



Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: [www.elsevier.com/locate/molliq](http://www.elsevier.com/locate/molliq)

## Specific behavior of excess enthalpy of binary fluid mixtures near critical loci

Koki Tsukamoto, Takahide Goto, GuoSong Fang, Masahiro Maebayashi, Masaharu Ohba \*

Faculty of Agriculture, Meijo University, Shiogamaguchi 1-501, Tempaku-ku, Nagoya 468-8502, Japan

### ARTICLE INFO

#### Article history:

Received 31 May 2015

Received in revised form 17 December 2015

Accepted 8 February 2016

Available online xxx

#### Keywords:

Supercritical fluid

Phase diagram

PY integral equation

LJ potential

### ABSTRACT

The excess enthalpies for model fluid mixture interacting through the Lennard-Jones potential were calculated using the Percus–Yevick integral equation over wide ranges of temperature and pressure and over the entire mole fraction range. The calculated results near the critical locus reproduced the several specific behaviors founded experimentally in many fluid mixtures, and all these specific behaviors were explained by the phenomena due to the change of the combination of the states of the mixture and its component fluids. Based on this result, the excess enthalpies of the model mixture and the mixture composed of ethane and ethene measured by Gruskiewicz et al. (J. Chem. Thermodynamics, 27, 1995, 507–524) were divided into two contributions, that is, the contribution due to the difference of the states between the mixture and its component fluids and the contribution which reflects the details of the molecular interactions for each mixture. The following results were found from these considerations. The specific behaviors of excess enthalpies near the critical locus are determined by the first contribution, and the excess enthalpies at states far from the critical locus are determined by the second contribution. In intermediate region, the new type specific behavior may arise because of the compensation of these two contributions with similar magnitude.

© 2016 Elsevier B.V. All rights reserved.

### 1. Introduction

Excess enthalpy  $H^E$  and excess volume  $V^E$  of various binary fluid mixtures in supercritical region have been reported by several researchers. The  $H^E$  and  $V^E$  have large positive or large negative values near the critical loci, and these values change complexly with the slight changes of temperature, pressure or composition. The many types of specific behaviors of  $H^E$  and  $V^E$  are found near the critical locus, and at a glance these various behaviors do not seem to be understandable. However, there are some important common features in the behaviors of  $H^E$  and  $V^E$  near the critical locus. For example, S-shaped curves are found in the composition dependences of  $H^E$  or  $V^E$  of many fluid mixtures at a constant temperature and pressure near the critical loci [1–6]. Almost all cases, the skewed composition dependences appear around the states where the S-shaped curves are found. The S-shaped composition dependence has been explained as the phenomena caused by the condensation of a gas-like (low density) fluid into a liquid-like (high density) fluid at the liquid-like fluid rich range and by the vaporization of a liquid-like fluid into a gas-like fluid at the gas-like fluid rich

range [5]. On the other hand, the clear explanation for the skewed composition dependences has not yet been given.

Wormald [7] focused on the relative position on the  $p-T$  plane of the critical points of the component fluids for the mixture, and found the following interesting facts. The mixtures composed of two fluids whose critical pressures are nearly equal show the S-shaped temperature dependences of  $H^E$  and  $V^E$ , and the mixtures composed of two fluids whose critical temperatures are nearly equal show the double maximum in the pressure dependences of  $H^E$  and  $V^E$ . These behaviors were explained as the phenomena caused by the fact that the combination of the states of the mixture and its component fluids changes with changing temperature or pressure. Wormald [7] also pointed out the importance of the shape of the critical locus on the  $p-T$  plane to understand the specific behaviors of  $H^E$  and  $V^E$  near the critical locus.

Previously, we have measured  $H^E$  of the mixture composed of benzene and cyclohexane over the wide ranges of temperature and pressure in liquid state and near the critical locus [8,9]. In these works, by comparing the behavior in the wide region of liquid state with that near the critical locus, the specific behavior of  $H^E$  near the critical locus was made clear. This means that the survey of the behavior over a wide region of states is important to understand the phenomena near the critical locus. And so, we have recently calculated the  $V^E$  [10] for the model mixture composed of two pure fluids whose critical pressures are equal by using the Percus–Yevick (PY) integral equation theory. The calculation was carried out over the wide region of states including the

\* Corresponding author.

E-mail addresses: [n0961501@ccalumni.meijo-u.ac.jp](mailto:n0961501@ccalumni.meijo-u.ac.jp) (K. Tsukamoto), [takahide\\_goto@nnmubpc.meijo-u.ac.jp](mailto:takahide_goto@nnmubpc.meijo-u.ac.jp) (T. Goto), [n0861502@ccalumni.meijo-u.ac.jp](mailto:n0861502@ccalumni.meijo-u.ac.jp) (G. Fang), [mmae@meijo-u.ac.jp](mailto:mmae@meijo-u.ac.jp) (M. Maebayashi), [ohba@meijo-u.ac.jp](mailto:ohba@meijo-u.ac.jp) (M. Ohba).

liquid state, the supercritical state and the gas state. In this recent work, we have shown that the specific behavior of  $V^E$  near the critical locus is caused by changing the combination of the states for the mixture and its component fluids.

In this paper, we calculate  $H^E$  for the same model mixture over a wide region of states including the liquid state, the supercritical state and the gas state, and compare the calculated  $H^E$  of the model mixture with the  $H^E$  of the mixture composed of ethane and ethene to get the total understandings of the various specific behaviors of  $H^E$  near the critical locus described above.

## 2. Model and calculation

### 2.1. Model

The model mixture is composed of two pure fluids A and B. The critical pressures  $p^c$  of the component fluids A and B are equal, and the critical temperatures  $T^c$  of these fluids are different. This model mixture is the same as the one for which we discussed the  $V^E$  in the previous paper [10]. The intermolecular potential is the 12-6 Lennard-Jones (LJ) potential. The Lorentz–Berthelot rule is used as the combining rule for the interaction parameters. The values of the LJ parameters and the critical constants of the component fluids A and B are summarized in Table 1. All quantities in this table and the calculation results described below are non-dimensionalized using the energy parameter and the size parameter of the LJ potential between the molecules A. In addition, in the calculation result in this paper the absolute temperature multiplied by the Boltzmann constant is simply called the “temperature  $T$ ”, though the term “temperature  $T$ ” normally means the absolute temperature.

Fig. 1 shows the critical points on the  $p-T$  plane for the component fluids and the model mixture at  $x_A=0.65$ . Here,  $x_A$  is the mole fraction of the component A. The vapor pressure curves of the component fluids and the critical locus are also shown in this diagram. The critical locus is drawn with a flexible curve to pass through the critical point of the mixture on the  $p-T$  plane. These critical constants and the vapor pressure curves were determined from the Gibbs energy  $G$  calculated by the PY integral equation. The essences of the calculation method of  $G$  using the PY integral equation and of the determination method of the critical point from  $G$  were presented at the 17th IUPAC Conference on Chemical Thermodynamics [11], and these details will be published. The critical locus of the model mixture is slightly curved upward on the  $p-T$  plane. This fact agrees with the experimental results of the binary mixtures in which the critical pressures of the component fluids are almost the same [12–14].

### 2.2. Calculation procedure

Excess enthalpy  $H^E$  of the model mixture composed of the pure fluids A and B is given by

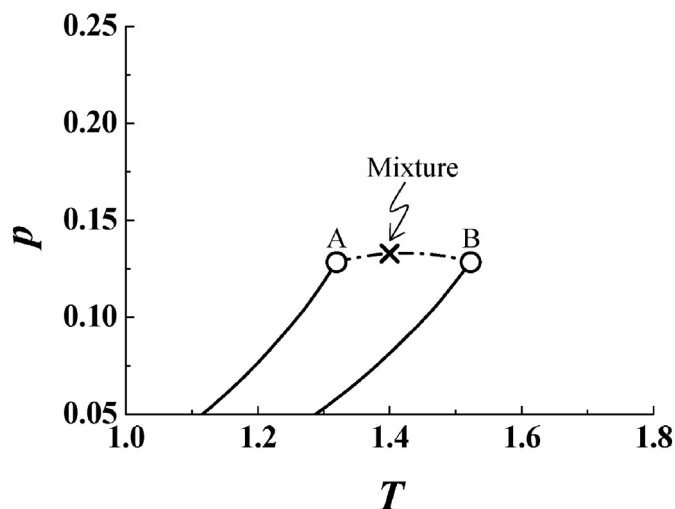
$$H^E(T, p, x_A) = H_m(T, p, x_A) - H_{m,id}(T, p, x_A). \quad (1)$$

$H_m(T, p, x_A)$  in this equation is the molar enthalpy, which is related to the molar internal energy  $U_m$  and the molar volume  $V_m$  by

$$H_m(T, p, x_A) = U_m(T, p, x_A) + pV_m(T, p, x_A). \quad (2)$$

**Table 1**  
The LJ parameters and the critical constants of each component fluid.

Component	$\sigma$	$\varepsilon$	$p^c$	$T^c$
A	1.000000	1.000000	0.129	1.320
B	1.048856	1.153846	0.129	1.523



**Fig. 1.** The critical points of the component fluids and the mixture on the  $p-T$  plane.  $\circ$ , the critical points of the component fluids A and B;  $\times$ , the critical point of the mixture at  $x_A=0.65$  ( $p^c=0.133$ ,  $T^c=1.40$ ); —, the vapor pressure curves of the component fluids A and B; - - -: the critical locus which is drawn by the flexible curve passing through the critical point of the mixture at  $x_A=0.65$ .

where  $V_m$  is related to the total number density  $\rho_t$  by

$$V_m(T, p, x_A) = \frac{1}{\rho_t(T, p, x_A)}. \quad (3)$$

$H_{m,id}(T, p, x_A)$  is the molar enthalpy of the ideal solution corresponding to the model mixture, which is defined by

$$H_{m,id}(T, p, x_A) = x_A H_m(T, p, x_A = 1) + (1 - x_A) H_m(T, p, x_A = 0). \quad (4)$$

Thus, we can calculate  $H^E$  if we obtain  $\rho_t$  and  $U_m$  at the same temperature, pressure and mole fraction. These calculation procedures are as follows. At first, we calculate the direct correlation function  $c_{ij}(r; T, \rho_t, x_A)$  and the radial distribution function  $g_{ij}(r; T, \rho_t, x_A)$  at given  $T$ ,  $\rho_t$  and  $x_A$  by solving the PY integral equation [15], where  $i$  and  $j$  mean A or B. The pressure  $p(T, \rho_t, x_A)$  is obtained by the following equation using the obtained  $c_{ij}$  as [16]

$$\frac{p}{T} = \rho_t + \frac{\rho_t^2}{2} \sum_i \sum_j x_i x_j \int \{ c_{ij}^2 / \tau_{ij} - 2c_{ij} \} dr + \frac{1}{2\pi^3} \int \{ \text{Tr}(\rho \tilde{c}) + \ln \det(1 - \rho \tilde{c}) \} dk, \quad (5)$$

where  $\rho = \rho_t x_i \delta_{ij}$ ,  $\delta_{ij}$  is the Kronecker delta,  $\tilde{c}$  is the matrix whose elements are the Fourier transforms of the  $c_{ij}$  and  $\tau_{ij}(r) = 1 - \exp\{u_{ij}(r)/T\}$  where  $u_{ij}(r)$  is the intermolecular potential. Eq. (5) is the analytically integrated form of the compressibility equation [15] holding only in the PY approximation.

Fig. 2 (a) shows the  $p$  as a function of the set of independent variables  $T$ ,  $\rho_t$  and  $x_A$ . In this diagram,  $T^{x_A}$  is the temperature satisfying that

$$\left( \frac{\partial p}{\partial \rho_t} \right)_{x_A} = \left( \frac{\partial^2 p}{\partial \rho_t^2} \right)_{x_A} = 0. \quad (6)$$

$T^{x_A}$  is not the critical temperature at  $x_A \neq 0$  and  $x_A \neq 1$ , though  $T^{x_A=1}$  and  $T^{x_A=0}$  are the critical temperatures of the pure fluids A and B, respectively. In Fig. 2 (a),  $p_1$  and  $p_2$  at  $T < T^{x_A}$  are the pressures of local minimum and local maximum, respectively. Fig. 2 (b) is the diagram exchanging the vertical axis  $p$  for the horizontal axis  $\rho_t$  in Fig. 2 (a). In Fig. 2 (b),  $\rho_t$  at  $T > T^{x_A}$  is a single-valued function of  $p$ . On the other hand,  $\rho_t$  at  $T < T^{x_A}$  is the triple valued function at  $p_1 < p < p_2$ . In this work, all calculation states are at  $T > T^{x_A}$ , thus  $\rho_t$  is a single-valued

Download English Version:

<https://daneshyari.com/en/article/5410079>

Download Persian Version:

<https://daneshyari.com/article/5410079>

[Daneshyari.com](https://daneshyari.com)