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Volumetric, acoustic and FT-IR spectroscopic study on ternary and constituent binary mixtures containing N-methylcyclohexylamine, nitrobenzene and 1-alkanols at 303.15 K

L. Venkatramana [a], C. Narasimha Rao [b], K. Sivakumar [c], R.L. Gardas [a,*]

[a] Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India
[b] Department of Chemistry, Sri Venkateswara University, Tirupati 517502, India
[c] Department of Chemistry, SV Arts UG & PG College (TTD'S), Tirupati 517502, India

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ABSTRACT

Excess volume (V^E_{123}) and speed of sound (u_{123}) data for three ternary mixtures, containing N-methylcyclohexylamine and nitrobenzene as common components and 1-alkanols, namely, 1-propanol, 1-butanol or 1-pentanol as non-common component were reported at 303.15 K. The experimental speeds of sound data of the mixtures were used to calculate the deviation in isentropic compressibility (Δk_{s123}). Further, experimental ternary excess volume data were compared with predictive relations in terms of Redlich–Kister, Kohler, Tsao–Smith and Hwang equations. Experimental results were analyzed on the basis of intermolecular interactions between component molecules with the help of FT-IR spectrum and also in terms of constituent binary mixtures.

1. Introduction

Thermodynamic properties of binary and ternary mixtures containing organic components capable of undergoing specific interactions, exhibit significant deviations from ideality not only arising from the difference in molecular size and shape but also due to structural changes [1]. Thermodynamic and transport property data are required in the oil and gas industries for flow assurance and oil recovery. In the chemical industries for the design of separation processes, in the pharmaceutical and polymer industries for solvent selection and emission control but also in the environmental science for the estimation of the distribution of chemicals in various ecosystems and also in biotechnology for the origin of many diseases data are traced to aggregation of proteins and several protein separations [2]. Many separation processes in chemical, biochemical and engineering as well as in petroleum industries depend on phase equilibrium data. Depending on the applications and compounds involved, different types of data are needed for example vapor–liquid equilibrium for many distillations, liquid–liquid equilibrium for liquid extractions and solid–liquid equilibrium for crystallization [3].

Study on thermodynamic properties is a valuable tool to learn about the liquid state because of the close connection between liquid structure and macroscopic properties. In this connection, we are engaged in systematic investigation of the thermodynamic properties of binary and ternary liquid mixtures [4]. The increasing uses of the alkylamine and alkanol in many industrial processes have greatly stimulated the need for extensive information on the thermodynamic property of alkylamine, alkanol and their mixtures. Thus, the thermo-physical properties of binary/ternary mixtures containing 1-alkanol and amine would be of great importance in chemical designing and also for researchers to understand the nature of molecular interactions [5] that are prevailing between these two components. Further, the study of molecular interactions in ternary non-electrolyte mixtures having 1-alkanol and amine may induce the change in the intermolecular hydrogen bonding, since both are strongly self-associated liquids through hydrogen bond [6] and can be associated with any other group having some degree of polar attractions [7].

In the present investigation, we reported here excess volume and speed of sound data for the ternary mixtures of N-methylcyclohexylamine (NMC) and nitrobenzene which were taken as common components and 1-alkanols such as 1-propanol, 1-butanol and 1-pentanol were considered as non-common component. The main intention of the present work was to study the effect of addition of a third component to a binary mixture which may influence not only the sign and magnitude of excess thermodynamic functions but also pair-wise interactions between component molecules. Amine and alkanols exist as associated structures in liquid state. Thus, upon mixing amine with alcohols of varying chain

* Corresponding author.
E-mail address: gardas@iitm.ac.in (R.L. Gardas).
URL: http://www.iitm.ac.in/info/fac/gardas (R.L. Gardas).

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Table 1
Density (ρ) and speed of sound (u) data of pure components at 303.15 K.

Compound	Density (ρ) kg·m^{-3}		Speed of sound (u) m·s^{-1}	
	Experimental	Literature	Experimental	Literature
N-methyl-cyclohexylamine	846.83	846.87 [16]	1356	1353 [16]
Nitrobenzene	1193.44	1193.41 [10]	1443	1446 [10]
1-Propanol	795.66	795.64 [17]	1189	1190 [17]
1-Butanol	802.05	802.03 [17]	1229	1228 [17]
1-Pentanol	807.64	807.62 [17]	1256	1258 [17]

lengths, provide interesting properties due to specific interactions arising from charge–transfer, dipole–dipole, donor–acceptor and hydrogen bond formation forces may be observed.

In addition, amines, alkanols and nitrobenzene are widely used in a variety of industrial and consumer applications such as fuel, perfumes, cosmetics, paints, varnishes, drugs, explosives, fats, waxes, resins, plastics, and in the production of pharmaceuticals and other chemical industries [8–10]. Further, nitrobenzene has higher dipole moment, dielectric constant values and flexible rotation along the C–N axis which gives more interaction to other molecules [11].

Moreover, a survey of literature has shown that no experimental ternary volumetric and sound speed data on NMC and nitrobenzene with 1-alkanols were reported earlier. Therefore, the present study was undertaken in order to have deeper understanding of the intermolecular interactions when NMC and nitrobenzene are mixed with 1-alkanols, as the chain length of 1-alkanol increases from 1-propanol

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

			V^E/10^3·m^3·mol^{-1}					
x_1	x_2	Density (ρ) kg·m^{-3}	Exp.	Redlich–Kister	Kohler	Tsao–Smith	Hwang	ΔV^E_{123}*
NMC (1) + nitrobenzene (2) + 1-propanol (3)								
0.1011	0.0721	845.46	−59.9	−60.1	−59.1	−59.6	−61.8	0.2
0.0621	0.1046	857.59	−42.8	−43.8	42.5	−43.0	−45.5	1.0
0.0891	0.1741	892.11	−56.0	−58.0	−56.0	−56.7	−59.4	2.0
0.1119	0.2506	926.15	−60.9	−63.9	−61.9	−62.4	−65.4	3.0
0.0967	0.3319	959.40	−50.5	−53.9	−51.7	−51.9	−55.8	3.4
0.0729	0.4526	1006.04	−34.4	−38.1	−35.9	−51.9	−40.3	3.7
0.0806	0.5519	1041.23	−23.9	−28.8	−27.3	−35.6	−32.2	4.9
0.1075	0.6230	1062.77	−13.7	−21.8	−21.1	−19.6	−26.2	8.1
0.1231	0.6974	1084.78	−11.8	−11.7	−11.1	−10.1	−16.0	9.9
0.0821	0.7618	1109.74	−1.1	−6.0	−5.6	−4.5	−8.7	4.9
0.0901	0.8028	1121.29	3.1	−1.9	−1.4	−0.7	−3.9	5.0
0.0660	0.8614	1142.53	1.1	−1.0	1.3	1.7	0.1	2.1
NMC (1) + nitrobenzene (2) + 1-butanol (3)								
0.0979	0.0618	837.55	−43.5	−44.6	−44.1	−44.4	−45.5	1.1
0.0711	0.1014	852.04	−35.5	−36.2	−35.4	−35.4	−37.1	0.7
0.1006	0.1916	890.62	−44.7	−46.4	−45.1	−45.6	−47.4	1.7
0.1129	0.2519	914.93	−45.6	−47.5	−46.0	−46.4	−48.6	1.9
0.0611	0.3119	936.87	−31.4	−32.3	−30.6	−31.0	−33.0	0.9
0.0878	0.4506	990.32	−27.7	−28.9	−27.2	−26.9	−30.8	1.2
0.1071	0.5276	1018.36	−22.5	−23.9	−22.6	−21.6	−26.7	1.4
0.1210	0.6519	1062.13	−10.4	−11.5	−10.6	−9.2	−14.6	1.1
0.0766	0.7016	1081.81	−5.7	−6.9	−6.0	−5.0	−9.0	1.2
0.0920	0.7542	1099.38	−1.3	−2.7	−2.1	−1.0	−4.7	1.4
0.0771	0.8016	1116.97	0.8	−0.1	0.5	1.3	−1.3	0.9
0.0919	0.8429	1130.18	3.8	3.0	3.6	3.9	2.3	0.8
NMC (1) + nitrobenzene (2) + 1-pentanol (3)								
0.0911	0.0819	844.88	−46.6	−47.5	−47.9	−48.3	−47.2	0.9
0.0873	0.1516	869.87	−43.5	−44.6	−45.1	−45.8	−43.7	1.1
0.1009	0.2219	896.08	−43.9	−45.1	−45.9	−47.0	−44.6	1.2
0.0716	0.3519	942.37	−29.8	−30.6	−31.1	−31.8	−29.7	0.8
0.1174	0.4223	969.63	−32.3	−32.3	−33.8	−34.8	−12.5	0.9
0.0912	0.5506	1016.44	−17.3	−18.2	−18.3	−18.8	−33.1	0.9
0.1214	0.6423	1053.08	−35.6	−37.6	−38.5	−36.0	−19.1	2.0
0.0619	0.6819	1065.86	−5.3	−6.0	−5.9	−6.0	−0.7	0.7
0.0701	0.7501	1091.85	−1.0	−1.9	−1.6	−1.7	−2.9	0.9
0.0962	0.7926	1107.58	2.5	1.1	1.7	1.5	0.2	1.4
0.0801	0.8219	1119.32	3.0	2.1	2.6	2.5	1.5	0.9
0.1031	0.8624	1134.33	5.9	5.1	5.6	5.4	4.9	0.4

The standard uncertainties are $u(T) = 0.01$ K, $u(\rho) = 0.01$ kg·m^{-3}, $u(\rho) = 0.1$ MPa, and $u(x_1) = 0.0001$ $u(V^E_{123}) = 0.003$ cm^3 mol^{-1}.

$$\Delta V^E_{123} = V^E_{123}(\text{Exp}) - V^E_{123}(bc)$$

where $V^E_{123}(bc)$ is computed from constituent binary data using Redlich–Kister equation.