Korean J. Chem. Eng., **26**(1), 220-224 (2009)

Measurement of excess enthalpies using a high-pressure flow microcalorimeter and determination of binary interaction parameters for thermodynamic models

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(*Received 29 August 2008 • accepted 17 November 2008*)

Abstract−While an equation of state (EOS) plays a critical role in estimating thermodynamic properties, employing it in the determination of binary interaction parameters is extremely important. In general, these parameters can be determined from phase equilibrium data. However, data collection from experiments is a time-consuming and tedious process. In this study, after measuring the excess enthalpies of binary systems containing CO_2 by high-pressure flow isothermal microcalorimetry (IMC), we determined the EOS binary interaction parameters, specifically, the Peng-Robinson EOS binary interaction parameters. These binary interaction parameters obtained by IMC were compared with those obtained by vapor-liquid equilibrium (VLE) experiments. Hence, high-pressure flow IMC appears to be an effective method for the determination of interaction parameters that are used in the estimation of thermodynamic properties. Further, the Flory-Huggins interaction parameters of a binary mixture CO_2 containing with various mole compositions were also estimated by employing high-pressure IMC.

Key words: Equation of State, Isothermal Microcalorimetry (IMC), Peng-Robinson EOS, Flory-Huggins Interaction Parameter

INTRODUCTION

Environmentally benign supercritical fluid solvents, in particular, CO_2, (T_C=304 K, P_C=7.4 MPa), have received a great deal of attention; these SCFs have replaced traditional toxic solvents in many chemical processes. However, the nonideal behavior of molecules at high pressures makes the determination of fundamental thermodynamic properties and parameters in mixtures a highly challenging task. There exist several methods for determining the interaction parameters of binary systems containing CO_2. Although vapor liquid equilibria (VLE) data are sufficiently reliable for the development of thermodynamic models, the data collection process itself is highly tedious; hence, there is a strong demand for an alternative approach. It is well known that calorimetry is a highly reliable method [1] that can be used to obtain excess molar enthalpies, H^E, for the determination of binary interaction parameters by regression.

Park and Lee [2] determined the H^E values of methyl *tert*-butyl ether and methanol system at 363.15 K and atmospheric pressure by employing IMC. At 313.15 K and 7.64 MPa the H^E values for a mixture of supercritical CO_2 and linalool were measured by using a high-pressure isothermal calorimeter [3]. The binary interaction parameters were reported as 0.116 and 0.1087 by applying both the Soave-Redlich-Kwong equation of state (EOS) and the Peng-Robinson (PR) EOS, respectively. Ochi et al. [4] performed experiments by using IMC to obtain the H^E values for a system containing supercritical CO_2 and alcohols. They reported large changes in the H^E values by varying the pressure.

The Flory-Huggins interaction parameter χ of a binary mixture in the presence of CO_2, in particular, at a high pressure plays a critical role in determining the osmotic repulsive potential in many chemical systems such as gas expanded liquid systems [5]. To our best knowledge, the estimation of χ using high-pressure IMC has not been reported yet. Because the H^E data are scarce, obtaining these data itself, especially, at a high pressure, would be a significant contribution.

In this study, the H^E values were determined for a {benzene+n-hexane} system at 298.15 K under atmospheric pressure and for {CO_2+n-hexane} and {CO_2+n-heptane} systems at 313.15 K and 8.27 MPa by employing the high-pressure IMC. The experimental IMC data were used to determine the PR EOS binary interaction parameters for the {CO_2+n-hexane} and {CO_2+n-heptane} systems, and these parameters were compared with those obtained by the VLE data. The H^E values of the {n-hexane+n-dodecane} binary system at 298.15 K and atmospheric pressure and that of the {CO_2+n-hexane} and {CO_2+n-dodecane} binary mixtures at 298.15 K and 6.89 MPa were reported, from which χ was estimated.

EXPERIMENTAL

1. Materials

n-Hexane (purity: >98.5%) and benzene (purity: >99.5%) were purchased from Aldrich Co., and n-heptane (purity: >99%) and n-dodecane (purity: >98%) were purchased from Kanto Chemical Co. and used as such. SFC-grade carbon dioxide supplied by a local gas company (Sebotech Inc., S. Korea) had a reported purity of 99.999%. All the chemicals were used as-received without further purification.

2. Experimental Apparatus and Methods

An isothermal high-pressure flow microcalorimeter (Computer Sciences Co. Lanham-Seabrook, MD., model CSC 6825), a thermostatic water bath (Poly Science, model 9501), a high pressure pump (M930 pump, Younglin, Korea), and an HPLC pump (Acu-

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flow series II) were used to conduct the experiment. The water bath controls the temperature of the heat sink where the mixing cell, reference cell, and thermoelectric sensors are located. The temperature of the bath is controlled to within ±0.05K. A typical experimental setup was used at atmospheric pressure, and a more detailed description has been reported elsewhere [6,7]. Fig. 1 illustrates an experimental setup used at a high pressure in the presence of CO_2. The liquid component was delivered by a high-pressure pump into a mixing tee that was placed just ahead of the microcalorimeter. CO_2 was delivered into the mixing tee by using a high-pressure booster in the other side stream. To determine the flow rate of the system, the flow meter was placed just after the microcalorimeter. The molar ratio of the two mixing streams was calculated from the molecular weight, densities, and volumetric flow rates. Great care is required to be taken to obtain the experimental data at a constant temperature because microcalorimetry is extremely sensitive to temperature variations during the course of the experiment. In this study, the temperatures of the streams were kept constant in a water thermostat and preheater.

The experimental results for the binary mixture are listed in Table 1. To confirm the experimental data obtained from this experiment, our data were compared with the previously published data [8]. As can be seen in Fig. 2, the 5th order polynomial regression deter-

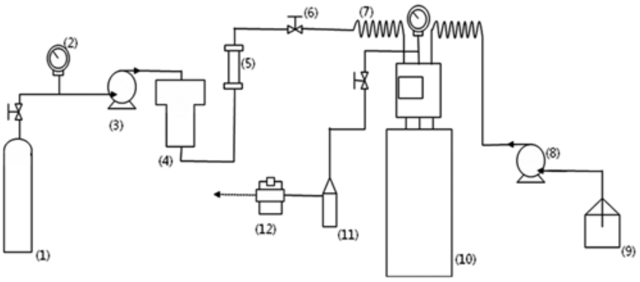

Fig. 1. Schematic diagram of experimental setup.

1. CO_2 gas cylinder	7. Preheater
2. Pressure gauge	8. High pressure pump
3. High pressure booster	9. Liquid reservoir
4. Buffer tank	10. Isothermal microcalorimeter
5. Check valve	11. Liquid trap
6. Valve	12. Fflow meter

Table 1. Comparison of experimental data of this study with Casas et al. [8] for {benzene+n-hexane} binary system at 298.15 K and 0.1013 MPa

Mole fraction of benzene	Lit. H^E [J/mol]	Mole fraction of benzene	Exp. H^E [J/mol]
0.069	200	0.071	246
0.145	399	0.108	365
0.215	562	0.217	581
0.267	657	0.439	879
0.283	689	0.542	922
0.344	785	0.631	904
0.385	839	0.668	882
0.404	857	0.720	825
0.462	899	0.860	599
0.537	939	0.920	466
0.557	938	0.946	280
0.558	939	0.981	181
0.567	933		
0.602	928		
0.633	901		
0.691	848		
0.734	793		
0.763	752		
0.826	614		
0.860	532		
0.897	402		
0.936	277		
0.966	153		

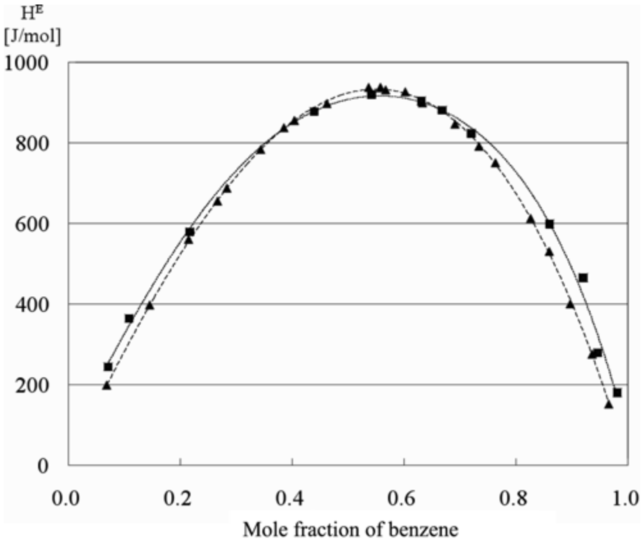

Fig. 2. Comparison of experimental data with that obtained from literature for {benzene+n-hexane} binary system at 298.15 K (▲: literature [8], ■: this work, lines are obtained by polynomial regression).

Table 2. Excess molar enthalpy, H^E, for the {carbon dioxide+n-hexane} system at 8.96 MPa and 313.15 K

Mole fraction of CO_2	Exp. H^E [J/mol]	Calc. H^E [J/mol]
1	0	0
0.84	−2167.41	−1829.87
0.61	−1763.73	−1556.63
0.54	−1568.82	−1420.04
0.49	−1407.49	−1297.54
0.44	−1274.74	−1191.21
0.38	−1092.93	−1038.09
0.31	−838.02	−866.27
0.32	−876.18	−903.34
0.26	−722.51	−752.20
0.21	−609.27	−611.09
0.18	−533.35	−535.66
0.16	−478.73	−480.63
0	0	0

mined standard deviation between literature values and the result of this work of 20.3 and the average of error of 31.2.

RESULTS AND DISCUSSION

The experimental H^E values of the {CO_2+n-hexane} and {CO_2+n-heptane} binary systems were obtained at 8.96 MPa and 313.15 K and listed in Tables 2 and 3, respectively, from which the Peng-Robinson EOS binary interaction parameters were also determined. The H^E values of the {n-hexane+n-dodecane} binary mixtures at 298.15 K and atmospheric pressure and that of the {CO_2+n-dodecane} binary mixtures at 298.15 K and 6.89 MPa were obtained so as to estimate the χ values at various molar concentrations. It appears that the experimental H^E data obtained by using (high-pressure) IMC compared to the traditional VLE data are quite reliable to determine both the Peng-Robinson interaction parameters and the Flory-Huggins interaction parameters.

Table 3. Excess molar enthalpy, H^E, for the {carbon dioxide+n-heptane} system at 8.96 MPa and 313.15 K

Mole fraction of CO_2	Exp. H^E [J/mol]	Calc. H^E [J/mol]
1	0	0
0.88	−2498.14	−2066.91
0.79	−2217.89	−2077.46
0.66	−1805.27	−1886.78
0.58	−1588.77	−1727.52
0.52	−1429.21	−1594.40
0.41	−1143.52	−1294.65
0.38	−1028.71	−1184.56
0	0	0

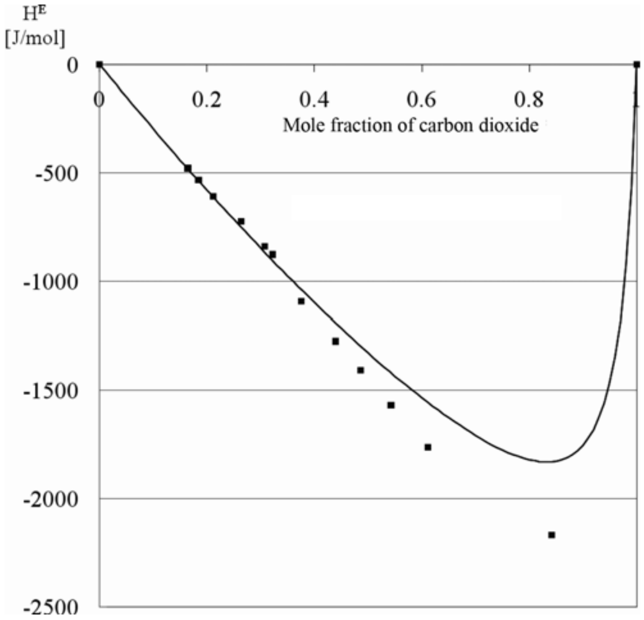

Fig. 3. Experimentally measured H^E values of {carbon dioxide+n-hexane} binary system at 8.96 MPa and 313.15 K (–: calculated result from the Peng-Robinson equation of state).

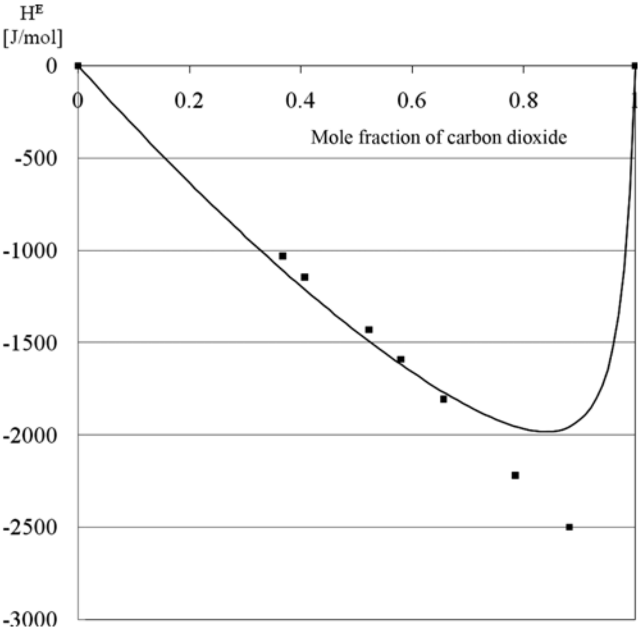

Fig. 4. Experimentally measured H^E values of {carbon dioxide+n-heptane} binary system at 8.96 MPa and 313.15 K (–: calculated result from the Peng-Robinson equation of state).

1. Determination of the Peng-Robinson (PR) EOS Interaction Parameters

Figs. 3 and 4 show the plots of the experimental H^E data of the {CO_2+n-hexane} and {CO_2+n-heptane} binary systems, respectively, versus various mole fractions of CO_2. It is evident that the H^E values of these binary mixtures were negative. We used the experimental results and the classical van der Waals mixing rule to obtain the Peng-Robinson EOS binary interaction parameters [9]. The lines in both Fig. 3 and 4 represent calculated results by using the PR equation of state. In Fig. 4, the estimated values are deviated from the values obtained experimentally, especially at higher CO_2 mole fraction. One possible explanation for this discrepancy between the data estimated and experimental data is that the mixing rule obtained at lower CO_2 mole fraction was applied to this estimation.

The PR EOS can be written in terms of the compressibility factor Z:

$$Z=\frac{1}{(1-b\rho)}-\frac{a\rho/RT}{(1+2b\rho-b^2\rho^2)} \tag{1}$$

where ρ is molar density and R is the universal gas constant.

The H^E values can be calculated by using the following equation [10]:

$$H^E=H^R-\sum(x_iH_i^R) \tag{2}$$

where H^R is the molar residual enthalpy. Lewis et al. [11] derived the following equation to obtain the H^R values from an equation of state.

$$\frac{H^R}{RT}=(Z-1)-\frac{1}{RT}\int_V^\infty\left\{T\left(\frac{\partial P}{\partial T}\right)_V-P\right\}dV \tag{3}$$

Combining Eqs. (1) and (6), Eq. (8) is obtained for a mixture and

(9) for a pure component i. A detailed derivation can be found elsewhere [7].

$$\frac{H^R}{RT}=(Z-1)+\left[\frac{T\left(\frac{\partial a}{\partial T}\right)-a}{2\sqrt{2}bRT}\ln\left(\frac{Z+2.414B}{Z-0.414B}\right)\right] \tag{4}$$

$$\frac{H_i^R}{RT}=(Z_i-1)+\left[\frac{T\left(\frac{\partial a_i}{\partial T}\right)-a_i}{2\sqrt{2}b_iRT}\ln\left(\frac{Z_i+2.414B_i}{Z_i-0.414B_i}\right)\right] \tag{5}$$

The binary interaction parameters obtained from the H^E data are presented in Table 4, and they were found to be very similar to those obtained by the VLE data [12]. Specifically, the binary interaction parameter for the {CO_2+n-hexane} system obtained by the VLE was 0.11 and that obtained by this study using high-pressure IMC was 0.0974.

2. Determination of the Flory-Huggins Interaction Paramters

To extend the usage of H^E for a binary system at a high pressure, a well-known equation was applied to estimate the χ value as shown below.

$$H^E=RTx_A\phi_B\chi \tag{6}$$

where x_A is the mole fraction of component A, and ϕ_B is the volume fraction of component B in the binary mixture. Table 5 shows the χ values of the n-hexane and dodecane binary system at 298 K and atmospheric pressure. As the mole fraction of n-hexane was increased from 0.2473 to 0.9295, the χ value decreased from 0.0574 to 0.0487. However, at a relatively high pressure of 6.89 MPa, the changes in the χ values of the binary system containing CO_2 were quite significant. Tables 6 and 7 show the χ values of the {CO_2+n-hexane} and {CO_2+dodecane} systems at 313.15 K and 6.89 MPa, respectively. As the mole fraction of CO_2 was decreased from 0.933 to 0.279 in the {CO_2+dodecane} binary system, the χ value decreased from 0.3181 to 0.1375. This result may illuminate the fact that the effect of pressure on the χ value in binary systems containing CO_2 is quite significant. Hence, it is strongly recommended that an accurate χ value be ascertained in molecular level thermodynamic calculations. This is partly because the dependence of the χ value on the composition and pressure is markedly higher than we expected. However, as the CO_2 mole fraction was increased from 0.615 to 0.749 χ value decreased from 0.1670 to 0.1576. This result may be triggered by the experimental error.

Table 4. Estimation of Peng-Robinson EOS binary interaction parameter by using the VLE data and H^E data

System	From VLE data [12]	From H^E data (this work)
CO_2+n-hexane	0.11	0.0974
CO_2+n-heptane	0.11	0.0996

Table 5. The Flory-Huggins interaction parameter χ of n-hexane and n-dodecane system at 298.15 K and atmospheric pressure

Mole fraction of n-hexane	Volume fraction of n-hexane	χ
0.9295	0.8834	0.0487
0.7759	0.6653	0.0408
0.7017	0.5746	0.0410
0.6764	0.5456	0.0428
0.6686	0.5368	0.0436
0.5036	0.3681	0.0505
0.2473	0.1587	0.0574

Table 6. The Flory-Huggins interaction parameter χ of CO_2 and n-hexane system at 313.15 K and 6.89 MPa

Mole fraction of CO_2	Volume fraction of CO_2	χ
0.9078	0.4634	0.1906
0.7108	0.1774	0.1243
0.4779	0.0743	0.1105
0.4368	0.0637	0.1093

Table 7. The Flory-Huggins interaction parameter χ of CO_2 and dodecane system at 313.15 K and 6.89 MPa

Mole fraction of CO_2	Volume fraction of CO_2	χ
0.933	0.5923	0.3181
0.839	0.3519	0.1771
0.749	0.2378	0.1576
0.615	0.1427	0.1670
0.553	0.1145	0.1457
0.279	0.0388	0.1375

CONCLUSIONS

By employing high-pressure flow IMC, the H^E values of {CO_2+n-hexane} and {CO_2+n-heptane} systems were obtained at 8.27 MPa and 313.15 K. Both binary systems were exothermic over the entire range of mole fractions of CO_2. The binary interaction parameters obtained from the H^E data were very similar to those obtained by the VLE data. The Flory-Huggins interaction parameter χ of the {n-hexane+n-dodecane} system at 298.15 K and atmospheric pressure was determined by using high-pressure IMC. The χ value was strongly dependent on the composition of the binary mixture. The χ values of the {CO_2+n-hexane} and {CO_2+n-heptane} systems at 313.15 K and 6.89 MPa were also determined. The dependence of χ on the mole composition of the binary mixtures containing CO_2 was so remarkable that an accurate estimation of χ at a high pressure is strongly recommended for molecular level thermdynamic calculations, for example, for the estimation of the ostmotic repulsion potential in gas-expanded liquid systems.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the Korea Ministry of Commerce, Industry & Energy and the Korea Energy Management Corporation.

APPENDIX A.
THE PENG-ROBINSON EQUATION OF STATE

For pure substances:

$$P=\frac{RT}{V-b}-\frac{a}{V(V+b)+b(V-b)} \tag{A-1}$$

$$a=\frac{0.45724R^2T_c^2\alpha}{P_c} \tag{A-2}$$

$$b=\frac{0.07780RT_c}{P_c} \tag{A-3}$$

$$\alpha=\left[1+\kappa\left(1-\sqrt{\frac{T}{T_c}}\right)\right]^2 \tag{A-4}$$

$$\kappa=0.37464+1.54226\omega-0.26992\omega^2 \tag{A-5}$$

where R is the ideal gas constant, and T_c is the critical temperature, and P_c is the critical pressure, and ω is the acentric factor.

For mixtures:

$$P=\frac{RT}{V-b_m}-\frac{a_m}{V(V+b_m)+b_m(V-b_m)} \tag{A-6}$$

where the constants a_m and b_m are expressed as functions of the concentration of the different components in the mixture, through mixing rules.

APPENDIX B. THE VAN DER WAALS MIXING RULE

$$a_m=\sum_i\sum_j x_ix_j\sqrt{a_ia_j}(1-k_{ij}) \tag{A-7}$$

$$b_m=\sum_i\sum_j x_ix_j\sqrt{b_ib_j}(1-\beta_{ij}) \tag{A-8}$$

where k_{ij} and β_{ij} are binary interaction parameters.

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