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Excess thermodynamic and spectroscopic study of ternary mixtures containing *N*-methylcyclohexylamine, bromobenzene, and 1-alkanols at 303.15 K

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Abstract Excess volume and sound speed data for three ternary mixtures, containing *N*-methylcyclohexylamine and bromobenzene as common components and 1-alkanols such as 1-propanol, 1-butanol, and 1-pentanol as third component, were measured at 303.15 K over the entire composition range. The experimental speeds of sound were used to compute isentropic compressibility and deviation in isentropic compressibility. The excess volume data of all mixtures were compared with data obtained from predictive expressions due to Redlich–Kister, Kohler, Tsao–Smith, and Hwang et al.'s equations. Further, the experimental results were analyzed in terms of molecular interactions between component molecules with FT-IR spectrum.

Graphical Abstract Excess volume and speed of sound measured at 303.15 K for three ternary mixtures containing *N*-methylcyclohexylamine (1), bromobenzene (2), and 1-alcohols (3). Results were used to calculate derived thermodynamic properties and analyzed in terms of intermolecular interactions between component molecules.

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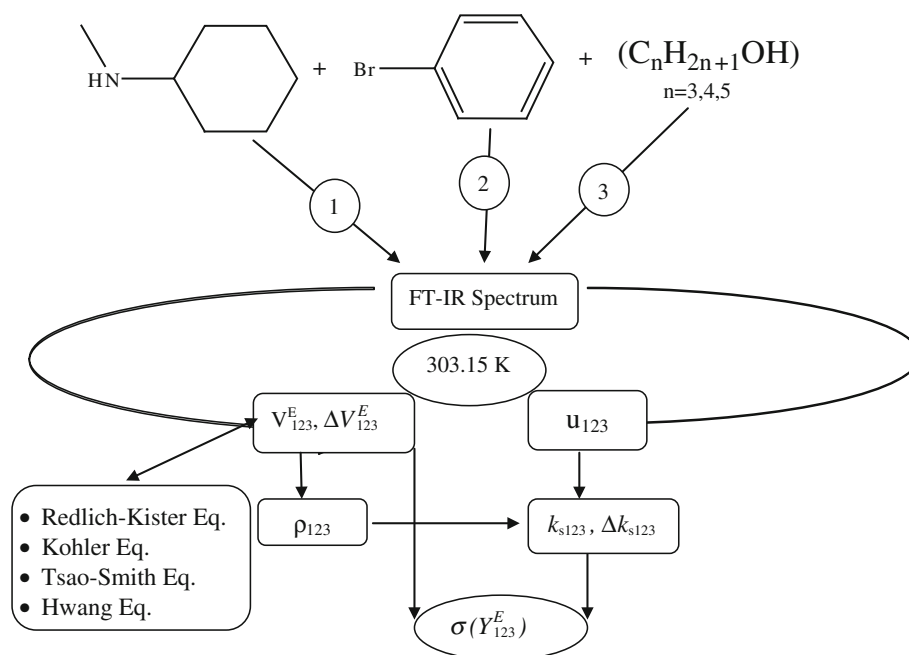
Keywords Ternary mixture · Isentropic compressibility · FT-IR spectrum · Molecular interaction

Introduction

Liquids and liquid mixtures were widely used in processing and product formulation in many industrial applications. Thermodynamic and transport properties of the liquids provide useful information about physical forces acting between the molecules of the same substance in pure liquids and molecules of different substances in liquid mixtures. When two liquids were mixed together, the resulting changes in physical and thermodynamic properties can be considered as a sum of several contributions due to free volume change, change in energy, change in molecular orientations, steric hindrances, etc. Properties such as speed of sound or surface tension and their variation with temperature and composition of the binary mixture are useful to design engineering processes and in chemical and biological industries. The qualitative and quantitative analysis of excess functions also provides information on the nature of molecular interactions in the binary mixtures [1–3]. So, our research group engaged in systematic studies on thermodynamic properties of binary and ternary liquid mixtures [4–8]. The present work is focused on the qualitative explanation of the influence of molecular structure on volumetric and sound speed data of ternary mixtures containing N-methylcyclohexylamine (NMC) and bromobenzene when mixed with 1-alkanols. Moreover, a survey of literature has shown that no experimental ternary volumetric and sound speed data on NMC and bromobenzene with 1-alkanols were reported earlier.

In addition, alkanols and amines were widely used in a variety of industrial and consumer applications, and hence, knowledge of their physical properties is also of great importance from a practical point of view. Alkanols are used as fuel, perfumes, cosmetics, paints, varnishes, drugs, explosives, fats, waxes, resins, plastics, rubber, detergents, etc. [9]. Cyclic amine is used in the production of pharmaceuticals and other chemicals including insecticides, pesticides, plasticizers, emulsifying agents, dyes, dry cleaning agents, and corrosion inhibitors [10]. In the present investigation, we report here new experimental data on excess volume and deviation in isentropic compressibility data of three ternary liquid systems containing N-methylcyclohexylamine and bromobenzene with 1-alkanols as the chain length of 1-alkanol increases from 1-propanol to 1-pentanol that may influence both the sign and magnitude of ternary excess volume (V_{123}^E) and deviation in isentropic compressibility (Δk_{s123}). Further, the ternary V_{123}^E data were analyzed in terms of predictive expressions, proposed in the literature [11–13]. The experimental data were discussed in terms of molecular interactions between component molecules that were explained on the basis of FT-IR spectrum.

Experimental

Materials

In the present investigation, N-methylcyclohexylamine (NMC) (Merck >99.5 %), bromobenzene (S.D. Fine Chemicals >99.5 %), 1-propanol (Merck >99.5 %), 1-butanol (Merck >99.5 %), and 1-pentanol (Merck >99.5 %)

Table 1 Name of the chemical, source, CAS number, purity, water content, density (ρ), and speed of sound (u) data of pure components at 303.15 K and $p = 0.1$ MPa

Compound	Source	CAS number	Purity in mass fraction	Water content/%	Density/ρ/g cm^{-3}		Speed of sound/u/ m s^{-1}	
					Exp.	Lit.	Exp.	Lit.
N-methylcyclohexylamine	Merck	100-60-7	0.995	0.032	0.84683	0.84687 [16]	1356	1353 [16]
Bromobenzene	S.D. Fine. Chem.	108-86-1	0.995	0.018	1.48149	1.48150 [14]	1163	1162 [17]
1-Propanol	Merck	71-23-8	0.995	0.024	0.79566	0.79564 [18]	1189	1190 [18]
1-Butanol	Merck	71-36-3	0.995	0.016	0.80205	0.80203 [18]	1229	1228 [18]
1-Pentanol	Merck	71-41-0	0.995	0.028	0.80764	0.80762 [18]	1256	1258 [18]

The standard uncertainties are $u(T) = 0.01$ K, $u(p) = 0.1$ kPa, $u(\rho) = 0.00002$ g cm^{-3}, and $u(u) = \pm 0.3$ %

were purified by the standard methods described in the literature [14, 15]. Further, the water content of solvents used in this work was measured by Analab (Micro Aqua Cal 100) Karl Fischer Titrator and Karl Fisher reagent from Merck. The density (ρ) and sound speed (u) data were compared with the literature values which were in good agreement [14, 16–18], and these data are given in Table 1 along with their CAS number, purity, and water content.

Measurements

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 had uniform bore and can be closed using a Teflon cap. The marks on the capillary were calibrated with triple distilled water.

An analytical balance (Afoset, ER-120A, India) with a precision of ± 0.1 mg has been used for all weight measurements. The uncertainty in the mole fraction was found to be ± 0.0001.

Excess volume (V_{123}^{E}) data for the ternary mixtures were measured using dilatometer, which was described earlier [19]. 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 weighing. The entire dilatometer was placed in a thermostat that could be maintained to 303.15 $\pm$ 0.01 K. All the measurements were taken at constant temperature employing a thermostat. The measured ternary excess volume data (V_{123}^{E}) were accurate to ± 0.003 cm^3 mol^{-1}.

The speed of sound (u) data of pure liquids and their mixtures were measured by using a single-crystal, variable-path multifrequency ultrasonic interferometer (M-82 Model, Mittal Enterprise, New Delhi, India) operated at 2 MHz, by using a digital constant temperature water bath

at 303.15 K. The total distance d (cm) moved by the reflector is given by $d = n\lambda/2$, where λ is the wavelength. The frequency, ν, of the crystal being accurately known (2.0 MHz), the speed of sound, u, in ms^{-1} is calculated by using the relation $u = \nu\lambda$. The uncertainty in the measurement of speed of sound was ± 0.3 %. The temperature stability was maintained within ± 0.01 K by digital, circulating thermostatic water bath around the cell with a circulating pump.

FT-IR spectra were recorded on a FT-IR spectrophotometer (JASCO FT-IR-4100, Japan; wave number range 7800–400 cm^{-1}; wavelength range 1282–25,000 nm). The devise has maximum resolution 0.9 cm^{-1} and has 22,000/1 signal-to-noise ratio.

Results and discussion

Excess volume

Excess volume data (V_{123}^{E}) of three ternary liquid systems containing NMC and bromobenzene with 1-propanol, 1-butanol, and 1-pentanol were measured at 303.15 K, and these are graphically represented in Figs. 1–3. Further, the experimental V_{123}^{E} data are given in Table 2 along with predictive expressions namely Redlich–Kister, Kohler, Tsao–Smith, and Hwang et al.'s equations.

Redlich–Kister equation [12] can be expressed as:

$$V_{123}^{E} = \sum_{i<j} V_{ij}^{E} (x_i, x_j) \tag{1}$$

where $V_{ij}^{E} = x_i x_j \sum_{s=0}^{n} (A_s)_{ij}(x_i - x_j)^s$ and x_i and x_j are the mole fractions of the components in a ternary mixture.

Kohler expression [11]:

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

where $V_{ij}^{E} = x_i' x_j' \sum_{s=0}^{n} (A_s)_{ij}(x_i' - x_j')^s$ at composition (x_i', x_j'), such that
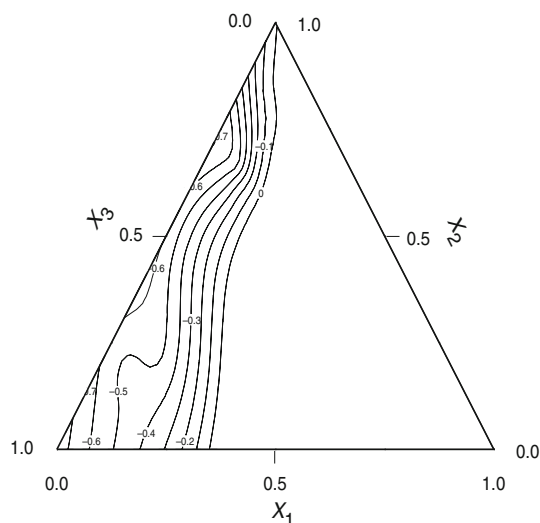
Fig. 1 Excess volume (V_{123}^E) data for N-methylcyclohexylamine (NMC) (1) + bromobenzene (2) + 1-propanol (3) at 303.15 K
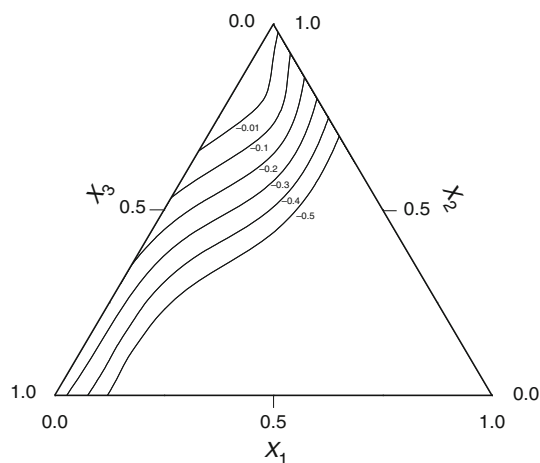

Fig. 2 Excess volume (V_{123}^E) data for N-methylcyclohexylamine (NMC) (1) + bromobenzene (2) + 1-butanol (3) at 303.15 K
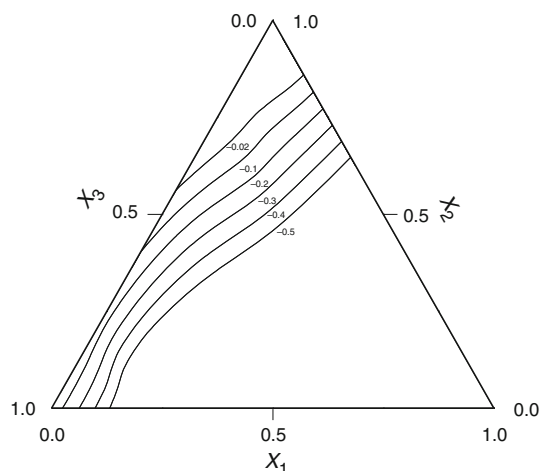

Fig. 3 Excess volume (V_{123}^E) data for N-methylcyclohexylamine (NMC) (1) + bromobenzene (2) + 1-pentanol (3) at 303.15 K

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

where x_i and x_j are the ternary mole fractions.

Tsao–Smith expression [11] is of the form:

$$V_{123}^E = x_2(1 + x_1)^{-1} V_{12}^E + x_3(1 - x_1)^{-1} V_{13}^E + (1 - x_1) V_{23}^E \tag{3}$$

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 $x_2' = \frac{x_2}{x_2 + x_3}$ for 2, 3 binary system.

Hwang et al. equation [13]:

$$
\begin{aligned}
V^{E(123)}/\text{cm}^3\,\text{mol}^{-1} &= x_1 x_2 \left(b_0^{(12)} + b_1^{(12)} x_1^3 + b_2^{(12)} x_2^3 \right) \\
&+ x_1 x_3 \left(b_0^{(13)} + b_1^{(13)} x_1^3 + b_3^{(13)} x_3^3 \right) \\
&+ x_2 x_3 \left(b_0^{(23)} + b_2^{(23)} x_2^3 + b_3^{(23)} x_3^3 \right) \tag{4}
\end{aligned}
$$

The magnitude ΔV_{123}^E and difference between measured ternary data and computed from the constituent binary data through the Redlich–Kister relation are given in Table 2. The binary data that are used to compute ternary excess volume data for the mixtures NMC + bromobenzene, NMC + 1-alkanols, and bromobenzene + 1-alkanols were collected from the literature [20–22], and these data are included in Table 3 along with SD values $\sigma(V^E)$.

An examination of curves of constant excess molar volumes which are plotted in Figs. 1–3 clearly suggests that these data were negative over the entire mole fraction range for the investigated ternary liquid mixtures. The important factors, which influence the sign and magnitude of excess thermodynamic function, were divided into physical, chemical, and structural contributions:

1. physical contribution comprises dispersion forces
2. chemical contribution includes charge transfer forces and formation of H bonds
3. geometrical fitting of the component molecule into each other's structure, and also due to difference in molar and free volumes.

The factor (1) will contribute to expansion in volume and (2) and (3) factors would contribute to contraction in volume. The actual value of excess volume would be determined by the relative strengths of the factors which were responsible for expansion and contraction. It is clearly evident from Table 2 that the negative magnitude of mixture decreases from 1-propanol to 1-pentanol due to increase in the chain length of 1-alkanols.

The negative excess volume data for the ternary mixtures of NMC and bromobenzene with 1-alkanols of the studied systems reveal that hetero-associates forming cross complexes in the alkanol+ amine mixtures have stronger

Table 2 Mole fractions of N-methylcyclohexylamine (x_1), bromobenzene (x_2), experimental, and predicted excess volume data for the ternary systems of N-methylcyclohexylamine (NMC) (1) + bromobenzene (2) + 1-alkanols (3) at 303.15 K

x_1	x_2	V_{123}^E/cm^3 mol^{-1}					ΔV_{123}^E*
		Exp.	(Redlich–Kister)	Kohler	Tsao–Smith	Hwang	
NMC (1) + bromobenzene (2) + 1-propanol (3)							
0.0919	0.1007	−0.516	−0.526	−0.511	−0.513	−0.545	0.010
0.0706	0.1826	−0.423	−0.432	−0.411	−0.413	−0.447	0.009
0.1129	0.2303	−0.566	−0.581	−0.561	−0.560	−0.600	0.015
0.1013	0.3411	−0.447	−0.463	−0.443	−0.436	−0.485	0.016
0.0876	0.4206	−0.344	−0.357	−0.339	−0.329	−0.382	0.013
0.0916	0.5179	−0.254	−0.269	−0.257	−0.241	−0.303	0.015
0.1029	0.6227	−0.157	−0.173	−0.169	−0.147	−0.214	0.016
0.1107	0.7191	−0.067	−0.084	−0.081	−0.064	−0.120	0.017
0.1212	0.7604	−0.033	−0.052	−0.044	−0.036	−0.148	0.019
0.0819	0.663	−0.699	−0.737	−0.689	−0.526	−0.082	0.038
0.1004	0.813	−0.009	−0.019	−0.011	−0.006	−0.037	0.010
0.0619	0.8402	0.008	0.002	0.004	0.013	−0.008	0.006
NMC (1) + bromobenzene (2) + 1-butanol (3)							
0.0929	0.0709	−0.439	−0.445	−0.442	−0.473	−0.452	0.006
0.1011	0.0987	−0.475	−0.485	−0.481	−0.527	−0.491	0.010
0.1119	0.1009	−0.512	−0.523	−0.520	−0.570	−0.528	0.011
0.0707	0.1911	−0.386	−0.394	−0.384	−0.447	−0.397	0.008
0.099	0.2207	−0.458	−0.47	−0.461	−0.554	−0.473	0.012
0.1041	0.3210	−0.413	−0.427	−0.415	−0.545	−0.433	0.014
0.1230	0.4106	−0.367	−0.383	−0.373	−0.541	−0.400	0.016
0.1147	0.5020	−0.267	−0.281	−0.271	−0.447	−0.303	0.014
0.0811	0.9161	−0.132	−0.144	−0.135	−0.291	−0.165	0.012
0.0901	0.7002	−0.075	−0.088	−0.082	−0.238	−0.108	0.013
0.1005	0.8017	−0.021	−0.030	−0.026	−0.116	−0.040	0.009
0.0612	0.8506	−0.001	−0.006	−0.005	−0.096	−0.010	0.005
NMC (1) + bromobenzene (2) + 1-pentanol (3)							
0.099	0.0714	−0.411	−0.520	−0.525	−0.532	−0.515	0.009
0.1017	0.1015	−0.515	−0.526	−0.534	−0.543	−0.518	0.011
0.1106	0.1926	−0.503	−0.522	−0.533	−0.548	−0.504	0.019
0.0610	0.2317	−0.336	−0.348	−0.355	−0.363	−0.335	0.012
0.0710	0.3308	−0.316	−0.332	−0.340	−0.349	−0.318	0.016
0.0828	0.4210	−0.278	−0.297	−0.305	−0.313	−0.288	0.019
0.1007	0.5150	−0.221	−0.246	−0.252	−0.260	−0.247	0.025
0.1149	0.5917	−0.164	−0.191	−0.194	−0.201	−0.119	0.027
0.1271	0.6420	−0.121	−0.151	−0.151	−0.158	−0.163	0.030
0.1020	0.6806	−0.087	−0.109	−0.110	−0.114	−0.119	0.022
0.0916	0.7510	−0.043	−0.059	−0.058	−0.06	−0.067	0.016
0.1210	0.8311	−0.005	−0.016	−0.012	−0.039	−0.020	0.011

The standard uncertainties are $u(x_1) = 0.0001$ and $u(V^E) = 0.003$ cm^3 mol^{-1}

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

O–H···N bonds than O–H···O and N–H···N bonds. This can be explained as follows: the free electron pair around the nitrogen atom with less "s" and more "p" character has a higher polarizability and acts as a good proton acceptor for the donor −OH groups of the alkanols, which are more efficient than the −OH group itself. As reported in the

Table 3 SD values (Redlich–Kister and Hwang equations) of binary systems of $\sigma(V^E)$ at 303.15 K

System	Redlich–Kister/cm^3 mol^{-1}				Hwang/cm^3 mol^{-1}			
	a_0	a_1	a_2	$\sigma(V^E)$	b_0	b_1	b_2	$\sigma(V^E)$
NMC (1) + bromobenzene (2)	0.088	0.006	−0.089	0.002	0.092	0.048	−0.084	0.006
Bromobenzene (2) + 1-propanol (3)	−0.281	0.913	0.138	0.007	−0.327	1.271	−0.904	0.008
Bromobenzene (2) + 1-butanol (3)	−0.382	0.989	−0.169	0.005	−0.327	0.960	−1.400	0.009
Bromobenzene (2) + 1-pentanol (3)	−0.283	0.714	−0.051	0.003	−0.266	0.782	−0.919	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

Table 4 SD $\sigma(\kappa_s)$ values of all the binary systems computed from Redlich–Kister equation at 303.15 K

System	a_0/TPa^{-1}	a_1/TPa^{-1}	a_2/TPa^{-1}	$\sigma(\kappa_s)$/TPa^{-1}
NMC (1) + bromobenzene (2)	−138.7	2.2	37.5	1
bromobenzene (2) +1-propanol (3)	−139.6	283.2	−156.2	3
bromobenzene (2) + 1-butanol (3)	−63.9	89.9	24.5	3
bromobenzene (2) + 1-pentanol (3)	−57.9	66.9	32.8	1
NMC (1) + 1-propanol (3)	−219.0	35.4	−68.3	2
NMC (1) + 1-butanol (3)	−166.5	21.8	89.7	2
NMC (1) + 1-pentanol (3)	−147.5	3.1	61.4	3

literature [23], in the liquid mixture consisting of amine and alcohol, it is estimated that nitrogen atom of amine group is more polarized and leads to contraction in volume. The negative sign of V_{123}^E indicates a net packing effect contributed by structural changes arising from interstitial accommodation [6]. It is evident from the ternary V_{123}^E data in Table 2 that the negative V_{123}^E values were larger in the mixture with 1-propanol and decrease as the chain length of the 1-alkanol increases from 1-propanol to 1- pentanol. This trend indicates that the strength of the intermolecular hydrogen bonding of N-methylcyclohexylamine with 1-propanol is much stronger than 1-butanol and 1-pentanol as follows the order:

1−propanol > 1−butanol > 1−pentanol

The longer 1-alkanols would increase the basicity of the oxygen and make the hydroxyl proton less available for H bonding. In addition, the most efficient packing can be attributed to the lower alkanols, which decreases with increasing chain length of 1-alkanols. The crowded molecules of amine, as a consequence of steric hindrance, are better packed in the more open structure of the longer alkanols. In the systems of 1-alkanols with N-methylcyclohexylamine, the absolute value of the V^E decreases with decreasing effective dipole moment of the 1-alkanols [24].

Bromo group in bromobenzene is an electron-withdrawing group, and it tends to decrease the electron density of the benzene ring, as a result bromobenzene becomes relatively poor electron donor toward electron-seeking H atom of 1-alkanol. However, the partial accommodation of linear alkanol molecules between the bromobenzene molecules and interactions due to the high polarity of bromobenzene lead to more negative V_{123}^E values for 1-propanol system when compared to 1-butanol and 1-pentanol. An examination of ternary data in Table 2 reveals that the predictive expressions proposed by Redlich–Kister, Kohler, Tsao–Smith, and Hwang et al. give satisfactory estimation in terms of ternary excess volumes with SD < 0.3 in all the mixtures.

Isentropic compressibility

The isentropic compressibility of ternary mixtures (κ_{s123}) was calculated from the expression

$$\kappa_{s123} = u_{123}^{-2}\rho_{mix123}^{-1} \qquad (5)$$

where u_{123} and ρ_{mix123} indicate sound speed and density of ternary mixtures, respectively.

The density of a ternary liquid mixture (ρ_{mix123}) was computed using the expression

$$\rho_{mix123} = (x_1 M_1 + x_2 M_2 + x_3 M_3)/(V \pm V_{123}^E) \qquad (6)$$

where x_1, x_2, and x_3 represent mole fractions and M_1, M_2, and M_3 are the molecular weights of NMC, bromobenzene,

Table 5 Volume fractions of N-methylcyclohexylamine (ϕ_1), bromobenzene (ϕ_2), density (ρ), speed of sound (u), isentropic compressibility (κ_{s123}), deviation in isentropic compressibility (κ'_{s123}), deviation in isentropic compressibility computed from computed constituent binary data and ($\kappa'_{s123(b)}$) and $\Delta\kappa_{s123}$ values for ternary systems N-methylcyclohexylamine (NMC) (1) + bromobenzene (2) +1-alkanols (3)

Φ_1	Φ_2	ρ/g cm^3	u/m s^{-1}	κ_{s123}/TPa^{-1}	κ'_{s123}/TPa^{-1}	$\kappa'_{s123(b)}$/TPa^{-1}	$\Delta\kappa_{s123}$/TPa^{-1}
NMC (1) + bromobenzene (2) + 1-propanol (3)							
0.1463	0.1271	0.89581	1225	744	−62	−64	2
0.1107	0.2271	0.96183	1205	716	−62	−66	4
0.1693	0.2737	0.99840	1207	687	−59	−65	6
0.1475	0.3937	1.07847	1183	663	−45	−53	8
0.1253	0.4769	1.13341	1268	549	−33	−42	9
0.1267	0.5678	1.19484	1156	626	−23	−31	8
0.1369	0.6566	1.25509	1154	598	−16	−24	8
0.1425	0.7336	1.30704	1157	571	−13	−19	6
0.1572	0.7620	1.32668	1163	557	−14	−19	5
0.1089	0.6991	1.28980	1145	591	−14	−19	5
0.1264	0.8119	1.35910	1160	547	−12	−15	3
0.0790	0.8502	1.38283	1148	549	−8	−10	2
NMC (1) + bromobenzene (2) + 1-butanol (3)							
0.1277	0.0773	0.86419	1235	759	−21	−23	2
0.138	0.1068	0.88510	1231	746	−23	−26	3
0.152	0.1088	0.88731	1233	741	−25	−28	3
0.0965	0.2067	0.95065	1205	724	−22	−27	5
0.133	0.235	0.97222	1207	706	−25	−32	7
0.1377	0.3365	1.04120	1192	676	−23	−32	9
0.1595	0.4221	1.10002	1185	647	−21	−31	10
0.1475	0.5116	1.15938	1172	628	−16	−27	9
0.1041	0.627	1.23440	1158	604	−12	−18	6
0.1140	0.7025	1.28543	1158	580	−11	−15	4
0.1250	0.7907	1.34528	1161	551	−11	−13	2
0.0768	0.8465	1.38078	1148	549	−5	−7	2
NMC (1) + bromobenzene (2) + 1-pentanol (3)							
0.1189	0.068	0.86128	1256	736	−12	−13	1
0.1221	0.0966	0.88163	1248	728	−12	−13	1
0.1329	0.1834	0.94077	1229	704	−12	−15	3
0.0742	0.2233	0.96409	1209	709	−5	−9	4
0.0864	0.3191	1.02912	1198	682	−5	−11	6
0.1008	0.4061	1.08812	1186	658	−4	−12	8
0.1224	0.4962	1.14921	1175	630	−6	−15	9
0.1395	0.5695	1.19897	1172	607	−7	−16	9
0.1541	0.6171	1.23103	1174	589	−11	−18	7
0.1245	0.6587	1.25738	1167	584	−9	−15	6
0.1123	0.7300	1.30460	1163	567	−9	−13	4
0.1477	0.8044	1.35567	1172	537	−15	−16	1

The standard uncertainty u (u) = ±0.3 %

and 1-alkanols, respectively; V is the molar volume of the mixture; and V_{123}^{E} is ternary excess volume.

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

$$\kappa'_{s123} = \phi_{s123} - \phi_1\kappa_{s1} - \phi_2\kappa_{s2} - \phi_3\kappa_{s3} \tag{7}$$

where ϕ_1, ϕ_2, ϕ_3, κ_{s1}, κ_{s2}, and κ_{s3} are the volume fractions and isentropic compressibilities of the pure components
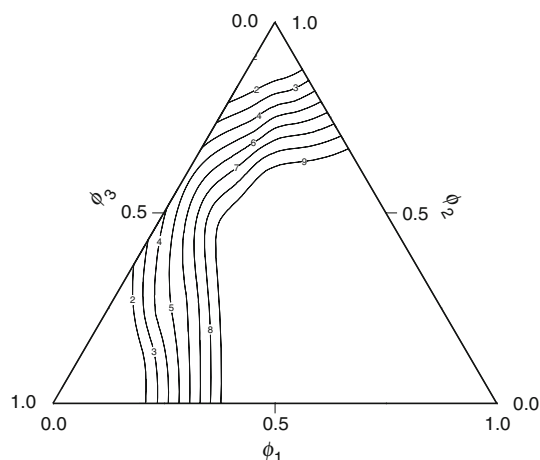
Fig. 4 Deviation in isentropic compressibility ($\Delta\kappa_{s123}$) data for *N*-methylcyclohexylamine (NMC) (1) + bromobenzene (2) + 1-propanol (3) at 303.15 K
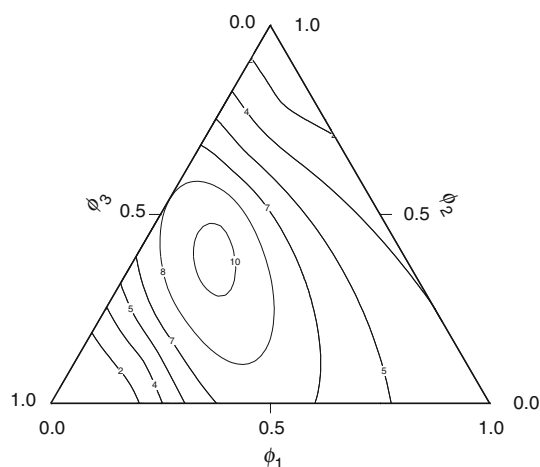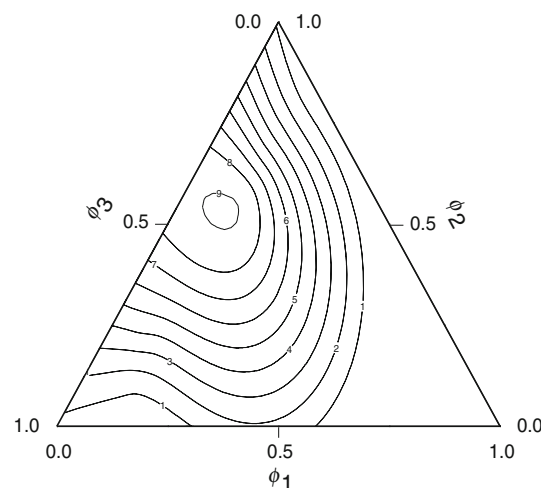

Fig. 6 Deviation in isentropic compressibility ($\Delta\kappa_{s123}$) data for *N*-methylcyclohexylamine (NMC) (1) + bromobenzene (2) + 1-pentanol (3) at 303.15 K

where a_0, a_1, and a_2 are the constants obtained by the least squares method. Further, the binary parameters that were required to compute $\kappa'_{s123(b)}$ for the mixtures of NMC with bromobenzene, NMC with 1-alkanols, and bromobenzene with 1-alkanols were collected from the literature [16, 25, 26], and these are given in Table 4 along with SD $\sigma(\Delta\kappa_s)$.

The speed of sound (u), density of the mixture ($\rho_{\mathrm{mix}123}$), isentropic compressibility (κ_{s123}), and deviation in isentropic compressibility (κ'_{s123}) for three ternary mixtures are given in Table 5. Further, the magnitude $\Delta\kappa_{s123}$ and the difference between measured data of κ'_{s123} and that of computed from the constituent binary data $\kappa'_{s123(b)}$ are also included in Table 5. Moreover, the deviations in isentropic compressibility ($\Delta\kappa_{s123}$) for the three ternary mixtures are also graphically represented in Figs. 4–6.

An examination of κ'_{s123} values that are present in Table 5 suggests that the values were positive over the entire composition range in all the binary mixtures of NMC and bromobenzene with 1-alkanols, and these were 3–4 times to the experimental error. This suggests that Redlich–Kister equation is capable of giving good estimation of deviation in isentropic compressibility of ternary mixtures from that of constituent binaries [16, 25, 26].

The deviation in isentropic compressibility ($\Delta\kappa_{s123}$) data arises due to structure-breaking and structure-making effects on mixing the component molecules and the consequent change in geometrical factors [27]. Structure-breaking effects contribute to an increase in free spaces [28] between the molecules, and structure-making effect cases to decrease in free spaces of the component molecules leading to positive and negative deviations in compressibilities, respectively. The actual deviation would depend up on the resultant effect of these two opposing

Fig. 5 Deviation in isentropic compressibility ($\Delta\kappa_{s123}$) data for *N*-methylcyclohexylamine (NMC) (1) + bromobenzene (2) + 1-butanol (3) at 303.15 K

1, 2, and 3, respectively. The magnitude $\Delta\kappa_{s123}$ and the difference between measured value of κ'_{s123} and that of computed from binary data $\kappa'_{s123(b)}$ have been calculated using the relation

$$\Delta\kappa_{s123} = \kappa'_{s123} - \kappa'_{s123(b)} \tag{8}$$

The latter magnitude, $\kappa'_{s123(b)}$, was computed using Redlich–Kister [12] relation

$$\kappa'_{s123(b)} = \kappa_{s12} + \kappa_{s13} + \kappa_{s23} \tag{9}$$

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

$$\kappa_{sij} = \phi_1\phi_2\left[a_0 + a_1(\phi_1 - \phi_2) + a_2(\phi_1 - \phi_2)^2\right] \tag{10}$$

Table 6 SD values $\sigma(\Delta V_{123}^E)$ and $\sigma(\Delta\kappa_{s123})$ for ternary systems of N-methylcyclohexylamine (NMC) (1) + bromobenzene (2) + 1-alcohols (3)

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}	$\sigma (\Delta\kappa_{s123})$/ TPa^{-1}
NMC (1) + bromobenzene (2) + 1-propanol(3)	0.739	0.935	137.4	0.001	316.9	1722.2	−850.2	1
NMC (1) + bromobenzene (2) +1-butanol(3)	0.732	0.350	92.4	0.001	375.5	−103.8	−14649.8	0
NMC (1) + bromobenzene (2) + 1-pentanol(3)	1.148	2.732	94.1	0.001	383.9	796.9	−25303.8	0
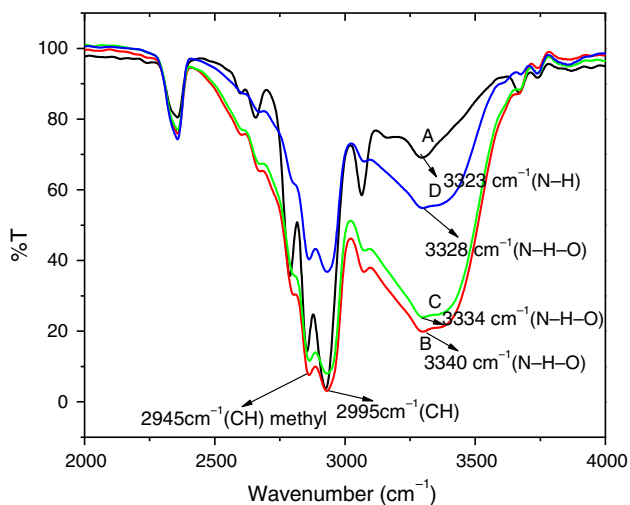
Fig. 7 Normalized FT-IR spectra of (N-methylcyclohexylamine + bromobenzene + 1-alkanols) ternary mixture over the range (2000–4000) cm^{-1}. *Peak A* NMC (1) + bromobenzene (2), *peak B* NMC (1) + bromobenzene (2) + 1-propanol (3), *peak C* NMC (1) + bromobenzene (2) + 1-butanol (3) and peak D: NMC (1) + bromobenzene (2) + 1-pentanol (3)

effects. A perusal of curves of constant deviation in isentropic compressibility in Figs. 4–6 indicates that structure-breaking effects were dominant in all the three ternary mixtures.

The experimental data ΔV_{123}^E and $\Delta\kappa_{s123}$ were fitted to the following equation proposed by Redlich–Kister:

$$\Delta V_{123}^E/\text{cm}^3\text{mol}^{-1} = x_1 x_2 x_3 \\ \times \left[A + B\, x_1(x_2 - x_3) + C\, x_1^2(x_2 - x_3)^2 \right] \quad (11)$$

$$\Delta\kappa_{s123}/\text{TPa}^{-1} = \phi_1 \phi_2 \phi_3 \\ \times \left[A + B\, \phi_1(\phi_2 - \phi_3) + C\, \phi_1^2(\phi_2 - \phi_3)^2 \right] \quad (12)$$

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

$$\sigma(Y_{123}^E) = \left[\sum \left(Y_{123\,\text{exp}}^E - Y_{123\text{cal}}^E \right)^2 \Big/ (m - n) \right]^{1/2} \quad (13)$$

where $\sigma(Y_{123}^E) = \Delta V_{123}^E$ (or $\Delta\kappa_{s123}$, "m" is the total number of experimental points and "n" is the number of coefficients in Eqs. (11) and (12), and the values of ternary constants A, B, and C along with their SD values are given in Table 6.

FT-IR studies

FT-IR spectroscopy has been used extensively to study intramolecular and intermolecular hydrogen bonding interactions between component molecules. Usually, intermolecular hydrogen bonds give rise to broad band, whereas sharp bands appear due to intramolecular hydrogen bonding. In aliphatic 1-alkanols, the sharp band appears around at 3650 cm^{-1} which is due to free -OH group in their pure state. When aliphatic 1-alkanols namely 1-propanol, 1-butanol, and 1-pentanol were mixed with NMC with bromobenzene mixture, the absorption band shifted to lower wave number. We can observe clearly the significant shifts in the wave numbers caused by the strong intermolecular interactions like hydrogen bonding between the oxygen in the hydroxyl group of 1-alkanols and hydrogen of NMC. Thus, the FT-IR analysis convinces intermolecular hydrogen bonding of the ternary mixture in all the systems effectively with proportionate variations in stretching wave numbers of –NH and –OH compared to their respective pure components [29].

In the present investigation, FT-IR spectrum studied at room temperature and the mole fraction of $x_1 = 0.1$, $x_2 = 0.5$. In Fig. 7, peaks B, C and D show that broad bands were observed around 3300 cm^{-1} due to hydrogen bonded –OH group of 1-propanol, 1-butanol and 1-pentanol. This contention was supported by the formation of intermolecular hydrogen bonding (N–H···O–H) between component molecules. When the chain length of 1-alkanols is increased, the absorption band shifted to shorter wave number because of decreases the strength of hydrogen bonding. Further, the peak A corresponds to NMC with bromobenzene mixture.

Conclusions

In the present investigation, ternary excess volume and isentropic compressibility data were reported for the systems of N-methylcyclohexylamine (NMC), bromobenzene, and 1-alkanols at 303.15 K. NMC, and bromobenzene was chosen as common components, and 1-alkanols namely 1-propanol, 1-butanol, and 1-pentanol were chosen as non-common components. The experimental ternary (V_{123}^E) data were compared with empirical relations proposed by Redlich–Kister, Kohler, Tsao–Smith, and Hwang et al. The experimental speed of sound (u) and density (ρ_{mix123}) of mixture were used to compute isentropic compressibility (κ_{s123}). Further, the data were analyzed in terms of intermolecular interactions between component molecules by FT-IR spectrum and also in the light constituents binaries. On the basis of V_{123}^E values, it can be concluded that the order of interaction for the ternary mixtures of NMC and bromobenzene follows the order: 1-propanol > 1-butanol > 1-pentanol. Redlich–Kister, Kohler, Tsao–Smith, and Hwang et al.'s equations gave satisfactory estimations for ternary excess volumes for all the three ternary mixtures.

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