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Molecular simulations of enthalpies for $CH_4-C_2H_6-CO_2$ mixtures at saturation conditions

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Abstract

Enthalpies for methane-ethane-carbon dioxide mixtures at low temperature and high pressure saturation conditions were calculated by the Gibbs ensemble Monte Carlo method. The Lennard-Jones potential function was employed to describe the site-site intermolecular interactions. Molecules of both methane and carbon dioxide were treated as spherical while those of ethane were treated as linear with two methyl groups. The total number of molecules adopted in all simulations was 300. A comparison of the simulated data with the results obtained from the Peng-Robinson equation of state yields a reasonable agreement.

Keywords: Gibbs ensemble Monte Carlo method; Heat of vaporization; Simulation; Ternary system; VLE

1. Introduction

The production, transportation and utilization of natural gas involve unit operations such as compression, expansion, adsorption, distillation and liquification. Thermodynamic properties, e.g. density and enthalpy, for light hydrocarbon mixtures containing carbon dioxide, nitrogen, etc., are essential for the design of these processes. The most reliable method to obtain these properties is through direct experimental determination. However, due to the extreme temperature and pressure conditions encountered by these mixtures, experimental measurements, especially at

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saturation conditions, are difficult to perform. Therefore, no experimental enthalpy data for such ternary systems have been reported in the literature.

Through the consideration of intermolecular interactions and application of statistical mechanics, molecular simulation can be carried out by either the Monte Carlo (MC) or the molecular dynamics (MD) methods for obtaining phase equilibria and thermodynamic properties of model fluids and their mixtures. With rapid development of computer technology and more appropriate potential functions, it is possible in principle to study real and complex systems. The Gibbs ensemble Monte Carlo (GEMC) method [1] is an efficient tool for simulation of phase equilibria. But, only binary mixtures have been studied extensively [2-4]. Calorimetric properties are rarely reported even for binary mixtures.

In this work, we have applied the GEMC method to calculate the enthalpies for a ternary system at saturation conditions. Several mixtures of $CH_4(1)$–$C_2H_6(2)$–$CO_2(3)$ at 220 and 233 K and at pressures from 2.5 to 5.5 MPa were investigated. A comparison of the enthalpy values has been made between the simulation results and the values calculated by the Soave–Redlich–Kwong equation of state.

2. Simulation method

The GEMC method was applied to perform all the simulations. A detailed procedure is available in the literature [1]. Only a brief description is presented here. Because the molecules of ethane were treated as linear, the alpha-face-centered cubic (α-FCC) lattice of dry ice was adopted as the starting configuration. This is different from the configuration originally proposed by Panagiotopoulos et al. [1]. Following the established computational procedures [1], the simulations were performed in cycles, with each cycle consisting of a number of attempted particle displacements, a single volume change attempt and a number of attempted particle interchanges.

In every cycle, 500 displacement trials were carried out within each simulation box in this work for reaching internal equilibrium. These displacements were made following the Monte Carlo algorithm of Metropolis et al. [5]. The maximum step length was dynamically adjusted to produce an approximately 50% acceptance ratio. For the linear ethane molecules, except for the displacement, a predesignated maximum change (12°) in the Euler angles was also made in which a space-fixed axis was selected at random and then a rotation about this axis was performed. A trial volume change was followed to satisfy the condition of equality of pressure in the two simulation boxes or regions. The maximum extent in the volume change was frequently adjusted to make approximately half of the trials successful. To ensure the equality of chemical potentials of all components in the two regions (coexisting phases), 500 random transfers of molecules from one region to the other were implemented by coupling the two regions. A schematic diagram of the computation has been presented by Panagiotopoulos and Stapleton [6].

In all simulations, the total number of molecules employed was 300. For each run, overall configurations of 1.2×10^6 were produced in which the first 3×10^5

states were used for equilibration and the remainder for obtaining the averages of properties.

3. Potential function

For close-packed molecules with no or weak polarities, such as CO_2, CH_4 and N_2, the Lennard-Jones (12-6) potential function has been found to be a reasonable approximation to describe their intermolecular interactions. For more structurally complicated molecules, the group-contribution concept could be adopted by dividing the molecules into several functional groups at first, and then summing up the interactions among all the groups on different molecules i and j

$$u_{ij} = \sum_{a}^{n} \sum_{b}^{m} 4\varepsilon_{ab} \left[\left(\frac{\sigma_{ab}}{r_{ab}} \right)^{12} - \left(\frac{\sigma_{ab}}{r_{ab}} \right)^{6} \right] \qquad r_{ab} = |\vec{r}_{ab}| = |\vec{r}_{ia} - \vec{r}_{jb}| \tag{1}$$

where a and b are groups on molecules i and j, respectively, n and m are the total number of groups for i and j, respectively, r_{ab} is the distance between the mass centers of the two groups, and ε_{ab} and σ_{ab} are the energy and size parameters, respectively, for a group pair of a and b. For hydrocarbons, the optimized parameters for liquid simulations (OPLS) of Jorgensen et al. [7] were employed and potential parameters for carbon dioxide were taken from Van Leeuwen et al. [8]. The potential parameters for the three groups used in this work are summarized in Table 1. The Lorentz–Berthelot (LB) mixing rules were applied to calculate the cross parameters

$$\sigma_{ab} = \frac{(\sigma_{aa} + \sigma_{bb})}{2} \qquad \varepsilon_{ab} = (1 - k_{ab})\sqrt{\varepsilon_{aa}\varepsilon_{bb}} \tag{2}$$

where k_{ab} is an empirical interaction parameter representing the deviation of the cross energy from the geometric average. For the present study, k_{ab} was taken to be zero except for the interaction between the methyl group and CO_2. The binary mixture of CO_2 and C_2H_6 has an azeotropic point indicating that the interaction between the methyl group and carbon dioxide is somewhat complicated. Consequently, there is a need to introduce a non-zero k_{ab} for these two groups.

Table 1
Potential parameters for different groups

Group	σ/Å	(ε/k)/K	Bond length/Å
$-CH_3$	3.775	104.6	1.53
CH_4	3.725	147.8	0.0
CO_2	4.694	243.4	0.0

4. Thermodynamic properties

With component 1 (methane) as the reference, the following reduced properties

$$\begin{aligned} T^* &= \frac{kT}{\varepsilon_{11}} \qquad U^* = \frac{U}{\varepsilon_{11}} \qquad \rho^* = \rho\sigma_{11}^3, \\ P^* &= \frac{P\sigma_{11}^3}{\varepsilon_{11}} \qquad \varepsilon_{ab}^* = \frac{\varepsilon_{ab}}{\varepsilon_{11}} \qquad L^* = \frac{L}{\sigma_{11}} \end{aligned} \tag{3}$$

were used in the course of simulation. Here, T, P, U, ρ and L represent temperature, pressure, energy, density of the system and side length of the central simulation box, respectively. Then the configurational energy and pressure are expressed by

$$U_c^* = \sum_i \sum_{j>i} \frac{u_{ij}}{\varepsilon_{11}} + U_{\mathrm{LRC}}^* \tag{4}$$

$$P^* = \rho^* T^* + \frac{8}{L^{*3}} \sum_i \sum_{j>i} \sum_a^n \sum_b^m \left\{ \frac{(\vec{r}_{ab}\vec{r}_{ij})}{r_{ab}^2} \left[2\left(\frac{\sigma_{ab}}{r_{ab}}\right)^{12} - \left(\frac{\sigma_{ab}}{r_{ab}}\right)^{6} \right] \varepsilon_{ab}^* \right\} + P_{\mathrm{LRC}}^* \tag{5}$$

where $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$. The usual spherical cut-off was made to save computation time. Therefore, the long-range corrections (LRC) to thermodynamic properties in the course of simulation were calculated by

$$\begin{aligned} U_{\mathrm{LRC}}^* &= \frac{8\pi}{3} N\rho^* \sum_a^n \sum_b^m x_{aa} x_{bb} \varepsilon_{ab}^* \left[\frac{1}{3}\left(\frac{\sigma_{ab}}{r_c}\right)^9 - \left(\frac{\sigma_{ab}}{r_c}\right)^3 \right] \\ P_{\mathrm{LRC}}^* &= \frac{16\pi}{3} \rho^{*2} \sum_a^n \sum_b^m x_{aa} x_{bb} \varepsilon_{ab}^* \left[\frac{2}{3}\left(\frac{\sigma_{ab}}{r_c}\right)^9 - \left(\frac{\sigma_{ab}}{r_c}\right)^3 \right] \end{aligned} \tag{6}$$

where r_c is the cut-off radius, taken to be half of the side length of the simulation box in this work, x_{aa} and N represent the mole fraction of the group a and the total number of molecules in one phase, respectively. In the derivation of Eq. (6), the radial distribution function $g(r)$ was taken to be unity for $r > r_c$.

Enthalpies can be readily obtained from the values of energy, pressure and volumes

$$H^* = (U_c^* + U_k^*) + P^*L^{*3} = (U_c^* + U_k^*) + NzT^* \tag{7}$$

where U_k^* is the dimensionless kinetic energy and z is the compressibility factor. For an ideal gas under the same state conditions

$$H_{\mathrm{id}}^* = U_k^* + NT^* \tag{8}$$

Subtracting Eq. (8) from Eq. (7) yields the enthalpy departure

$$\Delta H^{\neq *} = H^* - H_{\mathrm{id}}^* = U_c^* + N(z-1)T^* \tag{9}$$

The molar differential enthalpy of vaporization is the difference in the enthalpy departures between the two coexisting phases and is given by

$$\Delta_{\mathrm{vap}}H^* = \Delta H_{\mathrm{g}}^{\neq *} - \Delta H_{\mathrm{l}}^{\neq *} = (U_{\mathrm{c,g}}^* - U_{\mathrm{c,l}}^*) + N_{\mathrm{A}}(z_{\mathrm{g}} - z_{\mathrm{l}})T^* \tag{10}$$

where N_A is the Avogadro constant, and subscripts g and l denote the vapor and liquid phases, respectively.

5. Results and discussion

The saturation enthalpies for the mixtures of CH_4, C_2H_6 and CO_2 were simulated at the vapor–liquid equilibrium compositions previously simulated [9] by means of the GEMC method. The equilibrium compositions obtained at $T = 233$ K and $P = 4.0$ MPa were used to determine the k_{ab} value of Eq. (2) for the interaction between the methyl group and CO_2. It was found that a value of $k = 0.10$ could reproduce satisfactorily the VLE values measured experimentally by Knapp et al. [10] as shown in Fig. 1.

More simulations were then performed to estimate the saturation enthalpies at 233 and 220 K and as several high pressures. The data obtained are listed in Table 2.

It would be desirable to compare the simulated saturated enthalpies with experimental values, but these are unfortunately not available in the literature. We are not aware of any equations which are specifically developed for estimating saturation enthalpies for the mixtures under consideration. Notwithstanding the uncertainties involved in estimating saturation enthalpies from vapor–liquid equilibrium data by

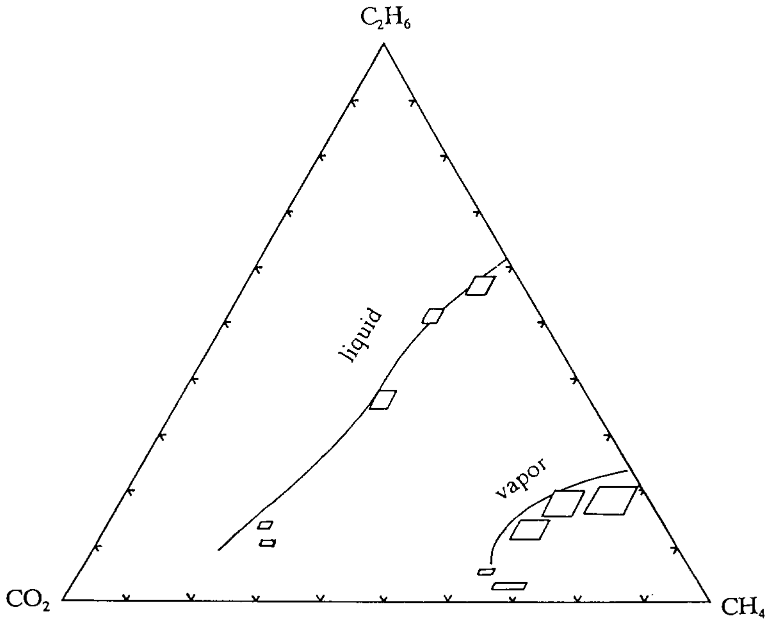

Fig. 1. Vapor–liquid equilibrium values for the mixture of $CH_4(1)$–$C_2H_6(2)$–$CO_2(3)$ at $T = 233$ K and $P = 4.0$ MPa: ——, experimental data from Ref. [10]; □, simulated results including error bonds [9].

Table 2
Simulated enthalpies (in kJ mol^{-1}) for $CH_4(1)$–$C_2H_6(2)$–$CO_2(3)$ under various conditions

x_1	x_2	y_1	y_2	$-\Delta H_g^{\neq PR}$	$-\Delta H_g^{\neq sim}$	$-\Delta H_l^{\neq PR}$	$-\Delta H_l^{\neq sim}$
$T = 220$ K, $P = 2.5$ MPa							
0.135	0.640	0.756	0.235	1.200	0.800	12.034	12.180
0.167	0.223	0.648	0.049	1.149	0.674	12.135	11.960
0.198	0.113	0.662	0.068	1.146	1.181	12.222	12.220
$T = 220$ K, $P = 3.5$ MPa							
0.201	0.086	0.646	0.048	1.809	1.380	12.329	11.140
0.232	0.745	0.727	0.248	1.998	1.443	11.579	12.230
0.237	0.287	0.650	0.101	1.878	1.273	11.213	11.530
0.269	0.534	0.706	0.151	1.828	1.217	10.899	11.320
$T = 220$ K, $P = 4.5$ MPa							
0.328	0.130	0.689	0.053	2.609	2.321	10.603	10.080
0.410	0.273	0.769	0.070	2.271	1.514	9.522	9.440
0.414	0.410	0.777	0.120	2.393	2.013	9.611	9.920
$T = 233$ K, $P = 2.5$ MPa							
0.080	0.263	0.421	0.107	1.328	0.970	12.361	12.220
0.089	0.477	0.468	0.188	1.316	0.862	11.803	12.690
0.094	0.647	0.458	0.362	1.498	1.349	11.795	13.190
0.113	0.756	0.482	0.343	1.445	1.884	11.830	12.540
$T = 233$ K, $P = 3.5$ MPa							
0.186	0.277	0.641	0.071	1.562	1.212	11.117	11.130
0.203	0.331	0.539	0.152	1.875	1.333	10.833	10.580
0.236	0.141	0.590	0.066	1.658	1.247	10.934	10.490
0.240	0.588	0.645	0.211	1.739	1.426	10.605	11.230
$T = 233$ K, $P = 4.0$ MPa							
0.247	0.139	0.634	0.055	1.867	1.288	10.822	9.420
0.264	0.107	0.681	0.033	1.726	1.288	10.730	10.220
0.314	0.363	0.662	0.131	1.911	1.260	9.708	9.620
0.321	0.512	0.690	0.176	1.928	1.587	9.846	10.440
0.367	0.562	0.761	0.183	1.795	1.774	9.625	10.600
$T = 233$ K, $P = 5.5$ MPa							
0.341	0.109	0.719	0.037	2.598	2.008	9.806	9.890
0.378	0.233	0.753	0.067	2.526	1.867	9.150	10.050
0.395	0.125	0.700	0.054	2.744	2.254	9.079	8.840
0.413	0.427	0.787	0.136	2.606	2.195	9.011	9.590

means of an equation of state, such estimations were made to provide an indication of the validity of the simulated values. As the estimated values would give only a qualitative comparison, it was decided to use a simple cubic equation of state for the task.

To begin the selection of a suitable equation, three equations, the Soave–Redlich–Kwong equation [11], the Peng–Robinson equation [12] and the Petel–Teja equation [13], were used to calculate the saturation enthalpies (heats of vaporization) of the three pure components. The calculated results were compared

Table 3
Comparison of calculated and literature values for vapor pressure and latent heat of vaporization for pure CH_4, C_2H_6 and CO_2

Equation of state	CH_4		C_2H_6		CO_2		Ave.
	$\Delta P^{sat}/\%$	$\Delta_{vap}H/\%$	$\Delta P^{sat}/\%$	$\Delta_{vap}H/\%$	$\Delta P^{sat}/\%$	$\Delta_{vap}H/\%$	$\Delta_{vap}H/\%$
Soave–Redlich–Kwong	1.18	3.57	0.78	3.62	1.10	2.97	3.39
Peng–Robinson	0.42	2.60	0.17	2.85	1.85	2.46	2.64
Petel–Teja	0.78	3.12	0.32	3.10	0.25	1.77	2.66

with the literature values compiled by Canjar and Manning [14], and the comparison is summarized in Table 3. It appears that the Peng–Robinson equation yields the best results. Consequently, the Peng–Robinson equation was selected for calculation of the saturation enthalpies for the mixtures of CH_4, C_2H_6 and CO_2. In the calculation, the conventional mixing rules were employed, namely

$$\begin{aligned} a &= \sum_i \sum_j x_i x_j (1 - l_{ij}) \sqrt{a_{ii} a_{jj}} \\ b &= \sum_i \sum_j x_i x_j \frac{b_{ii} + b_{jj}}{2} \end{aligned} \tag{11}$$

The enthalpy departure is expressed by

$$\Delta H^{\neq} = \frac{a}{b} \left(1 - \frac{T}{a} \frac{\partial a}{\partial T} \right) \ln \frac{z}{z + B^*} + RT(z - 1) \tag{12}$$

where

$$B^* = \frac{bP}{RT} \quad \text{and} \quad z = \frac{PV}{RT}$$

In Eqs. (11) and (12), values of l_{ij} for the three binary systems have been reported by Knapp et al. [15] for the Peng–Robinson equation. Their reported values for the three parameters are $l_{12} = -0.0059$, $l_{13} = 0.0978$, and $l_{23} = 0.1300$.

Using these binary l_{ij} values, the ternary vapor–liquid equilibrium values for the CH_4–C_2H_6–CO_2 mixtures predicted by means of the Peng–Robinson equation are in good agreement with the experimentally determined values [10]. The calculated $\Delta H^{\neq}$ values using the same l_{ij} values are also included in Table 2 for comparison. Although our simulated results are usually higher than the results calculated from the experimental vapor–liquid equilibrium values by an average of about 20%, the two sets of data are in reasonable agreement with each other. It appears that the MC method can be used not only for phase equilibria but also for calorimetric properties.

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