Excess Enthalpy and Vapor-Liquid Equilibrium Prediction Using Non-Random Fluid Lattice Equation of State[1]

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Abstract

Although an equation of state can be applied to volumetric properties, phase equilibria and excess enthalpy calculations, few works have been published for a unified application . This study presents the consistent application of lattice fluid model of You et al. Using pure component parameters fitted to saturation density and vapor pressure, binary interaction parameters were determined. The binary parameter was found more sensitive to enthalpy. The linear temperature dependence of this parameter was found adequate. The method yields good results except for polar-nonpolar mixtures, for which systems errors in vapor liquid equilibria appear magnified.

Introduction

Excess enthalpy is one of important thermophysical properties needed in the process design and simulation. However, compared with volumetric or phase equilibrium properties, less progress has been made done either in experiments or in prediction methods. Enthalpy may be calculated from Helmholtz free energy or Gibbs free energy using classical thermodynamic relations in principle. Thus methods based on UNIFAC[1] or on DISQUAC[2] have been proposed. Equation of state based methods[3,4,5] have also been proposed which are specific to enthalpy calculation. Enthalpy calculation is sensitive to temperature derivative of parameters. Other properties are calculated at a fixed temperature and parameters are less sensitive to temperature.

Authors has been working on a lattice fluid theory[6,7] and its group contribution methods[8,9]. This theory was found to provide good descriptions of volumetric and phase equilibrium properties of both vapor and condensed phases. In this work we explore the applicability of the theory in the excess enthalpy calculation.

Lattice-Hole Equation of State

You et al.[6,7] derived an approximate and explicit solution to the Guggenheim combinatory[10] by expanding Helmholtz free energy around the reference athermal solution. The model uses two temperature dependent parameters for pure species, ε_{ii} and V_i^*, and one binary energy parameter, λ_{ij}.

$$\varepsilon_{ii}/k = \varepsilon_a + \varepsilon_b T + \varepsilon_c \ln T \; ; \; \varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}(1-\lambda_{ij}) \tag{1}$$

$$V_i^* = V_a + V_b T + V_c \ln T \tag{2}$$

r_i is calculated from V_i^* by the relation,

$$V_i^* = r_i N_a V_H \tag{3}$$

and q_i is related to r_i,

$$zq_i = (z-2)r_i + 2 \tag{4}$$

where z and V_H are constants which are equal to 10 and 9.75 cm3/mol, respectively, and N_a is the Avogardro's number.

Expressions for thermodynamic properties are obtained from Helmholtz free energy. For equation of state and chemical potential,

$$P = \left(\frac{1}{\beta V_H}\right)\left\{\left(\frac{z}{2}\right)\ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right] - \ln(1-\rho)\right\} - \left(\frac{z}{2}\right)\theta^2\left(\frac{\varepsilon_M}{V_H}\right) \tag{5}$$

$$\frac{\mu_i^{\Pi}}{RT} = \gamma_i + r_i \ln(1-\rho) + \ln\left(\frac{\theta_i}{q_i}\right) + r_i \ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right] - \frac{zq_i\beta\varepsilon_M\theta^2}{2}$$

$$\times\left[1-\frac{r_i}{q_i} - \frac{2\sum\theta_j\varepsilon_{ij} + \beta\sum\sum\sum\theta_k\theta_l\theta_m\varepsilon_{ik}(\varepsilon_{ik}+\varepsilon_{lm}-\varepsilon_{kl}-\varepsilon_{il})}{\theta^2\varepsilon_M}\right] \tag{6}$$

where

$$\varepsilon_M = \left(\frac{1}{\theta^2}\right)\left[\sum\sum\theta_i\theta_j\varepsilon_{ij} + \left(\frac{\beta}{2}\right)\sum\sum\sum\sum\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}\left(\varepsilon_{ij}+3\varepsilon_{kl}-2\varepsilon_{ik}-2\varepsilon_{jk}\right)\right] \tag{7}$$

$$q_M = \sum x_i q_i \quad r_M = \sum x_i r_i \quad \sum X_i = 1 \tag{8}$$

$$\theta_i = x_i q_i/(x_0 + q_M) \qquad x_0 = N_0/\sum N_i \qquad \theta = \sum\theta_i \tag{9}$$

$$V = V_H\left(\sum N_i\right)(x_0 + r_M) \quad \rho = \sum V_i^*/V \tag{10}$$

Here N_i is the number of molecules of species i. The sum is over all molecular species and subscript 0 denotes holes.

The configurational internal energy is also obtained from Helmholtz free energy,

$$\frac{\beta U^c}{N} = \frac{zq_M'}{2}\ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right] + \frac{z\beta q_M}{2\theta}\left[\sum\sum\theta_i\theta_j\varepsilon_{ij}\left(\frac{q_i'}{q_i}+\frac{q_j'}{q_j}-\frac{q_M'}{q_M}\theta+\frac{\varepsilon_{ij}'}{\varepsilon_{ij}}-1\right)\right.$$
$$+\frac{\beta}{2}\sum\sum\sum\sum\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}\left\{\left(\varepsilon_{ij}+\varepsilon_{kl}-\varepsilon_{ik}-\varepsilon_{jk}\right)\times\left(\frac{q_i'}{q_i}+\frac{q_j'}{q_j}+\frac{q_M'}{q_M}\theta+\frac{\varepsilon_{ij}'}{\varepsilon_{ij}}-2\right)\right. \tag{11}$$
$$\left.\left.-\frac{q_M'}{q_M}\theta\left(2\varepsilon_{ij}+4\varepsilon_{kl}-3\varepsilon_{ik}-3\varepsilon_{jk}\right)+\varepsilon_{ij}'+\varepsilon_{kl}'-\varepsilon_{ik}'-\varepsilon_{jk}'+\frac{q_k'}{q_k}\left(\varepsilon_{kl}-\varepsilon_{ik}-\varepsilon_{jk}\right)+\frac{q_l'}{q_l}\varepsilon_{kl}\right\}\right]$$

where primed quantities denotes derivatives with respect to lnT.

$$\varepsilon_{ij}' = \frac{\varepsilon_{ij}}{2}\left(\frac{\varepsilon_{ii}'}{\varepsilon_{ii}}+\frac{\varepsilon_{jj}'}{\varepsilon_{jj}}-\frac{\lambda_{ij}'}{1-\lambda_{ij}}\right) \tag{12}$$

$$q_i' = r_i'\frac{z-2}{z} = \frac{(V_i^*)'}{N_a V_H}\frac{z-2}{z} \tag{13}$$

Finally, excess enthalpy is the departure from ideal solution behavior as follows.

$$H^E = (U^c + PV)_{mixture} - \sum x_i (U^c + PV)_{pure,i} \tag{14}$$

Result and Discussion

Parameters for ε_{ii} and V_i^* are given in references 6. They have been determined from saturated liquid density and vapor pressure below the critical temperature. Above the critical temperature volumetric properties are used. The binary energy parameter λ_{ij} are fitted to phase equilibrium properties and reported in the same references as constants for some selected systems in limited temperature ranges. However, the temperature derivative of the binary parameter in eqn (1) turns out to be very sensitive to the enthalpy calculation. Therefore we assume the linear temperature dependence which was determined by fitting both phase equilibrium properties and excess enthalpy data.

$$\lambda_{ij} = a + bT \tag{15}$$

The results are summarized in table 1. Vapor liquid equilibrium is seen generally well represented by the theory. Excess enthalpies for both nonpolar-nonpolar and polar-polar mixtures are satisfactory. However, it is seen that somewhat increased errors in vapor liquid equilibria for polar- nonpolar mixture are magnified in enthalpy calculation. It is likely that the difference of the specific interaction is more sensitive to the enthalpy calculation. Since no other methods for enthalpy calculation which is consistent with equilibrium calculation are known to the authors we do not present comparisons with other methods.

Results of significance are presented by figures to follow and discussed. Fig. 1 shows excess enthalpies for benzene - n-alkane mixtures. The large differences in molecular size is seen accurately reproduced for these nonpolar-nonpolar mixtures. An advantage with the use of an equation of state is that the pressure dependence can be calculated. Excess enthalpies for cyclohexane - n-hexane mixture in Fig. 2 shows that the pressure dependence is well described by the present method.

Methanol - 1-butanol mixture in Fig. 3 is an example of polar-polar mixtures and the calculated results are seen accurate. But a large error for n-hexane - 1-hexanol system as shown in Fig. 4 indicates that further work is needed for these systems. Probably the association effect need to be considered. We also need to explore the applicability of the method to systems with more complex concentration dependence.

Conclusion

Lattice fluid model of You et al. has been applied to both phase equilibria and excess

enthalpy calculations. Using pure component parameters fitted to saturation density and vapor pressure, binary interaction parameters were determined. The binary parameter was found more sensitive to enthalpy. The linear temperature dependence of this parameter was found adequate. The method yields good results except for polar-nonpolar mixtures, for which systems errors in vapor liquid equilibria appear magnifying.

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List of Symbols

H = Enthalpy

N_a = Avogardro′s number.

q_i = surface area parameter for molecule i

r_i = number of segment per molecule i

U = Internal Energy

V = molecular volume

V_i^* = molecular hard core volume of molecule i, cm^3/mol

V_H = lattice cell volume, cm^3/mol

z = lattice coordination number

Greek Letters

β = reciprocal temperature, $1/kT$

ε_{ij} = molecular interaction energy

λ_{ij} = binary energy parameter

μ = chemical potential

θ = surface area fraction

ρ = molar density

Subscript

i = property of component i

M = mixture quantity

Superscript

c = configurational quantity

References

[1] Aa. Fredenslund, R. L. Jones and J. M. Prausnitz, AIChE. J., 21 (1975), 1086

[2] K. V. Kehiaian, Fluid Phase Equilibria, 13 (1983), 1235

[3] A. G. Casielles, C. Pando, J. A. R. Renuncio, J. J. Christensen and R. M. Izatt, Themochim. Acta, 154 (1989), 57

[4] Y. Adachi and H. Sugie, J. Chem. Eng. Japan , 21 (1988), 57

[5] H. -M. Lin and M. -J. Lee, Fluid Phase Equilibria, 100 (1994), 139

[6] S.S. You, K.-P. Yoo and C.S. Lee, Fluid Phase Equilibria, 93 (1994), 193

[7] S.S. You, K.-P. Yoo and C.S. Lee, Fluid Phase Equilibria, 93 (1994), 215

[8] K.-P. Yoo, and C.S. Lee, Fluid Phase Equilibria, 117 (1996), 48

[9] S.J. Yoo, K.-P. Yoo and C.S. Lee, J. Phys. Chem. B, 101 (1997), 1072

[10] E. S. Guggenheim, Mixtures (1952), Oxford

[11]J. Gmehling, U. Onken and W. Arlt, Vapor-Liquid Equilibrium Data Collection.Vol. I (1980)

[12] M. Diaz Pena and C. Meduina, J. Chem. Thermodynamics, 6 (1974), 1097

Table 1. List of Binary parameters and Comparison of Results with Experimental Data

System	a	b	Temperature Range (K)	VLE Error $\Delta y / \Delta p$(%)	H^E Error (%)
Cyclohexane + Toluene	0.027926	-0.00004	298.15 - 323.15	0.4 1.3	4.9
Benzene + n-Octane	0.028096	-0.000035	298.15 - 348.15	- 0.2	1.4
Benzene + n-Hexadecane	0.040517	-0.000072	298.15 - 353.15	- 0.2	2.6
Benzene + 1-Hexene	-0.082482	0.00028	298.15 - 323.15	4.7 3.7	2.9
Benzene + CCl4	0.036346	-0.0001	298.15 - 313.15	0.6 0.1	2.0
CCl4 + n-Hexane	0.004508	-0.00005	298.15 - 323.15	0.2 0.1	2.5
CCl4 + n-Heptane	0.018526	-0.00004	308.15 - 318.15	0.2 0.2	4.4
CCl4 + n-Octane	0.017960	-0.000035	308.15 - 318.15	0.2 0.2	4.6
n-Hexane + Cyclohexane	0.021380	-0.000065	298.15 - 333.15	0.4 0.3	6.2
n-Hexane + 1-Hexene	0.021689	-0.00006	298.15 - 333.15	0.1 0.0	11.9
n-Hexane + 1-Hexanol	-0.087932	0.000402	298.23 - 313.15	- 8.4	53.6
n-Heptane + Diisopropyl Ether	0.021158	-0.00005	298.15 - 343.15	2.0 0.8	1.8
Methanol + n-Butanol	-0.036753	0.000133	298.15 - 313.15	0.2 0.6	1.4
Methanol + Acetone	-0.030973	0.00015	293.15 - 313.15	5.2 1.3	15.5
Ethanol + 2-Butanone	-0.008753	0.000133	298.15 - 328.15	4.5 2.1	6.4

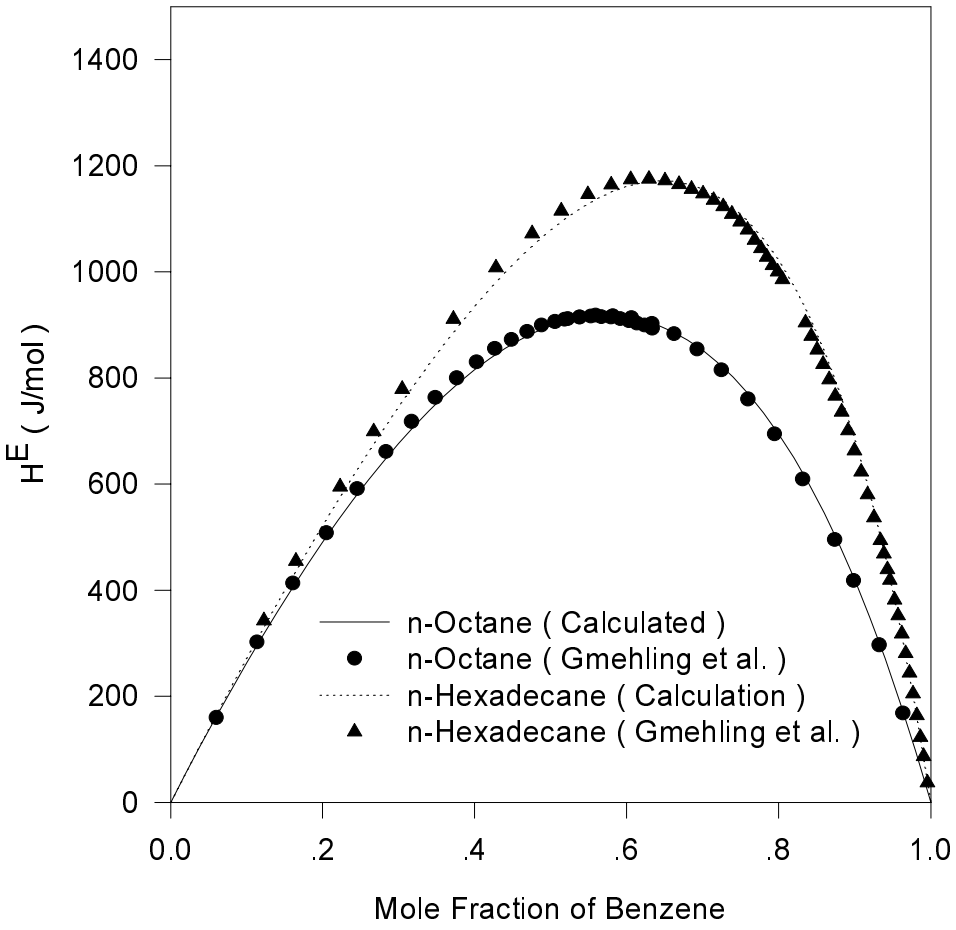
FIGURE CAPTIONS

Figure 1. Comparison of calculated excess enthalpies for benzene + n-alkane systems with experimental ones at 323.15 K and 1.01325 bar

Figure 2. Comparison of calculated excess enthalpies for cyclohexane + n-hexane system with experimental ones at 298.15 K and different pressures (1.01325 bar and 150.0 bar)

Figure 3. Comparison of calculated excess enthalpies for methanol + 1-butanol system with experimental ones at 298.15 K and 1.01325 bar

Figure 4. Comparison of calculated excess enthalpies for n-hexane + 1-hexanol system with experimental ones at 298.15 K and 1.01325 bar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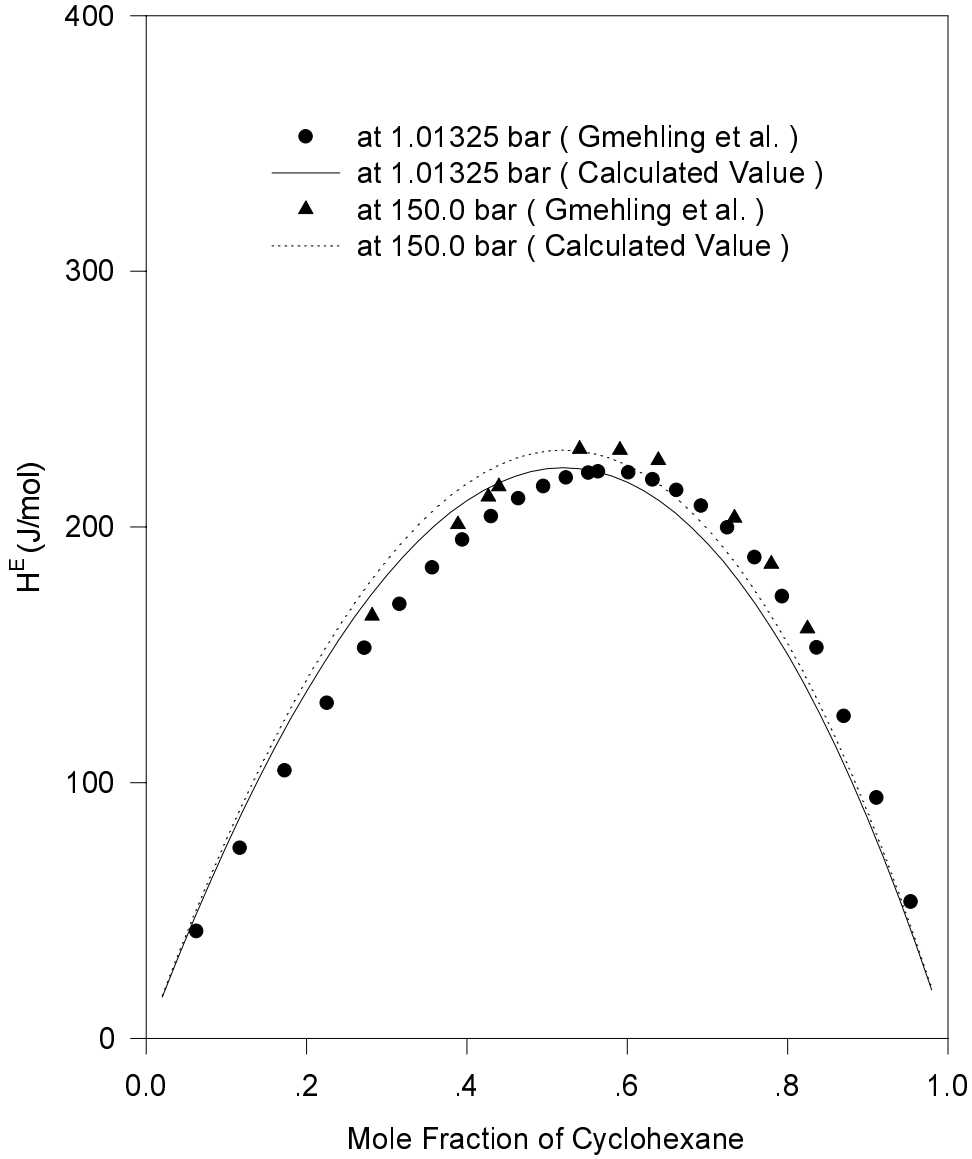
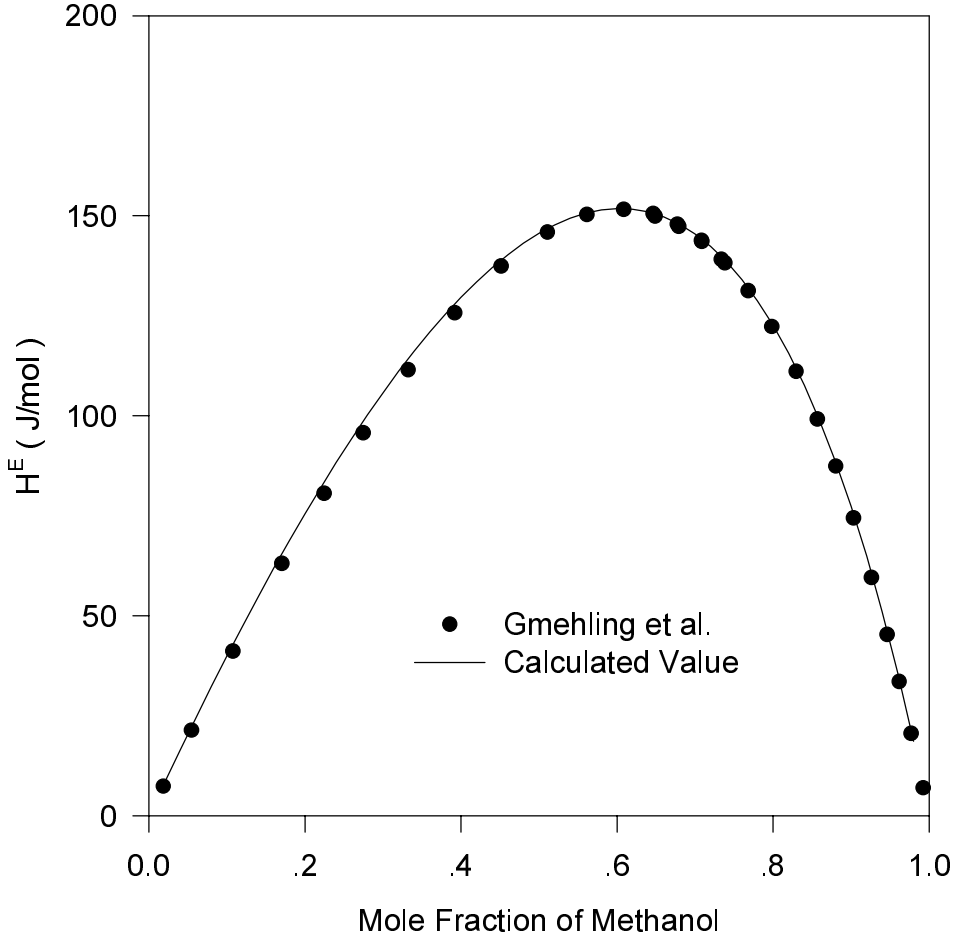
1200
1000
800
600
400
200
0
H^E (J/mol)
0.0
.2
.4
.6
.8
1.0
Mole Fraction of Benzene
n-Octane (Calculated)
n-Octane (Gmehling et al.)
n-Hexadecane (Calculation)
n-Hexadecane (Gmehling et al.)

< Fig. 1 >


400
300
200
100
0
0.0
.2
.4
.6
.8
1.0
H^E (J/mol)
Mole Fraction of Cyclohexane
at 1.01325 bar (Gmehling et al.)
at 1.01325 bar (Calculated Value)
at 150.0 bar (Gmehling et al.)
at 150.0 bar (Calculated Value)

< Fig. 2 >


200
150
100
50
0
H^E (J/mol)
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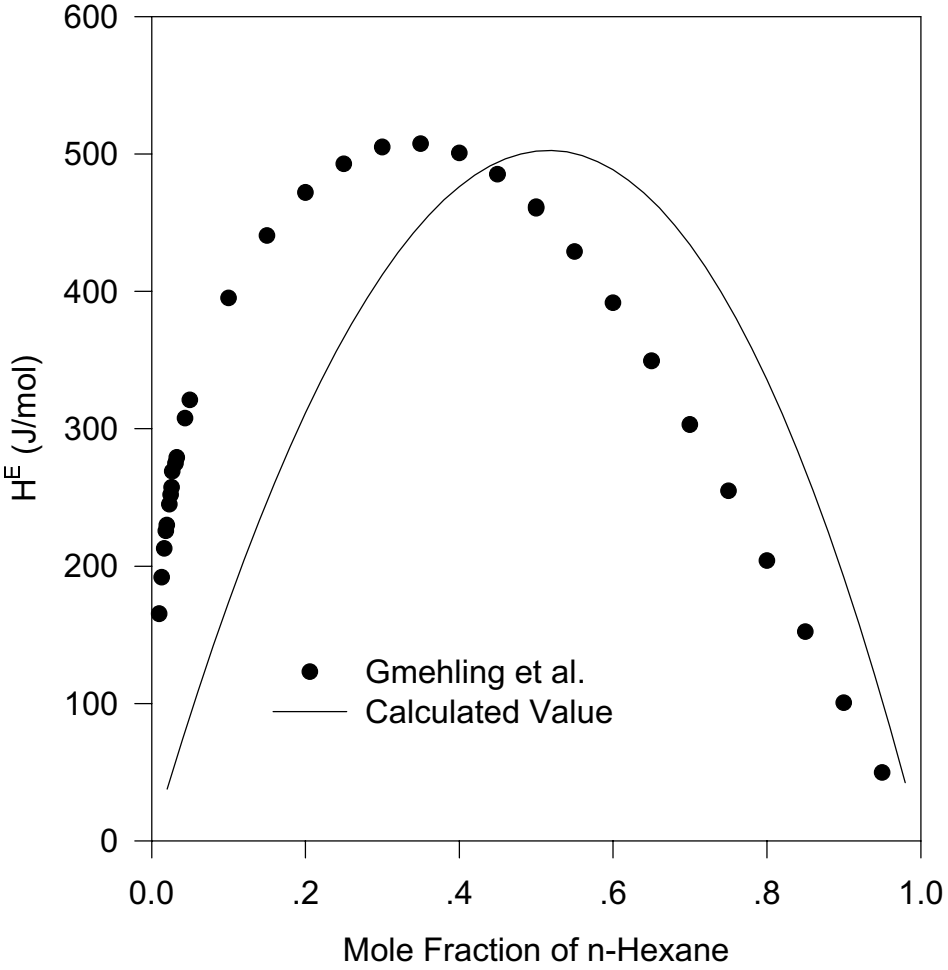
.2
.4
.6
.8
1.0
Mole Fraction of Methanol
Gmehling et al.
Calculated Value

< Fig. 3>


600
500
400
300
200
100
0
H^E (J/mol)
0.0
.2
.4
.6
.8
1.0
Mole Fraction of n-Hexane
Gmehling et al.
Calculated Value

< Fig. 4 >