J. Chem. Eng. Data **1995,** *40,* 1233−1236

Excess Enthalpies of Cyclohexane + Cyclohexanone, Cyclohexane + Methyl Methacrylate, and Cyclohexanone + Methyl Methacrylate at 298.15 K

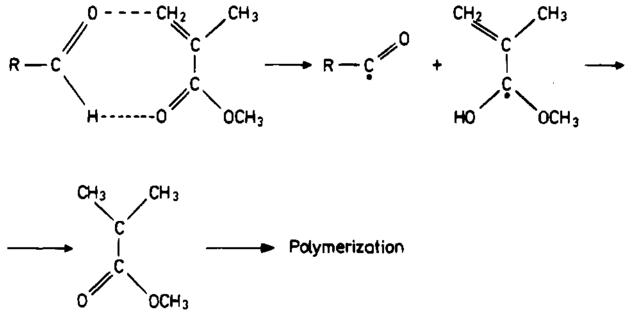
Hanna Wilczura, Mir Munsif Ali Talpur,[†] Andrzej Kaim, and Teresa Kasprzycka-Guttman*

Faculty of Chemistry, University of Warsaw, ul. Pasteura 1, 02-093 Warsaw, Poland

The excess enthalpies of cyclohexane + cyclohexanone, cyclohexane + methyl methacrylate, and cyclohexanone + methyl methacrylate have been measured at 298.15 K. The H^E values were compared with Prigogine−Flory−Patterson estimations. Both thermodynamic and spectroscopic results support the hypothesis of strong interactions between cyclohexanone and methyl methacrylate. The structure of the methyl methacrylate + cyclohexanone system is discussed.

Introduction

It has been reported that some organic compounds containing acidic hydrogen atoms can initiate the radical polymerization of polar vinyl monomers (Imoto et al., 1975; Ouchi et al., 1980; Kaim, 1984; Talpur and Kaim, 1994). The mechanism of the reaction involving transfer of the hydrogen radical abstracted from the active compound to the monomer originally proposed by Ouchi et al. (1980) for methyl methacrylate initiated with aldehydes, structure 1, and later discussed for methyl methacrylate polymerization started by cyclohexanone (Kaim, 1984) is based on strong interactions between methyl methacrylate and compounds containing acid hydrogen atoms. However, the proof of the discussed mechanism by kinetic (Kaim, 1984) as well as by spectral analysis using electron paramagnetic resonance (EPR) seems to be indecisive (Kaim and Kołodziejski, 1984). Additional information on the mechanism can be obtained from the molar excess enthalpies of mixtures formed by compounds associated into the complex, i.e., cyclohexanone and methyl methacrylate, from such results to estimate of the strength of interactions between the complex-forming agents. Additionally, IR and ^{1}H NMR measurements were made.



Experimental Section

Cyclohexane, cyclohexanone, and methyl methacrylate were purified according to the methods described previously (Kaim, 1984). Commercial grade methyl methacrylate was treated with aqueous KOH solution (10 mass-%), washed with distilled water until the washings were neutral, and then dried over $MgSO_4$ and distilled under reduced pressure at 293 K in an oxygen-free nitrogen atmosphere. Prior to use, it was immediately distilled as before. The properties and parameters for the purified components are listed in Table 1.

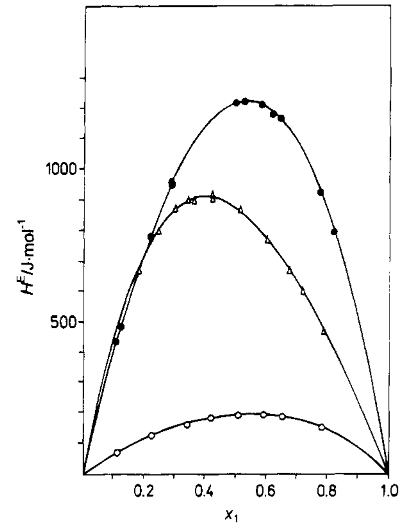


Figure 1. Excess enthalpy for (●) cyclohexane (1) + methyl methacrylate (2), (○) cyclohexanone (1) + methyl methacrylate (2) and (△) cyclohexanone (1) + cyclohexane (2): (—) R−K polynomial.

Enthalpies of mixing have been measured using a flow microcalorimeter UNIPAN type 600 (Wilczura et al., 1986). The accuracy of the H^E determination is estimated to be within 2 J·mol^{-1}.

Results and Discussion

The measured excess enthalpies at 298.15 K are listed in Table 2 and shown graphically in Figure 1. The results were fitted to the Redlich−Kister (R−K) polynominal:

$$H^E/(\mathrm{J\cdot mol^{-1}}) = x_1x_2\sum_{i=1}^{3}A_i(2x-1)^{i-1} \qquad (1)$$

where A_i are the coefficients for the binary systems. They are presented together with the standard deviation $\delta(H^E)$ in Table 3. For all the systems the H^E values are positive and decrease in the order cyclohexane (1) + methyl methacrylate (2) > cyclohexanone (1) + cyclohexane (2) > cyclohexanone (1) + methyl methacrylate (2).

[†] Permanent address: Department of Chemistry, Shah Abdul Latif University, Khairpur (Mir's) Sindh, Pakistan.

0021-9568/95/1740-1233$09.00/0

Table 1. Parameters of Pure Components

component	d^{20}/(g·cm^{-3}) (our result)	d^{20}/(g·cm^{-3}) (lit.)	n_D^{25} (our result)	n_D^{25} (lit.)	n_D^{20} (our result)	n_D^{20} (lit.)	purity/ % (GLC)
cyclohexane	0.77858	0.77856^a	1.4236	1.42354^d			99.9
cyclohexanone	0.95100	0.9466^b			1.4510	1.4522^e	99.8
methyl methacrylate	0.9401	0.936^c	1.4120	1.41198^f			99.9

^{a} Tamura et al. (1985). ^{b} Richards and Shipley (1916). ^{c} Kaye and Laby (1966). ^{d} Dreisbach (1955). ^{e} *Reagents Diagnostics Chemicals* (1990/1991). ^{f} Yu et al. (1980).

Table 2. Excess H^E at 298.15 K

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
Cyclohexane (1) + Methyl Methacrylate (2)			
0.1097	439.5	0.5854	1216.6
0.2183	780.4	0.6225	1184.9
0.2919	962.8	0.6442	1169.9
0.2919	952.4	0.7777	932.1
0.4969	1221.9	0.8232	794.0
0.5242	1223.3		
Cyclohexanone (1) + Methyl Methacrylate (2)			
0.1134	68.4	0.5077	194.4
0.2255	124.3	0.5953	193.2
0.3405	162.4	0.5953	191.3
0.4193	180.9	0.6538	187.1
0.5077	191.0	0.7846	152.1
Cyclohexanone (1) + Cyclohexane (2)			
0.1145	489.7	0.4216	905.2
0.1813	676.8	0.4216	914.7
0.2409	795.2	0.5108	872.6
0.3026	863.6	0.5978	773.3
0.3026	871.5	0.6758	665.1
0.3430	898.0	0.7144	599.8
0.3628	898.5	0.7870	465.6

Table 3. Parameters of the Redlich–Kister Equation (1) Obtained by Least Squares Together with Standard Deviation $\delta(H^E)$

system	A_1	A_2	A_3	$\delta(H^E)$/ J·mol^{-1}
cyclohexane + methyl methacrylate	4875.15	711.84	311.89	4.1
cyclohexanone + methyl methacrylate	776.46	167.41	99.92	1.5
cyclohexanone + cyclohexane	3494.99	−1439.92	349.62	4.2

For the series of binaries the H^E curves are nearly symmetrical. The maximum value of H^E for particular systems corresponds to the following molar fractions: H^E_{max} = 1225.0 J·mol^{-1} for cyclohexane (1) + methyl methacrylate (2) (x_1 = 0.55), H^E_{max} = 911.7 J·mol^{-1} for cyclohexanone (1) + cyclohexane (2) (x_1 = 0.40), and H^E_{max} = 194.1 J·mol^{-1} for cyclohexanone (1) + methyl methacrylate (2) (x_1 = 0.55).

Our results are consistent with literature data. The H^E maximum value for the cyclohexanone (1) + cyclohexane (2) mixture is about 20 J·mol^{-1} lower than that published by other authors (Amaya, 1961; Polo et al., 1982; Herrero et al., 1983), and the H^E maximum value for cyclohexane (1) + methyl methacrylate (2) is about 10 J·mol^{-1} lower than that obtained by Luo and co-workers (Luo et al., 1987).

The results are also compared with a model derived from the Prigogine–Flory–Patterson theory (Costas and Patterson, 1982; Orwoll and Flory, 1967; Orwoll and Flory, 1967; Flory et al., 1964). Comparisons of the model calculation with experiment are given graphically in Figure 2.

The Prigogine–Flory–Patterson model considers a contribution of physical interactions to the excess properties of mixtures. In calculations, the reduced and characteristic quantities were estimated using Flory's reduced equation of state (Flory et al., 1964) from the pure component properties given in Table 4. The adjustable parameter is the interaction energy parameter χ_{12}.

Table 4. Properties of Pure Components at 298.15 K Used in the Prigogine–Flory–Patterson Model Calculations

component	M	$\beta = -(1/v)(\partial v/\partial p)_T$/ TPa^{-1}	$\alpha \times 10^3$/ K^{-1}	S/A^{-1}
cyclohexanone	98.245	544.0^b	0.914^c	1.10^f
cyclohexane	84.162	1129.9^a	1.215^d	0.93^e

^{a} Tamura et al. (1985). ^{b} Richards and Shipley (1916). ^{c} Poradnik Fizykochemiczny (1974). ^{d} Jungera et al. (1988). ^{e} Costas and Paterson (1982). ^{f} Estimated from the data for other substances (Costas and Patterson, 1982) on a group contribution basis.

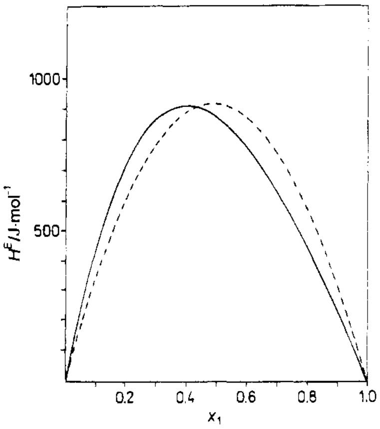


Figure 2. Excess enthalpy for cyclohexanone (1) + cyclohexane (2) at 298.15 K: (—) R–K polynominal; (- - -) calculated from the Prigogine–Flory–Patterson theory.

For methyl methacrylate, there are no results for the isobaric thermal expansivity α, and compressibility. Therefore, the calculation of H^E values has been done only for the cyclohexanone + cyclohexane mixture.

The calculated excess enthalpy using the Prigogine–Flory–Patterson method gives a good representation of both the H^E magnitude and its concentration dependence; however, some systematic shift of the calculated H^E curve toward the experimental one is observed. The values of the adjustable χ_{12} parameter and corresponding standard deviation of calculated H^E from experiment are as follows:

$$\chi_{12} = 48.8\ \mathrm{J{\cdot}cm^{-3}}; \qquad \delta(H^E) = 82.1\ \mathrm{J{\cdot}mol^{-1}}$$

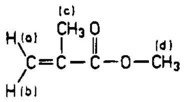
The concentration dependence of H^E calculated from the Prigogine–Flory–Patterson theory is compared with the experimental values in Figure 2.

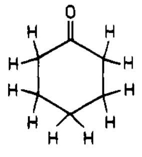
In addition to the excess enthalpy measurements IR and ^{1}H NMR investigations were made on the pure substances and the mixtures (Tables 5 and 6). From the concentration dependence of the frequency of the C=O and C=C bonds in the diluted cyclohexanone and methyl methacrylate solutions in cyclohexane and their mixtures, it is concluded that both compounds are self-associated substances and that the association between cyclohexanone and methyl methacrylate also takes place. Interaction of the oxygen

Table 5. IR Absorption Bands (cm^{-1}) of the C=O and C=C Groups for Methyl Methacrylate (MMA) and Cyclohexanone (Chn) in Cyclohexane (C_6H_{12}) Solutions (mol %)

methyl methacrylate						cyclohexanone		
C=O			C=C			C=O		
pure MMA	50 mol % solution in Chn	20 mol % solution in Chn	pure MMA	50 mol % solution in Chn	20 mol % solution in Chn	pure Chn	50 mol % solution in MMA	20 mol % solution in MMA
1725.7	1720.5	1714.9	1638.9	1637.6	1636.1	1714.9	1720.5	1714.9
1 mol % MMA + 1 mol % Chn in C_6H_{12}	1 mol % MMA + 5 mol % Chn in C_6H_{12}	1 mol % MMA in C_6H_{12}	1 mol % MMA + 1 mol % Chn in C_6H_{12}	1 mol % MMA + 5 mol % Chn in C_6H_{12}	1 mol % MMA in C_6H_{12}	1 mol % Chn + 1 mol % MMA in C_6H_{12}	5 mol % Chn + 1 mol % MMA in C_6H_{12}	1 mol % Chn in C_6H_{12}
1729.1	1722.0	1729.8	1640.3	1640.2	1640.4	1724.0	1722.0	1723.0

Table 6. ^1H NMR Results (δ, ppm) of Methyl Methacrylate (MMA) and Cyclohexanone (Chn) in Deuterated Cyclohexane (C_6D_{12}) Solutions (mol %) with Tetramethylsilane as Internal Reference Compound

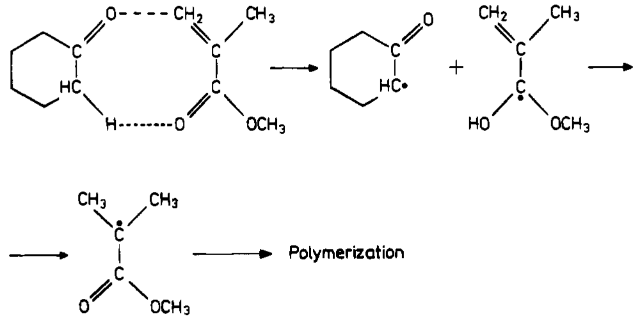




no.	description of sample	H_a	H_b	H_c	H_d	H_α	H_β	H_γ	CH_2 of C_6H_{12}
1	MMA (concentrated) in C_6D_{12}	6.033	5.526	1.963	3.69				
2	1% MMA in C_6D_12	6.014	5.380	1.883	3.343				1.39
3	1% MMA in Chn + C_6D_12	7.939	5.812	2.019	3.686	2.263	1.751	1.751	
4	1% Chn in MMA + C_6D_{12}	6.033	5.521	1.897	3.69	2.188	1.756	1.756	
5	20% MMA in Chn + $C_6{}_D12$	6.042	5.526	1.897	3.686	2.244	1.732	1.732	
6	Chn (concentrated) in C_6D_{12}					2.244	1.737	1.737	
7	5% MMA in Chn + C_6D_{12}	6.014	5.535	2.047	3.667	2.240	1.737	1.737	
8	5% MMA in C_6D_{12}	6.019	5.395	1.878	3.629				
9	5% Chn in MMA + C_6D_{12}	6.033	5.550	1.897	3.69	2.193	1.732	1.732	
10	Chn in C_6D_{12}					2.197	1.732	1.732	1.39

of the carbonyl group of cyclohexanone with the methylene group of the vinyl double bond of methyl methacrylate and simultaneous interaction of the acidic hydrogen atom of cyclohexanone with the oxygen of the carbonyl group of methyl methacrylate leads to the ^1H NMR and IR results as obtained here.

It can be said that the spectroscopic data complete the thermodynamic results and support the hypothesis of the complex formation of methyl methacrylate and cyclohexanone as discussed earlier (Kaim, 1984); see structure 2.



Thus, during the mixing of cyclohexanone with cyclohexane and methyl methacrylate with cyclohexane the structure of cyclohexanone and methyl methacrylate is destroyed. The total values of $H^E = f(x)$ are relatively large because of dissociation of cyclohexanone and methyl methacrylate and their nonspecific interactions with cyclohexane in the mixture.

The excess enthalpy effect for the system formed by cyclohexanone and methyl methacrylate is rather small in comparison to the remaining two. This is probably the consequence of dissociation of cyclohexanone and methyl methacrylate and association between the unlike molecules. The contribution of dissociation to H^E is in this case dominant over association. Therefore, the total excess enthalpy for the system cyclohexanone + methyl methacrylate is weakly endothermic.

Literature Cited

Amaya, K. Thermodynamical Studies on Binary Systems Consisting of Polar and Non-Polar Liquids. The Measurements of the Heats of Mixing for Binary Systems of Polar and Non-Polar Liquids. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 1278–1285.

Costas, M.; Patterson, D. Volumes of Mixing and the P* Effect: Part II. Mixtures of Alkanes with Liquids of Different Internal Pressures. *J. Solution Chem.* **1982**, *11* (11), 807–821.

Dreisbach, R. R. *Physical Properties of Chemical Compounds;* Advances in Chemistry Series 15; American Chemical Society: Washington, DC, 1955.

Flory, P. J.; Orwoll, R. A.; Vrij, A. Statistical Thermodynamics of Chain Molecule Liquids. I. An Equation of State for Normal Paraffin Hydrocarbons. *J. Am. Chem. Soc.* **1964**, *86*, 3507–3514.

Flory, P. J.; Orwoll, R. A.; Vrij, A. Statistical Thermodynamics of Chain Molecule Liquids. II. Liquid Mixtures of Normal Parafin Hydrocarbons. *J. Am. Chem. Soc.* **1964**, *86*, 3515–3520.

Flory, P. J.; Abe, A. Thermodynamic Properties of Nonpolar Mixtures of Small Molecules. *J. Am. Chem. Soc.* **1964**, *86*, 3563–3565.

Herrero, L. A.; Otin, S.; Gutierrez Losa, C. Thermodynamic Properties of Organic Oxygen Compounds. Excess Enthalpies for (Cyclohexanone or Methylcyclohexanone + Cyclohexane or Methylcyclohexane). *J. Chem. Thermodyn.* **1983**, *15*, 555–558.

Imoto, M.; Oishi, M.; Ouchi, T. Polymerization of Methyl Methacrylate Initiated with Poly(styrene-co-acrolein) or Poly(styrene-co-methyl vinyl ketone). *Makromol. Chem.* **1975**, *176*, 3287–3294.

Junquera, E.; Tardajos, G.; Aicart, E. Speed of Sound and Isentropic Compressibilities of (Cyclohexane + Benzene and (1-Chlorobutane + n-Hexane or n-Heptane or n-Octane) at 298.15K. *J. Chem. Thermodyn.* **1988**, *20*, 1461–1467.

Kaim, A. Polymerization of Vinyl Monomers Initiated with Cyclohexanone. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 203–208.

Kaim, A. Kinetics of Polymerization of Methyl Methacrylate Initiated with Cyclohexanone. Part I. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1891–1895.

Kaim, A.; Kołodziejski, W. Radicals in the Polymerization System of Valeraldehyde and Methyl Acrylate. *Polymer* **1984**, *25*, 8–9.

Kaye, G. W. C.; Laby, T. H. *Tables of Physical and Chemical Constants and Source Mathematical Functions*; Longman: Birmingham, AL, 1966.

Luo, B.; Haman, S. E.; Benson, G. C.; Lu, B. C-Y. Excess Volumes and Excess Entha;pies for Binary Mixtures of Methyl Methacrylate with Cyclopentane and Cyclohexane. *J. Chem. Eng. Data* **1987**, *32*, 81–82.

Orwoll, R. A.; Flory, P. J. Equation of State Parameters for Normal Alkanes. Correlation with Chain Lenght. *J. Am. Chem. Soc.* **1967**, *89*, 6814–6814.

Orwoll, R. A.; Flory, P. J. Thermodynamic Properties of Binary Mixtures of n-Alkanes. *J. Am. Chem. Soc.* **1967**, *89*, 6822–6829.

Ouchi, T.; Murayama, N.; Imoto, M. Radical Polymerization of Vinyl Monomer Initiated by Aliphatic Aldehyde. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 748–752.

Polo, C.; Otin, S.; Gutierrez Losa, C. Thermodynamic Properties of Organic Oxygen Compounds. Excess Enthalpies for (Cycloalkanone + Cycloalkane). *J. Chem. Thermodyn.* **1982**, *14*, 309–312.

Poradnik Fizykochemiczny; WNT: Warszawa, 1974.

Rastogi, R. P.; Nath, J.; Misra, J. Thermodynamics of Weak Interactions in Liquid Mixtures. I. Mixtures of Carbon Tetrachloride, Benzene, Toluene and p-Xylene. *J. Phys. Chem.* **1967**, *71* (5), 1277–1286.

Reagents Diagnostics Chemicals; E. Merck: Darmstadt, 1990/1991.

Richards, T. W.; Shipley, J. W. The Compressibility of Certain Typical Hydrocarbons, Alcohols and Ketones. *J. Am. Chem. Soc.* **1916**, *38*, 989–1011.

Talpur, M. M. A.; Kaim, A. Investigation of Methyl Methacrylate-Styrene Copolymerization System in Presence of Methyl Cyanoacetate. *J. Macromol. Sci., Chem.* **1994**, *5*, 535–541.

Tamura, K.; Murakami, S.; Doi, S. Speeds of Sound, Densities, and, Isentropic Compressibilities of $\{xc\text{-}C_6H_{12} + (1\text{-}x)C_6H_5CH_3\}$, $\{xc\text{-}C_6H_{11}CH_3 + (1\text{-}x)C_6H_6\}$, and $xc\text{-}C_6H_{11}CH_3 + (1\text{-}x)C_6H_5CH_3\}$, from 293.15 to 303.15K. *J. Chem. Thermodyn.* **1985**, *17*, 325–333.

Wilczura, H.; Kasprzycka-Guttman, T.; Randzio, S. Flow Microcalorimeter with a Separate Dosage System. *Bull. Pol. Acad. Sci., Chem.* **1986**, *34* (11–12), 483–488.

Yu, J.-M.; Ishikawa, T.; Lu, B. C.-Y. Vapor-Liquid Equilibria for Ethanol-Methyl Methacrylate. *J. Chem. Thermodyn.* **1980**, *12*, 57–63.

Received for review May 1, 1995. Accepted August 31, 1995.[⊗]

JE950103A

[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1995.