400 J. Chem. Eng. Data 1992, 37, 400–402

Excess Enthalpies of the Systems Acetone + Ethyl Acetate and Cyclohexane + Cyclohexanone

Shubao Shen, Yanru Wang, and Jun Shi

Department of Chemical Engineering, Nanjing Institute of Chemical Technology, Nanjing 210009,
People's Republic of China

George C. Benson* and Benjamin C.-Y. Lu

Department of Chemical Engineering, University of Ottawa, 770 King Edward Avenue,
Ottawa, Ontario, Canada K1N 9B4

Microcalorimetric measurements of excess enthalpies are reported for acetone + ethyl acetate at 308.15 K, and for cyclohexane + cyclohexanone at 323.15 K. Redlich–Kister forms were fitted to the results. Use of a unified model of excess thermodynamic properties to represent simultaneously the excess enthalpy and vapor–liquid equilibria of the systems was investigated. The errors of representing H_m^E are less than 3%, and the mean absolute deviations between calculated and experimental vapor-phase mole fractions are less than 0.01.

Introduction

The vapor–liquid equilibria of acetone + ethyl acetate (system A) and of cyclohexane + cyclohexanone (system B) have been investigated by Subrahmanyam and Murty (*1*) and by Boublik and Lu (*2*), respectively. The present study was undertaken to provide supplementary information about the excess enthalpies of these systems.

Experimental Section

An LKB flow microcalorimeter (model 2107-121) was used to measure the excess molar enthalpies, H_m^E. Flows of the component liquids were produced by infusion pumps (LKB 2150). Details of the equipment and the operating procedure have been described previously (*3, 4*). Over most of the mole-fraction range, the accuracies of the determinations of H_m^E and the mole fraction, x_1, are estimated to be better than 1% and 5×10^{-4}, respectively.

Acetone (reagent grade from Shanghai AG) and ethyl acetate and cyclohexane (both reagent grade from Merck) were all purified by standard procedures (*5*). Cyclohexanone (also reagent grade from Merck) was dried over anhydrous sodium sulfate and fractionated in a 1-m glass column filled with McMahon packing. The purities of the samples used in the calorimetric studies were checked by density and refractive index measurements with an Anton Paar densimeter and a five-digit precision refractometer. The observed values of the density, $\rho/(\text{kg m}^{-3})$, and refractive index, n_D, both at 293.15 K, were, respectively, 789.91 and 1.358 76 for acetone, 900.32 and 1.372 25 for ethyl acetate, 778.56 and 1.426 59 for cyclohexane, and 947.76 and 1.450 65 for cyclohexanone. These results agree reasonably well with the literature values (*5, 6*).

Results and Discussion

The experimental values of H_m^E are summarized in Table I, and plotted in Figures 1 and 2. The equation

$$H_m^E/(\text{J mol}^{-1}) = x_1x_2\sum_{j=0}^{n} h_j(x_2 - x_1)^j \qquad (1)$$

was fitted to the results for each system, by the method of least squares with all points weighted equally. The results of these analyses are given in the footnote of Table I, along with the standard deviations, *s*, of the representations.

Table I. Experimental Results for the Excess Molar Enthalpies, H_m^E

x_1	H_m^E/(J mol^{-1})	x_1	H_m^E/(J mol^{-1})	x_1	H_m^E/(J mol^{-1})
		Acetone (1) + Ethyl Acetate (2) at 308.15 K[a]			
0.1744	68.3	0.5502	133.1	0.7345	98.1
0.2550	98.5	0.5977	126.3	0.8012	80.0
0.3435	122.2	0.6033	125.7	0.8652	57.8
0.4436	134.8	0.6704	114.1	0.9212	36.1
		Cyclohexane (1) + Cyclohexanone (2) at 323.15 K[b]			
0.1055	318.0	0.3801	861.2	0.7645	833.9
0.2172	587.6	0.5322	970.5	0.8515	643.6
0.2373	629.8	0.6166	971.2	0.8730	577.4
0.3143	769.7	0.6977	924.6	0.9050	464.9

[a] $H_m^E/(\text{J mol}^{-1}) = x_1x_2[542.4 + 55.4(x_2 - x_1) - 132.8(x_2 - x_1)^2 - 168.9(x_2 - x_1)^3]$; $s = 0.5$ J mol^{-1}. [b] $H_m^E/(\text{J mol}^{-1}) = x_1x_2[3836.7 - 959.3(x_2 - x_1) + 815.2(x_2 - x_1)^2 - 485.6(x_2 - x_1)^3]$; $s = 1.8$ J mol^{-1}.

The curve for acetone (1) + ethyl acetate (2) is nearly symmetrical about $x_1 = 0.5$. That for cyclohexane (1) + cyclohexanone (2) shows much larger deviations from ideality, and is skewed toward higher mole fractions of cyclohexane.

The excess enthalpies of both of the present systems have been studied previously. More than 60 years ago, Hirobe (*7*) measured H_m^E for system A at 298.15 K. A broken curve representing those results is included in Figure 1 for comparison. It appears from this that $(\partial H_m^E/\partial T)_P$ is predominantly negative. However, this conclusion is questionable, in view of the uncertainty of the older data.

Prior studies of the excess enthalpies of system B (*8–12*) have also been limited to 298.15 K. Zhou et al. (*12*) have compared some of these sets of data. The broken curve in Figure 2 represents the results of the most recent of the investigations at 298.15 K (*12*). Figure 2 indicates that $(\partial H_m^E/\partial T)_P$ is positive for $0 < x_1 < 0.8$, and that it is essentially zero beyond that range. For an equimolar mixture, $(\partial H_m^E/\partial T)_P \approx 1$ J K^{-1} mol^{-1}.

0021-9568/92/1737-0400$03.00/0

Table II. Values of Model Parameters from Fit of Equation 2 to H_m^E Data

system	α	$\Delta\epsilon_{21}$/(J mol^{-1})	$\Delta\epsilon_{12}$/(J mol^{-1})	$\langle\lvert\delta H_m^E\rvert\rangle$/(J mol^{-1})	$100\langle\lvert\delta H_m^E/H_m^E\rvert\rangle$
acetone (1) + ethyl acetate (2)	4.7035	−105.539	0.965	3.1	3.0
cyclohexane (1) + cyclohexanone (2)	−1.0165	−1234.105	843.774	16.4	2.7

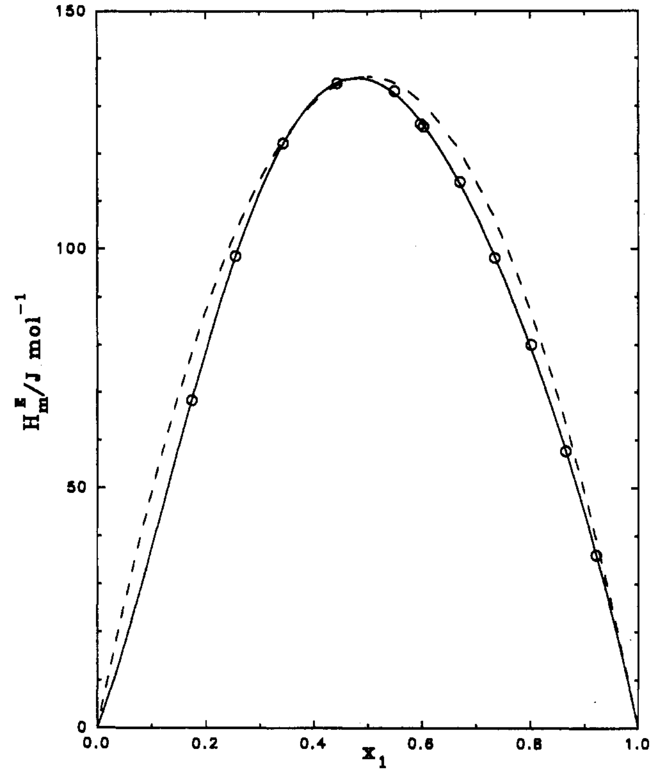

Figure 1. Excess molar enthalpies, H_m^E, of acetone (1) + ethyl acetate (2) as a function of the mole fraction, x_1, of acetone: present work at 308.15 K (—); Hirobe (*7*) at 298.15 K (- - -).

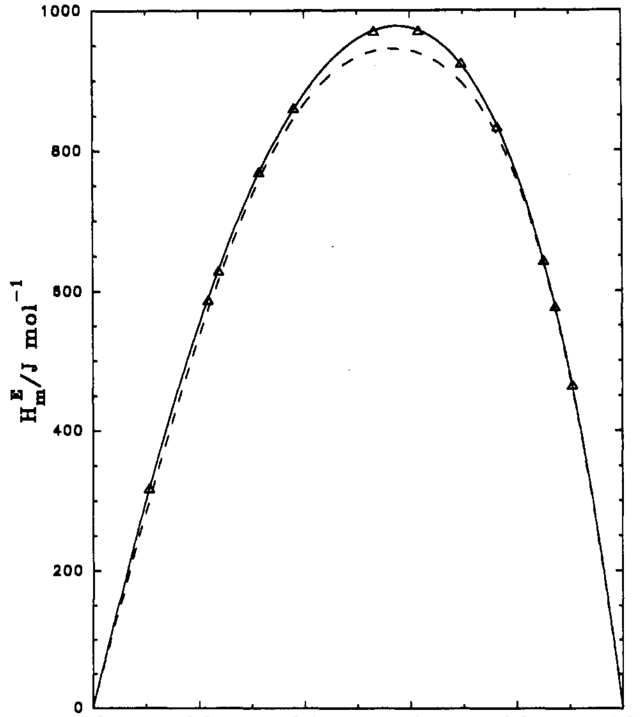

Figure 2. Excess molar enthalpies, H_m^E, of cyclohexane (1) + cyclohexanone (2) as a function of the mole fraction, x_1, of cyclohexane: present work at 323.15 K (—); Zhou et al. (*12*) at 298.15 K (- - -).

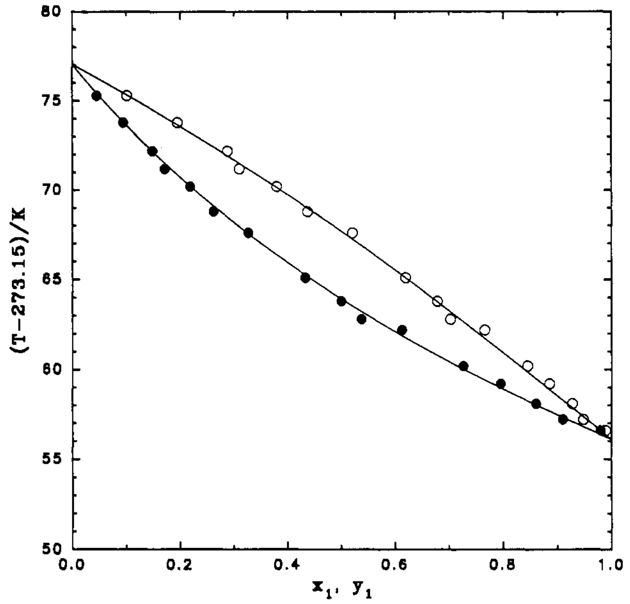

Figure 3. Comparison of calculated temperatures, T, and vapor mole fractions, y_1, with experimental results at liquid mole fractions, x_1, for acetone (1) + ethyl acetate (2) at 101.32 kPa: present calculation (—); Subrahmanyam and Murty (*1*) liquid–vapor results (●, ○).

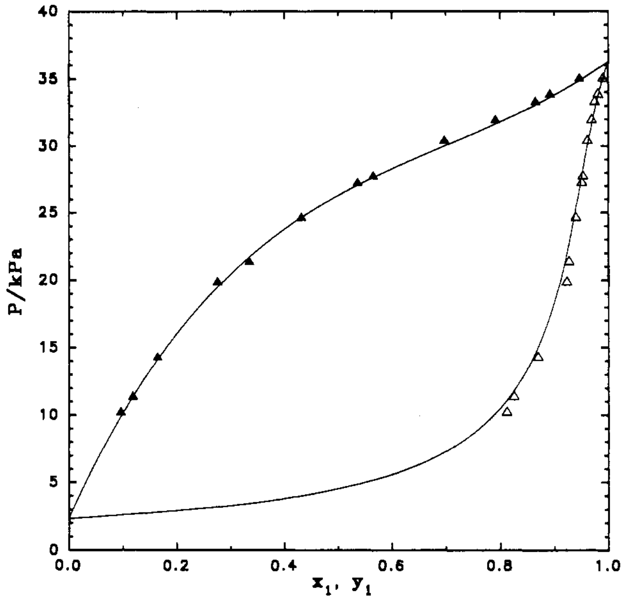

Figure 4. Comparison of calculated total pressures, P, and vapor mole fractions, y_1, with experimental results at liquid mole fractions, x_1, for cyclohexane (1) + cyclohexanone (2) at 323.15 K: present calculation (—); Boublik and Lu (*2*) liquid–vapor results (▲, △).

The unified model of excess thermodynamic properties, developed by Shen et al. (*13*), was used to represent simultaneously the H_m^E and vapor–liquid equilibria of systems A and B. According to this model

$$H_m^E = \frac{z x_1 x_2}{2}\left[\frac{\Delta\epsilon_{21}A_{21}}{x_1 + x_2 A_{21}} + \frac{\Delta\epsilon_{12}A_{12}}{x_2 + x_1 A_{12}}\right] \qquad (2)$$

and the excess molar Gibbs energy, G_m^E, is given by

$$\frac{G_m^E}{RT} = x_1 \ln \frac{\phi'_1}{x_1} + x_2 \ln \frac{\phi'_2}{x_2} + \frac{z}{2}\left(q_1 x_1 \ln \frac{\theta_1}{\phi_1} + q_2 x_2 \ln \frac{\theta_2}{\phi_2}\right) - \frac{z}{2\alpha}[x_1 \ln (x_1 + x_2 A_{21}) + x_2 \ln (x_2 + x_1 A_{12})] \quad (3)$$

where

$$A_{ij} = \left(\frac{V_i + V_j}{2V_j}\right) \exp[-\alpha\, \Delta\epsilon_{ij}/RT] \quad (4)$$

$$i, j = 1, 2 \qquad i \neq j$$

and

$$\theta_i = x_i q_i / \sum_{j=1}^{2} x_j q_j$$

$$\phi_i = x_i r_i / \sum_{j=1}^{2} x_j r_j \quad (5)$$

$$\phi'_i = x_i r_i^{3/4} / \sum_{j=1}^{2} x_j r_j^{3/4}$$

The values of the molecular area parameter q_i, volume parameter r_i, and saturated liquid volume V_i/(cm^3 mol^{-1}), tabulated for component i by Gmehling et al. (*14*), were adopted in the calculations. They are, respectively, 2.3360, 2.5735, and 74.05 for acetone; 3.1160, 3.4786, and 98.49 for ethyl acetate; 3.2400, 4.0464, and 108.75 for cyclohexane; and 3.3400, 4.1433, and 104.18 for cyclohexanone.

Assuming that the three model parameters α, $\Delta\epsilon_{21}$, and $\Delta\epsilon_{12}$ were temperature independent over a modest temperature interval, their values were determined for each system by simultaneously fitting the model to the present H_m^E data and the vapor–liquid equilibria (*1*, *2*). The results of these calculations are summarized in Table II, where the mean absolute and relative deviations, $\langle|\delta H_m^E|\rangle$ and $\langle|\delta H_m^E/H_m^E|\rangle$, of the fits are also listed.

In Figure 3, curves of calculated T plotted against x_1 and against calculated y_1 values are shown, together with the experimental T–x_1 and T–y_1 data for acetone (1) + ethyl acetate (2) at 101.32 kPa (*1*). The mean absolute deviations between calculated and experimental vapor-phase mole fractions, $\langle|\delta y_1|\rangle$, and equilibrium temperature, $\langle|\delta T|\rangle$, are 0.0058 and 0.17 K, respectively. Similarly in Figure 4, curves of calculated P plotted against x_1 and against calculated y_1 values are compared with the experimental P–x_1 and P–y_1 data for cyclohexane (1) + cyclohexanone (2) at 323.15 K (*2*). The mean absolute deviations $\langle|\delta y_1|\rangle$ and $\langle|\delta P|\rangle$ for this system are 0.0060 and 0.31 kPa, respectively. Thus, for both systems, the simultaneous representations of H_m^E and vapor–liquid equilibria are satisfactory.

Glossary

A_{ij}	parameter in eqs 2 and 3, defined by eq 4
G_m^E	excess molar Gibbs energy
H_m^E	excess molar enthalpy
P	pressure
q_i	molecular area parameter for component i
R	molar gas constant, 8.31451 J K^{-1} mol^{-1}
r_i	molecular volume parameter for component i
T	thermodynamic temperature
V_i	molar volume of saturated liquid component i
x_i	mole fraction of component i in liquid phase
y_i	mole fraction of component i in vapor phase
z	coordination number, assumed to be 10
α	model nonrandomness parameter (eqs 3 and 4)
δQ	deviation between calculated and experimental values of Q ($Q \equiv H_m^E, P, T, y_1$)
$\Delta\epsilon_{ij}$	model energy parameter (eqs 2–4)
ϕ_i,ϕ'_i,θ_i	volume, modified volume, and surface fractions of component i, defined by eq 5

Literature Cited

(1) Subrahmanyam, V.; Murty, P. D. *J. Appl. Chem.* **1964**, *14*, 500.
(2) Boublik, T.; Lu, B. C.-Y. *J. Chem. Eng. Data* **1977**, *22*, 331.
(3) Zhang, Y.; Wang, Y.; Shi, J. *Acta Phys.-Chim. Sin.* **1988**, *4*, 411.
(4) Shen, S.; Wang, Y.; Shi, J.; Benson, G. C.; Lu, B. C.-Y. *J. Chem. Thermodyn.* **1990**, *22*, 387.
(5) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. Techniques of Chemistry. In *Organic Solvents*, 4th ed.; Weissberger, A., Ed.; John Wiley and Sons: New York, 1986; Vol. II.
(6) *Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1990.
(7) Hirobe, H. *J. Fac. Sci., Imp. Univ. Tokyo* **1926**, *1*, 155.
(8) Amaya, K. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 1278.
(9) Polo, C.; Otin, S.; Gutierrez Losa, C. *J. Chem. Thermodyn.* **1982**, *14*, 309.
(10) Herrero, L. A.; Otin, S.; Gutierrez Losa, C. *J. Chem. Thermodyn.* **1983**, *15*, 555.
(11) Marongiu, B. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1987**, 27.
(12) Zhou, L.; Wang, Y.; Zhang, Y.; Shi, J.; Benson, G. C.; Lu, B. C.-Y. *Thermochim. Acta* **1991**, *189*, 57.
(13) Shen, S.; Wang, Y.; Shi, J. International Symposium on Thermodynamics in Chemical Engineering and Industry, Beijing, China, May 30–June 2, 1988.
(14) Gmehling, J.; Onken, U.; Arlt, W. In *Vapor-Liquid Equilibrium Data Collection*; Behrens, D., Eckermann, R., Eds.; Chemistry Data Series; DECHEMA: Frankfurt, 1979; Vol. 1, Parts 3 and 4 (see Appendix A).

Received for review December 30, 1991. Revised April 28, 1992. Accepted May 9, 1992. S.S., Y.W., and J.S. thank the National Science Foundation of China and the China National Petroleum and Natural Gas Corp. for financial support. G.C.B. and B.C.-Y.L. are indebted to the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support.

Registry No. Acetone, 67-64-1; ethyl acetate, 141-78-6; cyclohexane, 110-82-7; cyclohexanone, 108-94-1.