J. Chem. Eng. Data 1987, 32, 81-82

Excess Volumes and Excess Enthalpies for Binary Mixtures of Methyl Methacrylate with Cyclopentane and with Cyclohexane

Beichen Luo, Salah E. M. Hamam,† George C. Benson,* and Benjamin C.-Y. Lu

Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4

Successive dilution dilatometric measurements of excess volumes and flow calorimetric determinations of excess enthalpies are reported for binary mixtures of methyl methacrylate with cyclopentane and with cyclohexane at 298.15 K.

Introduction

Ester interchange reactions between methyl methacrylate (MMA) and higher alcohols are usually carried out in the presence of an inert solvent. A knowledge of the properties of ester–solvent mixtures is therefore useful in the design of an efficient transesterification process. Recently we investigated the excess volumes and enthalpies of binary mixtures of MMA with *n*-hexane and *n*-heptane (*1*). We now report the results of similar studies of mixtures of MMA with cyclopentane and cyclohexane.

Experimental Section

Chemicals. The MMA was Aldrich Analyzed-grade material stabilized with 65 ppm hydroquinone monomethyl ether. The cyclohexane was Spectranalyzed reagent from the Fisher Scientific Co.

In the course of the investigation two samples, A and B, from different lots of Research-grade cyclopentane (99 mol % minimum purity) from the Phillips Petroleum Co. were used. The volumetric studies were carried out with sample A as received from the manufacturer. Sample B was further purified by fractional distillation prior to its use in the calorimetric measurements.

The densities of the component liquids were determined in an Anton-Paar densimeter. At 298.15 K, the values of ρ/(kg·m^{-3}) were 937.66 for MMA, 772.27 for cyclohexane, and 739.92 and 740.22, respectively, for cyclopentane samples A and B.

Apparatus. Excess molar volumes, V_m^E, were determined in a successive dilution tilting dilatometer. This apparatus and its operation have been described by Kumaran and McGlashan (*2*). The error in the measurement of V_m^E is estimated to be about 0.2%. A modified LKB flow microcalorimeter was used to determine the excess molar enthalpies, H_m^E. Details of this equipment have also been described previously (*3*, *4*). Over most of the mole fraction range, the error in H_m^E is estimated to be less than 0.5%.

Table I. Experimental Results for the Excess Molar Volume, V_m^E, of MMA–Cycloalkane Mixtures at Mole Fraction x of MMA and 298.15 K

x	V_m^E/(cm^3·mol^{-1})	x	V_m^E/(cm^3·mol^{-1})
MMA–Cyclopentane		MMA–Cyclohexane	
0.0344	0.1284	0.0352	0.1999
0.0659	0.2319	0.0935	0.4824
0.1070	0.3468	0.1607	0.7227
0.1486	0.4427	0.2212	0.8894
0.1972	0.5297	0.2670	0.9808
0.2388	0.5888	0.3486	1.0822
0.2760	0.6303	0.3972	1.1128
0.3106	0.6601	0.4429	1.1204
0.3463	0.6804	0.4789	1.1141
0.3879	0.6932	0.4908	1.1057
0.4208	0.6960	0.5042	1.1020
0.4536	0.6896	0.5221	1.0918
0.4588	0.6918	0.5238	1.0842
0.4774	0.6838	0.5807	1.0325
0.4891	0.6836	0.6305	0.9664
0.4980	0.6764	0.6704	0.8999
0.5203	0.6668	0.7208	0.8037
0.5500	0.6499	0.7694	0.6927
0.5834	0.6266	0.8002	0.6153
0.6247	0.5904	0.8764	0.3984
0.6718	0.5393	0.9146	0.2797
0.7233	0.4754		
0.7859	0.3850		
0.8438	0.2903		
0.8979	0.1925		

Table II. Experimental Results for the Excess Molar Enthalpy, H_m^E, of MMA–Cycloalkane Mixtures at Mole Fraction x of MMA and 298.15 K

x	H_m^E/(J·mol^{-1})	x	H_m^E/(J·mol^{-1})
MMA–Cyclopentane		0.8000	552
0.0500	241	0.8506	429
0.0999	439	0.9499	155
0.1499	597		
0.2001	721	MMA–Cyclohexane	
0.3001	888	0.0499	299
0.4000	965	0.1003	547
0.4002	968	0.1996	901
0.4698	971	0.3000	1121
0.4992	962	0.3998	1221
0.4995	960	0.5011	1230
0.5495	932	0.6002	1140
0.5495	930	0.6986	972
0.6000	883	0.7994	720
0.6003	886	0.8996	397
0.7018	746	0.9499	208

Results and Discussion

The experimental V_m^E and H_m^E of $\{x\text{MMA} + (1-x)\text{c-C}_n\text{H}_{2n}\}$ mixtures at 298.15 K for $n = 5$ and 6 are listed in Tables I and II, and plotted in Figures 1 and 2. Equations of the form

$$X_m^E = x(1-x)\sum_{j=1}^{m} c_j(1-2x)^{j-1} \qquad (1)$$

were fitted to the results for V_m^E/(cm^3·mol^{-1}) and H_m^E/(J·mol^{-1}) by least-squares analyses with unit statistical weight assigned to each point. The coefficients c_j and standard deviations s for

---

† Visiting Scientist from the Department of Chemical Engineering, College of Engineering and Petroleum, Kuwait University, Kuwait.

0021-9568/87/1732-0081$01.50/0

Table III. Coefficients, c_j, and Standard Deviations, s, for Least-Squares Representation of V_m^E and H_m^E for MMA-Cycloalkane Mixtures at 298.15 K by Eq 1

X_m^E	c_1	c_2	c_3	c_4	c_5	s
		MMA-Cyclopentane				
$V_m^E/(cm^3·mol^{-1})$	2.7103	0.8381	0.2660	0.1865		0.0013
$H_m^E/(J·mol^{-1})$	3840.6	809.6	389.1	241.1		1.9
		MMA-Cyclohexane				
$V_m^E/(cm^3·mol^{-1})$	4.4109	1.0565	0.3464	0.2963		0.0020
$H_m^E/(J·mol^{-1})$	4912.8	850.9	336.1	293.7	241.1	1.6

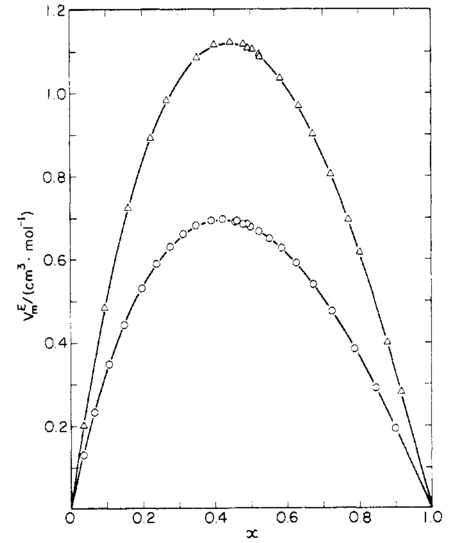

Figure 1. Excess molar volumes, V_m^E, of MMA–cycloalkane mixtures at mole fraction x of MMA and 298.15 K: O, cyclopentane; Δ, cyclohexane; —, least-squares representations of results by eq 1.

these representations are given in Table III. The solid curves in Figures 1 and 2 were calculated from eq 1 with these coefficients.

V_m^E and H_m^E are positive for both of the present mixtures, and at corresponding values of x their magnitudes increase with increasing size of the cycloalkane molecule. We are not aware of any directly comparable investigations of the excess volumes or excess enthalpies of these mixtures. However, the shapes and magnitudes of the curves in Figures 1 and 2 are similar to those found for MMA–n-alkane mixtures (*1*).

Vapor–liquid equilibria of MMA–cyclohexane mixtures at 318.12, 333.13, and 348.14 K have been studied recently and the activity coefficients γ_i of the components in the liquid phase have been reported (*5*). Values of H_m^E at 298.15 K were estimated from these results by using the thermodynamic relations

$$G_m^E = RT[x \ln \gamma_{MMA} + (1 - x) \ln \gamma_{C_6H_{12}}] \tag{2}$$

$$H_m^E = G_m^E - T(\partial G_m^E/\partial T)_p \tag{3}$$

and assuming that the variation of the excess molar Gibbs function, G_m^E, with the temperature T was of the form

$$G_m^E = A_1(x) + A_2(x)T + A_3(x)T \ln T \tag{4}$$

where A_1, A_2, and A_3 are functions of x only. The results of these calculations are shown as a dotted curve in Figure 2. The deviations from the experimental results for H_m^E seem reasonable in view of the uncertainties arising from the assumed temperature dependence of G_m^E and the extrapolation to a temperature below the range of the vapor–liquid studies.

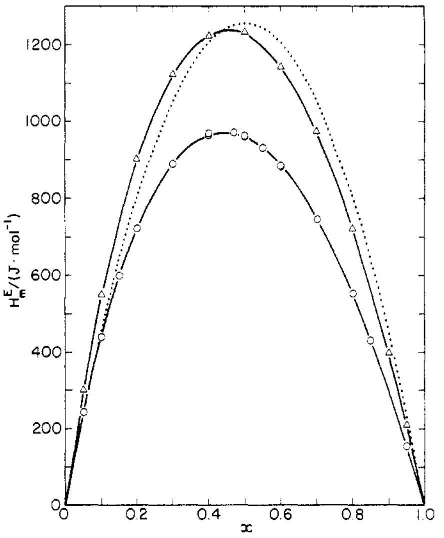

Figure 2. Excess molar enthalpies, H_m^E, of MMA–cycloalkane mixtures at mole fraction x of MMA and 298.15 K: O, cyclopentane; Δ, cyclohexane; —, least-squares representations of results by eq 1; ···, calculated from G_m^E for MMA–cyclohexane (*5*).

Glossary

A_1, A_2, A_3	functions of x in eq 4
c_j	coefficient in representation of X_m^E by eq 1
G_m^E	excess molar Gibbs function, $J·mol^{-1}$
H_m^E	excess molar enthalpy, $J·mol^{-1}$
m	number of coefficients in eq 1
R	gas constant, $J·K^{-1}·mol^{-1}$
s	standard deviation of least-squares representation by eq 1
T	thermodynamic temperature, K
V_m^E	excess molar volume, $cm^3·mol^{-1}$
x	mole fraction of MMA
X_m^E	excess molar thermodynamic function
γ_i	activity coefficient of component i in the liquid phase
ρ	density, $kg·m^{-3}$

Registry No. MMA, 80-62-6; cyclohexane, 110-82-7; cyclopentane, 287-92-3.

Literature Cited

(1) Luo, B. C.; Hamam, S. E. M.; Benson, G. C.; Lu, B. C.-Y. *J. Chem. Thermodyn.*, in press.

(2) Kumaran, M. K.; McGlashan, M. L. *J. Chem. Thermodyn.* **1977**, *9*, 259.

(3) Tanaka, R.; D'Arcy, P. J.; Benson, G. C. *Thermochim. Acta* **1975**, *11*, 163.

(4) Kumura, F.; Benson, G. C.; Halpin, C. J. *Fluid Phase Equilib.* **1983**, *11*, 245.

(5) Hull, D. M.; Lu, B. C.-Y. *J. Chem. Eng. Data* **1984**, *29*, 417.

Received for review April 22, 1986. Accepted July 8, 1986. We thank the Natural Sciences and Engineering Research Council of Canada for their financial support of this investigation.