pairs of hydrogen bonds given by

$$v^{\mathrm{HB}} = \sum_{m=1}^{K}\sum_{n=1}^{L} N_{mn}^{\mathrm{HB}}/\sum_{i=1}^{c} N_i r_i \quad (2)$$

where, N_{mn}^{HB} is total number of hydrogen bonds between donor of type m and acceptor of type n. The chemical potential of component i in a mixture can be written as the summation of physical contribution and hydrogen bonding contribution. These contributions are expressed as

$$\mu_i = \mu_i^{\mathrm{P}} + \mu_i^{\mathrm{HB}} \quad (3)$$

The chemical potential for species i is given by the sum of physical and chemical (i.e., hydrogen bonding) contributions. These contributions are expressed as

$$\frac{\mu_i^{\mathrm{P}}}{RT} = \lambda_i(T) - r_i\ln(1-\rho) + \ln\frac{\theta_i}{q_i} + r_i\ln\left[1+\left(\frac{q_{\mathrm{M}}}{r_{\mathrm{M}}}-1\right)\rho\right] + \frac{zq_i\theta}{2}\left\{1 - \frac{r_i}{q_i} - \frac{1}{\theta}\left[\ln\sum_{k=0}^{c}\theta_k\tau_{ki} + \beta\epsilon_{ii} + \sum_{l=1}^{c}\frac{\theta_l(\tau_{il} - \tau_{0l}(r_i/q_i))}{\sum_{k=0}^{c}\theta_k\tau_{kl}}\right]\right\} \quad (4)$$

$$\frac{\mu_i^{\mathrm{HB}}}{RT} = -\left(\sum_{m}^{M} d_m^i \ln\frac{N_{\mathrm{d}}^m}{N_{mo}^{\mathrm{HB}}} + \sum_{n}^{N} a_n^i \ln\frac{N_{\mathrm{a}}^n}{N_{on}^{\mathrm{HB}}}\right) \quad (5)$$

where N_{mo}^{HB} is the number of unbonded donors of type m and N_{on}^{HB} is the number of unbonded acceptors of type n. To apply the present MF−NLF−HB model to real systems with specific interaction, it is necessary to estimate the fraction of hydrocarbon bonds in the systems, v^{HB}, given by the fraction summed for mn pairs of hydrogen bonds v_{mn}^{HB}.

The minimization condition for alcohol (1) + hydrocarbon (2) systems gives

$$(N_1 - N_{11}^{\mathrm{HB}})^2 = N_{11}^{\mathrm{HB}} r_{\mathrm{M}} N \frac{1}{\rho}\exp\left(\frac{A_{11}^{\mathrm{HB}}}{RT}\right) \quad (6)$$

The solution of above quadratic is

$$v^{\mathrm{HB}} = \frac{N_{11}^{\mathrm{HB}}}{r_{\mathrm{M}}N} = \frac{2y_1/r_{\mathrm{M}} + Y - (4Yy_1/r_{\mathrm{M}} + Y^2)^{1/2}}{2} \quad (7)$$

where

$$Y = \frac{1}{\rho}\exp\left(\frac{A_{11}^{\mathrm{HB}}}{RT}\right)$$

and $A_{11}{}^{\mathrm{HB}}$ is the Helmholtz free energy for hydrogen bonding of alcohol, which was obtained by the fundamental thermodynamic relation

$$A_{11}^{\mathrm{HB}} = U_{11}^{\mathrm{HB}} - TS_{11}^{\mathrm{HB}} \quad (8)$$

The hydrogen bonding contribution of the chemical potential of alcohol in the binary system is

$$\frac{\mu_1^{\mathrm{HB}}}{RT} = -2\ln\left(\frac{x_1/r_{\mathrm{M}}}{x_1/r_{\mathrm{M}} - v^{\mathrm{HB}}}\right) \quad (9)$$

The hydrogen bonding parameters (U_{11}^{HB}, S_{11}^{HB}) for alcohol were given by Yeom et al.[6] There are four molecular parameters in the physical tem of MF−NLF−HB EOS for pure fluids: z, V_{H}, r_1, and ϵ_{11}. As in the previous study,[3,4,6] we set $z = 10$ and $V_{\mathrm{H}} = 9.75$ cm^3 mol^{-1}. Thus, for a pure fluid we need to determine only two independent molecular parameters, r_1 and ϵ_{11}. The parameters r_1 and ϵ_{11} were regressed at each isotherm and represented as functions of temperature given by

$$\epsilon_{11}/k = E_{\mathrm{a}} + E_{\mathrm{b}}(T - T_0) + E_{\mathrm{c}}[T\ln(T_0/T) + T - T_0] \quad (10)$$

$$r_1 = R_{\mathrm{a}} + R_{\mathrm{b}}(T - T_0) + R_{\mathrm{c}}[T\ln(T_0/T) + T - T_0] \quad (11)$$

where $T_0 = 298.15$ K is a reference temperature. We have one binary energy parameter λ_{12} for a binary, which is defined by

$$\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}(1 - \lambda_{12}) \quad (12)$$

where λ_{12} was determined by regression.

Results and Discussion

The vapor- and liquid-phase equilibrium data were measured for two binary propane + methanol and propane + ethanol systems at temperature ranges from (313.15 to 349.78) K. At an isothermal condition, the vapor- and liquid-phase compositions were measured continuously by increasing the mole fraction of propane. The experimental data for propane + methanol and propane + ethanol systems are summarized in Tables 1 and 2, respectively.

The reliability of the presented system was tested for the CO_2 + methanol system, and the results were given in our previous work.[2] Measured data of CO_2 + methanol at 313.15 K agreed with the high-accuracy data at the same temperature. Further, the results of present work for propane + methanol and propane + ethanol systems were compared with existing reliable data[7,8] in Figures 1 and 2, respectively. The VLE data of the propane + methanol system measured at 313.55 K and the propane + ethanol system measured at 349.78 K agreed quantitatively with existing data.

Measured VLE data were correlated with the MF−NLF−HB EOS. For a VLE data correlation, pure thermodynamic properties are needed such as liquid density and vapor pressure.

Table 1. Measured VLE Data for the Propane(1) + Methanol(2) System

P/MPa	x_1	y_1	P/MPa	x_1	y_1	P/MPa	x_1	y_1
			T = 313.55 K					
0.28	0.0240	0.8300	0.77	0.0931	0.9290	1.34	0.5235	0.9629
0.35	0.0313	0.8615	1.05	0.1590	0.9525	1.38	0.8181	0.9656
0.52	0.0512	0.9112	1.15	0.2146	0.9639	1.39	0.9753	0.9792
0.53	0.0514	0.8989	1.31	0.3575	0.9606			
			T = 327.95 K					
0.35	0.0192	0.7501	1.17	0.1102	0.9165	1.83	0.4059	0.9540
0.66	0.0493	0.8721	1.46	0.1697	0.9402	1.88	0.5083	0.9549
0.94	0.0791	0.9085	1.75	0.2946	0.9518	1.90	0.7414	0.9566
			T = 343.21 K					
0.40	0.0143	0.6380	1.79	0.1468	0.9112	2.48	0.4068	0.9387
0.74	0.0374	0.7864	2.30	0.2068	0.9253	2.54	0.6108	0.9367
1.13	0.0684	0.8610	2.23	0.2455	0.9333	2.58	0.7627	0.9455
1.46	0.1006	0.8933	2.36	0.3187	0.9363			

Table 2. Measured VLE Data for the Propane(1) + Ethanol(2) System

P/MPa	x_1	y_1	P/MPa	x_1	y_1	P/MPa	x_1	y_1
			T = 313.58 K					
0.48	0.0900	0.9651	1.03	0.2710	0.9820	1.32	0.8203	0.9892
0.84	0.1843	0.9781	1.28	0.5432	0.9868	1.34	0.8997	0.9902
			T = 333.99 K					
0.37	0.0415	0.8012	1.39	0.2346	0.9620	2.08	0.8587	0.9790
0.72	0.0925	0.9269	1.74	0.3724	0.9699	0.9699	0.9699	0.9699
1.05	0.1536	0.9486	1.97	0.6556	0.9750	0.9750	0.9750	0.9750
			T = 349.78 K					
0.47	0.0373	0.7646	1.39	0.1552	0.9244	2.33	0.4050	0.9525
0.72	0.0653	0.8533	1.70	0.2146	0.9340	2.66	0.7101	0.9613
1.03	0.1026	0.8914	2.03	0.2968	0.9457	2.83	0.9100	0.9700

The basic property constants for methanol, ethanol, and propane are summarized in Table 3. The pure energy and size parameters of the pure alcohols for the MF−NLF−HB model were computed by using liquid-density and vapor-pressure data.[9] The computed values of the parameter coefficients of eqs 10 and 11 are summarized in Table 4.

The binary interaction parameters, λ_{12}, were regressed with the measured VLE data for each system. The binary adjustable interaction energy parameters (λ_{12}) for MF−NLF−HB EOS are summarized in Table 5. The calculated λ_{12} parameters of EOS model are the independent constants with respect to the variation of the whole range of temperatures. The objective function for evaluating the binary parameter, λ_{12}, was written as

$$\mathrm{OBJ} = \frac{1}{N}\sum_{J} |(x_j^{\mathrm{cal}} - x_j^{\mathrm{exp}})| + \frac{1}{N}\sum_{J} |(y_j^{\mathrm{cal}} - y_j^{\mathrm{exp}})| \quad (13)$$

The average errors between the measured and calculated mole fractions of the liquid phase (Δx) and the vapor phase (Δy) are summarized in Table 5. The average errors in the liquid mole fraction and the vapor mole fraction of propane + methanol system are 0.0331 and 0.0003. Further, the average errors in the liquid mole fraction and the vapor mole fraction of propane + methanol system are 0.0081 and 0.0002. These calculated results were compared with the measured data for propane + methanol and propane + ethanol systems in Figures 1 and 2, respectively. The MF−NLF−HB EOS produced a good correlation in the range from (313.5 to 349.78) K for these nonideal mixtures of alkane + alcohol binary systems.

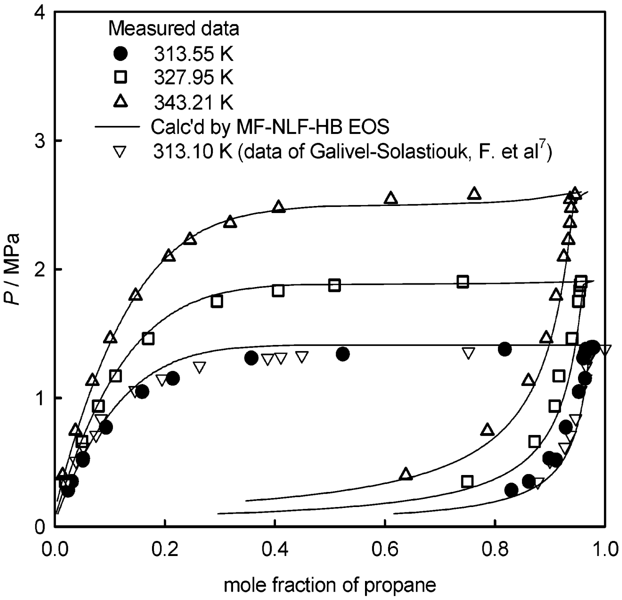

Figure 1. Comparison of measured data with correlated values calculated with the MF−NLF−HB EOS for the propane + methanol system.

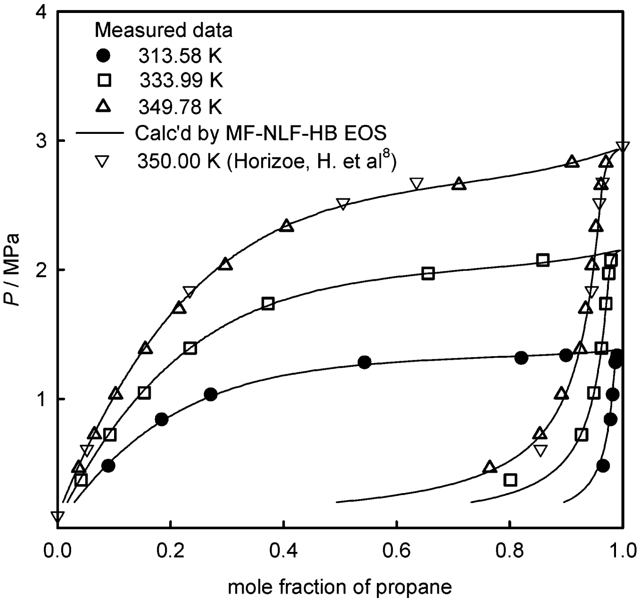

Figure 2. Comparison of measured data with correlated values calculated with the MF−NLF−HB EOS for the propane + ethanol system.

Table 3. Physical Properties of Chemicals Used in This Work

chemical	M_W	T_b/K	T_c/K	P_c/MPa
propane	44.09	231.1	369.7	4.25
methanol	32.04	337.7	512.6	8.09
ethanol	46.07	351.4	513.9	6.14

Table 4. Coefficients of Molecular Parameters for Equations 10 and 11

chemicals	E_a	E_b	E_c	R_a	R_b	R_c
propane	81.2828	0.02206	0.1608	7.0340	−0.0027	−0.0190
methanol	94.1974	0.0506	0.0598	4.9806	0.0024	0.0121
ethanol	101.8944	0.0327	0.1091	5.2337	0.0018	0.0003

Table 5. Binary Interaction Parameters and Average Absolute Deviations for the Equilibrium Data

system	λ_{12}	Δx^a	Δy^b
propane + methanol	0.0719	0.0331	0.0003
propane + ethanol	0.0205	0.0081	0.0002

[a] $\Delta x = 1/N\ \sum_J|(x_j^{\mathrm{cal}} - x_j^{\mathrm{exp}})|$. [b] $\Delta y = 1/N\ \sum_J|(y_j^{\mathrm{cal}} - y_j^{\mathrm{exp}})|$.

List of Symbols

N_i	number of molecular species i
$N_a{}^n$ and $N_d{}^m$	total number of acceptor groups of type n and donor group of type m
P	pressure (Pa)
q_i	surface area parameter
r_i	segment number
R	universal gas constant ($\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$)
S_{mn}^{HB}	entropy of $m-n$ hydrogen bond formation ($\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$)
U_{mn}^{HB}	energy of $m-n$ hydrogen bond formation ($\mathrm{J{\cdot}mol^{-1}}$)
V_{H}	volume of unit cell, 9.75 ($\mathrm{cm^3{\cdot}mol^{-1}}$)
z	lattice coordination number ($z = 10$)

Greek Letters

β	$1/kT$ ($\mathrm{J^{-1}}$)
ϵ_{ij}	interaction energy for ij segment contacts (J)
ν^{HB}	volume fraction of hydrogen bond
θ	surface area fraction
ρ	reduced density defined by $\rho = \sum_{i=1}^{c} N_i r_i / N_r$
τ_{ij}	nonrandomness defined by$\tau_{ji} = \exp\{\beta\ (\epsilon_{ji} - \epsilon_{ii})\}$

Superscripts

HB	hydrogen bonding contribution
P	physical contribution

Subscripts

i, j, k, and l	components i, j, k, and l
ij and mn	interaction pairs ij and mn
M	property of mixture

Literature Cited

(1) McHugh, M. A.; Krukonis, V. J., *Supercritical Fluid Extraction: Principles and Practice;* Butterworth-Heinemann: Boston, 1994.

(2) Joung, S. N.; Yoo, C. W.; Shin, H. Y.; Kim, S. Y.; Yoo, K.-P.; Lee, C. S.; Huh, W. S. Measurements and Correlation of High-Pressure VLE of Binary CO_2−Alcohol Systems (Methanol, Ethanol, 2-Methoxyethanol and 2-Ethoxyethanol). *Fluid Phase Equilib.* **2001**, *185*, 219−230.

(3) Yoo, K.-P.; Shin, H. Y.; and Lee, C. S. Approximate Nonrandom Two-Fluid Lattice-Hole Theory. General Derivation and Description of Pure Fluids. *Bull. Korean Chem. Soc.* **1997**, *18*, 965−972.

(4) Yoo, K.-P.; Shin, H. Y.; Lee, C. S. Approximate Nonrandom Two-Fluid Lattice-Hole Theory. Thermodynamic Properties of Real Mixtures. *Bull. Korean Chem. Soc.* **1997**, *18*, 841−850.

(5) Veytsman, B. A. Are Lattice Models Valid for Fluids with Hydrogen Bonds? *J. Phys. Chem.* **1990**, *94*, 8499−8500.

(6) Yeom, M. S.; Yoo, K.-P.; Park, B. H.; Lee, C. S. A Nonrandom Lattice Fluid Hydrogen Bonding Theory for Phase Equilibria of Associating Systems. *Fluid Phase Equilib.* **1999**, *158*, 143−149.

(7) Galivel-Solastiouk, F.; Laugier, S.; Richon D. Vapor-Liquid Equilibrium Data for the Propane Methanol and Propane Methanol Carbon-Dioxide System. *Fluid Phase Equilib.* **1986**, *28*, 73−85.

(8) Horizoe, H.; Tanimoto, T.; Yamamoto, I.; Kano, Y. Phase Equilibrium Model for the Separation of Ethanol−Water Solution Using Super- and Subcritical Propane Solvent Extraction. *J. Chem. Eng. Jpn.* **1993**, *26*, 482−489.

(9) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 2000.

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