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Excess Molar Volumes of Binary Mixtures of 4-Methyl-2-pentanone and Some Hydrocarbons

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Summary. Excess molar volumes (V^E) for binary mixtures of 4-methyl-2-pentanone and some hydrocarbons (cyclohexane, benzene, toluene, and *p*-xylene) over the whole mole fraction range are determined by density measurement at 293.15 K. The variation of the V^E values with the composition for all binary systems is symmetrical except for benezene where the dependence is sigmoid. The V^E values are positive for the binary mixture of the ketone with cyclohexane. For the other hydrocarbons, the V^E values are progressively negative over the entire mole fraction range except the system containing benzene, where a few values at higher mole fractions of benzene are positive. The results are discussed in terms of molecular interactions steric effects.

Keywords. Excess molar volumes; Molecular interaction; Binary mixtures.

Molare Zusatzvolumina von binären Mischungen von 4-Methyl-2-pentanon und einigen Kohlenwasserstoffen

Zusammenfassung. Molare Zusatzvolumina (V^E) von binären Mischungen von 4-Methyl-2-pentanon und einigen Kohlenwasserstoffen (Cyclohexan, Benzol, Toluol und *p*-Xylol) wurden bei 293.15 K durch Dichtemessungen über den gesamten Molenbruchbereich bestimmt. Mit Ausnahme der binären Mischung mit Benzol (sigmoide Kurvenform) ist die Änderung von V^E in Abhängigkeit von der Zusammensetzung der Mischungen symmetrisch. Für das System Keton/Cyclohexan sind die V^E-Werte stark positiv, während sie für die anderen Gemische negativ sind. Eine Ausnahme bildet wieder das System mit Benzol als Kohlenwasserstoff, wo einige Werte bei höheren Molenbrüchen von Benzol positiv sind. Die Ergebnisse werden im Zusammenhang mit intermolekularen Wechselwirkungen und dem Einfluß sterischer Faktoren diskutiert.

Introduction

Molecular interactions in binary mixtures of two unlike molecules have been extensively studied by excess molar volume measurements [1]. *Nigam et al.* [2] have determined excess volumes dilatometrically as a function of temperature and composition for various categories of binary systems such as polar–polar, polar–non-polar, and non-polar–non-polar liquid mixtures and examined the different theories of solution. Excess volumes for the binary mixtures of methyl ethyl ketone as one component and liquids with increasing steric demand such as di-, tri- and tetrachloromethane as the second component have been determined recently by *Jain et al.* [3] and the results have been discussed in terms of the existence of specific interactions between unlike molecules. Although excess volume measurements for binary mixtures of lower ketones [3, 4] and hydrocarbons have been performed, hardly any data exist for the study of molecular interactions between higher ketones and hydrocarbons.

In continuation with our earlier work on molecular interactions between polar molecules and hydrocarbons by dipole moment [5], viscosity [6], and excess volume [7, 8] measurements, it was intended to employ excess molar volume measurements for binary mixtures to study the molecular interactions between a higher ketone (4-methyl-2-pentanone) and aromatic hydrocarbons progressively differing in their steric environment (benzene, toluene, and *p*-xylene) and the effect of steric hindrance in such interactions. Cyclohexane has been used as an inert solvent in order to have a reference point for comparing the molecular interactions of the ketone with the other hydrocarbons.

Results and Discussion

The densities (ρ_{12}) and excess molar volumes (V^E) of the binary systems are reported in Table 1. Fig. 1 shows that the variation of V^E with the composition is symmetrical for the binary mixtures of 4-methyl-2-pentanone with cyclohexane, toluene, and *p*-xylene. The V^E *vs.* x graph is sigmoid for the ketone–benzene system with generally negative values over the region rich in ketone and very few positive values in the region rich in hydrocarbon. Table 1 shows that V^E is large positive for the 4-methyl-2-pentanone-cyclohexane system over the entire composition range. It becomes negative when cyclohexane is replaced by benzene, toluene, or *p*-xylene. However, the excess volume becomes positive for the ketone–benzene system at a higher mole fractions (about 0.78) of the hydrocarbon. The V^E values for equimolar

Table 1. Mole fractions of the hydrocarbon (x_2), densities (ρ_{12}) and excess molar volumes of mixing (V^E) at 293.15 K

x_2	ρ_{12} (g·cm^{-3})	V^E (cm^3·mol^{-1})	x_2	ρ_{12} (g·cm^{-3})	V^E (cm^3·mol^{-1})
	4-methyl-2-pentanone-cyclohexane			4-methyl-2-pentanone-benzene	
0.0000	0.8018	–	0.0000	0.8018	–
0.0923	0.7987	0.207	0.1142	0.8088	−0.061
0.2263	0.7945	0.442	0.2605	0.8181	−0.080
0.3353	0.7912	0.601	0.3972	0.8276	−0.099
0.4773	0.7874	0.710	0.5215	0.8368	−0.089
0.5154	0.7862	0.763	0.5625	0.8399	−0.072
0.5566	0.7850	0.803	0.6009	0.8430	−0.071
0.5935	0.7844	0.767	0.639[illegible]	0.8461	−0.056
0.7094	0.7818	0.753	0.7482	0.8555	−0.042
0.8212	0.7804	0.567	0.8471	0.8640	+0.052
0.9254	0.7794	0.345	0.9395	0.8733	+0.059
1.0000	0.7800	–	1.0000	0.8804	–

Table 1 (*Contd.*)

x_2	ρ_{12} (g·cm^{-3})	V^E (cm^3.mol^{-1})
	4-methyl-2-pentanone-toluene	
0.0000	0.8018	–
0.0993	0.8085	−0.154
0.2283	0.8168	−0.245
0.3542	0.8248	−0.272
0.4817	0.8330	−0.265
0.5236	0.8357	−0.253
0.5588	0.8381	−0.258
0.5965	0.8405	−0.234
0.7114	0.8482	−0.192
0.8214	0.8560	−0.170
0.9278	0.8633	−0.083
1.0000	0.8682	–

x_2	ρ_{12} (g·cm^{-3})	V^E (cm^3·mol^{-1})
	4-methyl-2-pentanone-*p*-xylene	
0.0000	0.8018	–
0.2745	0.8201	−0.322
0.4648	0.8317	−0.365
0.5359	0.8360	−0.373
0.5672	0.8378	−0.362
0.5986	0.8396	−0.350
0.7347	0.8474	−0.298
0.8638	0.8546	−0.217
1.0000	0.8613	–

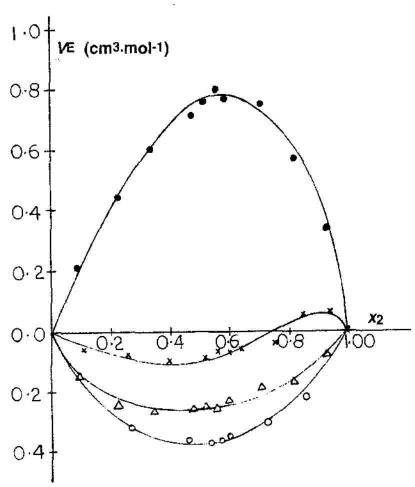

Fig. 1. Excess molar volume (V^E) *vs.* mole fraction (x_2) of hydrocarbons at 293.15 K; ●: cyclohexane, ×: benzene, △: toluene, ○: *p*-xylene

mixtures of ketone and different hydrocarbons have the order cyclohexane > benzene > toluene > *p*-xylene.

Anderson et al. [9] measured the V^E values for nitroethane and a number of hydrocarbons of increasing electron donating power and found that V^E increases with the ionization potential of the hydrocarbon. The order of the ionization potential of different hydrocarbons is the same as that of the V^E values of the equimolar mixtures of ketone and different hydrocarbons in the systems studied [9]. *Duncan et al.*, on the basis of the excess volume measurement of hexafluorobenzene with several hydrocarbons at 313.15 K, indicated that the extent of interaction increases with the electron donating power of the hydrocarbon [10]. It has been shown that the magnitude of the excess molar volume decreases with the increase of the number of substituted methyl groups on the benzene ring [11]. The V^E values for the binary mixture of ketone with benzene, toluene, and *p*-xylene have the similar trend with decreasing values (increasing negative values) of V^E for the three hydrocarbons, respectively, except for very few positive values at higher mole fractions of the hydrocarbon in the ketone–benzene system.

Powell and *Swinton* suggested that large positive V^E values indicate a weak unlike interaction, whereas large negative V^E values usually show the presence of strong interactions to form an intermolecular complex [12]. The large positive V^E values for the entire composition range of the ketone–cyclohexane system show the presence of weak forces between unlike pairs of molecules rather than that between similar molecules. This is quite obvious in view of the known associating tendency of the ketone. The forces between unlike molecules seem to be of the dispersion type. The V^E values for the equimolar binary mixtures of the ketone with benzene, toluene, and *p*-xylene are negative and their absolute values increase in the above order. This shows the presence of appreciable forces between the two unlike molecules in the ketone–benzene system. The forces between unlike molecules seem to increase when benzene is replaced with toluene or *p*-xylene, respectively.

It seems that the polar ketone polarizes the non-polar aromatic hydrocarbon benzene, resulting in an induced dipole moment in the ketone; the resultant forces between unlike pairs of molecules are of dipole-induced dipole type. However, a few positive values of V^E for this system at higher mole fractions of the hydrocarbon could not be explained. Enhanced forces between unlike pairs of molecules for the polar ketone–toluene system are expected due to dipole–dipole interaction, the hydrocarbon toluene being a polar molecule with a gas phase dipole moment of 0.36 D [13]. The unlike forces are still higher in the binary mixture of ketone–*p*-xylene as is evident from the increased negative values of V^E. This seems to be due to the locking effect by the further methylation of toluene where the ketone molecule is trapped by the methyl groups of *p*-xylene [14].

Experimental

The binary systems studied consisted of 4-methyl-2-pentanone and cyclohexane, benzene, toluene, and *p*-xylene, respectively. All compounds were commercially available and fractionally distilled over one meter column prior to use. The middle fractions were used for the measurements.

A series of binary mixtures of ketone and hydrocarbon covering the whole mole fraction range was prepared gravimetrically by injecting the components in vials sealed with rubber stoppers with a syringe in order to avoid evaporation losses. The densities of the liquids and liquid mixtures were measured with a single capillary pycnometer after equilibrating in a thermostat regulated at 293.15 K. The densities were accurate to $\pm 0.0001\,\mathrm{g \cdot cm^{-3}}$. The excess molar volumes for the binary mixtures were calculated from the densities of the pure liquids and liquid mixtures with an accuracy of $\pm 0.001\,\mathrm{cm^3 \cdot mol^{-1}}$ by equation 1 where ρ_1, ρ_2, and ρ_{12} are the densities of the pure components and binary liquid mixtures, respectively, at the experimental temperature. M_1, M_2, x_1, and x_2 are the molecular weights and mole fractions of the components in the liquid mixtures.

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho_{12}} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \qquad 1$$

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