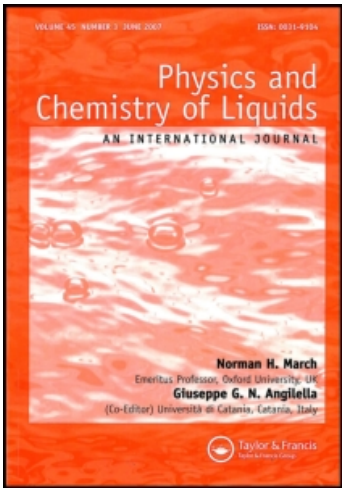

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Excess Volumes of Methylcyclohexane with Ketones and Esters at 303.15 K

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Excess Volumes of Methylcyclohexane with Ketones and Esters at 303.15 K

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Excess volumes for the binary liquid mixtures of methylcyclohexane with methylethylketone, methylisobutylketone, cyclohexanone, ethylacetate, *n*-propylacetate and *n*-butylacetate have been measured at 303.15 K. Excess volumes are positive over the entire range of mole fraction in all systems except the system containing cyclohexanone. In this system, excess volumes change sign from negative to positive with increase in the concentration of methylcyclohexane. The results have been discussed in terms of the influence of chain length and loss of dipolar association in the polar components.

KEY WORDS: Chain length, dipolar association, binary mixtures.

1 INTRODUCTION

As a part of our study on the measurement of excess thermodynamic properties of binary liquid mixtures[1,2] we have reported here the excess volumes of methylcyclohexane with methylethylketone methylisobutylketone, cyclohexanone, ethylacetate, *n*-propylacetate and *n*-butylacetate measured at 303.15 K. The influence of chain length of the esters and the effect of molecular shape of the ketones on excess volumes have been examined. Excess volume data for these systems are not available in the literature and hence we could not compare our results.

2 EXPERIMENTAL

Excess volumes were determined using the batch dilatometer technique described earlier[3]. The values were accurate to $\pm 0.003\ cm^3 \cdot mole^{-1}$.

Table 1 Boiling points and densities of the pure components.

Compound	Boiling point/K		Density/g cm^{-3}	
	Expt.	Lit.	Expt.	Lit.
Methylcyclohexane	100.15	100.93	0.76125	0.7606[a]
Methylethylketone	79.20	79.50	0.79399	0.79452[a]
Methylisobutylketone	115.58	115.70	0.79660	0.7961[b]
Cyclohexanone	155.46	155.65	0.93732	0.93761[a]
Ethylacetate	77.30	77.11	0.88804	0.8885[a]
n-Propylacetate	101.55	101.54	0.87760	0.8773[a]
n-Butylacetate	126.18	126.11	0.87573	0.87636[b]

[a] at 303.15 K.
[b] at 298.15 K.

All the chemicals were analytical-grade commercial products. Methylethylketone(BDH), methylisobutylketone(BDH) were further purified by the methods described earlier[3,4]. Cyclohexanone(BDH) was dried for one day over anhydrous sodium sulphate and fractionally distilled. Ethylacetate(BDH) and *n*-propylacetate(Sisco) were dehydrated over potassium carbonate for two days, filtered and fractionally distilled. The middle fractions of the esters were redistilled with a fractionating column over phosphorous pentoxide. *n*-Butylacetate (SD s) was kept over anhydrous magnesium sulphate for one day and fractionally distilled. Methylcyclohexane (SD s) was fractionally distilled over sodium wire and the middle fraction was collected. The purity of the compounds was checked by comparing the densities and boiling points with the literature values[5,6]. The boiling points were corrected to 1 atm. pressure and the data for the pure components are given in Table 1 along with the literature values[5,6].

3 RESULTS AND DISCUSSION

Excess volumes are given in Table 2 and also presented as a function of mole fraction in Figure 1. The results may be expressed by an empirical equation of the form

$$V^E = x_1x_2[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \quad (1)$$

The values of the parameters a_0, a_1 and a_2 are obtained by the method of least squares and are given in Table 3 along with the standard deviation $\sigma(V^E)$.

Table 2 Mole fraction of methylcyclohexane, x_1, and excess volumes, V^E, at 303.15 K.

x_1	V^E / $cm^3\ mol^{-1}$	ΔV^E / $cm^3\ mol^{-1}$
Methylcyclohexane + methylethylketone		
0.1209	0.287	−0.005
0.2196	0.474	0.007
0.3363	0.615	0.003
0.3763	0.655	0.008
0.4732	0.694	−0.007
0.5090	0.713	0.004
0.6430	0.677	−0.006
0.7870	0.526	−0.008
0.8339	0.460	0.007
Methylcyclohexane + methylisobutylketone		
0.1549	0.223	−0.001
0.2561	0.341	0.003
0.3806	0.446	−0.003
0.4385	0.482	−0.003
0.5159	0.517	0.006
0.6332	0.501	0.005
0.7240	0.444	−0.008
0.8330	0.335	0.004
Methylcyclohexane + cyclohexanone		
0.1311	−0.010	0.002
0.1861	−0.014	−0.003
0.3398	0.010	−0.001
0.3953	0.034	0.01
0.5019	0.045	−0.007
0.5936	0.082	0.005
0.7099	0.100	−0.009
0.8049	0.102	0.005
0.8748	0.080	0.000
Methylcyclohexane + ethylacetate		
0.1573	0.487	−0.002
0.2298	0.652	0.002
0.3411	0.815	−0.008
0.4557	0.902	−0.009
0.5340	0.909	−0.01
0.6579	0.837	−0.006
0.7882	0.648	0.009
0.8771	0.435	0.015

Table 2 (*continued*).

x_1	V^E / $cm^3\ mol^{-1}$	ΔV^E / $cm^3\ mol^{-1}$
	Methylcyclohexane + propylacetate	
0.1413	0.303	0.006
0.2612	0.496	−0.01
0.3778	0.634	−0.002
0.4354	0.673	0.006
0.4918	0.678	0.004
0.5840	0.632	−0.004
0.7009	0.520	0.008
0.8296	0.296	−0.004
	Methylcyclohexane + butylacetate	
0.1607	0.325	−0.01
0.2049	0.400	0.009
0.3079	0.488	0.005
0.4188	0.540	−0.004
0.4713	0.563	−0.001
0.6595	0.572	−0.007
0.8143	0.473	0.004
0.8467	0.420	0.001

$\Delta V^E = V^E(\text{exp}) - V^E(\text{Eq. 1})$.

The results shown in figure and in the table reveal that the V^E values are positive in the systems methylcyclohexane with methylethylketone, methylisobutylketone, ethylacetate, *n*-propylacetate and *n*-butylacetate. In methylcyclohexane with cyclohexanone, V^E values are changing sign from negative to positive with increase in mole fraction of methylcyclohexane. However, excess volumes in this system are small in magnitude. The results may be attributed to the loss of dipolar association of polar components in presence of methylcyclohexane. Further, the decrease in V^E values with increase in chain length and size of the polar components may be ascribed to the reduction in size difference between unlike components. The small and negative values of V^E observed in the mixtures of methylcyclohexane with cyclohexanone, may be explained as the effect of the molecular shapes of the unlike components which are roughly similar in this system. In mixtures containing esters the algebraic values of V^E at 0.5 mole fraction are in the order:

ethylacetate > *n*-propylacetate > *n*-butylacetate

and the V^E values in the systems containing ketones are in the sequence:

methylethylketone > methylisobutylketone > cyclohexanone.

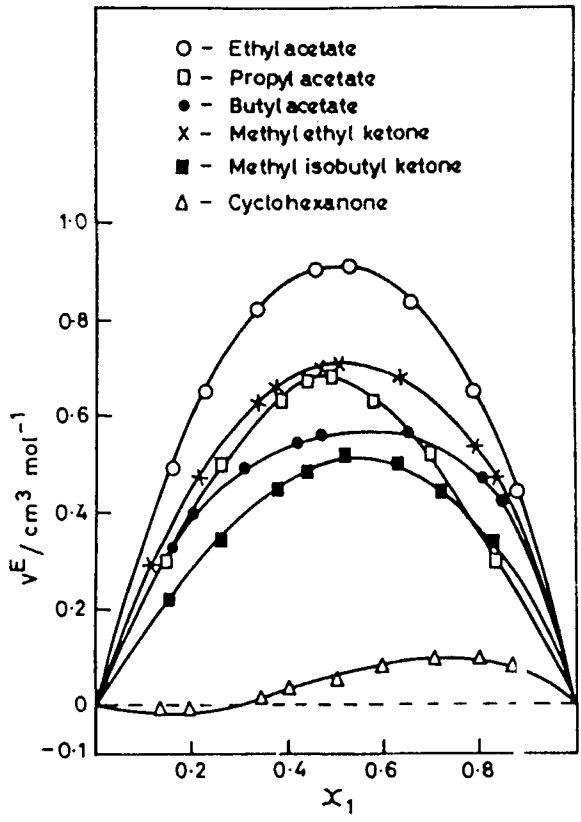

Figure 1 Mole fraction versus excess volumes at 303.15 K.

Table 3 Least square parameters and the standard deviation at 303.15 K.

System	a_0	a_1	a_2	$\sigma(V^E)$
	cm^3 mol^{-1}			
Methylethylketone	2.8323	0.3994	0.3788	0.007
Methylisobutylketone	2.0309	0.5320	0.0075	0.005
Cyclohexanone	0.2092	0.5602	0.1839	0.007
Ethylacetate	3.6847	0.1300	0.2026	0.010
Propylacetate	2.6904	0.2839	−0.8740	0.007
Butylacetate	2.2881	0.5277	1.2115	0.007

A comparison of the two similar systems, methylcyclohexane + ethylacetate and methylcyclohexane + methylethylketone, which differ only in their functional groups, reveals that the expansion in volume due to loss of dipolar association is relatively less in mixtures containing methylethylketone than in mixtures of ethylacetate.

References

1. K. P. Rao, K. S. Reddy, *Phy. Chem. Liq.*, **15**, 147 (1985).
2. T. Jayalakshmi, K. S. Reddy, *J. Chem. Eng. Data*, **30**, 51 (1985).
3. K. S. Reddy, P. R. Naidu, *Can. J. Chem.*, **55**, 76 (1977).
4. K. S. Reddy, P. R. Naidu, *Aust. J. Chem.*, **32**, 687 (1979).
5. J. A. Riddic, W. S. Bunger, Organic Solvents in techniques of Chemistry, 3rd ed. Vol. II, Wiley Interscience (New York, 1970).
6. J. Timmermans, Physico-chemical constants of pure Organic Compounds, Elsevier Publishing Company (Amsterdam, 1965).