Excess Thermodynamic Properties of Ternary Mixtures of *N*-Methylcyclohexylamine and Toluene with 1-Alcohols

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Excess volume and speed of sound data for the ternary mixtures were reported at 303.15 K over the entire composition range for three ternary mixtures containing *N*-methylcyclohexylamine and toluene as common components and 1-alcohols as third component, namely 1-propanol, 1-butanol, and 1-pentanol. The experimental speed of sound and density of ternary mixtures were used to compute isentropic compressibility ($\acute{k}_{s123}$) and the quantity Δk_{s123}, the difference between measured value and that computed from the constituent binary data. Further, the experimental ternary excess volume data were compared with calculated data obtained by empirical relations proposed by Redlich–Kister, Kohler, Tsao–Smith, and Hwang. The results were analyzed on the basis of intermolecular interactions between component molecules and also in terms of constituent binary data.

The mixing of different compounds gives rise to properties such as volumes, enthalpies, and entropies of mixing, which give an idea of the extent of the deviations from nonideality. A thorough knowledge of thermodynamic properties of binary–ternary component liquid mixtures is essential in many industrial applications such as design calculation, heat transfer, mass transfer, fluid flow, and so forth.[1] In general, mixtures of associated liquids exhibit nonideal behavior in respect to properties like excess volume.[2] Any excess thermodynamic property may be considered as made up of two parts: one corresponding to breaking up of the hydrogen bonds in component liquids and the other is due to van der Waals type interactions between the alkane chain of the 1-alcohol and other solvents.

Further, nonideal thermodynamic behavior of liquid mixtures may be discussed in terms of differences in molecular size and shape, dispersion forces, polarity, polarizability, molecular association, etc. In many liquid mixtures, dipolar interactions contribute significantly to the thermodynamic properties.[3,4] The components selected for making the ternaries are well-known organic liquids and also have wide range of applications in various fields of chemistry besides being used in industries and routine analytical work.

The present work is a part of our systematic study on thermodynamic properties of ternary organic liquid mixtures containing molecules of significantly different sizes.[5–7] The aim of the present investigation is to study the molecular interactions in *N*-methylcyclohexylamine (NMC) (1) + toluene (2) + 1-alcohol (3) by measuring the excess volume (V_{123}^E) and isentropic compressibility ($\acute{k}_{s123}$) data at 303.15 K. Furthermore, no experimental work has been reported in the literature for these ternary mixtures in terms of excess volume and isentropic compressibility data. The measured excess volume data have been compared with those predicted from binary data in terms of empirical equations.[8,9]

Experimental

Materials. For the present investigations, *N*-methylcyclohexylamine (NMC) (Merck >99.5%) was degassed with ultrasound, and was purified by fractional distillation. Toluene (Sigma-Aldrich >99.9%), 1-propanol (Merck >99.5%), 1-butanol (S. D. Fine chem., >99.5%), and 1-pentanol (Sigma-Aldrich, >99.9%) were purified by standard methods described in the literature.[10,11] The purity of the chemical products was compared by measuring the densities (ρ) and speed of sound (u) which were in good agreement with literature values[12,13] and these are given in Table 1.

Experimental Procedure. The densities of all the pure liquids were measured by using a single-stem bicapillary pycnometer (made of borosil glass) of bulb capacity 12 cm[3], with graduated marks and uniform bore, and can be closed using a Teflon cap. The marks on the capillary were calibrated with triple distilled water.

Excess volume (V_{123}^E) data for the ternary mixtures were measured with a dilatometer described earlier.[14,15] The mixing cell contained three bulbs of different capacities that were connected by a W-tube. Mercury was used to separate three component liquids. One of the three bulbs was fitted with a capillary and the other two were fitted with ground-glass stoppers. Each bulb of the dilatometer was filled with a component whose mass was determined directly by weighting. The entire dilatometer was placed in a thermostat that could be maintained

Table 1. Density (ρ) and Speed of Sound (u) of Pure Components at 303.15 K

Compound	Density (ρ)/g cm^{-3}		Speed of sound (u)/m s^{-1}	
	Experimental	Literature	Experimental	Literature
N-methylcyclohexylamine	0.84683	0.84687 (ref 12)	1356	1353 (ref 12)
toluene	0.85767	0.85764 (ref 12)	1284	1282 (ref 12)
1-propanol	0.79566	0.79564 (ref 13)	1189	1190 (ref 13)
1-butanol	0.80205	0.80203 (ref 13)	1229	1228 (ref 13)
1-pentanol	0.80764	0.80762 (ref 13)	1256	1258 (ref 13)
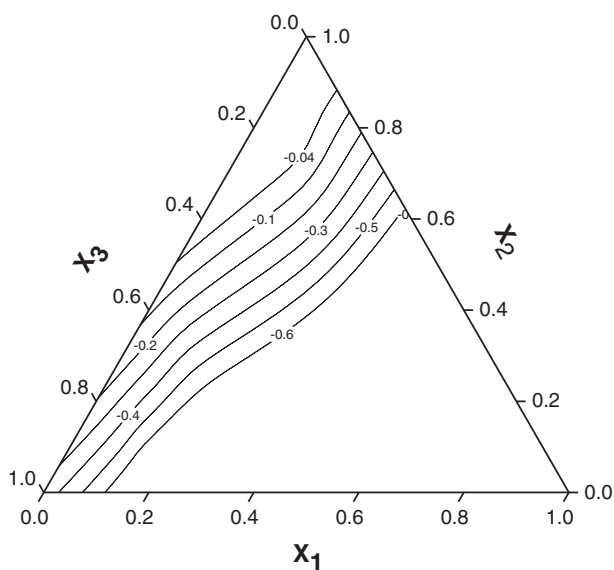
Figure 1. Excess volumes (V^E_{123}) data for *N*-methylcyclohexylamine (NMC) (1) + toluene (2) + 1-propanol (3) at 303.15 K.
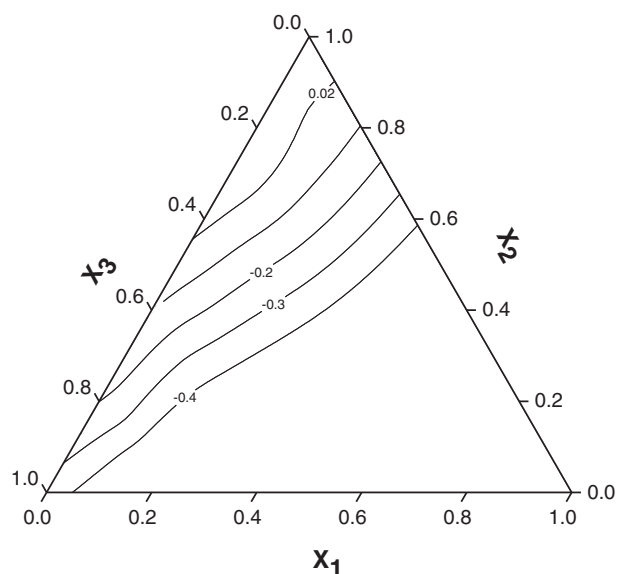
Figure 2. Excess volumes (V^E_{123}) data for *N*-methylcyclohexylamine (NMC) (1) + toluene (2) + 1-butanol (3) at 303.15 K.

to 303.15 ± 0.01 K. All the measurements were made at constant temperature employing a thermostat. The uncertainty in ternary excess volume data (V^E_{123}) is 0.005 cm^3 mol^{-1}.

The speed of sound (u) of pure liquids and in their mixtures were measured by using a multifrequency ultrasonic interferometer (M-82 Model, Mittal Enterprise, New Delhi, India) single-crystal variable-path at 303.15 K by using a digital constant temperature water bath. The uncertainty in the measurement of speed of sound was $\pm 0.3\%$. The temperature stability was maintained within ± 0.01 K by circulating thermostatic water bath around the cell with a circulating pump.

Results and Discussion

Excess Volume. The experimental ternary excess volume (V^E_{123}) data for the mixtures of NMC and toluene with 1-propanol, 1-butanol, and 1-pentanol are graphically represented in Figures 1–3. The density of ternary mixture was computed using the relation

$$\rho_{mix123} = (X_1 M_1 + X_2 M_2 + X_3 M_3)/V + V^E_{123} \qquad (1)$$

where X_1, X_2, and X_3 denote molefractions and M_1, M_2, and M_3 are the molecular weights of NMC, toluene and 1-alcohols respectively; V is the molar volume and V^E_{123} is experimental ternary excess volume.
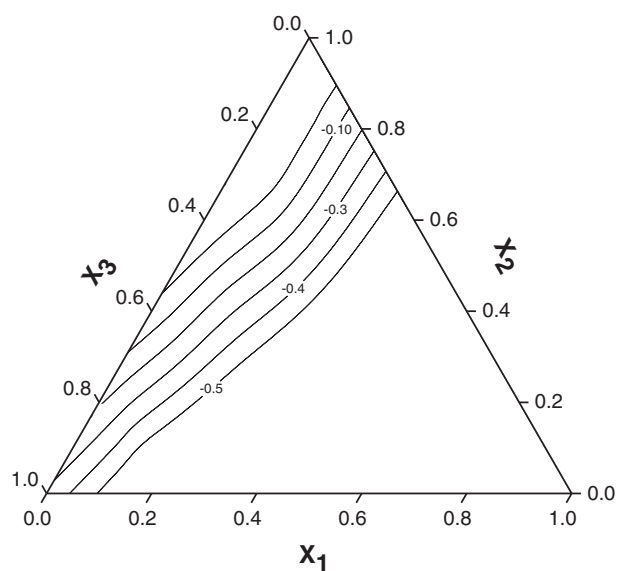

Figure 3. Excess volumes (V^E_{123}) data for *N*-methylcyclohexylamine (NMC) (1) + toluene (2) + 1-pentanol (3) at 303.15 K.

Table 2. Mole Fractions of *N*-Methylcyclohexylamine (X_1), Toluene (X_2), Experimental and Predicted Excess Volumes for the Ternary Mixtures of *N*-Methylcyclohexylamine (NMC) (1) + Toluene (2) + 1-Alkanols (3) at 303.15 K

X_1	X_2	$V^E/\text{cm}^3\,\text{mol}^{-1}$					
		Experimental	Redlich–Kister	Kohler	Tsao–Smith	Hwang	ΔV_{123}^{E} [a]
N-Methylcyclohexylamine (NMC) (1) + toluene (2) + 1-propanol (3)							
0.1285	0.0961	−0.638	−0.648	−0.631	−0.636	−0.669	0.010
0.1081	0.1010	−0.541	−0.550	−0.532	−0.536	−0.572	0.009
0.1122	0.1617	−0.533	−0.554	−0.525	−0.527	−0.565	0.011
0.0972	0.2302	−0.436	−0.445	−0.426	−0.424	−0.497	0.009
0.1218	0.3010	−0.462	−0.472	−0.462	−0.454	−0.493	0.010
0.0968	0.4206	−0.282	−0.292	−0.285	−0.270	−0.315	0.010
0.1288	0.5526	−0.194	−0.209	−0.219	−0.191	−0.248	0.015
0.1020	0.6376	−0.084	−0.097	−0.103	−0.076	−0.128	0.013
0.1107	0.6970	−0.046	−0.016	−0.066	−0.042	−0.090	0.015
0.1231	0.7510	−0.022	−0.039	−0.036	−0.023	−0.064	0.017
0.0970	0.8029	0.002	−0.009	−0.006	0.005	−0.025	0.011
0.0864	0.8506	0.005	−0.002	0.002	0.007	−0.013	0.007
N-Methylcyclohexylamine (NMC) (1) + toluene (2) + 1-butanol (3)							
0.1027	0.0866	−0.396	−0.407	−0.399	−0.403	−0.417	0.011
0.0782	0.1421	−0.287	−0.296	−0.287	−0.290	−0.304	0.009
0.0934	0.2017	−0.301	−0.317	−0.307	−0.308	−0.322	0.016
0.1081	0.3113	−0.263	−0.281	−0.275	−0.268	−0.284	0.018
0.0962	0.4027	−0.168	−0.185	−0.181	−0.168	−0.187	0.017
0.1304	0.5129	−0.131	−0.157	−0.161	−0.138	−0.170	0.026
0.1288	0.5710	−0.086	−0.112	−0.117	−0.092	−0.128	0.026
0.0713	0.6519	0.018	0.002	0.001	0.018	−0.017	0.016
0.0973	0.7011	0.005	−0.015	−0.019	0.001	−0.036	0.020
0.0818	0.7502	0.024	0.010	0.007	0.023	−0.013	0.014
0.1255	0.8069	−0.005	−0.020	−0.018	−0.012	−0.035	0.015
0.0644	0.8611	0.018	0.013	0.012	0.020	−0.004	0.005
N-Methylcyclohexylamine (NMC) (1) + toluene (2) + 1-pentanol (3)							
0.1002	0.0919	−0.438	−0.445	−0.445	−0.451	−0.445	0.007
0.1176	0.1024	−0.495	−0.503	−0.503	−0.511	−0.501	0.008
0.0969	0.2120	−0.341	−0.347	−0.357	−0.363	−0.339	0.006
0.0763	0.3316	−0.200	−0.206	−0.220	−0.223	−0.197	0.006
0.1210	0.4410	−0.209	−0.218	−0.238	−0.241	−0.216	0.009
0.0819	0.5076	−0.089	−0.097	−0.113	−0.111	−0.097	0.008
0.1060	0.5820	−0.065	−0.079	−0.092	−0.088	−0.084	0.014
0.1102	0.6504	−0.019	−0.038	−0.046	−0.039	−0.046	0.019
0.0982	0.7127	0.018	0.003	0.001	0.007	0.004	0.015
0.0762	0.7608	0.048	0.037	0.036	0.042	0.003	0.011
0.1001	0.8217	0.022	0.010	0.015	0.018	0.004	0.012
0.0862	0.8518	0.021	0.013	0.017	0.019	0.008	0.008

a) $\Delta V_{123}^{E} = V_{123}^{E}(\text{Exp}) - V_{123}^{E}(\text{bc})$, where $V_{123}^{E}(\text{bc})$ is computed from constituent binary data using the Redlich–Kister equation.

Further, the ternary excess volume data predicted from the binary data through the use of empirical relations[8] in terms of Redlich–Kister, Kohler, Tsao–Smith, and Hwang[9] equations are also included in Table 2 along with experimental ternary excess volume and the methods of calculation given as follows

Redlich–Kister equation is of the form:

$$V_{123}^{E} = \sum_{i<j} V_{ij}^{E}(x_i, x_j) \tag{2}$$

where

$$V_{ij}^{E} = x_i x_j \sum_{s=0}^{n} (A_s)_{ij}(x_i - x_j)^s \tag{3}$$

and x_i, x_j are the mole fractions of the components in a ternary mixture.

Kohler equation takes the following form:

$$V_{123}^{E} = (x_1 + x_2)^2 V_{12}^{E} + (x_1 + x_3)^2 V_{13}^{E} + (x_2 + x_3)^2 V_{23}^{E} \tag{4}$$

where

Table 3. The Standard Deviation Values (Redlich–Kister and Hwang eqs) of Binary Systems of $\sigma(V^E)$ (cm^3 mol^{-1}) at 303.15 K

System	Redlich–Kister				Hwang			
	a_0	a_1	a_2	$\sigma(V^E)$	b_0	b_1	b_2	$\sigma(V^E)$
NMC (1) + toluene (2)	0.355	0.891	0.002	0.001	0.354	1.063	−1.055	0.009
toluene (2) + 1-propanol (3)	0.142	0.849	0.349	0.005	0.026	1.475	−0.540	0.002
toluene (2) + 1-butanol (3)	0.387	0.646	0.016	0.003	0.463	0.2937	−0.898	0.003
toluene (2) + 1-pentanol (3)	0.359	0.645	0.577	0.002	0.167	1.537	0.022	0.002
NMC (1) + 1-propanol (3)	−6.237	2.703	3.925	0.002	−7.545	8.449	2.015	0.002
NMC (1) + 1-butanol (3)	−5.219	0.847	1.908	0.001	−5.852	3.461	1.531	0.002
NMC (1) + 1-pentanol (3)	−5.243	0.955	0.417	0.002	−5.382	1.695	−0.580	0.003

$$V_{ij}^E = x_i' x_j' \sum_{s=0}^{n} (A_s)_{ij}(x_i' - x_j')^s \tag{5}$$

at composition (x_i', x_j'), such that

$$x_i' = 1 - x_j' = \frac{x_i}{x_i + x_j} \tag{6}$$

where x_i and x_j are the ternary mole fractions.

Tsao–Smith equation can be expressed as:

$$V_{123}^E = x_2(1 + x_1)^{-1} V_{12}^E + x_3(1 - x_1)^{-1} V_{13}^E + (1 - x_1)V_{23}^E \tag{7}$$

where V_{12}^E, V_{13}^E, and V_{23}^E are the binary excess volumes at composition (x_i', x_j'), such that $x_i' = x_1$ for 1,2 and 1,3 binary systems and $x_2' = x_2/(x_2 + x_3)$ for 2,3 binary system.

Hwang equation is represented as:

$$\begin{aligned}
V_{123}^E/\text{cm}^3\,\text{mol}^{-1} &= x_1 x_2 (b_0^{(12)} + b_1^{(12)} x_1{}^3 + + b_2^{(12)} x_2{}^3) \\
&+ x_1 x_3 (b_0^{(13)} + b_1^{(13)} x_1{}^3 + + b_3^{(13)} x_3{}^3) \\
&+ x_2 x_3 (b_0^{(23)} + b_2^{(23)} x_2{}^3 + + b_3^{(23)} x_3{}^3)
\end{aligned} \tag{8}$$

The methods of calculation of ternary (V_{123}^E) were discussed earlier.[16,17] To generate ternary V^E data, through binary V^E data in terms of different pairs of the binary system namely NMC with toluene,[18] NMC and 1-alcohols[19] and toluene and 1-alcohols[20] were collected from literature and these data are included in Table 3 along with standard deviation $\sigma(V^E)$ values.

An examination of results in Table 2 show that the ternary excess volume data were negative at higher composition of 1-alcohol and the quantity tends to become positive as the alcohol composition was gradually decreased. The excess and deviation values reflect the interactions between component species, mainly depend upon the composition, the different molecular size and shape of the components. The important effects, which influence the sign and magnitude of excess thermodynamic functions were divided into physical, chemical, and structural contributions:

1) Physical contributions which comprise nonspecific physical interaction namely dispersion forces or weak dipole–dipole interactions leading to a positive contribution towards ternary excess volume.

2) Chemical effect includes charge transfer forces formation of H-bonds and other complex forming interactions making negative contribution to excess volume.

3) Geometric fitting of the component molecules to each other's structure and also due to difference in molar and free volumes.

Table 4. The Standard Deviation $\sigma(k_s)$ (TPa^{-1}) Values of All the Binary Systems Computed from the Redlich–Kister Equation at 303.15 K

System	a_0	a_1	a_2	$\sigma(k_s)$
NMC (1) + toluene (2)	70.77	22.22	−30.03	1
toluene (2) + 1-propanol (3)	7.00	163.00	−31.00	1
toluene (2) + 1-butanol (3)	70.00	55.00	44.00	1
toluene (2) + 1-pentanol (3)	67.00	64.00	−17.00	1
NMC (1) + 1-propanol (3)	−219.00	35.40	−68.30	2
NMC (1) + 1-butanol (3)	−166.50	21.84	89.70	2
NMC (1) + 1-pentanol (3)	−147.50	3.05	61.40	3

4) Association between unlike molecules through N–H⋯π interaction between amino group and π-electrons in aromatic ring.

The factor (i) will contribute to destruction of order and hence leads to expansion in volume and (ii), (iii), and (iv) factors would contribute to creation of order and causes contraction in volume. The actual value of excess volume would be determined by the relative strengths of the factors which were responsible for creation and destruction of orders.

It is well established that 1-alcohols are self-associated through hydrogen bonding. Dipole–dipole interactions too affect the properties of 1-alcohols.[21] Thus mixing of an amine with toluene and 1-alcohols may be expected to induce changes in hydrogen bonding equilibria and electrostatic interactions with different resultant contributions to the volume of the mixtures. Weakening of the interactions between the component molecules tends to result in an increase in volume. Perhaps, this is the most decisive factor in determining the sign and magnitude of deviation from ideal solution law.[22]

Generally, for ternary and quaternary mixtures fewer interactions have been reported. This is due to the fact that the addition of the third or fourth component to a mixture weakens the energy of interaction and the mixture tends to approach ideal behavior.[23,24] Thus, on the basis of V_{123}^E values it can be concluded that the order of interaction for the ternary mixtures of NMC and toluene with 1-alcohols follow the order:

$$1\text{-propanol} > 1\text{-butanol} > 1\text{-pentanol} \tag{9}$$

The positive excess volumes suggest that the higher 1-alcohols possess less proton-donating ability than the lower alcohols, and hence heteroassociation effects decrease in the ternary mixtures with an increase of chain length of linear alcohols.[25]

Table 5. Volume Fractions of *N*-Methylcyclohexylamine (φ_1), Toluene (φ_2), Density (ρ), Speed of Sound (u), Isentropic Compressibility (k_{s123}), Deviation in Isentropic Compressibility ($\acute{k}_{s123}$), Deviation in Isentropic Compressibility Computed from Computed Constituent Binary Data and ($\acute{k}_{s123(b)}$) and Δk_{s123} Values for Ternary Systems *N*-Methylcyclohexylamine (NMC) (1) + Toluene (2) + 1-Alkanols (3)

φ_1	φ_2	ρ /g cm^{-3}	u /m s^{-1}	k_{s123} /TPa^{-1}	$\acute{k}_{s123}$ /TPa^{-1}	$\acute{k}_{s123(b)}$ /TPa^{-1}	Δk_{s123} /TPa^{-1}
N-Methylcyclohexylamine (NMC) (1) + toluene (2) + 1-propanol (3)							
0.1955	0.1199	0.81935	1253	777	−41	−42	1
0.1699	0.1276	0.81744	1248	785	−39	−40	1
0.1719	0.1991	0.82180	1251	777	−33	−36	3
0.1467	0.2793	0.82452	1248	779	−23	−29	6
0.1765	0.3506	0.83057	1252	768	−14	−23	9
0.1368	0.4777	0.83475	1250	767	−2	−10	8
0.1710	0.5898	0.84259	1269	737	3	−4	7
0.1339	0.6728	0.84491	1265	739	6	1	5
0.1420	0.7186	0.84784	1273	728	5	1	4
0.1543	0.7565	0.85062	1279	718	1	−1	2
0.1214	0.8077	0.85192	1280	716	2	0	2
0.1072	0.8486	0.85370	1284	710	0	−1	1
N-Methylcyclohexylamine (NMC) (1) + toluene (2) + 1-butanol (3)							
0.1401	0.0950	0.81690	1255	777	−13	−12	−1
0.1069	0.1560	0.81791	1249	784	−5	−6	1
0.1258	0.2182	0.82230	1253	775	−3	−5	2
0.1423	0.3293	0.82887	1261	759	3	−3	6
0.1255	0.4224	0.83250	1266	749	9	2	7
0.1652	0.5223	0.83953	1280	727	12	2	10
0.1619	0.5771	0.84206	1281	724	13	4	9
0.0906	0.6661	0.84299	1277	727	15	10	5
0.1216	0.7042	0.84660	1281	720	12	7	5
0.1021	0.7528	0.84828	1282	717	11	7	4
0.1529	0.7901	0.85286	1288	707	1	−1	2
0.0797	0.8565	0.85309	1286	709	4	3	1
N-Methylcyclohexylamine (NMC) (1) + toluene (2) + 1-pentanol (3)							
0.1202	0.0886	0.82000	1276	749	−10	−11	1
0.1405	0.0984	0.82169	1278	745	−11	−12	1
0.1165	0.2049	0.82498	1273	748	−3	−6	3
0.0923	0.3226	0.82888	1267	752	6	1	5
0.1453	0.4255	0.83618	1270	741	10	2	8
0.0993	0.4945	0.83693	1266	746	14	7	7
0.1279	0.5646	0.84138	1271	736	13	6	7
0.1330	0.6311	0.84455	1274	729	11	6	5
0.1190	0.6940	0.84687	1276	725	10	6	4
0.0928	0.7450	0.84816	1276	724	9	6	3
0.1214	0.8011	0.85229	1287	708	1	0	1
0.1049	0.8334	0.85326	1287	708	1	0	1

The quantity ΔV_{123}^{E}, difference between measured ternary data and computed from the constituent binary data through the Redlich–Kister relation are given in the last column of Table 2.

Further, the positive values of ΔV_{123}^{E} are attributed to the weakening of charge-transfer interactions by the addition of a third component.[26] In general, thermodynamic properties of ternary mixtures on nonelectrolytes should in principle, be determined from the properties of respective binary mixtures[27,28] and the behavior[29] of a ternary system is assumed to be closely dependent on the interaction of the constituent binary mixtures, and hence it should be possible to evaluate V_{123}^{E} of nonelectrolytes considering the corresponding excess volume of the binary systems.

A perusal of V_{123}^{E} data in Table 2 suggest that predictive expressions proposed by Redlich–Kister, Kohler, and Tsao–Smith and Hwang give satisfactory estimations in ternary excess volume in all the three ternary mixtures.

Isentropic Compressibility. The isentropic compressibility of ternary mixtures (k_{123}) was calculated from the expression

$$k_{123} = u^{-2}{}_{123}\rho^{-1}{}_{\text{mix}123} \qquad (10)$$

where u_{123} and $\rho_{\text{mix}123}$ denotes speed of sound and density of ternary mixture respectively.

The deviation in isentropic compressibility ($\acute{k}_{s123}$) was estimated using the relation

$$\acute{k}_{s123} = k_{s123} - \varphi_1 k_{s1} - \varphi_2 k_{s2} - \varphi_3 k_{s3} \qquad (11)$$

where φ_1, φ_2, φ_3, k_{s1}, k_{s2}, and k_{s3} are the volume fractions and isentropic compressibilities of the pure components 1, 2, and 3 respectively. The quantity Δk_{s123} the difference between measured value of $\acute{k}_{s123}$ and that computed from binary data $\acute{k}_{s123(b)}$ has been calculated using the relation

$$\Delta k_{s123} = \acute{k}_{s123} - \acute{k}_{s123(b)} \qquad (12)$$

The latter quantity $\acute{k}_{s123(b)}$ was computed using Redlich–Kister relation[30]

$$\acute{k}_{s123(b)} = k_{s12} + k_{s13} + k_{s23} \qquad (13)$$

where k_{s12}, k_{s13}, and k_{s23} denote the deviation in isentropic compressibilities for the three binary mixtures and these are estimated using the smoothing equation

$$k_{sij} = \varphi_1\varphi_2[a_0 + a_1(\varphi_1 - \varphi_2) + a_2(\varphi_1 - \varphi_2)^2] \qquad (14)$$

where a_0, a_1, and a_2 are the constants obtained by the method of least squares; φ_1 and φ_2 are the volume fraction of components 1 and 2 respectively. Further, the binary parameters that were required to compute ternary compressibility data for the mixtures of NMC with toluene,[12] NMC with 1-alcohol[31] and toluene with 1-alcohols[32] were collected from the literature. The constants of all the binary systems computed from eq 14, were given in Table 4 along with $\sigma(k_{sij})$.

The speed of sound (u), density of the mixture ($\rho_{\text{mix}123}$), isentropic compressibility (k_{123}), and deviation in isentropic compressibility ($\acute{k}_{s123}$) for the three ternary mixtures are given in Table 5. Further, the quantity Δk_{s123}, the difference between measured data of $\acute{k}_{s123}$ and that computed from the constituent binary data $\acute{k}_{s123(b)}$ are also included in Table 5. The deviation in isentropic compressibility (Δk_{s123}) for the three ternary mixtures are also graphically represented in Figures 4–6.

As examination of Δk_{s123} data that were present in Table 5 suggests that the values were positive over the entire composition range in all the binary mixtures of NMC and toluene with 1-alcohols and these were 3 to 4 times the experimental error. This suggests that Redlich–Kister equation was capable of giving good estimation of deviation in isentropic compressibility from that of constituent binaries.[12,31,32]

In general, the isentropic compressibility data of ternary liquid mixture depends upon an increase or a decrease in free space[33] in liquid state, and arise generally due to loose packing of molecules which leave some free space between them. The intermolecular free space and its dependent properties are related to intermolecular interactions and may reveal the information regarding the interaction, which may be occurring when the liquids are mixed together.

The actual deviation in isentropic compressibility would depend upon the balance between the two opposing effects (increase and decrease in free space between molecules in liquid mixture).[34] The experimental Δk_{s123} values in Table 5
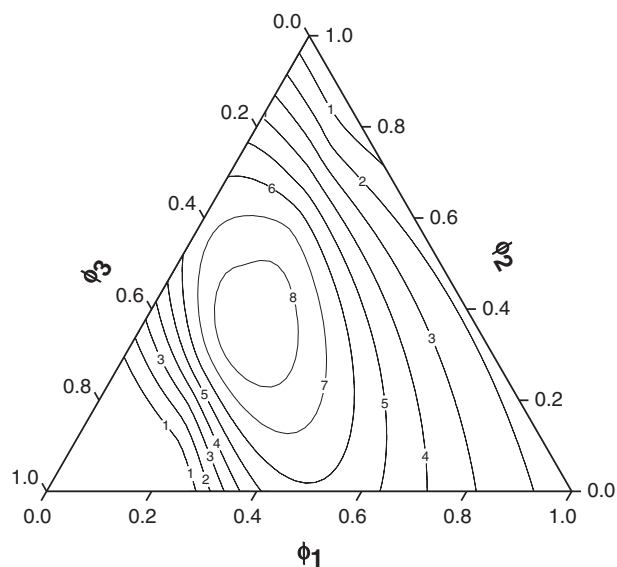

Figure 4. Deviation in isentropic compressibility (Δk_{s123}) data for *N*-methylcyclohexylamine (NMC) (1) + toluene (2) + 1-propanol (3) at 303.15 K.
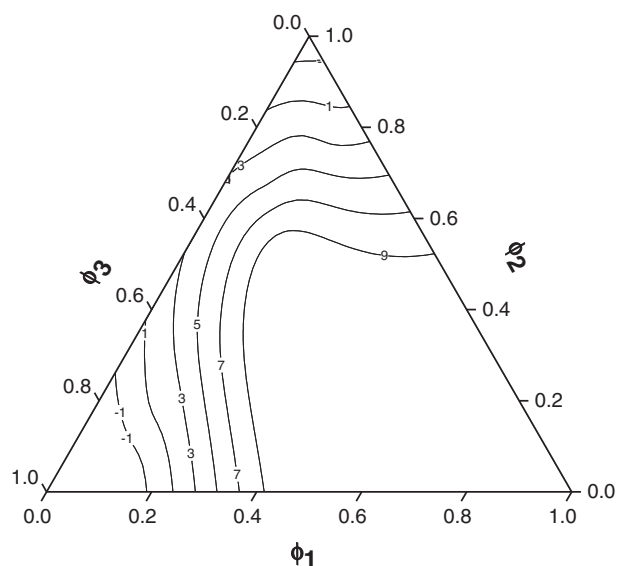

Figure 5. Deviation in isentropic compressibility (Δk_{s123}) data for *N*-methylcyclohexylamine (NMC) (1) + toluene (2) + 1-butanol (3) at 303.15 K.

suggest that the former effect was dominant in all three ternary mixtures. Further, Δk_{s123} values also indicate that constituent binaries behave in the same way in the ternary mixtures as they behave in indusial binaries. Transference of charge due to the partial double bond character in toluene is responsible for compact structural arrangement of molecules resulting in decrease in deviation in isentropic compressibility.[35]

The dependence of ΔV_{123}^E and Δk_{s123} were fitted with an equation proposed by Redlich–Kister[30] and it is expressed by the following relation:

$$\Delta V_{123}^E/\text{cm}^3\,\text{mol}^{-1} = x_1 x_2 x_3[A + Bx_1(x_2 - x_3) + Cx_1^2(x_2 - x_3)^2] \qquad (15)$$

Table 6. The Standard Deviation Values $\sigma(\Delta V_{123}^E)$ and $\sigma(\Delta k_{s123})$ for Ternary Systems of NMC (1) + Toluene (2) + 1-Alcohols (3) at 303.15 K

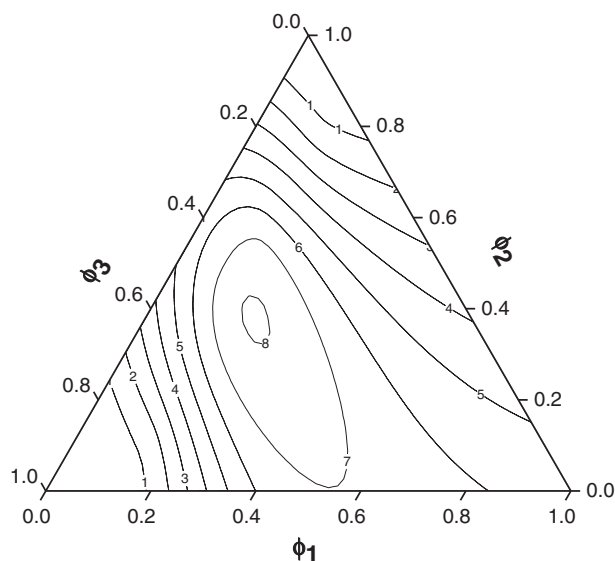| System	A /cm^3 mol^{-1}	B /cm^3 mol^{-1}	C /cm^3 mol^{-1}	$\sigma(\Delta V_{123}^E)$ /cm^3 mol^{-1}	A /TPa^{-1}	B /TPa^{-1}	C /TPa^{-1}	$\sigma(\Delta k_{s123})$ /TPa^{-1}
NMC (1) + toluene (2) + 1-propanol (3)	0.489	3.726	129.865	0.001	311.712	795.424	16038.775	0
NMC (1) + toluene (2) + 1-butanol (3)	0.953	2.258	123.551	0.001	352.446	2366.301	−29045.291	1
NMC (1) + toluene (2) + 1-pentanol (3)	0.415	6.985	173.263	0.001	318.098	332.517	−24875.677	0

Figure 6. Deviation in isentropic compressibility (Δk_{s123}) data for N-methylcyclohexylamine (NMC) (1) + toluene (2) + 1-pentanol (3) at 303.15 K.

$$\Delta k_{123}^s/\text{TPa}^{-1} = \varphi_1 \varphi_2 \varphi_3 [A + B\varphi_1(\varphi_2 - \varphi_3) + C\varphi_1^2(\varphi_2 - \varphi_3)^2] \quad (16)$$

where A, B, and C are the ternary constants which were obtained by least square method. The values of coefficients were in turn used to compute standard deviation $\sigma(Y_{123}^E)$.

$$\sigma(Y_{123}^E) = \Delta V_{123}^E/\Delta k_{s123}$$
$$= [\Sigma(Y_{123\text{exp}}^E - Y_{123\text{cal}}^E)^2/(m-n)]^{1/2} \quad (17)$$

where 'm' is the total number of experimental points and 'n' is the number of coefficients in eqs 15 and 16 and these are given in Table 6.

Conclusion

For three ternary mixtures of N-methylcyclohexylamine and toluene as common components and 1-alcohols, namely, 1-propanol, 1-butanol, and 1-pentanol, excess volume and isentropic compressibility were calculated from experimental density and speed of sound data measured at 303.15 K. The experimental ternary (V_{123}^E) data were compared with empirical relations proposed by Redlich–Kister, Kohler, Tsao–Smith, and Hwang. The experimental speed of sound (u) and density (ρ_{mix123}) of mixture were used to compute isentropic compressibility (k_{s123}). Further, the data were analyzed in terms of intermolecular interactions between component molecules and also in the light constituent binaries. Thus, on the basis of V_{123}^E values it can be concluded that the order of interaction

for the ternary mixtures of NMC and toluene with 1-alcohols follow the order: 1-propanol > 1-butanol > 1-pentanol. Redlich–Kister, Kohler, Tsao–Smith, and Hwang gives satisfactory estimations in ternary excess volume in all the three ternary mixtures.

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