

Thermoacoustic Parameters of Some Liquid Mixtures of O-chloroaniline with F, NMF and N, N-DMF

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Abstract

In this study, the density (ρ), speed of sound (u), and viscosity (η) of the binary liquid mixtures of an industrially important solvent O-Chloroaniline (O-CA) with Formamide (F), N-Methylformamide (NMF) and N,N-Dimethyl formamide (N,N-DMF) have been measured over the entire composition range and From these experimental values, thermo-acoustic parameters like Z , K_s , V , L_f , V_f , π_i , H and τ are calculated at temperatures from $T = 303.15, 308.15$ and 313.15K at atmospheric pressure. These results were compared with literature values.

Keywords: Ultrasonic velocity, Density, Viscosity, Binary liquid mixture and Acoustic parameters.

Introduction

The speed of sound (U) density (ρ) and viscosity (η) of binary or ternary liquids are indispensable in most fluid mechanics, solution theory, molecular thermodynamics, and various methodical uses.¹⁻⁵ These values carry a significant role to elucidate the behavior of liquids and their mixtures.^{6, 7} The analysis of excess functions and deviations from ideality is essential to interpret the interactions in the mixing process. Therefore, the assessment and forecast of these mixtures as functions of temperature and composition are of noticeable importance. Researchers are highly devoted to discovering the real causes of possible interaction of organic molecules in binary mixtures using physical property data.⁸⁻¹⁰ We display ρ and η values in the pure state and for their binary systems of O-Chloroaniline (O-CA) with amides, formamide (F), N-Methylformamide (NMF), and N, N-dimethyl formamide (N, N-DMF) at $T = (303.15 \text{ to } 318.15) \text{ K}$ and atmospheric pressure over the entire range of composition. All liquids are used for laboratory and industrial purposes. Here, the O-Chloroaniline liquid (O-CA) has been considered as first component, while the other amides liquids F, NMF, and N,N-DMF have been considered as second component. This work is part of our program to give information/data for the characterization of molecular interactions between solvents in binary systems.^{11,12} The liquids were chosen for the present study on the basis of their medical and Industrial importance. O-Chloroaniline is Intermediate for rubber chemicals, pigments, pesticides and dyes. On the other hand, Formamide is an amide derived from formic acid used as a feedstock in the manufacture of formate esters, as an ionizing solvent, as an RNA stabilizer in gel electrophoresis, and in tissue preservation. More intriguingly, it may be a key compound in the origin of life on Earth. N-Methylformamide (NMF) is closely related to other formamides, not ably formamide and dimethyl formamide (DMF). However, industrial use and production of NMF are far less than for either of these other formamides. DMF is favored over NMF as a solvent due to its greater stability. NMF is mainly used as a reagent in various

organic syntheses with limited applications as a highly polar solvent.^{13,14} *N, N*-Dimethyl formamide (DMF) Dimethyl formamide is odorless whereas technical grade or degraded samples often have a fishy smell due to impurity of dimethylamine. DMF is a polar aprotic solvent with a high boiling point. It facilitates reactions that follow polar mechanisms, such as SN_2 reactions. In the present study¹⁵, our focus is on the study of liquid mixtures of substituted amides with *O*-Chloroaniline because there have been a few studies on these mixtures.¹⁵⁻¹⁹ It is expected that there will be a significant degree of H-bonding in these binary mixtures.²⁰

The liquid mixtures of *O*-CA+F (*O*-Chloroaniline + Formamide), *O*-C+NMF (*O*-Chloroaniline + *N*-Methylformamide), *O*-CA+N, *N*-DMF (*O*-Chloroaniline + *N, N*-Dimethyl formamide) are considered here and their U , ρ , η are measured using the relevant apparatus. From these experimental values, thermo-acoustic parameters like Z , K_s , V , L_f , V_f , π_i , H and τ are calculated. All the above said parameters were measured composition range and at 303.15, 308.15 and 313.15K.

The expression used to find the ultrasonic speed is

$$U = f * \lambda \text{ ms}^{-1}$$

Where, f is the frequency of the generator which is utilized to energize the quartz crystal. In the present examination, a steady frequency (2 MHz) interferometer was utilized and henceforth ' f ' value is 2×10^6 hertz.

THERMO ACOUSTIC PARAMETERS

Different thermo acoustic parameters like, acoustic impedance (Z), isentropic compressibility (K_s), molar volume (V), free length (L_f), free volume (V_f), internal pressure (π_i), enthalpy (H) and relaxation time (τ) are calculated utilizing the experimentally determined values of U , ρ and η . Experimental and literature values of U , ρ and η are shown in table 1, 2 & 3.

TABLE.1

Examination of trial and writing estimations of ρ, η, U at 303.15 K.

Liquid	T/K	$\rho \cdot 10^{-3} / (\text{kg} \cdot \text{m}^{-3})$		$\eta \cdot 10^3 / (\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1})$		$U / (\text{m} \cdot \text{s}^{-1})$		α (kK^{-1})	C_p ($\text{J mol}^{-1} \text{K}^{-1}$)
		Exp.	literature	Exp.	literature	Exp.	literature		
<i>O</i> -CA	303.15	1.2026	1.2026	3.8257	3.8256	1469.5	1469.6	---	131.6
F	303.15	1.1238	1.1237	2.8018	2.8018	1585.4	1585.4	0.9967	107.11
NMF	303.15	0.9947	0.9946	1.5860	1.5859	1408.6	1408.5	0.9967	124.95
<i>N,N</i> -DMF	303.15	0.9388	0.9386	0.7532	0.7485	1467.2	1469.8	0.9967	152.00

TABLE.2

 Examination of trail and writing estimations of ρ, η, U at 308.15 K.

Liquid	T/K	$\rho \cdot 10^{-3} / (\text{kg} \cdot \text{m}^{-3})$		$\eta \cdot 10^3 / (\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1})$		$U / (\text{m} \cdot \text{s}^{-1})$		α (kK^{-1})	C_p ($\text{J mol}^{-1} \text{K}^{-1}$)
		Exp.	literature	Exp.	literature	Exp.	literature		
O-CA	308.15	1.1980	1.1980	3.4123	3.4122	1453.4	1453.3	---	133.8
F	308.15	1.1195	1.1194	2.4980	2.4980	1580.5	1580.6	0.9961	105.20
NMF	308.15	0.9902	0.9903	1.4624	1.4627	1400.64	1400.6	0.9961	126.05
N,N-DMF	308.15	0.9353	0.9357	0.7210	0.7210	1432.96	1433.2	0.9961	153.02

TABLE. 3

 Examination of trail and writing estimations of ρ, η, U at 313.15 K.

Liquid	T/K	$\rho \cdot 10^{-3} / (\text{kg} \cdot \text{m}^{-3})$		$\eta \cdot 10^3 / (\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1})$		$U / (\text{m} \cdot \text{s}^{-1})$		α (kK^{-1})	C_p ($\text{J mol}^{-1} \text{K}^{-1}$)
		Exp.	literature	Exp.	literature	Exp.	literature		
O-CA	313.15	1.1930	1.1930	3.0606	3.0602	1435.3	1435.2	---	136.0
F	313.15	1.1155	1.1154	2.2435	2.2435	1572.0	1572.0	0.9998	108.56
NMF	313.15	0.9859	0.9861	1.3528	1.3520	1383.24	1382.5	0.9998	129.47
N,N-DMF	313.15	0.9304	0.9302	0.6923	0.6900	1418.12	1418.0	0.9998	157.14

RESULTS AND DISCUSSION

The liquid mixtures are chosen such that they contain O-CA as solute and F/ NMF/ N, N-DMF as solvents. The experimentally determined values of ρ , U , η along with the literature values for these parameters are given in tables 1, 2 and 3. To find the molecular interactions strength, values of acoustic, thermodynamic and excess parameters were calculated. For the mixtures of O-CA+F, O-CA+NMF, O-CA+N, N-DMF, the experimental values of ρ , U , η are given in fig. 1(a, b, c) to fig. 3(a, b, c). Using these values, various parameters like Z , K_s , V , L_f , V_f , π_i , H and τ are calculated.

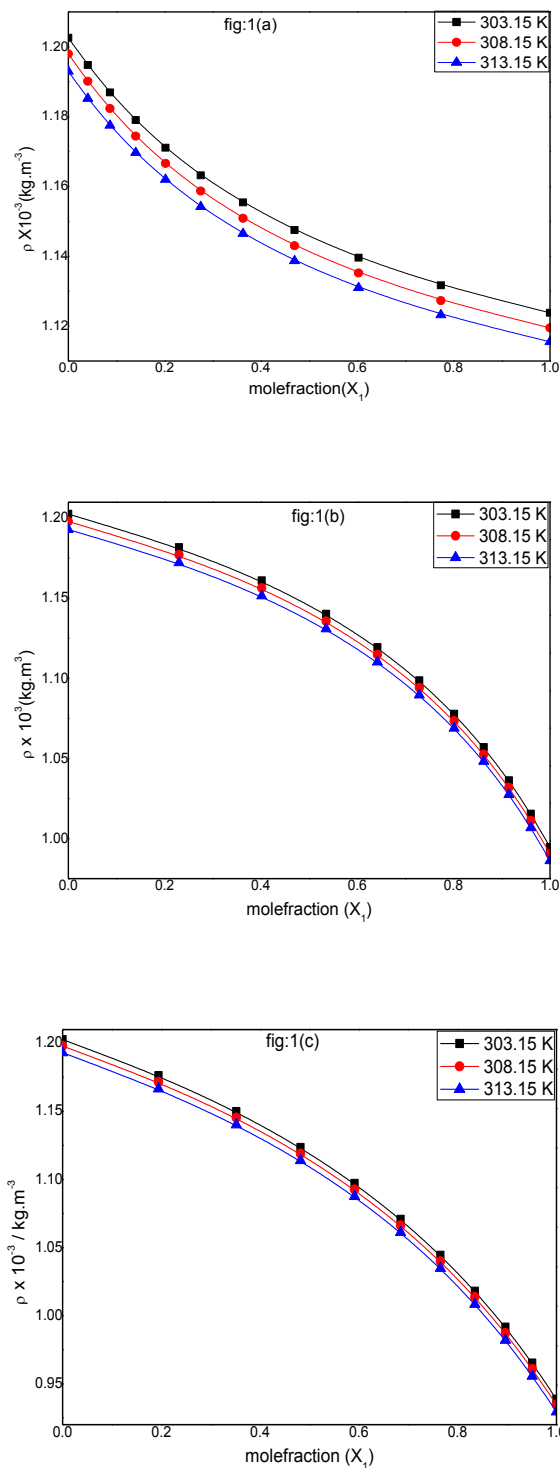


Fig. 1. Variation of ρ with mole fraction at various temperatures for (a) O-CA+F (b) O-CA+NMF(c) O-CA+N, N-DMF.

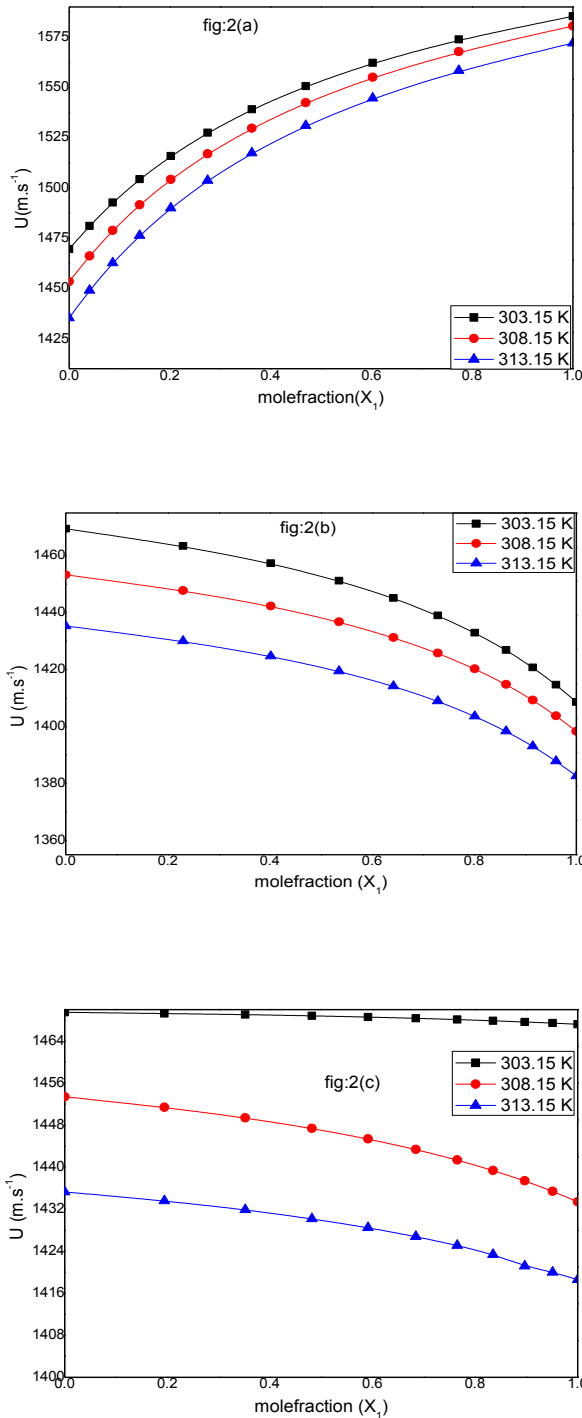


Fig. 2. Variation of U with mole fraction at various temperatures for (a) O-CA+F (b) O-CA+NMF(c) O-CA+N, N-DMF.

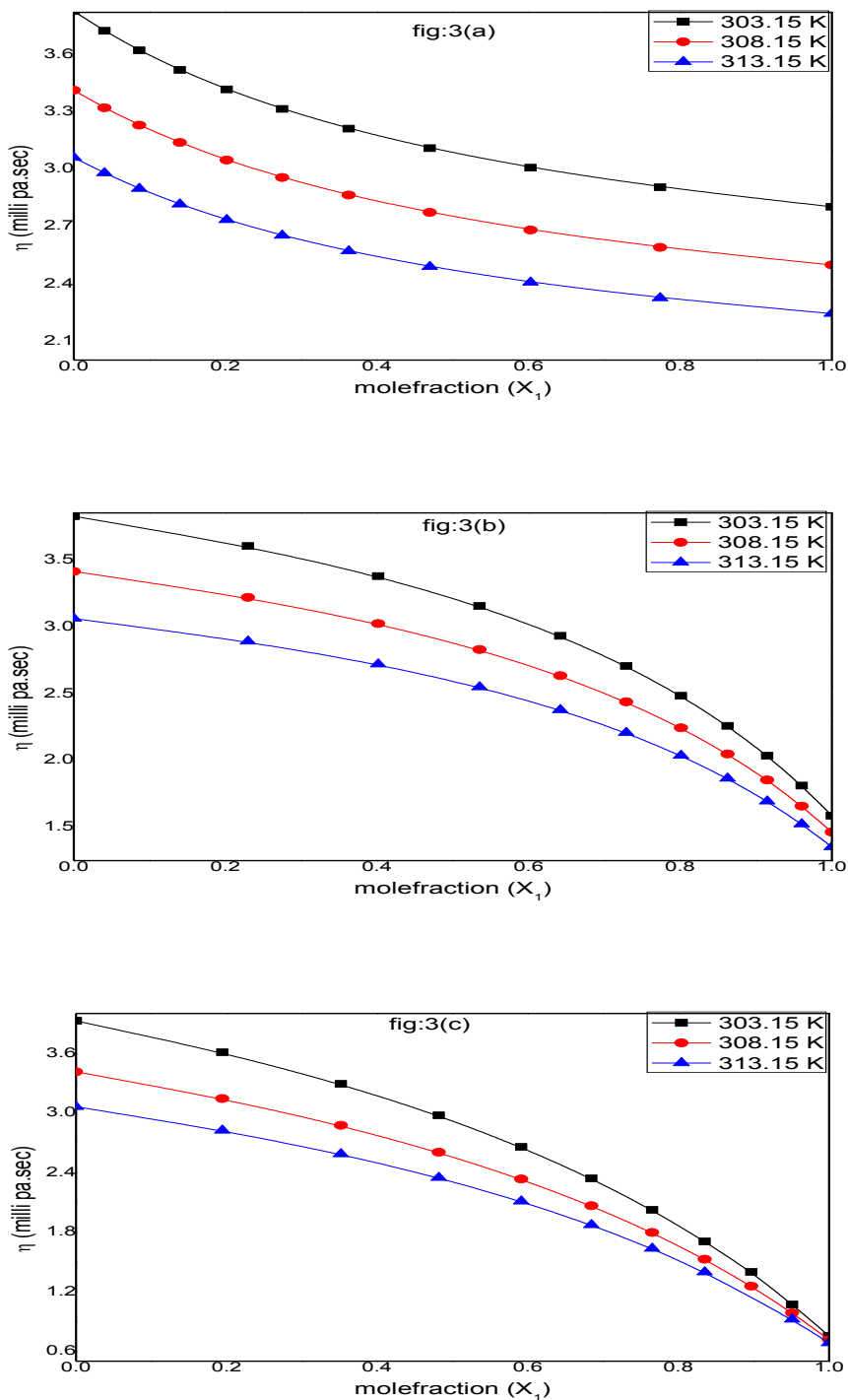


Fig. 3. Variation of η with mole fraction at various temperatures for (a) O-CA+F (b) O-CA+NMF(c) O-CA+N, N-DMF.

Speed of sound (U), Viscosity (η) and Density (ρ)

Figures 1(a, b, c) tell us that in all these liquid mixtures, the U values are increasing with rise in concentration of O-CA at the specified temperatures. The increasing U values indicate that, strong

molecular interactions are present among the molecules of liquid systems under study. The cause of these interactions may be forces due to dipole-induced dipole or due to hydrogen bonding. With the increasing temperature the U values are decreasing for all our mixtures. With the increasing temperature thermal agitation increases in the molecules of liquid, there by distance between the molecules increases and it causes the decrease in interactions. So the estimations of U are diminishing with expanding temperature.²⁰⁻²⁶ We can also observe in fig.2 (a, b, c) and fig.3 (a, b, c) that the values of ρ , η are increasing with increasing concentration of O-CA in the liquids. The increasing values of ρ and η with increasing concentration of O-CA indicates the increase in magnitude of intermolecular interactions in these systems under study. The decrease in values of ρ and η with increasing temperature reflects the decrease in intermolecular forces due to thermal agitation in the liquid systems under consideration.

CONCLUSION

Ultrasonic speeds (U), viscosities (η) and densities (ρ) of formamide (F), N-Methylformamide(NMF) and N, N-dimethyl formamide (DMF) at different temperatures over the entire composition range have been measured. Examination of Table 2 shows that the speed of sound(U), density (ρ) and viscosity (η) of the pure amides follow the order at 303.15 K, F ($\rho = 1.1237 \text{ g } \sim \text{cm}^{-3}$) > NMF ($\rho = 0.9946 \text{ g } \sim \text{cm}^{-3}$) > DMF ($\rho = 0.9386 \text{ g } \sim \text{cm}^{-3}$) and F ($\eta = 2.8018 \text{ mp.s}$) > NMF ($\eta = 1.5859 \text{ mp.s}$) > DMF ($\eta = 0.7485 \text{ mp.s}$). The physical data suggest that F is extensively associated through H-bonding. NMF is also associated through H-bonding, but much less extensively, as can be understood by the existence of only one aminic hydrogen capable of H-bond formation and by the steric effect. Unlike these two amides, DMF is associated through weak physical forces, such as, dipole- dipole and dipole-induced dipole interactions. The results are used to qualitatively discuss specific interactions between unlike molecules.

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