Asian Journal of Organic & Medicinal Chemistry **ISSN Online: 2456-8937**
Vol. 7 No. 2 (April-June, CRNSS 2022) **UGC CARE APPROVED JOURNAL**

Thermophysical, Acoustic and FTIR Study on Binary Mixtures of Nitrobenzene and Aniline with 2-Methyl-2-propanol at Temperature 308.15 K and Atmospheric Pressure

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ABSTRACT

Densities, viscosities and speeds of sound of binary mixtures of nitrobenzene and aniline with 2-methyl-2-propanol have been measured at temperature 308.15 K and atmospheric pressure. From the experimental densities, viscosities and speeds of sound, the excess molar volumes V^{E}, deviations in viscosity $\Delta\eta$, and deviations in isentropic compressibility ΔK_S have been calculated. The excess molar volumes and deviations in isentropic compressibility are positive for the binary systems studied over the whole composition, while deviations in viscosities are negative. The excess molar volumes, deviations in viscosity, and deviations in isentropic compressibility have been fitted to a Redlich–Kister type polynomial equation. FTIR study of these mixtures is also reported.

KEYWORDS: Density, Viscosity, Speed of sound, IR.

INTRODUCTION

The thermophysical, acoustic, and transport properties of non-electrolyte liquid-liquid mixtures are important for engineering calculation, research of mass transfer, heat transfer, and fluid flow. They provide information about type and extent of molecular interactions and can be used for the development of molecular models for describing the behavior of solutions [1-5].

Marsh et.al. [6,7] investigated the variation of density, viscosity, speed of sound, and isentropic compressibility of binary liquid mixtures of protic, aprotic, and associating liquids with changing mole fraction of one of the components. The trends of changes, either positive or negative, have been interpreted by these workers in terms of differences in size of molecules and the strength of specific or nonspecific interactions taking place between the components of the mixtures. Nikam et al., 1997 [8] reported the effect of molecular size, shape and molecular association of alkanols. In the present study, the densities and viscosities for the binary system of nitrobenzene and aniline with 2-methyl-2-propanol at 308.15 K and atmospheric pressure have been measured. The nature of interactions in binary systems studied have been explained on the basis of certain thermophysical properties, such as excess volumes V^E, deviations in viscosity $\Delta\eta$, deviations in isentropic compressibility ΔK_S.

EXPERIMENTAL

Nitrobenzene (s.d.fine chem., purity 99%), aniline (s.d.fine chem., purity 99%) and 2-methyl-2-propanol (Qualigens 99%) were used after a single distillation. The purities of the solvents, after purification, were ascertained by comparing their densities, viscosities and ultrasonic velocities with the corresponding literature values at 308.15 K (Table 1). Binary mixtures were prepared by mass in air-tight stoppered glass bottles. The masses were measured using an Adairdutt balance to an accuracy of ±0.0001 g. Care was taken to avoid evaporation and contamination during mixing. The estimated uncertainty in mole fraction is <±0.0001.

Table 1: Comparison of Experimental Densities, ρ, Viscosities, η, and Speed of Sound, u, of pure components with literature values at 308.15 K.

Pure liquid	ρ (g·cm^{-3})		η (mPa.s)		u (m.s^{-1})	
	Exptl.	Lit	Exptl.	Lit	Exptl.	Lit
2-methyl-2-propanol	0.7700	0.7702[9]	2.642	2.644[10]	1094	1093[11]
Nitrobenzene	1.1883	1.1883[12]	1.430	1.437[13]	1423	1423[14]
Aniline	1.0087	1.0084[15]	2.521	2.510[16]	1599	1595.1[17]

Densities of pure liquids and their binary mixtures were measured using DMA 35 Anton Paar digital density meter. The instrument has a resolution of 0.0001 g $\cdot$cm^{-3}. The average uncertainty in the measured density was ±0.1 %.

Dynamics viscosity η measurements of all pure components and their binary mixtures were determined by using LVDV-II+ Pro Brookfield viscometer, calibrated with triply distilled water with an accuracy ± 1% of full scale of range and viscosity repeatability ± 2%.

The speed of sound was measured with a single-crystal variable path digital interferometer (Mittal Enterprises, New Delhi, India) operating at a frequency of 2 MHz that had been calibrated with water and benzene. The uncertainty in the speed of sound was found to be ± 2 %. In all property measurements the temperature was controlled within ± 0.01 K using a constant temperature bath (INSREF model IRI O16C, India) by circulating water from the thermostat.

FTIR spectra of the studied binaries were recorded on a FTIR spectrometer model-SHIMADZU 8400S PC by using KBr pellet in the region (400 to 4000) cm^{-1} with 4.0 cm^{-1} resolution. The transmission values were read in steps of 5 %. The spectrometer possesses out to aligned energy optimization and a dynamically aligned interferometer. It is fitted with a KBr beam splitter and a DLATGS detector. A baseline correction was made for the spectra recorded.

RESULTS AND DISCUSSION

Experimental values of the densities ρ, viscosities η, and speed of sound u of mixtures at 308.15 K are listed as a function of mole fraction in Table 2.

The density values were used to calculate excess molar volumes V^E using the following equation:

$$V^E\ (\text{cm}^3.\text{mole}^{-1}) = (x_1M_1 + x_2M_2)/\ \rho_{12} - (x_1M_1/\ \rho_1) - (x_2M_2/\rho_2) \qquad (1)$$

where ρ_{12} is the density of the mixture, x_1, M_1, ρ_1 and x_2, M_2, ρ_2 are the mole fractions, molecular weights and densities of pure components 1 and 2 respectively.

The viscosity deviations Δη from binary mixing were calculated using

$$\Delta\eta = \eta_{12} - x_1\,\eta_1 - x_2\,\eta_2 \qquad (2)$$

where η_{12} is the viscosity of the mixture, x_1, x_2 and η_1, η_2 are the mole fractions and viscosities of the pure components 1 and 2 respectively.

The isentropic compressibility was calculated using the Laplace relation

$$K_s\ (\text{TPa}^{-1}) = 1/(u^2\rho) \qquad (3)$$

where *u* is the ultrasonic velocity and ρ the density.

The deviations from isentropic compressibility, Δ K_s, were obtained using the relation,

$$\Delta K_s\ (\text{TPa}^{-1}) = K_{s,\,12} - x_1\,K_{s,\,1} - x_2\,K_{s,\,2} \qquad (4)$$

where $K_{s,\,12}$ is the experimental isentropic compressibility of the mixture, and x_1, x_2 and $K_{s,\,1}$, $K_{s,\,2}$ are the mole fractions and isentropic compressibilities respectively, of the pure components.

Table 2: Densities ρ, viscosities η, speeds of sound *u*, isentropic compressibilities K_s , excess molar volumes V^E, deviations in viscosity Δη, and deviations in isentropic compressibility ΔK_s for 2-methyl-2-propanol (1) + nitrobenzene (2) and + aniline (2) at 308.15 K.

x_1	ρ x10^{-3} (Kg.m^{-3})	V^E (cm^3.mol^{-1})	η (mPa.s)	Δη (mPa.s)	*u* (ms^{-1})	K_s (TPa^{-1})	ΔK_s (TPa^{-1})
2-methyl-2-propanol (1) + nitrobenzene (2)							
0.0000	1.1883	0.000	1.430	0.000	1423	416	0
0.0929	1.1533	-0.120	1.118	-0.425	1416	433	-41
0.1964	1.1129	-0.184	0.984	-0.684	1385	468	-71
0.3000	1.0719	-0.258	0.924	-0.870	1350	512	-94
0.3940	1.0339	-0.305	0.927	-0.981	1309	564	-104
0.5000	0.9901	-0.330	1.017	-1.019	1272	624	-114

0.6008	0.9474	-0.313	1.193	-0.965	1231	697	-109
0.6998	0.9047	-0.280	1.460	-0.818	1192	777	-96
0.8009	0.8602	-0.216	1.788	-0.613	1158	867	-76
0.8995	0.8160	-0.131	2.201	-0.319	1126	967	-46
1.0000	0.7700	0.000	2.642	0.000	1094	1085	0
2-methyl-2-propanol (1) + aniline (2)							
0.0000	1.0087	0.000	2.521	0.000	1599	388	0
0.1007	0.9863	-0.240	2.311	-0.222	1572	410	-47
0.1985	0.9638	-0.395	2.005	-0.540	1534	441	-87
0.2962	0.9409	-0.496	1.818	-0.739	1486	482	-113
0.3979	0.9169	-0.571	1.658	-0.911	1426	536	-127
0.4986	0.8927	-0.581	1.591	-0.990	1366	601	-131
0.5998	0.8682	-0.551	1.620	-0.974	1306	676	-126
0.6998	0.8438	-0.475	1.746	-0.860	1248	761	-110
0.7992	0.8195	-0.367	1.958	-0.660	1194	856	-85
0.9003	0.7947	-0.215	2.267	-0.363	1143	964	-53
1.0000	0.7700	0.000	2.642	0.000	1094	1085	0

The excess molar volumes and deviations in viscosity and isentropic compressibility were fitted to a Redlich–Kister [18] equation of the type:

$$Y = x_1 x_2 \sum_i^n a_i (x_1 - x_2)^i \qquad (5)$$

where Y is V^E, Δη, or ΔK_s, and n is the polynomial degree. The a_i coefficients were obtained by fitting the parameters of Eq. 3 to experimental results using a least-squares regression method. In each case, the optimum number of coefficients was ascertained from an examination of the variation of the standard deviation σ . The values of σ were calculated using the relation:

$$\sigma(Y) = \left\{\frac{\sum_n \left(Y_{expt,i} - Y_{cacl})\right)}{N-n}\right\}^{1/2} \qquad (6)$$

where N is the number of data points and n is the number of coefficients. The calculated values of the a_i coefficients along with the standard deviations σ of the fits are given in Table 3.

Table 3: Parameters and standard deviations *σ* of Eqs. 3 and 4 at 308.15 K.

		a_0	a_1	a_2	a_3	a_4	σ
2-methyl-2-propanol+nitrobenzene	V^E ($cm^3.mol^{-1}$)	-1.3212	-0.1929	0.5352	0.2314	-1.0851	0.0065
	Δη (mPa.s)	-4.0727	0.0044	0.3943	1.3718	-1.0699	0.0108
	ΔK_s (TPa^{-1})	-449.812	-24.4270	12.5779	12.1234	-132.7420	0.48
2-methyl-2-propanol+nitrobenzene	V^E ($cm^3.mol^{-1}$)	-2.3312	0.1635	0.0973	-0.0057	-0.6246	0.0036
	Δη (mPa.s)	-3.9266	-0.4184	0.0101	-0.8558	1.6231	0.0172
	ΔK_s (TPa^{-1})	-568.113	0.1589	-34.5159	-48.320	33.0312	0.25

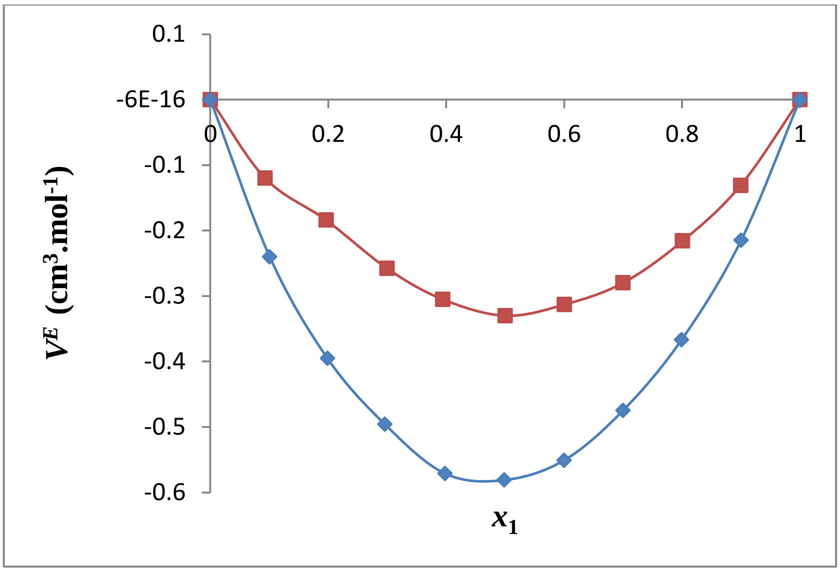


Fig. 1: Excess molar volumes V^E at 308.15 K for 2-methyl-2-propanol + nitrobenzene (■) and aniline (◆)

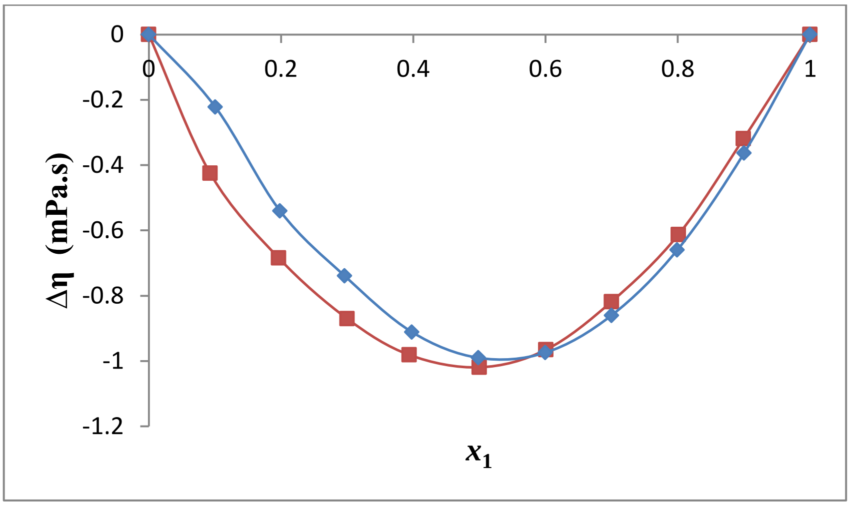


Fig. 2: Deviations in viscosity (Δη) at 308.15 K for 2-methyl-2-propanol + nitrobenzene (■) and aniline (◆)

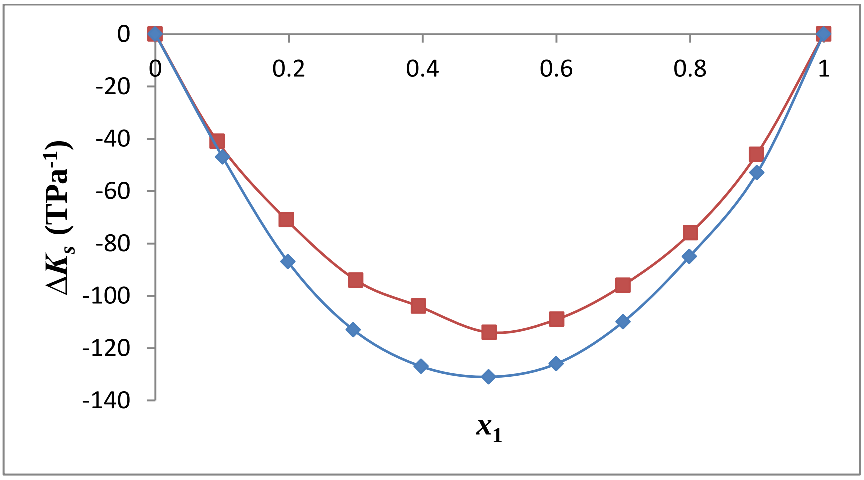


Fig. 3: Deviations in isentropic compressibility (ΔK_s) at 308.15 K for 2-methyl-2-propanol + nitrobenzene (■) and aniline (◆)

The variation of V^E with the mole fraction $x_1$of 2-methyl-2-propanol in mixtures with nitrobenzene and aniline at 308.15 K is represented in Fig. 1. It is seen that the V^E values are negative for binary mixtures of 2-methyl-2-propanol with nitrobenzene and aniline over the entire composition range at 308.15 K. The observed excess molar volume values in the present investigation may be discussed in terms of several effects which may be arbitrarily divided into physical, chemical, and geometrical contributions. The physical interactions involve mainly dispersion forces giving a positive contribution to V^E [19]. The chemical or specific interactions between constituent molecules of the mixture result in a volume decrease. In the present investigation, specific interaction between 2-methyl-2-propanol with nitrobenzene and aniline molecules takes place through dipole-dipole interactions, forming the complex through hydrogen bond formation. The structural contributions arising from the geometrical fitting of one component into the other, due to differences in the molar volumes and free volumes between components, lead to negative contributions to V^E**.**

Figure **2** indicates that the deviations in viscosity are negative for both the binary systems studied, suggesting that the dispersive forces like rupture of the self association in 2-methyl-2-propanol are predominant.

The variation of ΔK_S with mole fraction of 2-methyl-2-propanol is represented in Fig. 3.

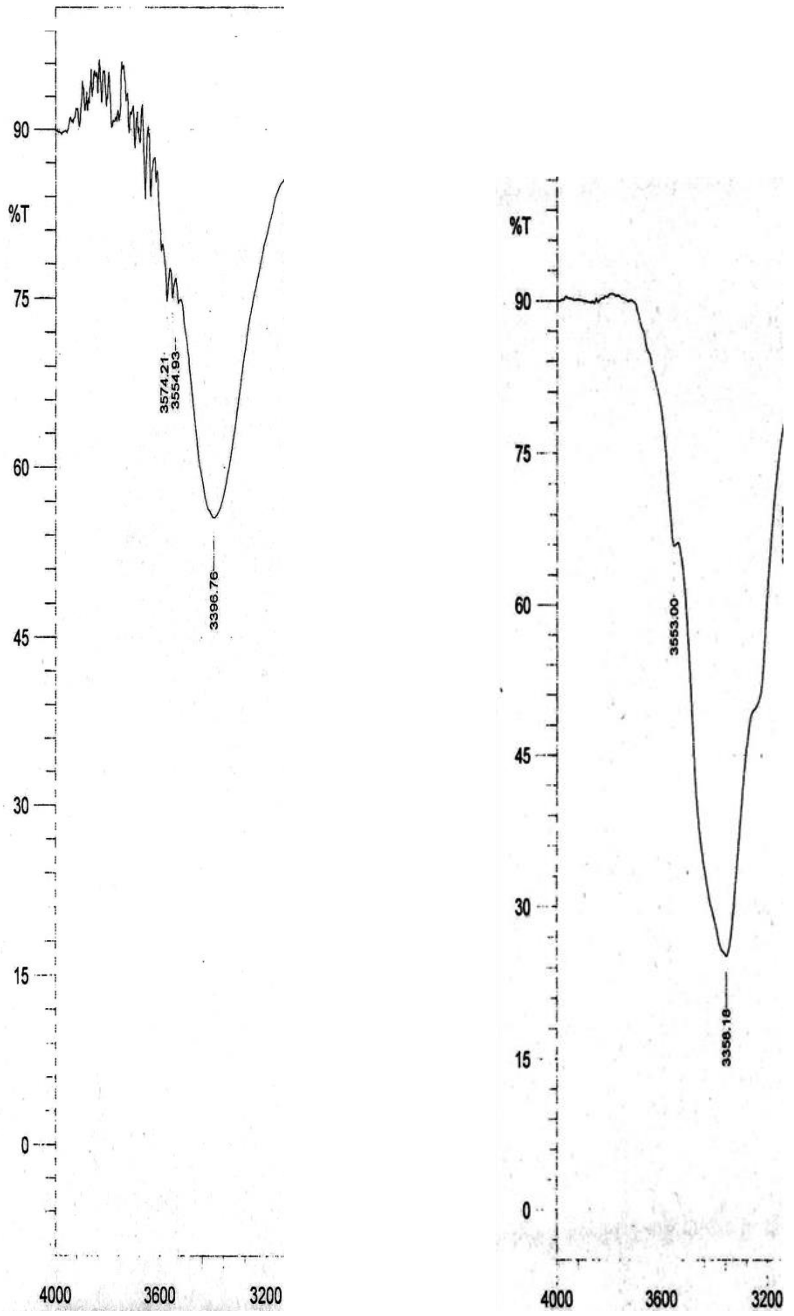
Kiyohara and Benson [20] have suggested that ΔK_S is the result of several opposing effects.

Strong molecular interactions occur through charge transfer, dipole induced-dipole and dipole-dipole interactions [21], interstitial accommodation and orientational ordering all lead to a more compact structure making ΔK_S negative, whereas breakup of the alkanol structures tends to make ΔK_S positive. The negative values of ΔK_S for mixtures of 2-methyl-2-propanol with nitrobenzene and aniline implies that the interactions between unlike molecule are stronger as compared with the interactions in pure component. It is seen that the maxima in V^E and ΔK_S occur at about the same mole fraction of 2-methyl-2-propanol for both the binary mixtures, suggesting the formation of a similar types of complexes in the both investigated binary mixtures.

It can be seen from table 4 that the -OH stretching frequency for 2-methyl -2-propanol is observed at 3377.47 cm^{-1}. For 2-methyl -2-propanol + nitrobenzene and + aniline at $x_1 \approx 0.5$ it appears at 3396.76 cm^{-1} and 3358.18 cm^{-1} respectively and the cut sections of the same are shown in figure 4. These shifts in -OH stretching frequency indicates that intermolecular interactions are present in the binary mixtures studied. This strongly supports the conclusion reached from the density, viscosity and speed of sound data.

Table 4 Neat FT-IR stretching frequencies of –OH (cm^{-1})

x_1	2-methyl-2-propanol + nitrobenzene	2-methyl-2-propanol + aniline
0.1	3377.47	3377.47
0.2	3381.56	3372.92
0.3	3385.21	3367.38
0.4	3387.83	3362.45
0.5	3396.76	3358.18
0.6	3386.19	3364.15
0.7	3384.35	3367.43
0.8	3382.69	3370.25
0.9	3380.74	3374.30
1.0	3377.47	3377.47



$x_1 = 0.5$ $x_1 = 0.5$

Figure 4 : Neat FTIR -OH Frequency (cm^{-1}) Cut Section (Spectrum) of 2-methyl-2-propanol + Nitrobenzene and + aniline.

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