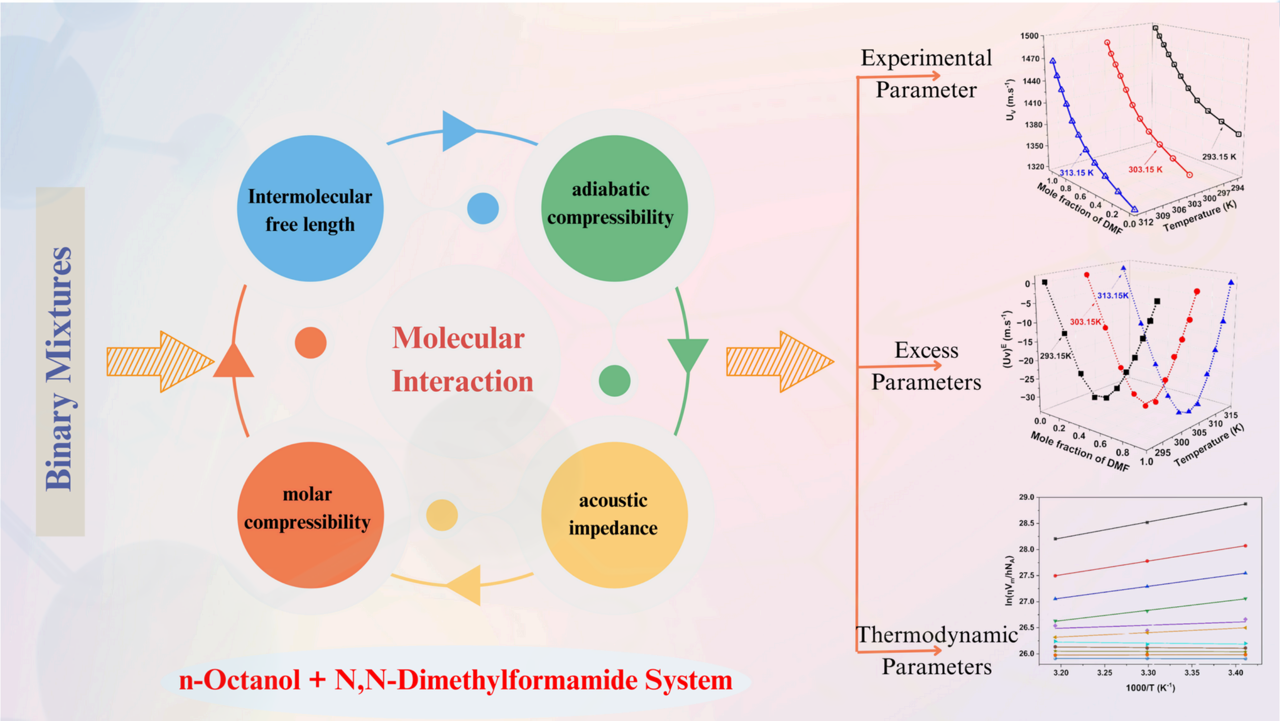
Chapter

7

Acoustic, Volumetric and Thermodynamics study of Binary Mixtures of n-Octanol and N, N-Dimethylformamide

Contents



7.1 Introduction

Extensive studies on molecular interactions in liquid systems have been conducted using various physical methods such as the Raman technique, Infrared Radiation (IR) technique, NMR technique, Ultraviolet, and ultrasonic methods [1-2]. Understanding the intermolecular interactions between the molecules in a mixture requires doing studies on liquid mixtures using ultrasonic techniques Ultrasonic sound vibrations can be used to investigate the properties of both liquid and solid materials. These studies have significant applications in a variety of industrial and scientific processes [3-4]. Liquid-liquid mixtures and solutions have found wide application in medical, pharmaceutical, chemical, and related industries [1-5]. The ultrasonic study of liquids and liquid mixtures has gained significant importance in recent years for understanding the nature of molecular interactions in pure liquids and binary liquid mixtures. This ultrasonic measurement is a part of the present chapter study, which aims to investigate the molecular interactions between the components of binary mixtures of N, N-Dimethylformamide (DMF) and n-octanol systematically. The excess thermodynamic functions are sensitive not only to intermolecular forces but also to the size of the molecules [2]. The non-rectilinear behavior of ultrasonic velocity, compressibility, and other thermodynamic parameters in liquid mixtures also indicates the strength of interactions between molecules. Different acoustical parameters such as free length, adiabatic compressibility, molar volume, and acoustic impedance, along with different excess parameters, are useful to obtain further insights into the nature and strength of molecular interactions. Ultrasonic methods have secured a permanent place in science, with new applications continually being found for solving both theoretical and practical problems [6-8].

Alcohol has been found in various applications and commercial uses in medical and other fields [9]. Recently, the longer-chain alcohol, n-octanol, has been recognized as a biofuel candidate derived from biomass-derived platform chemicals [10]. Primary alcohols of medium chain length are crucial industrial products, serving as valuable compounds for detergent and surfactant production, as well as in perfumery and flavor applications. Notably, 1-octanol holds significance and is employed in synthesizing 1-octene, a key co-monomer in polyethylene production and petrochemical processes [11]. Amides are highly polar and have a strong ability to dissolve substances, making them crucial solvents in industries and biological processes [12-13]. N, N-Dimethylformamide (DMF) is an important member of the amides solvent group and is used in the production of acrylic fibers and plastics [14]. It consists of two hydrophobic -CH_3 groups and one highly polar C=O group. DMF can easily form C-H…O and C=O…H type hydrogen bonds with other molecules, such as alcohols, enhancing its solvent capabilities [15]. Limited physical property measurements are available for binary mixtures of DMF with 1-alkanols, especially for higher 1-alkanols (C4–C10), according to an extensive examination of the literature. Singh et al. [16] reported excess volumes for DMF with methanol at temperatures of 303.15 K and 308.15 K. Bakshi and Kaur [17] provided measurements for excess volumes, viscosities, and ultrasonic speeds for the same system but at a temperature of 298.15 K. Gopal and Agarwal [18] studied excess molar volumes for DMF with ethanol at temperatures of 303.15 K and 313.15 K. Saleh et al. [19] reported densities and excess molar volumes for DMF with propanol at a temperature of 303.15 K, while Saleh and Uddin [20] reported viscosities in the temperature range of 303.15 K to 323.15 K. For higher alkanols, Rauf et al. [21] investigated excess molar volumes for binary mixtures of DMF with n-heptanol, n-octanol, n-nonanol, and n-decanol at a temperature of 298.15 K. Zegers and Somsen [22] obtained excess volumes for DMF with eight n-alkanols (methanol to octanol) at the same temperature. Additionally, Rao and Reddy [23] studied excess volumes and isentropic compressibility for DMF with methanol to heptanol at a temperature of 303.15 K. Garcia et al. [24] reported excess volumes for DMF with n-alkanols (C_1–C_{10}) at a temperature of 298.15 K. Iloukhani and Rostami [25] obtained excess volumes and isentropic compressibility for DMF with methanol to hexanol at a temperature of 303.15 K. While the properties reported above were at one or two temperatures only, Aminabhavi et al. [26], Ali et al. [27], Yang et al. [28], and Bhuiyan and Uddin [29] reported excess volumes for DMF with methanol, ethanol, or a mixture of methanol and ethanol (lower alkanols) at several temperatures. However, no more physical properties such as (intermolecular free length (L_f), adiabatic compressibility (β), acoustic impedance (Z), molar sound velocity (R), molar compressibility (B), surface tension (σ), relaxation time (τ)) for DMF with higher order alcohol (n-Octanol) at several temperatures were previously reported.

The present chapter involves the experimentally measured values of ultrasonic velocity (u), Density (ρ) and Viscosity (η) for binary mixtures of n-Octanol and N, N-Dimethylformamide at different temperatures (293.15 K, 303.15K, 313.15 K) are reported. From the experimental data the physiochemical parameters such as molar volume (Vm), adiabatic compressibility (β), intermolecular free length (Lf), acoustic impedance (Z), molar sound velocity (R), molar compressibility (B), relaxation strength (r), surface tension (σ), internal pressure (Pint), free volume (Vf) and relaxation time (τ), enthalpy (ΔH), entropy (ΔS), Gibbs free energy (ΔG) were calculated, which are more useful to predict and confirm the molecular interaction in the binary liquid mixtures. The Redlich-Kister equation has been associated with the excess and deviation functions that have been computed from experimental data. These functions were further discussed in terms of molecular interactions existing in the mixtures as well as the influence of temperature on them.

7.2 Material and Experimental Details

n-Octanol (Synthesis Grade) and N, N-Dimethylformamide (DMF) (AR grade) were procured from Loba Chemi Pvt Ltd, India, and used without further purification. Binary mixtures of n-Octanol and DMF were prepared at eleven different volume-based concentrations. These concentrations were subsequently converted into the mole fraction of DMF using a referenced Equation (3.1) (detail in chapter 3) [14]. The ultrasonic velocity (Uv) of the binary mixtures was measured using a digital ultrasonic interferometer (Model F-05, Mittal Enterprises, New Delhi, India) with an accuracy of ±2 m/s. The densities (ρ) of the binary mixtures were determined using a specific gravity bottle. The viscosity (η) of the pure liquids and their binary mixtures was measured using an Ostwald viscometer. The temperature of the binary liquid mixtures was maintained constant using an electronically operated digital constant temperature bath. All measurements were carried out at constant temperature at different temperatures. The temperature was controlled by continuously circulating water around the sample. The experimental values of ultrasonic velocity (Uv), density (ρ) and viscosity (η) of the pure liquids, along with literature values, are tabulated in Table 7.1 at different temperatures [30-39].

Table 7.1 Comparison of experimental and literature values of ultrasonic velocity (Uv), density (ρ) and viscosity (η) for pure liquids (n-Octanol and N, N-Dimethylformamide (DMF)) at different temperatures.

Parameters	**Temperatures**	**n-Octanol**		**DMF**	
(Uv)		Exp.	Lit.	Exp.	Lit.
	293.15 K	1373.09	1365.25 [30]	1493.65	1492.00 [35]

	303.15K	1338.26	1338.00 [31]	1481.93	1462.00 [36]
	313.15 K	1317.22	1303.00 [32]	1466.86	1434.80 [37]
(ρ)	293.15 K	0.8254	0.8251 [33]	0.9470	0.9485 [38]
	303.15K	0.8183	0.8183 [33]	0.9420	0.9394 [38]
	313.15 K	0.8113	0.8114 [33]	0.9382	0.9301 [38]
(η)	293.15 K	8.7764	9.1850 [34]	0.9200	0.8830 [39]
	303.15K	6.0962	6.0402 [31]	0.9190	0.7690 [39]
	313.15 K	4.4124	4.6280 [31]	0.9160	0.6830 [39]

7.3 Results and Discussion

7.3.1 Experimental and evaluated parameters

Comparison of experimental and literature values of Ultrasonic velocity (Uv), density (ρ), viscosity (η), of n-Octanol and DMF at different temperatures is shown in Table 7.1. The experimental value shows good agreement with literature for pure n-Octanol and pure N, N-Dimethylformamide (DMF). Figure 7.1 shows the variation of ultrasonic velocity (Uv) across the entire miscibility range (mole fraction of DMF) in N, N-dimethylformamide (DMF) and n-Octanol mixtures at various temperatures (293.15 K to 313.15 K). At all measured temperatures and concentrations, the plot is divided into two linear segments with different slopes, intersecting at a mole fraction of X = 0.5768, indicating a deviation from ideal mixing behavior, similar to the DMF/methanol system [8]. Additionally, the ultrasonic velocity (Uv) increases with the mole fraction of DMF and decreases with temperature. This linear increase in Uv with concentration suggests significant interactions between unlike molecules through hydrogen bonding (OH–O), causing displacement of electrons and nuclei [47]. Figure 7.2 depicts the variation of density as a function of the mole fraction of DMF at different temperatures. The density increases nonlinearly with the concentration of DMF at all measured temperatures, indicating that the mixture becomes more compact with the addition of DMF. This suggests the presence of attractive interactions between the components, causing a nonlinear increase in density [48]. The rate of increase in density is higher in the lower and mid concentration range ($0 \le X \le 0.5768$) compared to the higher concentration range ($X > 0.5768$). For instance, at 293.15 K, the density of n-Octanol and DMF is 0.8254 g.cm^{-3} and 0.9470 g.cm^{-3}, respectively, which decreases to 0.8113 g.cm^{-3} and 0.9382 g.cm^{-3} at 313.15 K. This decrease in density with increasing temperature is observed in all n-Octanol and DMF mixtures, attributed to a less organized structure and increased intermolecular gaps at higher temperatures.

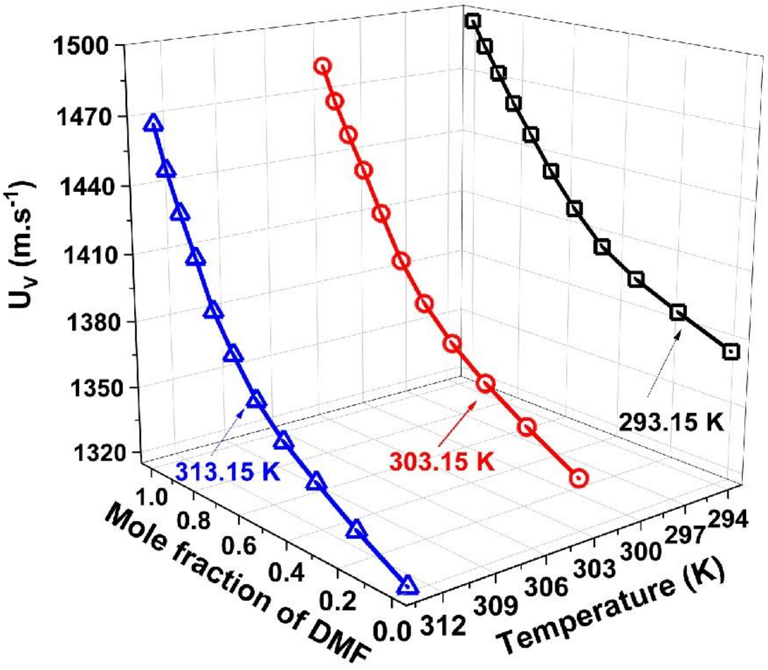


Fig. 7.1 Ultrasonic velocity (Uv) against mole fraction of DMF in n-Octanol at different temperatures.

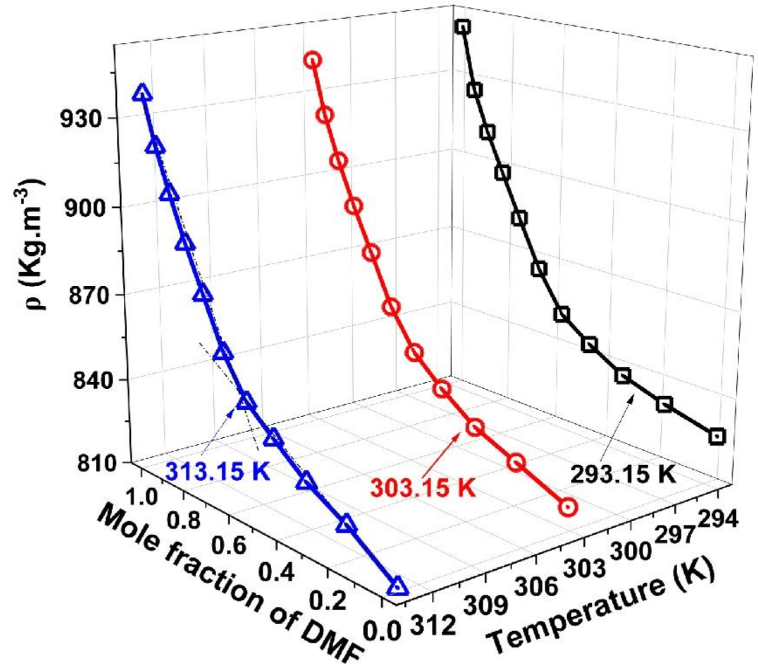


Fig. 7.2 Variation of density (ρ) against mole fraction of DMF in n-Octanol at different temperatures.

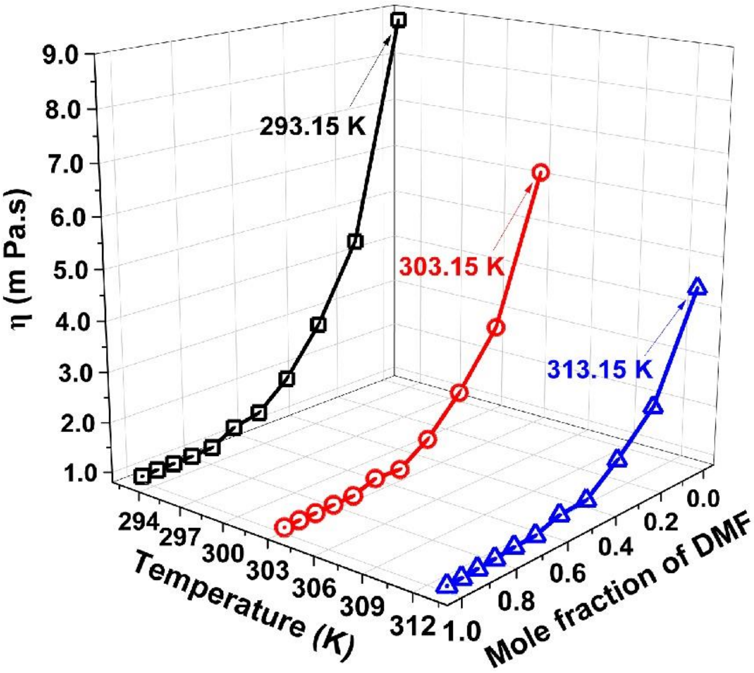


Fig. 7.3 Variation of viscosity (η) against mole fraction of DMF in n-Octanol at different temperatures.

Figure 7.3 shows the variation in viscosity with varying DMF composition in the mixture at different temperatures. Viscosity increases nonlinearly with the mole fraction of DMF at all temperatures, consistent with reports by Yue et al. [49] and Fort and Moore [50], which observed nonlinear variation or higher viscosity values in polar liquid mixtures. This nonlinear increase in viscosity indicates specific interactions between mixture constituents, such as hydrogen bond formation and charge transfer complexes, leading to higher viscosity in the mixtures compared to pure components [51]. Experiment measured Uv, ρ, η value use determined acoustic parameter namely adiabatic compressibility (β), intermolecular free length (L_f), acoustic impedance (Z), molar sound velocity (R) and molar compressibility (B) for different concentrations and temperatures are presented in Table 7.2.

The experimentally measured values of ultrasonic velocity (Uv) density (ρ) and viscosity (η) were used to determine various acoustic parameters, including molar volume (Vm), adiabatic compressibility (β), intermolecular free length (Lf), acoustic impedance (Z), molar sound velocity (R), molecular compressibility (B) and relaxation time (τ). These parameters are described in Chapter 3 and were calculated using Equations (3.42) to (3.47) [40-46]. The close pursual Table 7.2 shows that ultrasonic velocity decreases as the temperature increases. However, it increases with higher mole fractions of DMF in n-Octanol. This suggests that at higher concentrations of DMF in the binary mixture, dipole-dipole interactions become stronger. The increase in ultrasonic velocity indicates strong molecular interactions, likely due to hydrogen bonding between the solute and solvent molecules. A nonlinear decrease in adiabatic compressibility is observed with an increase in the mole fraction of DMF as the temperature rises. The adiabatic compressibility values increase with temperature for all compositions ranges from 0.0 →1.0. In the DMF + n-Octanol system, the adiabatic compressibility is lower compared to the DMF + n-Hexanol system. For instance, at 293.15 K, the adiabatic compressibility value for the DMF + n-Hexanol system is 4.73 $m^2 \cdot N^{-1}$, while for the DMF + n-Octanol system, it is 6.43 $m^2 \cdot N^{-1}$. The changes in adiabatic compressibility, which affect ultrasonic velocity, are due to structural changes in the liquid mixtures. When molecules interact, they break up molecular clusters, releasing dipoles for further interactions, leading to an increase in compressibility. Similar results have been observed in other systems [52-54]. At higher alcohol concentrations, more alcohol molecules surround the ester molecules, strengthening dipole-dipole interactions. At lower alcohol concentrations, fewer alcohol molecules result in weaker hydrogen bonding interactions with the ester molecules. The free length (L_f) of a system indicates the degree of intermolecular attraction between components in binary mixtures. As shown in Table 7.2, L_f increases with the increasing mole fraction of DMF, and also with rising temperature. The L_f values exhibit a nearly linear trend in both the DMF + n-Hexanol and DMF + n-Octanol systems. Additionally, the increase in compressibility brings the molecules closer together, leading to an increase in intermolecular free length. The decrease in intermolecular free length (L_f) with increasing solute concentration suggests significant interactions between the solute and solvent, indicating that the solutes promote structural changes in the mixture. Additionally, the increase in ultrasonic velocity with solute concentration points to stronger intermolecular forces within the mixtures. Furthermore, it was observed that acoustic impedance (Z) increases with both the mole fraction of DMF and temperature, suggesting that complex formation is occurring in the liquid system due to enhanced solute-solvent interactions. This behavior is consistent with theoretical predictions, as ultrasonic velocity also rises with increasing mole fraction of DMF in liquid mixtures. The increase in acoustic impedance (Z) with solute concentration reflects stronger inter- and intra-molecular interactions between the molecules in the mixture, indicating significant molecular interactions within the system. The decrease in molar sound velocity and compressibility with increasing mole fraction of DMF and temperature suggests the presence of hydrogen bonding and dipole-dipole interactions. These interactions strengthen solute-solvent associations, reducing molecular mobility. As temperature rises, thermal energy disrupts these interactions, leading to structural reorganization that further lowers sound velocity and compressibility [8].

Table 7.2 The values of ultrasonic velocity (Uv), adiabatic compressibility (β), intermolecular free length (Lf), acoustic impedance (Z), Rao constant (R) and molar compressibility (B) for binary mixtures of DMF + n-Octanol at different temperatures.

X	**U (m/s)**	**$\beta \times 10^{-10}$ ($m^2.N^{-1}$)**	**$L_f \times 10^{-11}$ (m)**	**$Z \times 10^{6}$ ($Kg.m^{-2}.\ s^{-1}$)**	**$R \times 10^{-3}$ ($S^{1/3}\cdot mol^{-1}$)**	**$B \times 10^{-3}$ $m^{3}\cdot Pa^{1/7}\cdot mol^{-1}$**
T=293.15 K						
0.0000	1373.09	6.43	5.17	1.13	1.71	3.24
0.1851	1383.13	6.30	5.11	1.15	1.57	2.97
0.3382	1392.22	6.18	5.07	1.16	1.45	2.75
0.4670	1402.56	6.04	5.01	1.18	1.34	2.55
0.5768	1416.62	5.86	4.93	1.20	1.25	2.38
0.6715	1431.28	5.65	4.84	1.24	1.17	2.23
0.7541	1446.00	5.43	4.75	1.27	1.09	2.08
0.8267	1458.80	5.24	4.67	1.31	1.03	1.96
0.8910	1471.47	5.08	4.59	1.34	0.97	1.85
0.9484	1482.78	4.92	4.52	1.37	0.92	1.76
1.0000	1493.65	4.73	4.43	1.41	0.86	1.66
T=303.15 K						
0.0000	1338.26	6.82	5.42	1.10	1.71	3.24
0.1851	1351.16	6.63	5.35	1.12	1.56	2.97
0.3382	1363.04	6.47	5.28	1.13	1.44	2.74
0.4670	1375.13	6.29	5.21	1.16	1.34	2.54
0.5768	1388.53	6.10	5.13	1.18	1.25	2.37
0.6715	1404.11	5.88	5.03	1.21	1.16	2.22
0.7541	1422.69	5.61	4.92	1.25	1.09	2.08
0.8267	1439.76	5.39	4.82	1.29	1.02	1.96
0.8910	1453.86	5.21	4.74	1.32	0.96	1.85
0.9484	1467.39	5.03	4.65	1.36	0.91	1.75

1.0000	1481.93	4.83	4.56	1.40	0.86	1.66
T=313.15 K						
0.0000	1317.22	7.10	5.63	1.07	1.72	3.25
0.1851	1329.55	6.87	5.54	1.09	1.56	2.96
0.3382	1341.27	6.69	5.47	1.11	1.44	2.73
0.4670	1352.03	6.52	5.39	1.14	1.33	2.53
0.5768	1364.39	6.34	5.32	1.16	1.24	2.36
0.6715	1379.78	6.10	5.22	1.19	1.16	2.21
0.7541	1395.09	5.85	5.11	1.22	1.08	2.07
0.8267	1415.19	5.59	5.00	1.26	1.02	1.95
0.8910	1432.07	5.37	4.90	1.30	0.96	1.84
0.9484	1448.81	5.17	4.80	1.34	0.91	1.75
1.0000	1466.86	4.95	4.70	1.38	0.86	1.66

The variation in surface tension indicates the attractive interactions between the two solutions. Table 7.3 observed the surface tension of the mixture increases with the mole fraction of DMF. According to Karla Granados [55], strong interactions in the liquid mixture lead to an increase in the surface tension (σ) value. This suggests that the interactions in the mixture are strong, resulting in higher σ values as the mole fraction increases. Additionally, the observed decrease in surface tension with increasing temperature supports the fundamental concept of surface tension, where the formation of an interface involves the migration of species from a high surface tension liquid state to a low surface tension vapor state. Furthermore, observed in relaxation time (τ) value decrease with increase in concentration with temperature increasing τ value decreases. The relaxation time is contingent upon the viscosity of the liquid. The τ usually on the order of 10^{-12} seconds, results from the structural relaxation process. This suggests a cooperative rearrangement of molecules. At 293.15 K, the relaxation time for the DMF + n-Hexanol system was observed to be 4.4215 ps, whereas the DMF + n-Octanol system exhibited a significantly longer relaxation time of 7.1596 ps. This indicates that the relaxation time for the DMF + n-Octanol system is approximately 1.61 times larger than that of the DMF + n-Hexanol system. The longer relaxation time of the DMF + n-Octanol system suggests stronger or more long molecular interactions, likely due to the larger molecular size and higher viscosity of n-Octanol compared to n-Hexanol. These factors could contribute to a slower reorientation of dipoles, thus increasing the relaxation time. In contrast, the smaller and less viscous n-Hexanol facilitates faster molecular reorientation, leading to a shorter relaxation time.

Table 7.3 Evaluated parameters of surface tension (σ) and relaxation time (τ) for mole fraction of DMF (0.0→1.0) at various temperatures.

	293.15 K		**303.15 K**		**313.15 K**	
X	**σ (N/m)**	**τ (10^{-12} s)**	**σ (N/m)**	**τ (10^{-12} s)**	**σ (N/m)**	**τ (10^{-12} s)**
0.0000	26.5838	7.5196	25.3587	5.5463	24.5512	4.1794
0.1851	27.0257	3.6118	25.9652	2.8253	25.2558	2.1976
0.3382	27.4569	2.2740	26.5059	1.8389	25.8237	1.4976
0.4670	28.0028	1.4752	27.1401	1.2078	26.4214	1.0335
0.5768	28.6882	1.0340	27.8358	0.8690	27.0461	0.9846
0.6715	29.6214	0.9113	28.7453	0.8626	27.9333	0.8178
0.7541	30.6642	0.6966	29.8884	0.7082	28.9569	0.7786
0.8267	31.6084	0.6586	30.9328	0.6759	30.0871	0.7170
0.8910	32.5141	0.6318	31.8936	0.6469	31.1347	0.6748
0.9484	33.4138	0.6114	32.8700	0.6244	32.1849	0.6360
1.0000	34.6041	0.5806	34.0170	0.5923	33.3643	0.6050

7.3.2 Excess parameters for binary mixtures

Figure 7.4 shows the variation of $(Uv)^E$ across different mole fractions of DMF at three distinct temperatures is shown. Across the composition range, the excess velocity tends to become more negative as the interaction strength between the component molecules increases. Additionally, the decrease in negative deviation and the shift of the velocity maximum point towards higher 'X_A' values with increasing temperature suggest the presence of strong hydrogen bonding. This bonding reaches its peak at the minima, indicating a significant influence on the mixture's behavior. Figure 7.5 presents the variation of excess molar volume $(V_m)^E$ with respect to the mole fraction of DMF across the entire composition range (0.0→1.0) at different temperatures. The strength of intermolecular interactions in liquid mixtures can be elucidated through the sign and magnitude of the $(V_m)^E$ values. Positive values of $(V_m)^E$ suggest a loose packing of molecules in the binary mixture compared to the pure components. In this figure, the $(Vm)^E$ values increase for the liquid mixtures as the interactions between unlike molecules weaken, particularly with the increase in the alkanol chain length. Figure 7.6

shows that positive adiabatic compressibility $(\beta)^E$ values indicate the presence of dispersive forces, suggesting weak interactions and structure-breaking tendencies between hetero-molecules in the mixtures. This leads to loosely packed molecular arrangements, reflecting positive deviations in $(\beta)^E$ in binary liquid systems. $(\beta)^E$ shows a higher deviation at around 0.578 mole fraction of DMF in n-Octanol, indicating significant attractive and repulsive forces between the components of the binary mixture. Figure 7.7 shows the excess free length $(L_f)^E$ in the DMF-n-Octanol mixture at various temperatures is depicted. At lower DMF mole fractions (around X = 0.578), $(L_f)^E$ rises, indicating strong interactions between different molecules. The shift to positive $(L_f)^E$ values suggests increased detachment between components, resulting in higher compressibility and volume.

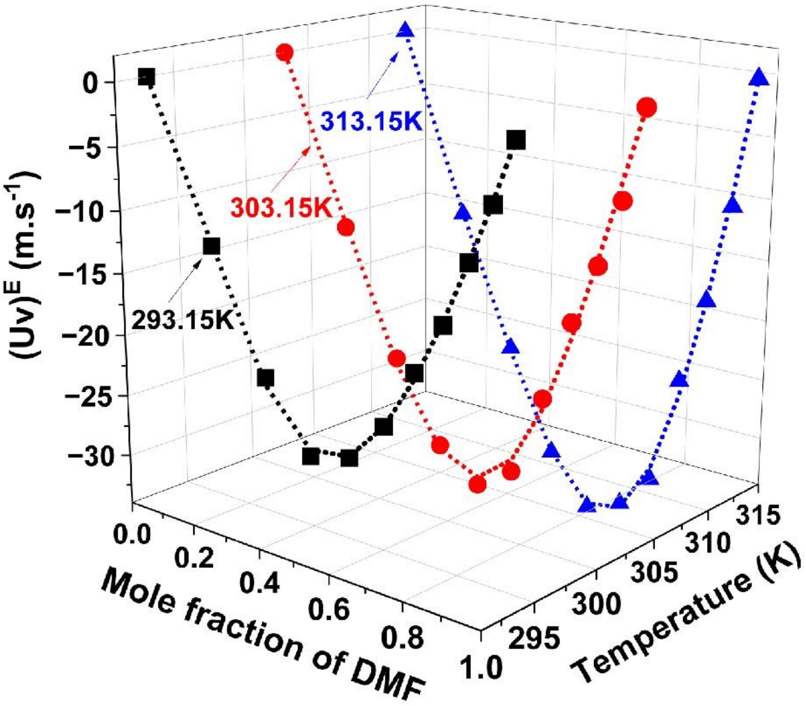


Fig.7.4 Excess ultrasonic velocity $(U_V)^E$ against mole fraction of DMF at different temperatures.

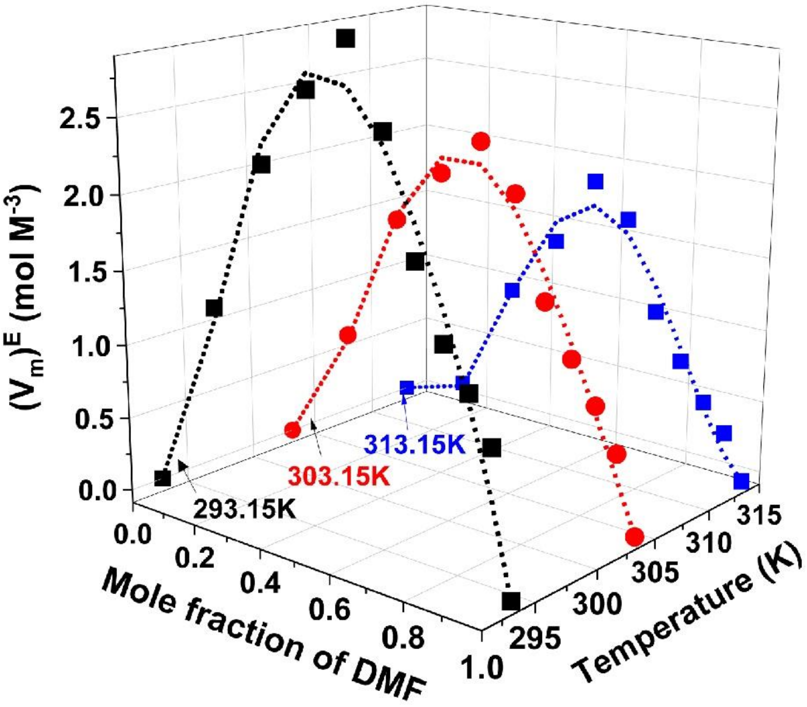


Fig.7.5 Excess molar volume $(V_m)^E$ against mole fraction of DMF at different temperatures.

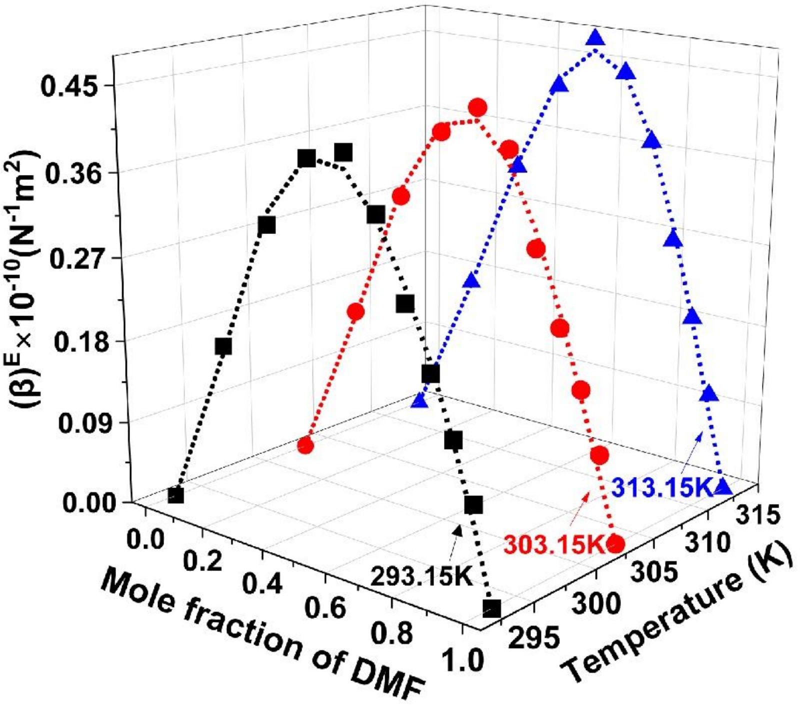


Fig.7.6 Excess adiabatic compressibility $(\beta)^E$ against mole fraction of DMF at different temperatures.

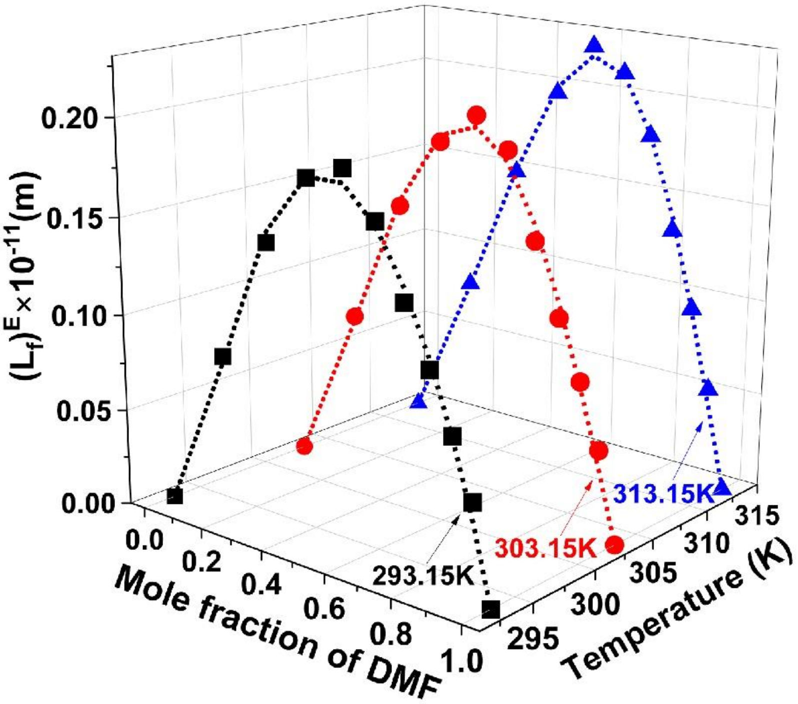


Fig.7.7 Excess intermolecular free length $(L_f)^E$ against mole fraction of DMF at different temperatures.

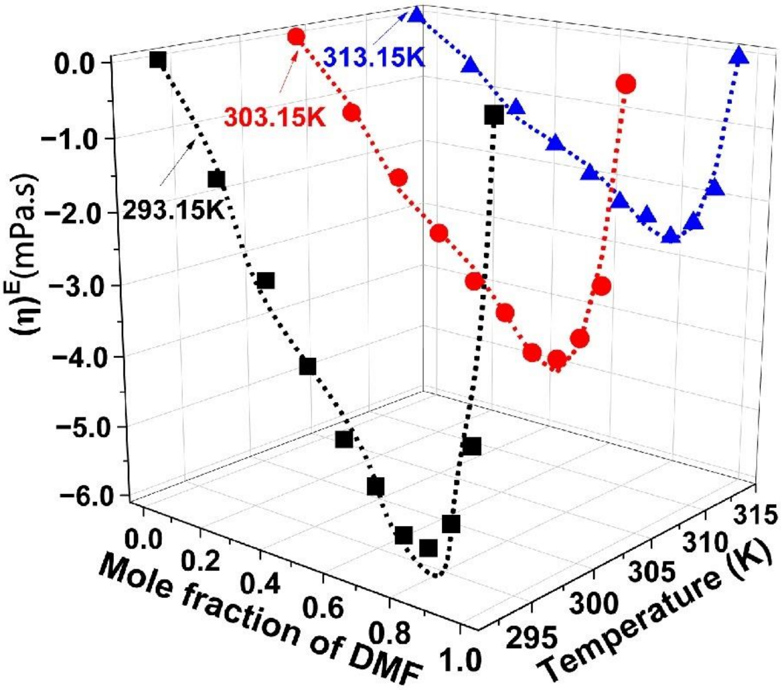


Fig. 7.8 Plot of excess viscosity $(\eta)^E$ against mole fraction of DMF in binary mixtures at different temperatures.

The negative values of excess viscosity $(\eta)^E$ observed across n-Octanol+DMF binary systems (Fig. 7.8) throughout the entire composition range (0.0→1.0) indicate that the viscosities of the heteromolecular complexes formed between n-Hexanol/n-Octanol and DMF are lower than those of the pure components. These negative deviations from an ideal linear dependence on mole fraction are often attributed to the dominance of dispersion forces, particularly in systems where the molecules differ significantly in size [50] as in this study. The excess values $(U)^E$, $(Vm)^E$, $(\beta)^E$, $(L_f)^E$ and $(\eta)^E$are fitted to the R. K. polynomial equation using the least squares method. Table 7.4 lists the coefficients a_0, a_1, a_2, and a_3 along with their standard deviation δ.

Table 7.4 Values of coefficients (a_0, a_1, a_2, a_3) of R. K. polynomials with correlation coefficients (R) at different temperatures.

Parameters	**a_1**	**a_2**	**a_3**	**a_4**	**R**
T = 293.15 K					
$(U_v)^E$	-106.3373	-4.0390	45.7044	-23.7668	0.9994
$(V_m)^E$	11.7507	0.6303	-4.994	5.2441	0.9864
$(\beta)^E$	1.6226	0.1012	-0.6083	0.5407	0.9972
$(L_f)^E$	0.7434	0.0908	-0.231	0.2354	0.9974
$(\eta)^E$	-12.5488	6.3217	-5.3335	4.7767	0.9993
T = 303.15 K					
$(U_v)^E$	-125.5903	-41.9581	40.3272	21.7376	0.9976
$(V_m)^E$	8.9209	1.3215	-5.6743	2.3600	0.9916
$(\beta)^E$	1.6472	0.397	-0.6756	-0.0467	0.9967
$(L_f)^E$	0.7703	0.225	-0.2559	-0.0204	0.9971
$(\eta)^E$	-8.5782	4.1108	-2.1819	2.5247	0.9983
T = 313.15 K					
$(U_v)^E$	-146.4458	-85.2688	4.7219	40.5627	0.9990
$(V_m)^E$	6.4728	4.3948	-7.8021	-1.2111	0.9863
$(\beta)^E$	1.7618	-0.9076	-0.5702	-0.5187	0.9986
$(L_f)^E$	0.8287	0.4489	-0.1975	-0.2181	0.9988
$(\eta)^E$	-5.8019	3.7018	-1.6470	0.6148	0.9980

7.3.3 Thermodynamic parameters

The thermodynamic parameters associated with the activation of viscous flow were derived from the measured dynamic viscosity values. The viscosity of liquid mixtures is quantitatively described by the formalism of Eyring's transition state theory, as articulated through the absolute rate equation [56,57].

$$\eta = \frac{hN_A}{V_m}\exp^{\left(\frac{\Delta G}{RT}\right)} \tag{7.1}$$

$$\Delta G = RT\ln\eta\left(\frac{V_m}{hN_A}\right) \tag{7.2}$$

Here, h represent Planck's constant, N_A is Avogadro's number, V_m denotes the molar volume, R is gas constant, T is temperature and ΔG corresponds to the activation Gibbs free energy associated with viscous flow. By combining this equation with the appropriate thermodynamic relations, the following expression is obtained, facilitating the evaluation of the activation enthalpy (ΔH) and entropy (ΔS) associated with viscous flow [58]

$$\Delta G = \Delta H_e - T\Delta S \tag{7.3}$$

$$\ln\left(\frac{\eta V_m}{hN_A}\right) = \frac{\Delta H_e}{RT} - \frac{\Delta S}{R} \tag{7.4}$$

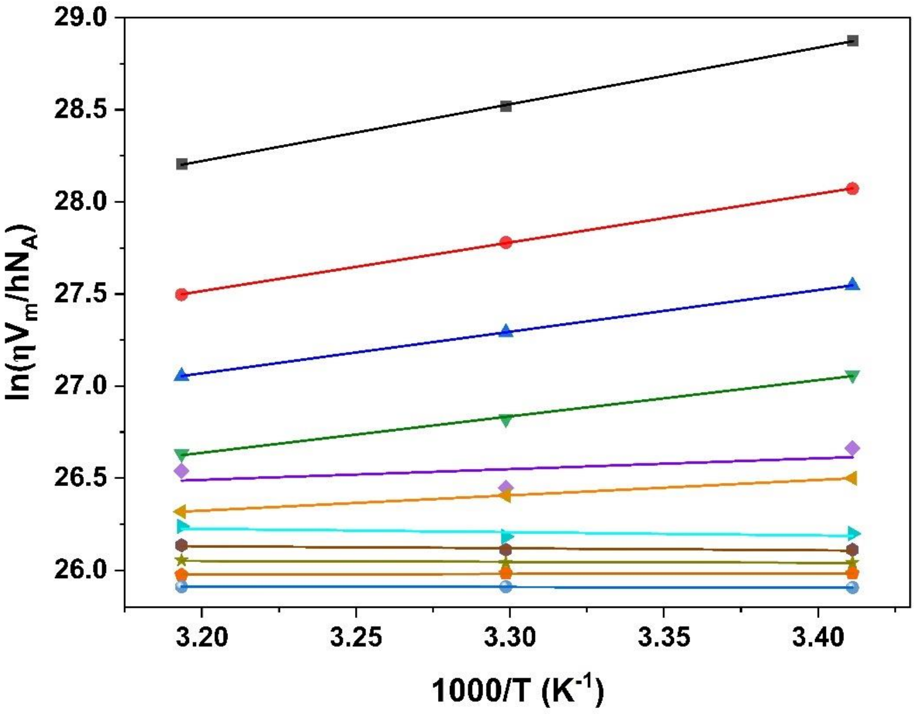


Fig. 7.9 Plots of ln(ηVm/hNA) vs inverse of temperature (1000/T) for different mole fraction of DMF in n-Octanol.

The term on the left-hand side of Equation 7.4 ($\ln\left(\frac{\eta V_m}{hN_A}\right)$) was plotted against the reciprocal of temperature, as shown in Fig. 7.9. The resulting linear trend within the temperature range of 293.15→323.15 K indicates Arrhenius behavior. From this plot, the activation enthalpy (ΔH) and activation entropy (ΔS) for viscous flow were determined from the slope and intercept, respectively. To assess the thermodynamic properties of the n-octanol and N, N-dimethylformamide (DMF) mixture, several activation thermodynamic parameters for viscous flow were calculated. These parameters, including activation Gibbs energy (ΔG), activation enthalpy (ΔH) and activation entropy (ΔS), were determined using Equations 7.2 to 7.4. The computed values at various temperatures are summarized in Table 7.5. This parameters provide detailed insights into the energy and entropy changes associated with the viscous flow of the mixture. A thorough examination of Table 7.5 shows that the activation Gibbs free energy (ΔG) increases with temperature, indicating a temperature-dependent activation process. Additionally, as the mole fraction of N, N-dimethylformamide (DMF) increases, the ΔG values across the entire composition range (0.0→1.0) exhibit anomalous behavior. Specifically, the ΔG values remain positive for all compositions (0.0→1.0), suggesting that the viscous flow is influenced by specific molecular interactions. The positive ΔG values imply the presence of specific interactions, such as complex formation through intermolecular hydrogen bonding and dipolar interactions between unlike molecules, rather than between similar molecules. This observation suggests that the interaction strength between different molecular species in the mixture is greater than that between like molecules, indicating the formation of more ordered structures due to intermolecular forces [59,60]. The activation entropy (ΔS) values are observed to decrease and become more negative as the mole fraction of DMF in the mixtures increases, alongside an increase in temperature. This trend suggests that, during viscous flow, the DMF and n-octanol mixture becomes more structured compared to its initial state due to the formation of activated species [58,61]. Moreover, the consistently negative ΔS values indicate that the viscous flow process is highly ordered, involving contiguous liquid layers that maintain their structural configuration even while moving in a steady, stationary state. This implies that the flow behavior is influenced by the formation of organized structures within the mixture [62,63]. The determined values of activation enthalpy (ΔH) exhibit anomalous behavior across the entire composition range of the mixture. ΔH decreases with the addition of a small amount of n-Octanol (X = 0.8910) to DMF, but then increases as the n-Octanol content decreases. This indicates that the formation of activated species required for viscous flow is relatively easier in the n-Octanol-rich region. However, as the mole fraction of DMF increases, the formation of these activated species becomes more difficult, suggesting that the energy required for viscous flow increases in the DMF-rich region [58].

Table 7.5 Determined values of Gibbs energy (ΔG), entropy (ΔS) and enthalpy (ΔH) of activation of viscous flow for different mole fraction of DMF in n-Octanol.

X	**ΔG ($KJmol^{-1}$)**			**ΔS ($JK^{-1}mol^{-1}$)**			**ΔH ($KJmol^{-1}$)**
	293.15 K	**303.15 K**	**313.15 K**	**293.15 K**	**303.15 K**	**313.15 K**	
0.0000	70.38	71.88	73.43	-39.02	-42.69	-46.29	58.94
0.1851	68.42	70.02	71.59	-60.78	-64.04	-67.02	50.60
0.3382	67.14	68.79	70.44	-81.44	-84.19	-86.77	43.26
0.4670	65.95	67.60	69.33	-96.17	-98.43	-100.83	37.76
0.5768	64.98	66.66	69.09	-183.46	-182.94	-184.86	11.20
0.6715	64.59	66.55	68.52	-165.90	-166.92	-167.86	15.95
0.7541	63.85	65.99	68.31	-229.46	-228.94	-229.04	-3.41
0.8267	63.64	65.81	68.04	-224.28	-224.04	-224.03	-2.11
0.8910	63.47	65.63	67.83	-219.94	-219.83	-219.82	-1.01
0.9484	63.32	65.48	67.63	-213.94	-214.01	-214.01	0.61
1.0000	63.14	65.30	67.46	-216.88	-216.86	-216.82	-0.44

7.4 Conclusions

- In the study of the n-Octanol+DMF binary system, the concentration-dependent behaviors of ultrasonic velocity (Uv), density (ρ), and viscosity (η) were examined across different temperatures.
- Good agreement was found between the experimental and literature values for the ultrasonic velocity, density and viscosity of the n-Octanol and DMF mixture at studied temperatures (293.15 K, 303.15 K and 313.15 K).
- The non-linear changes observed in parameters like β, L_f, σ, and τ shed light on the intricate molecular interactions underlying complex formation via hydrogen bonding between solute molecules.

- Additionally, the contrasting positive and negative shifts in excess values concerning concentration and temperature for these acoustic parameters provided further evidence of interactions between unlike molecules.
- The thermodynamic analysis of the n-octanol and N, N-Dimethylformamide (DMF) mixture shows Arrhenius-type behavior with positive activation Gibbs energy (ΔG), indicating specific intermolecular interactions such as hydrogen bonding and dipolar interactions between unlike molecules.
- The negative activation entropy (ΔS) suggests a more ordered viscous flow, with increased structuring during flow. The activation enthalpy (ΔH) decreases in the n-octanol-rich region and increases in the DMF-rich region, implying that the formation of activated species is easier in the n-octanol region but requires more energy in the DMF region.

References

[1] A. Ali, A. K Nain and S. Hyder, Study of molecular interaction in binary liquid mixtures through ultrasonic speed measurement, J. Pure Appl. Ultrason. 23 (2001) 73-79.

[2] S. Anuradha, S. Prema and K. R. Rajagopal, Ultrasonic studies on molecular interactions in binary mixtures of acetonitrile with carbonyl molecules, J. Pure Appl. Ultrason. 27 (2005) 49-54.

[3] S. Thirumaran, J. Jayakumar, Ultrasonic study of n-alkanols in toluene with nitrobenzene, Indian J. Pure Appl. Phy. 47 (2009) 265–272.

[4] A. N. Prajapati, Acoustic and refractometric study of binary mixtures of 1-Propanol + Benzonitrile at 313 K, Indian J. Pure Appl. Phy. 55 (2017) 297-303.

[5] S. T. Murugan and D. Priya, Acoustical and excess thermodynamic studies of ternary liquid mixtures of some primary alkanols in mixed binary solvent at varying temperatures, Indian J. Pure Appl. Phy. 51 (2013) 413-420.

[6] M. Gupta, J. P. Shukla, Indian Ultrasonic investigation of molecular association in binary mixtures-Dioxan plus formic acid, salicylic acid and benzoic acid, Indian J. Pure Appl. Phy. 34 (1966) 769-772.

[7] A. N. Kannappan, R. Palani, Studies on molecular interaction in ternary liquid mixtures by ultrasonic velocity measurements, Ind. J. Phys. 70 (1996) 59-65.

[8] A. M. E. Raj, L. B. Resmi, V. B. Jothy, M. Jayachandran, C. Sanjeeviraja, Ultrasonic study on binary mixture containing dimethylformamide and methanol over the entire miscibility range ($0 < x < 1$) at temperatures 303–323 K, Fluid Ph. Equilib. 281 (2009) 78-86.

[9] S. P. Patel, A. N. Prajapati, H. P. Vankar and V. A. Rana, Dielectric Dispersion Response of Binary Mixtures of n-Butanol and Valeronitrile, Adv. Mater. Res. 1169 (2022) 73-77.

[10] L. Cai, Y. Uygun, C. Togbe, H. Pitsch, H. Olivier, P. Dagaut, S. M. Sarathy, An experimental and modeling study of n-octanol combustion, Proc. Combust. Inst. 35 (2015) 419-427.

[11] J. Julis and W. Leitner, Synthesis of 1-Octanol and 1,1-Dioctyl Ether from Biomass-Derived Platform Chemicals, Angew. Chem. Int. Ed. 51 (2012) 1-6.

[12] W. D. Kumar, C. W. Porter, Dipole Moments and Molecular Structure of Amides, J. Am. Chem. Soc. 56 (1934) 2549-2554.

[13] M. Rabinovitz, A. Pines, Hindered internal rotation and dimerization of N, N-dimethylformamide in carbon tetrachloride, J. Am. Chem. Soc. 91 (1969) 1585-1589.

[14] L. Yang, K. Huang, X. Yang, Dielectric Properties of N, N-Dimethylformamide Aqueous Solutions in External Electromagnetic Fields by Molecular Dynamics Simulation, J. Phys. Chem. A. 114 (2009) 1185-1190.

[15] R. J. Sengwa, V. Khatri, S. Sankhla, Structure and hydrogen bonding in binary mixtures of N, N-dimethylformamide with some dipolar aprotic and protic solvents by dielectric characterization, Indian J. Chem. 48A (2009) 512-519.

[16] P. P. Singh, D. V. Verma, P. S. Arora, Thermodynamics of binary methanol solutions, Thermochim. Acta. 15 (1976) 267-280.

[17] M. S. Bakshi, G. Kaur, Thermodynamic Behavior of Mixtures. 4. Mixtures of Methanol with Pyridine and N, N-Dimethylformamide at 25 °C, J. Chem. Eng. Data. 42 (1997) 298-300.

[18] R. Gopal, S. Agarwal, Excess volumes of some polar and non-polar liquids with N, N-dimethylformamide, J. Chem. Thermodyn. 8 (1976) 1205-1207.

[19] M. A. Saleh, S. Begum, M. H. Uddin, Excess molar volumes of 1-propanol+ formamide,+ N-Methylformamide,+ N, N-dimethylformamide at 303.15 K, J. Mol. Liq. 94 (2001)155-161.

[20] M. A. Saleh, M. H. Uddin, Viscosity and Thermodynamics of Viscous Flow of the Systems, 1-Propanol + Formamide, +N methyl formamide, + N, N-Dimethylformamide, Phys. Chem. Liq. 37 (1999) 701-718.

[21] M. A. Rauf, M. Arfan, A. Farhataziz, Excess molar volumes of (N, N-dimethylformamide+ an aliphatic alcohol) at 298.15 K, J. Chem. Thermodyn, 15 (1983) 1021-1023.

[22] H. C. Zegers, G. Somsen, Partial molar volumes and heat capacities in (dimethylformamide+ an n-alkanol), J. Chem. Thermodyn. 16 (1984) 225-235.

[23] K. P. Rao, K. S. Reddy, excess volumes and excess isentropic compressibility of binary mixtures of N, N-dimethyl formamide with n-alcohols at 303.15 K, Phys. Chem. Liq. 15 (1985) 147-154.

[24] B. Garcia, R. Alcalde, J. M. Leal, J. L. Trenzado, Volumetric behaviour of N-Methylformamide-(C1-C10) alkan-1-ol and N, N-Dimethylformamide – (C1-C10) alkan-1-ol solvent systems, J. Phys. Org. Chem. 10 (1997) 138-144.

[25] H. Iloukhani, Z. Rostami, Measurement of Some Thermodynamic and Acoustic Properties of Binary Solutions of N, N-Dimethylformamide with 1-Alkanols at 30◦C and Comparison with Theories, J Solution Chem. 32 (2003) 451-462.

[26] V. A. Aminabhavi, T. M. Aminabhavi, R. H. Balundgi, Evaluation of Excess Parameters from Densities and Viscosities of Binary Mixtures of Ethanol with Anisole, N, N-Dimethylformamide, Carbon Tetrachloride, and Acetophenone from 298.15 to 313.15 K, Ind. Eng. Chem. Res. 29 (1990) 2106-2111.

[27] A. Ali, A. K. Nain, M. Kamil, Physico-chemical studies of non-aqueous binary liquid mixtures at various temperatures, Thermochim. Acta. 274 (1996) 209-221.

[28] C. Yang, Y. Sun, Y. He, P. Ma, Volumetric Properties and Viscosities of Binary Mixtures of N, N-Dimethylformamide with Methanol and Ethanol in the Temperature Range (293.15 to 333.15) K, J. Chem. Eng. Data. 53 (2008) 293-297.

[29] M. M. H. Bhuiyan, M. H. Uddin, Excess molar volumes and excess viscosities for mixtures of N, N-dimethylformamide with methanol, ethanol and 2-propanol at different temperatures, J. Mol. Liq. 138 (2008) 139-146.

[30] M. Dzida, Speeds of Sound, Densities, Isobaric Thermal Expansion, Compressibilities, and Internal Pressures of Heptan-1-ol, Octan-1-ol, Nonan-1-ol, and Decan-1-ol at Temperatures from (293 to 318) K and Pressures up to 100 MPa, J. Chem. Eng. Data 52 (2007) 521-531.

[31] J. A. Al-Kandary, A. S. Al-Jimaz and A. M. Abdul-Latif, Physicochemical Properties for Binary Mixtures of Anisole with 1-Hexanol, 1-Heptanol, 1-Octanol, 1-Nonanol, and 1-Decanol at 298.15, 303.15, 308.15, and 313.15 K, Chem. Eng. Comm., 195 (2008) 1585-1613.

[32] M. Hasan, U. B. Kadam, A. P. Hiray and A. B. Sawant, Densities, Viscosities, and Ultrasonic Velocity Studies of Binary Mixtures of Chloroform with Octan-1-ol and Decan-1-ol at (303.15 and 313.15) K, J. Chem. Eng. Data. 51 (2006) 1797-1801.

[33] E. Zorebski and A. Waligora, Densities, Excess Molar Volumes, and Isobaric Thermal Expansibilities for 1,2-Ethanediol + 1-Butanol, or 1-Hexanol, or 1-Octanol in the Temperature Range from (293.15 to 313.15) K, J. Chem. Eng. Data 53 (2008) 591-595.

[34] C. W. Ye and J. Li, Density, Viscosity, and Surface Tension of n-Octanol–Phosphoric Acid Solutions in a Temperature Range 293.15–333.15 K, Russ. J. Phys. Chem. A 86 (2012) 1515-1521.

[35] R. D. Singha and M. Gupta, Molecular interaction Study in binary mixture of DMSO with formamide and N, N-dimethylformamide, Indian J. Pure Appl. Phy. 55 (2017) 729-736.

[36] P. Venkatesu, G. C. Sekhar and M. V. P. Rao, Ultrasonic studies of N, N-dimethylformamide 1 cyclohexanone 1 1-alkanols at 303.15 K, Phys. Chem. Liq. 44 (2006) 287-291.

[37] D. S. Choudhary, C. A. Ladole, A. S. Aswar, Interaction of 5-Chloro-2-hydroxy-3-nitroacetophenone in N, N-Dimethylformamide at Various Temperatures: A Viscometric, Volumetric and Ultrasonic Study, Proc. Natl. Acad. Sci., India, Sect. A Phys. Sci., 85 (2015) 221-226.

[38] S. J. Peng, H. Y. Hou, C. S. Zhou, T. Yang, Densities and excess volumes of binary mixtures of N, N-dimethylformamide with aromatic hydrocarbon at different temperature, J. Chem. Thermodynamics 39 (2007) 474-482.

[39] C. Hao, L. Zhao, X. Yue, Y. Pang, J. Zhang, Density, dynamic viscosity, excess properties and intermolecular interaction of triethylene glycol+ N, N-dimethylformamide binary mixture. J. Mol. Liq. 274 (2019) 730-739.

[40] V. Vanathi, S. Mullainathan, S. Nithiyanatham, V. Ramasamy, L. Palaniappan, Ultrasonic velocity, density, viscosity for the ternary mixture of (benzene þ chloroform þ cyclohexane) at different temperatures, Heliyon 5 (2019) 2203.

[41] M. I. Aralaguppi, C. V. Jadar, T. M. Aminabhavi, Density, viscosity, refractive index, and speed of sound in binary mixtures of acrylonitrile with methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol, heptan-1-ol, and butan-2-ol, J. Chem. Eng. Data. 44 (1999) 216-221.

[42] B. Jacobson, Ultrasonic velocity in liquids and liquid mixtures, J. Chem. Phys. 20 (1952) 927-928.

[43] N. S. Shah, V. A. Rana, Density and ultrasonic velocity of binary mixtures of benzaldehyde and methanol at different temperatures, AIP Conf. Proc. 2100 (2019) 020118.

[44] A. Saini, H. Joshi, K. Kukreja, R. Dey, A study of viscometric, optical and interfacial properties of binary and ternary liquid mixtures, J. Mol. Liq. 223 (2016) 165-173.

[45] M. K. Praharaj, A. Satpathy, P. Mishra and S. Mishra, Ultrasonic studies of ternary liquid mixtures of N-N-dimethylformamide, nitrobenzene, and cyclohexane at different frequencies at 318 K, J Theor Appl Phys. 7 (2013) 23-28.

[46] Glasstone, Laidler and Erying, Theory of Rate Processes, McGraw Hill Book Company, Inc., New York and London, (1941) 548.

[47] M. Rastogi, A. Awasthi, M. Gupta, J. P. Shukla, Molecular association of aliphatic ketones and phenol in a nonpolar solvent-ultrasonic and IR study, J. Mol. Liq. 107 (2003) 185-204.

[48] M. C. Sekhar, T. M. Mohan, T. V. Krishna, A. Venkatesulu, K. Siva Kumar, Density, refractive Index, speed of sound and computational studies of intermolecular interactions in binary mixtures of 2-Chloroaniline with butanols (1- butanol, 2-butanol) at T= (303.15–318.15) K, J. Solution Chem. 44 (2015) 237–263.

[49] X. Yue, L. Zhao, L. Ma, H. Shi, T. Yang, J. Zhang, Density, dynamic viscosity, excess property and intermolecular interplay studies for 1, 4-butanediol+ dimethyl sulfoxide binary mixture, J. Mol. Liq. 263 (2018) 40-48.

[50] R. J. Fort, W. R. Moore, Viscosities of binary liquid mixtures, Trans. Faraday Soc. 62 (1966) 1112-1119.

[51] D. Rahul, T. S. Krishna, M. Gowrisankar, D. Ramachandran, Molecular interactions and theoretical estimation of ultrasonic speeds using scaled particle theory in binary mixtures of 3-chloroaniline and 1-alkanols (C6–C10) at different temperatures, J. Mol. Liq. 212 (2015) 618-628.

[52] U. Sridevi, K. Samatha, A.V. Sarma, Excess thermodynamic properties in binary liquids, J. Pure Appl. Ultrason. 26 (4) (2004) 01-11.

[53] V. Kannappan, R. J. Shanthi, Ultrasonic study of induced dipole-dipole interactions in binary liquid mixtures, Indian J. Pure Appl. Phys. 43 (10) (2005) 750-754.

[54] W. Kerboub, Z. Atik, A thermodynamic study on solubility and liquid–liquid phase behaviour for 2,2,2-trifluoroethanol + cyclohexane + 1-butanol at three temperatures and pressure 101.3 kPa, J. Chem. Thermodyn. 42 (11) (2010) 1330-1334.

[55] K. Granados, J. G. Fredrique, Refractive Index, Surface Tension, and Density of Aqueous Mixtures of Carboxylic Acids at 298.15 K. J. Chem. Eng. Data. 51 (2006)1356-1360.

[56] H. Eyring, M. S. Jhon, Significant Liquid Structures John Wiley and Sons, Inc., New York, USA. (1969).

[57] A. Ali, A.K. Nain, S. Hyder, Ion-Solvent Interaction of Sodium Iodide and Lithium Nitrate in N, N-Dimethylformamide + Ethanol Mixtures at Various Temperatures, J. Indian Chem. Soc. 75 (1998) 501-505.

[58] R. Zarrougui, M. Dhahbi, D. Lemordant, Transport and thermodynamic properties of ethylammonium nitrate-water binary mixtures: Effect of temperature and composition, J. Solution Chem. 44 (2015) 686-702.

[59] J. Pires, L. Timperman, J. Jacquemin, A. Balducci, M. Anouti, Density, conductivity, viscosity, and excess properties of (pyrrolidinium nitrate-based Protic Ionic Liquid + propylene carbonate) binary mixture, J. Chem. Thermodyn. 59 (2013) 10-19.

[60] N. Ouerfelli, Z. Barhoumi, R. Besbes, N. Amdouni, The reduced Redlich–Kister excess molar Gibbs energy of activation of viscous flow and derived properties in 1, 4-dioxane+ water binary mixtures from 293.15 to 309.15 K, Phys. Chem. Liq. 49 (2011) 777-800.

[61] M. A. Saleh, S. Akhtar, M. S. Ahmed, Density, viscosity and thermodynamics for viscous flow of water+ 1, 2-dimethoxyethane, Phys. Chem. Liq. 46 (2008) 140-153.

[62] Z. Guo, J. Zhang, T. Zhang, C. Li, Y. Zhang, J. Bai, Liquid viscosities, excess properties, and viscous flow thermodynamics of triethylene glycol+ water mixtures at T=(298.15, 303.15, 308.15, 313.15, and 318.15) K, J. Mol. Liq. 165 (2012) 27-31.

[63] L. Li, J. Zhang, Q. Li, B. Guo, T. Zhao, F. Sha, Density, viscosity, surface tension, and spectroscopic properties for binary system of 1, 2-ethanediamine+ diethylene glycol, Thermochim. Acta. 590 (2014) 91-99.