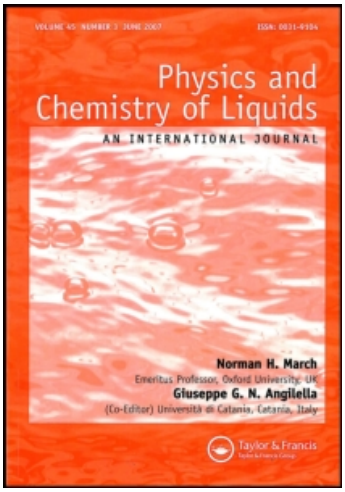

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Excess Volumes of Ternary Mixtures Containing *N*-Methylcyclohexylamine, Benzene with 1-Alkanols at 303.15 K

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EXCESS VOLUMES OF TERNARY MIXTURES CONTAINING *N*-METHYLCYCLOHEXYLAMINE, BENZENE WITH 1-ALKANOLS AT 303.15 K

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New excess volume data have been measured for three ternary mixtures at 303.15 K. The mixtures included *N*-methylcyclohexylamine and benzene as common components. 1-propanol, 1-butanol and 1-pentanol were chosen as non-common components. The data were compared with those predicted by empirical relations. The experimental results have been analysed in terms of intermolecular interactions between unlike molecules.

Keywords: Ternary mixtures; Dilatometer; Intermolecular interactions

INTRODUCTION

This work forms a part of our study on the measurements of thermodynamic properties of non-electrolyte solutions [1, 2]. In the present investigation we report here experimental ternary excess volume data for three ternary mixtures containing *N*-methylcyclohexylamine and benzene with 1-propanol, 1-butanol and 1-pentanol. The excess volumes have been measured to understand the nature and degree of interaction between the components. The ternary excess volumes are

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compared with those predicted from binary data using empirical equations [3, 4]. The methods of calculation of empirical equations aspect have been already discussed in the literature [5, 6].

EXPERIMENTAL DETAILS

Apparatus

Excess volumes for ternary mixtures were measured with the dilatometer described by Naidu and Naidu [7]. The mixing cell contains three bulbs of different capacities that were connected through W-tube. Mercury was taken at the bottom of the bulbs of dilatometer to separate the three components. One of the bulbs was fitted with a capillary and the other two bulbs were fitted with ground glass stoppers. Four dilatometers of the aforesaid types were used to cover the entire range of composition. All the measurements were made at constant temperature employing a thermostat that could be maintained to ± 0.01 K. The measured V^E values were accurate to $\pm 0.003\,cm^3\,mole^{-1}$.

Materials

All the liquids used were of analytical grade and purified as described in the literature [8]. The purity of the components was checked by measuring the densities and boiling points. Densities were measured using a bicapillary pycnometer, giving an accuracy of two parts in 10^5. Boiling points were measured using Swietoslawski-type ebuliometer, yielding an accuracy of ± 0.2°C. The measured values are included in Table I along with the literature [8, 9] values.

TABLE I Densities of pure components at 303.15 K

	Density ρ $(g\,cm^{-3})$	
Compounds	*Present work*	*Literature* [8, 9]
N-methylcyclohexylamine	0.84687	0.84690
benzene	0.86846	0.86850
1-propanol	0.79562	0.79567
1-butanol	0.80203	0.80203
1-pentanol	0.80762	0.80764

Results and Discussion

The measured excess volume data for the ternary mixtures are listed in Table II. Binary V^E parameters to compute ternary data for the systems *N*-methylcyclohexylamine with benzene, *N*-methylcyclohexylamine with 1-alkanols and benzene with 1-alkanols were taken from the literature [10–12]. The least square parameters for all these binary systems are given in Table III. The ternary excess volume data, predicted by using the binary data through the empirical equations [3,4] proposed by Redlich-Kister, Kohler, Tsao-Smith and Hwang *et al.*, are given in columns 4–7 of Table II.

The experimental ternary excess volume data for all the mixtures are negative over the entire range of composition studied. This can be explained on the basis of the following factors:

(i) addition of benzene and 1-alkanols to associated liquid, *N*-methylcyclohexylamine may lead to break up of hydrogen bonds in amine aggregates,
(ii) loss of dipolar association due to the addition of non-common components and
(iii) hydrogen bond interactions of the type *N*—*H*...Π amine and Π electrons in aromatic ring may be expected.

The first two factors above are responsible for expansion in volume and the last factor contributes to contraction in volume. The experimental ternary V^E data in the present investigation suggest that the factor which is responsible for contraction in volume is dominant in nature over the entire range of mole fraction in all three ternary mixtures.

The dependence of experimental ternary excess volume V^E_{123} (exptl) on composition is expressed by the polynomial

$$V^E_{123}(\text{exptl}) = V^E_{123}(b) + X_1X_2X_3[A + BX_1(X_2 - X_3) + CX_1^2(X_2 - X_3)^2] \quad (1)$$

and

$$V^E_{123}(b) = V^E_{12} + V^E_{23} + V^E_{13} \quad (2)$$

where X_1, X_2 and X_3 are the mole fractions of *N*-methylcyclohexylamine, benzene and 1-alkanol respectively. A, B and C are ternary

TABLE II Experimental and predicted ternary excess volume (V^E_{123}) of ternary mixtures of *N*-methylcyclohexylamine (1) + benzene (2) + 1-alkanols (3) at 303.15 K

		$V^E_{123}(exp)$	$V^E_{123}(cm^3\,mol^{-1})$				ΔV^E_{123} [a]
X_1	X_2	$(cm^3\,mol^{-1})$	*Redlich-Kister*	*Kohler*	*Tsao-Smith*	*Hwang et al.*	$(cm^3\,mol^{-1})$
			N-methylcyclohexylamine(1) + benzene(2) + 1-propanol(3)				
0.0896	0.1070	−0.392	−0.400	−0.384	−0.392	−0.417	0.008
0.1013	0.1604	−0.397	−0.408	−0.391	−0.398	−0.423	0.011
0.0989	0.2210	−0.334	−0.344	−0.331	−0.334	−0.356	0.010
0.1320	0.3411	−0.325	−0.335	−0.342	−0.336	−0.341	0.010
0.1147	0.4027	−0.223	−0.232	−0.246	−0.233	−0.232	0.009
0.1065	0.5106	−0.123	−0.135	−0.162	−0.142	−0.126	0.012
0.0971	0.5719	−0.073	−0.086	−0.116	−0.095	−0.074	0.013
0.1102	0.6302	−0.065	−0.085	−0.122	−0.101	−0.072	0.020
0.0902	0.7104	−0.022	−0.038	−0.068	−0.047	−0.029	0.016
0.0762	0.7629	−0.016	−0.027	−0.052	−0.037	−0.015	0.011
0.1019	0.8002	−0.047	−0.064	−0.081	−0.077	−0.056	0.017
0.0874	0.8516	−0.055	−0.064	−0.072	−0.076	−0.060	0.009
			N-methylcyclohexylamine(1) + benzene(2) + 1-butanol(3)				
0.1039	0.0972	−0.340	−0.359	−0.348	−0.366	−0.368	0.009
0.1136	0.1106	−0.371	−0.382	−0.371	−0.395	−0.391	0.011
0.0917	0.1927	−0.228	−0.240	−0.234	−0.291	−0.247	0.012
0.1210	0.2410	−0.273	−0.288	−0.284	−0.371	−0.293	0.015
0.0876	0.3282	−0.120	−0.132	−0.137	−0.222	−0.129	0.012
0.1009	0.4106	−0.100	−0.113	−0.127	−0.237	−0.103	0.013
0.0972	0.5125	−0.041	−0.055	−0.078	−0.193	−0.038	0.014
0.0766	0.5908	0.015	0.044	−0.019	−0.117	0.022	0.011
0.0971	0.6429	−0.011	−0.023	−0.052	−0.158	0.000	0.012
0.1173	0.7117	−0.030	−0.045	−0.073	−0.145	−0.022	0.015
0.1002	0.7488	−0.022	−0.032	−0.056	−0.118	−0.012	0.010
0.0869	0.8317	−0.037	−0.044	−0.057	−0.059	−0.034	0.007

N-methylcyclohexylamine(1) + benzene(2) + 1-pentanol(3)

0.1029	0.0986	−0.419	−0.430	−0.435	−0.451	−0.535	0.011
0.0921	0.1517	−0.327	−0.337	−0.348	−0.364	−0.488	0.010
0.1109	0.2110	−0.325	−0.339	−0.357	−0.378	−0.521	0.014
0.0864	0.3512	−0.133	−0.140	−0.172	−0.181	−0.395	0.007
0.1329	0.4329	−0.158	−0.167	−0.206	−0.222	−0.400	0.009
0.1210	0.5106	−0.079	−0.090	−0.131	−0.139	−0.325	0.011
0.1176	0.5820	−0.035	−0.048	−0.086	−0.091	−0.265	0.013
0.1071	0.6524	0.000	−0.015	−0.048	−0.048	−0.210	0.015
0.0912	0.7019	0.022	0.009	−0.020	−0.018	−0.174	0.013
0.1010	0.7622	0.002	−0.014	−0.034	−0.034	−0.142	0.016
0.1212	0.8230	−0.004	−0.012	−0.026	−0.025	−0.114	0.008
0.1421	0.8614	−0.056	−0.062	−0.067	−0.068	−0.108	0.006

[a] $\Delta V^E_{123} = V^E_{123}(\text{exp}) - V^E_{123}(b)$, where $V^E_{123}(b)$ is the excess volume calculated from the Redlich-Kister equation.

TABLE III Standard deviation $\sigma(\Delta V^E)$ and the values of binary constants from the equations of Redlich-Kister and Hwang

	Redlich-Kister equation				*Hwang equation*			
	a_0	a_1	a_2	$\sigma(\Delta V^E)$	b_0	b_1	b_2	$\sigma(\Delta V^E)$
System	cm^3mol^{-1}							
N-methylcyclohexylamine(1) + benzene(2)	0.7690	1.5660	0.9160	0.002	1.0740	0.6430	3.0860	0.009
N-methylcyclohexylamine(1) + 1-propanol(3)	−6.2370	2.7030	3.9250	0.002	−7.5451	8.4492	2.0154	0.002
benzene(2) + 1-propanol(3)	0.6789	0.2527	−0.1489	0.002	0.7283	0.1036	−0.4980	0.002
N-methylcyclohexylamine(1) + benzene(2)	0.7690	1.5660	−0.9160	0.002	1.0740	0.6430	−3.0860	0.009
N-methylcyclohexylamine(1) + 1-butanol(2)	−5.2180	0.8473	1.9080	0.001	−5.8516	3.4605	1.5312	0.002
benzene(2) + 1-butanol(3)	0.7109	0.2540	−0.0616	0.002	1.7317	0.2188	−3.0650	0.009
N-methylcyclohexylamine(1) + benzene(2)	0.7690	1.5660	−0.9160	0.002	1.0740	0.6430	−3.0860	0.009
N-methylcyclohexylamine(1) + l-pentanol(3)	−5.2430	0.9548	0.4169	0.002	−5.3823	1.6945	−0.5790	0.003
benzene(2) + 1-pentanol(3)	0.7324	0.5084	0.0311	0.003	0.7225	0.6460	−0.5660	0.003

TABLE IV Values of ternary constants A, B and C and the standard deviation $\sigma(\Delta V^E_{123})$ at 303.15 K

System	A	B	C	$\sigma(\Delta V^E_{123})$
	($cm^3\ mol^{-1}$)			
N-methylcyclohexylamine(1) + benzene(2) + 1-propanol(3)	0.4345	6.1146	243.7530	0.001
N-methylcyclohexylamine(1) + benzene(2) + 1-butanol(3)	0.6681	0.2975	88.6792	0.001
N-methylcyclohexylamine(1) + benzene(2) + 1-pentanol(3)	0.4097	1.8066	204.8071	0.001

constants and their values obtained by the least squares method are given in Table IV along with standard deviation $\sigma(\Delta V^E_{123})$.

Analysis of the data in Table II, indicates that the agreement between measured V^E_{123} and that calculated from empirical equations is satisfactory in all three ternary systems.

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