Chapter

8

Study of Refractometric and various mixing relations for (ϵ_0, u, n,η) of Binary Mixtures (n-Hexanol +N, N-Dimethylformamide, n-Octanol + N, N-Dimethylformamide)

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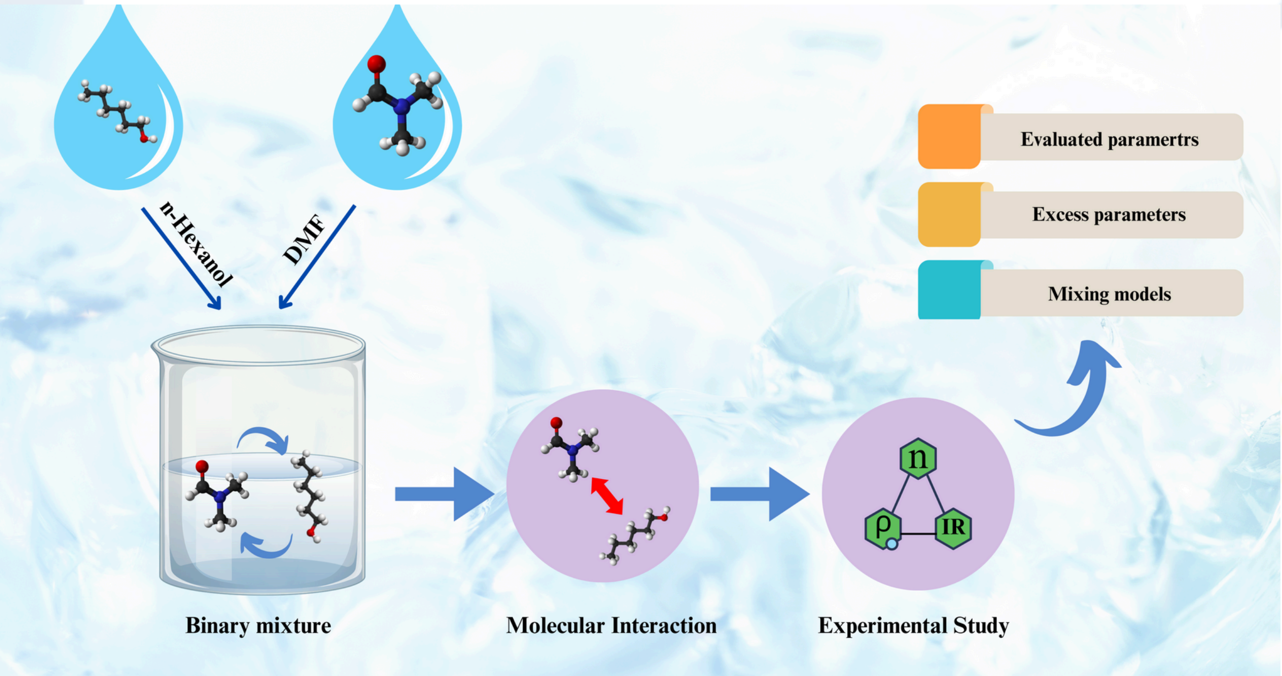

8.1 Introduction

In the past, studying the physico-chemical characteristics of liquid mixtures to comprehend molecular interactions has seen significant success through measurements and analysis of refractive index (n) and density (ρ). Variations in molecule size and interaction strength contribute to the non-linear behavior observed in many properties of liquid mixtures concerning mole or volume fractions. Many fields such as chemical processing, medical diagnostics, semiconductor manufacturing, organic synthesis, and quantitative analysis benefit a great deal from the measurements of liquid compositions [1]. To this date, the optimal yield of the product is ensured by the in-line, real-time temperature monitoring of the liquid chemical compositions. These ideal compositions are defined by the physical properties, like refractive index and the density, of the molecules present in the mixtures [2]. The refractive index measurements along with other properties like melting point, boiling point, density; and other analytical data proved to be very helpful in industries and laboratories for the investigation of the oils, sugar syrups, waxes, etc. An extended literature survey reveals that there is an immediate need of such data on the liquid mixture systems whose constituents are widely used in chemical industries and other research fields [3]. Such a data set provides with us, in ideal case, with an opportunity to use various in-situ measurements of the above-mentioned physical properties as a monitoring tool for the composition of a liquid mixture. In-situ quality check in the manufacturing of the pharmaceutical chemicals through the metrology of process fluids (i.e. measurement of the refractive index) has proven to be a viable and superior mode of this concept [4]. Even more powerful yet simple quality control technique can be realized by the combination of the simultaneous measurements of the refractive index and the density for some applications due to the ease of implementations and availability of automation of such measurements [1-5]. Many binary liquid system quantities are widely utilized for the investigation and the interpretation of the medium effects in different chemical reactions and molecular interactions [6-10]. The excess properties which depend on the temperature and the composition have also proven to be a great tool to study various interactions among the mixed constituents. Both, the density and refractive index measurements of the liquid mixtures are expected to provide deeper insights in the solvent-solvent interactions and the spatial configuration of their mixtures [11-12]. The excess properties such as dielectric quantities and the refractive index are shown to not follow linear relation with the composition when a binary mixture is formed. This deviation from the linear behaviour of these parameters is called the "excess parameters" which are very helpful in investigating the nature of bonding and interactions among the molecules present in the two liquids. these kinds of studies make it possible to provide a direct information even on the molecular dynamics of the pure liquids and their mixtures. From the vast pool of different liquids, alcohols are often found to be the most interesting to study [13-15]. The several reasons for which are: crucial role in the applied sciences and ability to form hydrogen bonds in many liquid systems. Since the molecules containing the -OH group is responsible for the formation of the associative liquid owing to the hydrogen bonding, it is necessary to study the effect of other molecules with non-hydroxyl groups on these molecules to probe the characteristics of the hydrogen bonding in such scenarios [16-21]. Alcohols have found their applications in variety of industries such as agriculture, medical, and chemical. Among all the alcohols, n-Hexanol is usually used as an insecticide (agriculture), antibacterial (medical), and flavoring additives (chemical). An important amide N, N Dimethylformamide (DMF) has applications as an avid solvent in many industries where the evaporation rate is low. It is also used in the manufacturing of many plastics and acrylic fibers. some major applications of the DMF are as a solvent in pharmaceuticals for the peptide coupling, in the manufacturing of pesticides, in the production of adhesives, fibers, synthetic leathers, and surface coatings. DMF is observed to penetrate most of the plastics, making them swelled up. As a result, making DMF a suitable candidate in the synthesis and as one of the components of paint strippers. DMF is well known for its use as an important raw material in the production of solvent dyes [22-24]. There are several theories reported in the literature for the prediction of the static dielectric constant, refractive index, ultrasonic velocity and viscosity of different types of binary mixture liquids [25-27]. These theoretical models are based on computer simulations, analytical methods, structural parameters of the involved molecules, and in some cases other phenomenological models.

The present chapter contains experimentally measured values refractive index (n) and density (ρ) of binary mixtures of n-Hexanol with N, N-Dimethylformamide over varying concentration of composition at different temperature (293.15K, 303.15 K, 313.15K). The measured data are utilized to evaluate various refractometric parameters namely, molar volume (Vm), molar refraction (Rm), atomic polarization (P_A), polarizability (α), molecular radii (r) and internal pressure (P_{int}) of the liquids and their mixtures. Excess of refractive index $(n)^E$ molar volume $(Vm)^E$ reduced free volume $(Vm/Rm)^E$ and internal pressures $(P_{int})^E$ are determined and fitted with Redlich-Kistler polynomial to derive the binary coefficients and correlation coefficient [28]. The nature of deviations of these parameters are discussed in light of hetero-molecular interactions between the participating molecules. Furthermore, in this chapter deals with the validation of static dielectric constant (ε_0), refractive index (n), ultrasonic velocity (Uv) and viscosity (η) of binary mixtures of (n-Hexanol +N, N-Dimethylformamide, n-Octanol + N, N-Dimethylformamide) systems. A comparison of the predicted values of static dielectric constant (ε_0), refractive index (n), ultrasonic velocity (v) and viscosity (η) of the liquid mixtures using various mixing relations with the experimentally determined values have been assessed in terms of Average Percentage Deviation (APD) [25].

8.2 Material and Experimental Details

n-Hexanol and DMF (AR grade) were procured from Loba Chemie (India) and were used without further purification. These two liquids were used to prepare binary mixture systems, which were created at a constant temperature in hermetically sealed glass vials with 11 volume concentrations spanning the entire mixing range (0.0→1.0). These concentrations were subsequently converted into the mole fraction of n-Hexanol using a Equation (3.1) (chapter 3) [26]. The refractive index (n) of the binary mixtures was measured using an Abbe refractometer with a sodium D-line source (wavelength 589 nm) and accuracy of ±0.0001. For measuring the density of liquid binary mixtures, a standard specific gravity bottle was used. All the measurements were carried out at three different temperatures and were controlled by the constant temperature water bath with an accuracy of ± 0.1 K.

Table 8.1 Comparison of experimental and literature values of refractive index and density (ρ) for pure liquids (n-Hexanol and N, N-Dimethylformamide (DMF)) at different temperatures.

Parameters	**Temperatures**	**n-Hexanol**		**DMF**	
		Exp.	Lit.	Exp.	Lit.
(n)	293.15 K	1.4170	1.4178 [29]	1.4305	1.4305 [30]
	303.15K	1.4168	1.4175 [31]	1.4286	1.4266 [32]
	313.15 K	1.4126	1.4100 [33]	1.4246	1.4220 [23]
	293.15 K	0.8182	0.8188 [29]	0.9470	0.9502 [30]

(ρ)	303.15K	0.8158	0.8185 [29]	0.9425	0.9461 [26]
	313.15 K	0.7960	0.8034 [34]	0.9382	0.9311 [35]

8.3 Results and Discussion

- The results and discussion section is organized into two main parts.
  I. Temperature-Dependent Refractive Index Analysis of the (DMF + n-Hexanol) System
  II. Validation of various mixing Models for n, ε_0, U and η in (DMF + n-Hexanol) and (DMF + n-Octanol) Systems.

8.3.1 Temperature-Dependent Refractive Index Analysis of the (DMF + n-Hexanol) System

8.3.1.1 Experimentally and Evaluated Parameters of Binary Liquid Mixtures

Table 8.1 presents a comparative analysis of refractive index (n) and density (ρ) values for pure organic liquids, n-Hexanol and N, N-Dimethylformamide (DMF), derived from both experimental data and existing literature. The experimental values in Table 8.1 closely match with literature values from prior studies, confirming the reliability of our measurements [26,29-35]. The variation of refractive index (n) and density (ρ) of the binary mixture of n-Hexanol with DMF is graphically represented in Fig. 8.1. It is apparent that as the concentration of n-Hexanol increase in the mixture, the refractive index and density decreases in nonrectilinear manner at 293.15 K. The measured refractive indices and densities for the (DMF + n-Hexanol) system were used to calculate key refractometric parameters such as molar volume (V_m) [15], molar refraction (R_m) [36], atomic polarization (P_A) [15], polarizability (α) [37], molecular radii (r) [38] and internal pressure (P_{int}) [39] using Equations (3.29) to (3.34) detailed in Chapter 3.

The refractive index is defined as the ratio of the speed of light in a vacuum to its speed in a material. When light passes through a medium other than a vacuum, its interaction with the atoms of the material causes a delay. The atoms absorb and re-emit the light, effectively reducing the speed at which it propagates through the substance. It is apparent from Table 8.2 that there is a considerable difference between the refractive index, density, and molar mass values of n-hexanol and DMF refractive index (n), density (ρ) and molar mass (M) values of n-Hexanol and DMF ((n) n-Hexanol-1.4170, (n) DMF-1.4305, (ρ) n-Hexanol-0.8182, (ρ) DMF-0.9470, (M) n-Hexanol-102.18, (M)

DMF-73.09) at 293.15 K temperature respectively. Therefore, the internal field in the pure state would be expected to differ significantly from the internal field in the mixed state. In binary liquid mixtures, there is a wide range of possible molecular interactions between the constituents, including hydrogen bonding, molecular association, dipole–dipole, and dipole–induced dipole interactions, whereas in the case of n-hexanol and DMF, there is a small difference in the refractive index values at studied temperatures. These interactions result in a deviation from the ideal behavior of the refractive index with the concentration of the mixture constituents. When DMF is added into the n-hexanol, the refractive index of the binary mixture decreases as temperatures increase.

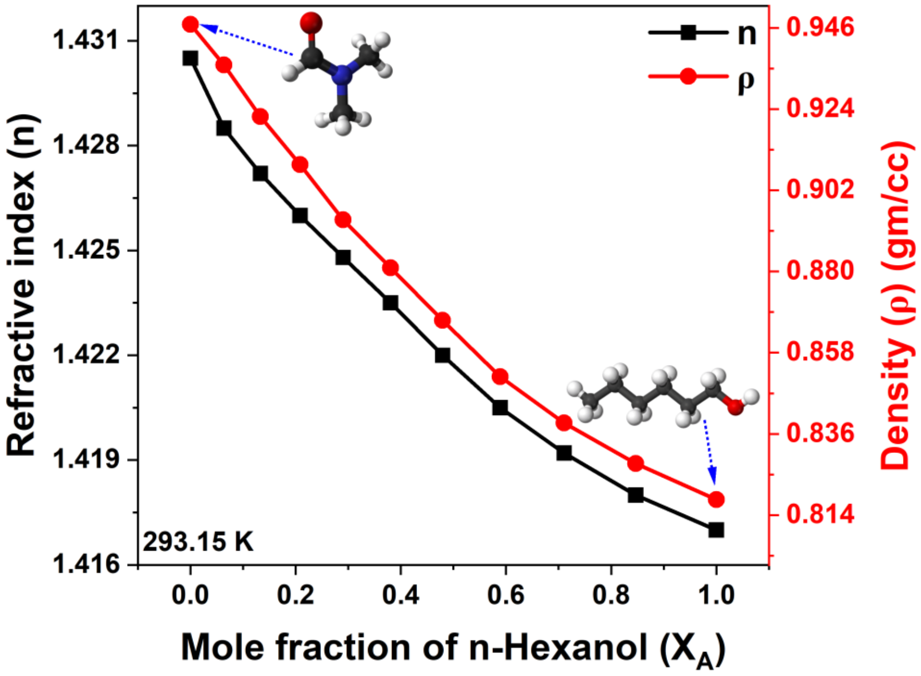

Fig.8.1 Graphically represent refractive index (n) and density (ρ) against mole fraction of n-Hexanol at 293.15 K.

A close perusal of Table 8.2 reveals that the experimentally measured refractive index (n) and density (ρ) of the binary liquid mixtures decrease as the mole fraction of n-Hexanol increases and with increasing temperature. This behavior can be attributed to the low packing density and open structure of n-Hexanol, where the molecules are held together by hydrogen bonds. The observed decrease in refractive index with rising temperature suggests that light propagates faster, due to a reduction in molecular density and weaker intermolecular interactions [40]. Furthermore, as the temperature increases, the molecular structure becomes less ordered, and the molecules are spaced further apart, leading to a decrease in density [41]. The measured density values are further used to calculate the molar volume of the system. The molar volume for the binary mixture of n-Hexanol and DMF at three different temperatures is presented in Table 6.2. It is observed that the molar volume of the binary mixture increases with an increase in the mole fraction of n-Hexanol. This can be attributed to the fact that molar volume is directly proportional to molecular weight [42]. Since the molecular weight of n-Hexanol (102.17 g/mol) is about 1.39 times greater than that of DMF (73.09 g/mol), n-Hexanol has a stronger effect on the molar volume of the mixture. It is also found that at a fixed mole fraction of n-Hexanol (0.0→1.0), the molar volume increases with increase in temperature. This is due to the added thermal energy, which causes greater separation between molecules, resulting in an increase in the molar volume (Vm) of the mixture [42]. According to the refractive index, molar refraction (Rm) is an estimation of the volume occupied by an atom or molecule. It can be observed that the molar volume (Vm), molar refraction (Rm), polarizability (α), molecular radii (r), and average molecular radii (rave) increase as the mole fraction of n-hexanol increases in the binary liquid mixtures at different temperatures (293.15 K, 303.15 K, 313.15 K). The increased concentration of n-hexanol leads to an increase in the molecular radii because of the lower packing fraction of n-hexanol and reduction in the number of DMF molecules in the mixture system, while the opposite trend is observed for atomic polarization (P_A) and internal pressure (P_{int}) as temperature increases. There is a large difference in internal pressure values of the pure components (Pint=64.58 MPa [n-hexanol] and Pint=106.79 MPa [DMF] at 293.15 K) that suggests a strong possibility of hetero interaction in molecular species [27]. Bhatia et al. [43] have similarly trend reported nonlinear decrease behavior in internal pressure for the binary mixture of octan-1-ol with chloroform, 1,2-dichloroethane and 1,1,2,2-tetrachloroethane at 298.15 and 308.15 K.

Table 8.2 Values of refractive index (n), density (ρ), molar volume (Vm), molar refraction (Rm), atomic polarization (P_A), polarizability (α), molecular radii (r) and internal pressure (P_{int}) for the binary liquid mixtures of n-Hexanol with N, N-Dimethylformamide at different temperatures.

X	n	ρ (gm/cm^3)	V_m (cm^3/mol)	R_m (cm^3/mol)	P_A (cm^3/mol)	α Å^3	r Å	P_{int} (MPa)
T=293.15 K								
0.0000	1.4305	0.9470	77.1806	19.96	2.15	0.79	1.99	106.80

0.0639	1.4285	0.9360	80.2279	20.66	2.14	0.82	2.02	102.41
0.1331	1.4272	0.9220	83.5300	21.46	2.14	0.85	2.04	98.16
0.2084	1.4260	0.9090	87.1202	22.32	2.14	0.89	2.07	93.93
0.2905	1.4248	0.8940	91.0382	23.27	2.13	0.92	2.10	89.71
0.3805	1.4235	0.8810	95.3307	24.30	2.13	0.96	2.13	85.50
0.4795	1.4220	0.8668	100.0543	25.43	2.12	1.01	2.16	81.26
0.5890	1.4205	0.8515	105.2773	26.67	2.12	1.06	2.20	77.04
0.7107	1.4192	0.8390	111.0833	28.06	2.11	1.11	2.23	72.86
0.8468	1.4180	0.8280	117.5757	29.63	2.11	1.18	2.27	68.71
1.0000	1.4170	0.8182	124.8839	31.41	2.11	1.25	2.32	64.58
T=303.15 K								
0.0000	1.4286	0.9425	77.5491	19.98	2.14	0.79	1.99	109.58
0.0639	1.4275	0.9350	80.2013	20.61	2.14	0.82	2.01	105.77
0.1331	1.4255	0.9176	83.9602	21.49	2.13	0.85	2.04	100.71
0.2084	1.4242	0.9061	87.5761	22.36	2.13	0.89	2.07	96.35
0.2905	1.4230	0.8907	91.5163	23.30	2.13	0.92	2.10	92.02
0.3805	1.4220	0.8768	95.8238	24.35	2.12	0.97	2.13	87.74
0.4795	1.4210	0.8604	100.5559	25.50	2.12	1.01	2.16	83.48
0.5890	1.4196	0.8513	105.7745	26.75	2.12	1.06	2.20	79.18
0.7107	1.4184	0.8385	111.5608	28.14	2.11	1.12	2.23	74.93
0.8468	1.4178	0.8244	118.0101	29.73	2.11	1.18	2.28	70.77
1.0000	1.4168	0.8158	125.2513	31.48	2.11	1.25	2.32	66.57
T=313.15 K								
0.0000	1.4246	0.9382	77.9045	19.90	2.13	0.79	1.99	111.96
0.0639	1.4236	0.9270	81.1280	20.68	2.13	0.82	2.02	107.33
0.1331	1.4220	0.9190	84.6211	21.50	2.12	0.85	2.04	102.64
0.2084	1.4202	0.9130	88.4191	22.38	2.12	0.89	2.07	97.94
0.2905	1.4192	0.8990	92.5636	23.39	2.11	0.93	2.10	93.41
0.3805	1.4180	0.8920	97.1044	24.47	2.11	0.97	2.13	88.87
0.4795	1.4168	0.8640	102.1011	25.67	2.11	1.02	2.17	84.35
0.5890	1.4160	0.8390	107.6262	27.01	2.11	1.07	2.20	79.92
0.7107	1.4146	0.8230	113.7680	28.47	2.10	1.13	2.24	75.43

0.8468	1.4134	0.8060	120.6359	30.11	2.10	1.19	2.29	71.00
1.0000	1.4126	0.7960	128.3668	31.98	2.10	1.27	2.33	66.64

8.3.1.2 Excess Parameters of Binary Liquid Mixtures

The excess function provides an idea of the amount of deviation of a given liquid mixture from ideality. The nature of molecular movement and intermolecular interactions in hetero molecules is fundamentally dependent on excess properties. In the present study, we calculated the excess refractive index $(n)^E$, excess molar volume $(Vm)^E$, excess reduced molar free volume $(Vm/Rm)^E$ and excess internal pressure $(Pint)^E$ of the binary mixtures. They are evaluated using Equations (3.35) to (3.40) detailed in Chapter 3 [15, 38,39].

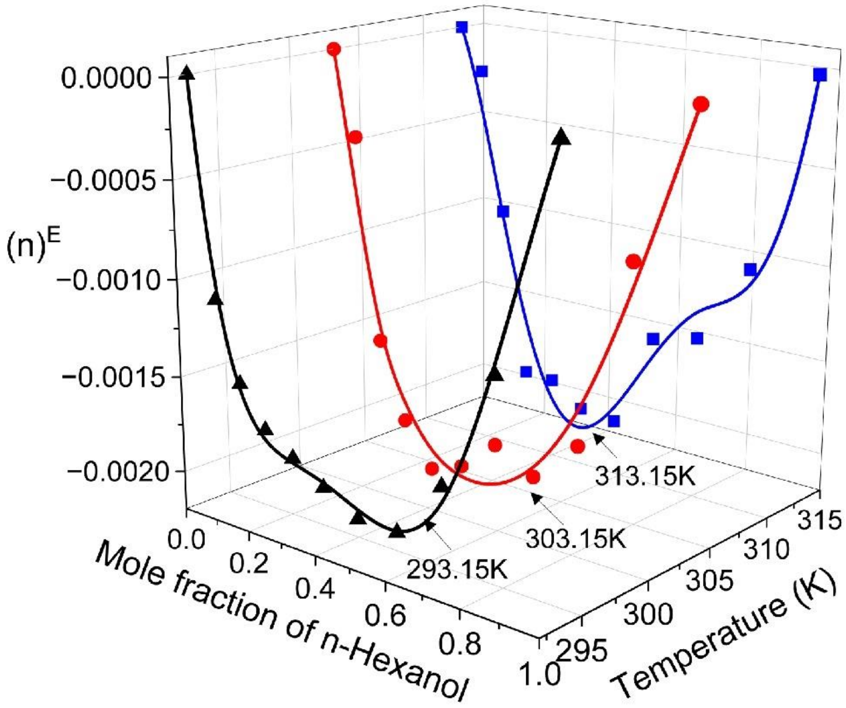

Fig. 8.2 Plot of excess refractive index $(n)^E$ against mole fraction of n-Hexanol in binary mixtures at different temperatures.

Figure 8.2 shows the excess refractive index $(n)^E$ against mole fraction of n-Hexanol at different temperatures (293.15 K, 303.15 K and 313.15K). The solid line (curve) in this figure shows the calculated values (RK polynomial-fitted), and the round points represent the experimental values of excess functions. It can be observed negative deviation over the entire composition range (0.0→1.0) at studied temperatures. The negative$(n)^E$ values show a maximum at around 0.38 mole fraction of n-Hexanol at 303.15 K. It is observed that the variation in the refractive index is influenced by a number of different energetic and structural effects. [44] The negative deviation $(n)^E$ indicates a weak interaction between the mixture components [45]. A negative value indicates weak molecular interactions when DMF is added to n-Hexanol, primarily due to the breaking of hydrogen bonds in the system [37].

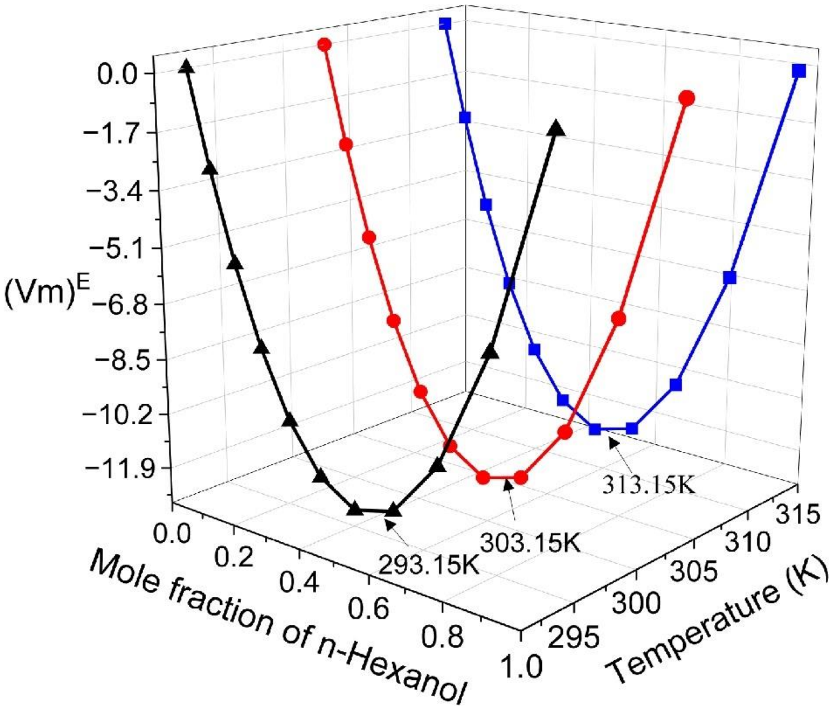

Fig. 8.3 Plot of excess molar volume $(V_m)^E$ against mole fraction of n-Hexanol in binary mixtures at different temperatures.

Furthermore, observed refractive index deviations become less negative as temperature increases. This behavior can be attributed to the weakening of intermolecular interactions at higher temperatures. The strength of hydrogen bonding in n-Hexanol and dipole–dipole interactions in DMF decreases due to enhanced Brownian motion caused by the rise in thermal energy [43]. According to Bhatia et al. [43], the excess refractive index $(n)^E$ exhibits an opposite sign to the excess molar volume $(Vm)^E$ when the refractive index behavior is approximately linearity. For these mixtures, $(n)^E$ demonstrates a similar trend to $(Vm)^E$ but with reversed polarity. Since $(n)^E$ values are negative while $(Vm)^E$ values are positive, Brocos et al. [46] proposed that $(n)^E$ represents an inverse measure of the deviation of reduced free volume from ideality, thereby indicating changes in intermolecular interactions. The variation of excess molar volume $(V_m)^E$ with the mole fraction of n-Hexanol at different temperatures is shown in Fig. 8.3. Negative $(V_m)^E$ values are observed across the entire range of composition (0.0→1.0) and different temperatures (293.15 K,303.15K and 313.15 K). The sign of

$(V_m)^E$ of a system depends on the relative magnitude of the expansion and contraction upon mixing of two liquids. When the factors causing expansion outweigh the factors causing contraction, $(V_m)^E$ becomes positive, but if the contractive factors become more powerful than expansion factors, $(V_m)^E$ becomes negative. The factors causing positive $(V_m)^E$ include (i) the breaking of H bonds of one compound by another, or breaking up of links held together by weaker physical forces, such as dipole–dipole or dipole–induced dipole interactions, (ii) the geometry of the molecular structure which does not favor fitting of the molecules with each other, and (iii) steric hindrance, which opposes the proximity of the constituent molecular species. The factors causing negative ΔVm include (i) chemical interactions between the components though H bonds, (ii) association through weaker physical forces, such as dipolar forces or any other forces of this kind, (iii) lodging of molecules of one component into the interstitials of the structural network of molecules of another component, and (iv) geometry of molecular structures which favors fitting of the component molecules with each other. [47] The $(V_m)^E$ values for the binary mixture n-Hexanol+DMF are found to be negative for the whole concentration range of n-hexanol. When n-hexanol is added to DMF, at least some proportion of n-hexanol (in the form of multimers in pure form) is dissociated into monomers, which results in volume expansion. The monomers so formed are thought to enter into the interstitial sites of DMF, causing volume contraction because $(V_m)_{DMF} > (V_m)_{n\text{-hexanol}}$. This contraction is believed to be larger than expansion; the net effect is therefore negative excess molar volume $(V_m)^E$. The other factors responsible for the volume contraction include the possible association between n-hexanol and DMF through H bonds and some weak association of DMF through physical forces such as dipolar types of interactions. The excess reduced molar free volume $(V_m/R_m)^E$ is shown in Fig. 8.4, and it is positive over the whole composition range $(0.0 \rightarrow 1.0)$ at different temperature. The refractive index deviation function must be computed on a volume fraction basis, whereas the molar refraction deviation function must be computed on a mole fraction basis. [46] This makes it possible for it to be directly understood as a measure of the expressed deviations of reduced free volumes from ideality. Positive values of $(V_m/R_m)^E$ where Vm is the molar volume and Rm is the molar refraction, indicate weak intermolecular interactions between the components of liquid mixtures. This is because positive deviations often suggest that the molecular packing is less efficient, leading to weaker cohesive forces and greater free volume in the mixture compared to the pure components [43].

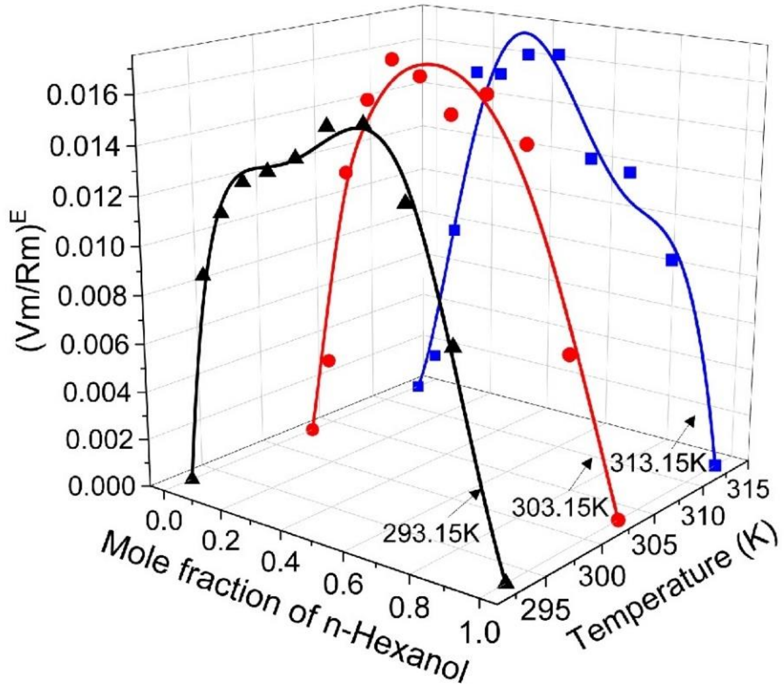

Fig. 8.4 Plot of excess reduced free volume $(V_m/R_m)^E$ against mole fraction of n-Hexanol in binary mixtures at different temperatures.

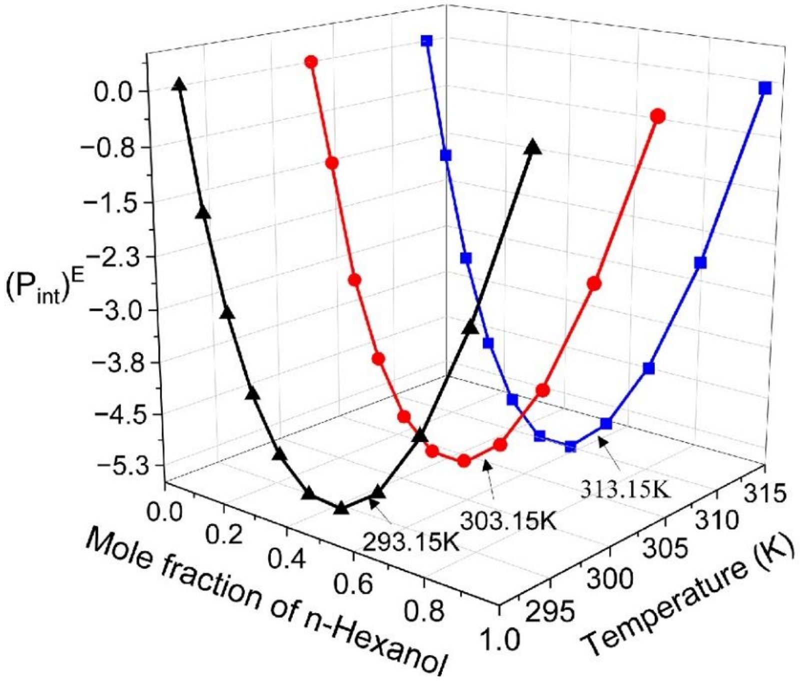

Fig. 8.5 Plot of excess internal pressure $(P_{int})^E$ against mole fraction of n-Hexanol in binary mixtures at different temperatures.

Figure 8.5 observed the negative deviation of internal pressure for all composition range at different temperatures. This negative deviation suggests that there are more repulsive forces than attractive forces [48]. A similar trend of negative $(P_{int})^E$ values was reported by Bhatia et al. for binary liquid mixtures of octan-1-ol with chloroform, 1,2-dichloroethane and 1,1,2,2-tetrachloroethane at 298.15 and 308.15 K. This behavior was attributed to weak interactions between the constituent molecules [43]. The evaluated excess parameters values such as excess refractive index, excess molar volume, excess reduce volume and excess internal pressure (Eq. 3.35 to 3.40)[15,38] (detail in chapter 3) were fitted to the R. K. polynomial equation [28] using the least squares method, with equal weighting for all data points. The coefficients (a_0), (a_1), (a_2) and (a_3), along with the correlation coefficients (R), are tabulated in Table 8.3.

Table 8.3 Value of coefficients of R. K. Polynomial, correlation coefficients (R) for excess refractive index $(n)^E$, excess molar volume $(V_m)^E$, excess reduce volume $(V_m/R_m)^E$ and excess internal pressure $(P_{int})^E$ at different temperatures.

Parameters	Temperatures	a_0	a_1	a_2	a_3	R
$(n)^E$	293.15 K	-0.0079	-0.0014	-0.0049	0.0094	0.9976
	303.15 K	-0.0084	0.0019	-0.0024	0.0003	0.9843
	313.15 K	-0.0077	0.0060	-0.0026	-0.0117	0.9850
$(V_m)^E$	293.15 K	-47.7033	-0.0015	0.0044	-0.0039	0.9999
	303.15 K	-48.1603	-0.0033	0.0027	-0.0073	0.9968
	313.15 K	-50.4624	-0.0013	0.0050	-0.0045	0.9999
$(V_m/R_m)^E$	293.15 K	0.0612	0.0183	0.0356	-0.0897	0.9965
	303.15 K	0.0619	-0.0133	0.0185	-0.0026	0.9831
	313.15 K	0.0609	-0.0483	0.0217	0.0968	0.9845
$(P_{int})^E$	293.15 K	-20.9707	4.6356	-1.9252	2.1111	0.9999
	303.15 K	-21.3677	5.3276	-1.6821	0.6976	0.9999
	313.15 K	-23.2274	6.5637	-1.8171	-1.3186	0.9999

8.3.2 Validation of various mixing Models for n, ε₀, U and η in (DMF + n-Hexanol) and (DMF + n-Octanol) Systems.

8.3.2.1 Validation of different mixing models for refractive index (n)

The mixing rules for refractive index (n) are found on the electromagnetic theory of light. This theory conceptualizes molecules as dipoles or collections of dipoles influenced by an external electromagnetic field [2]. Predicting the refractive indices of binary liquid mixtures is important for understanding their composition and has many industrial applications. When combined with properties like density, boiling point, and melting point, refractive index measurements help analyze materials like oils, waxes, and sugar syrups. However, a review of existing research shows that data on the studied systems is missing, even though their components are widely used in chemical and industrial processes [3]. Several molecular interactions can be observed in binary mixtures since their constituents are composed of different types of compounds. In that sense, we test the applicability of the most important mixing rules suitable for predicting the refractive index in different physical situations to the binary mixtures under consideration. In the present chapter various mixing rules are applied to predict the refractive index of binary mixtures. These rules take into account the density of the mixtures along with the refractive indices of the pure components. Such study we have tested the validity of eight different mixing rules, namely Arago – Biot (A-B) [49], Newton (NW) [50], Gladstone – Dale (G-D) [51], Eyring – John (E-J) [52], Lorentz-Lorentz (L-L) [53], Weiner (Wi) [54], Oster [55] and Eykman (Eyk) [56] to determine their applicability to the systems under investigation (DMF + n-Hexanol & DMF + n-Octanol). The deviation of mixing models/rules are expressed in average percentage deviation (APD).

Eyring-John (E-J) model:

$$n = n_A X_A^2 + 2(n_A n_B)^{1/2} X_A X_B + n_B X_B^2 \tag{8.1}$$

Gladstone-Dale (G-D) model:

$$n - 1 = [n_A - 1]X_A + [n_B - 1]X_B \tag{8.2}$$

Arago-Biot (A-B) model:

$$n = n_A X_A + n_B X_B \tag{8.3}$$

Newton (Nw) model:

$$n^2 - 1 = [n_A^2 - 1]X_A + [n_B^2 - 1]X_B \tag{8.4}$$

Lorentz-Lorentz (L-L) model:

$$\frac{n^2-1}{n^2+2}=\left[\frac{n_A^2-1}{n_A^2+2}\right]X_A+\left[\frac{n_B^2-1}{n_B^2+2}\right]X_B \tag{8.5}$$

Weiner (Wi) model:

$$\frac{\mathrm{n}^2-\mathrm{n}_\mathrm{A}^2}{\mathrm{n}^2+2\mathrm{n}_\mathrm{A}^2}=\left[\frac{\mathrm{n}_\mathrm{B}^2-\mathrm{n}_\mathrm{A}^2}{\mathrm{n}_\mathrm{B}^2+2\mathrm{n}_\mathrm{A}^2}\right]\mathrm{X}_\mathrm{B} \tag{8.6}$$

Eykman (Eyk) model:

$$\frac{\mathrm{n}^2-1}{\mathrm{n}+0.4}=\left[\frac{\mathrm{n}_\mathrm{A}^2-1}{\mathrm{n}_\mathrm{A}+0.4}\right]\mathrm{X}_\mathrm{A}+\left[\frac{\mathrm{n}_\mathrm{A}^2-1}{\mathrm{n}_\mathrm{B}-0.4}\right]\mathrm{X}_\mathrm{B} \tag{8.7}$$

Oster (Ost) model:

$$\frac{(n^2-1)(2n^2+1)}{n^2}=\left[\frac{(n_A^2-1)(2n_A^2+1)}{n_A^2}\right]X_A+\left[\frac{(n_B^2-1)(2n_B^2+1)}{n_B^2}\right]X_B \tag{8.8}$$

APD is determined,

$$\mathrm{APD}=\frac{100}{\mathrm{n}}\sum_{\mathrm{i=n}}\left(\frac{|\,\delta_{\mathrm{expi}}-\delta_{\mathrm{cali}}\,|}{\delta_{\mathrm{expi}}}\right) \tag{8.9}$$

In the formula given, the variables n_m, n_A, and n_B indicate the refractive indices of the mixture, the solvent, and the solute, respectively. The variables X_A and X_B denote the volume fractions of the solvent and the solute, respectively.

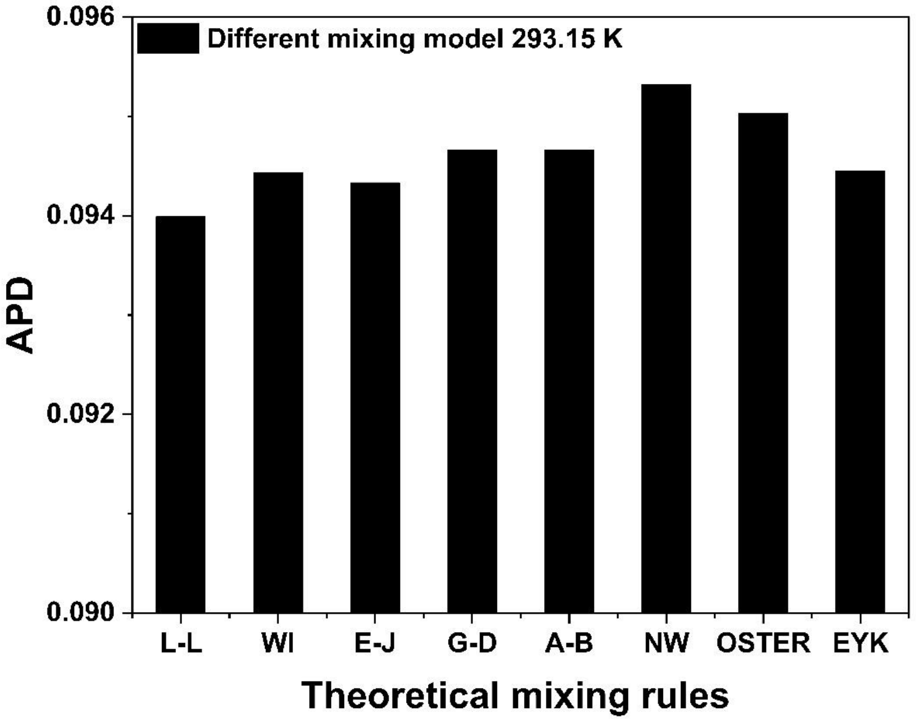

Fig. 8.6 (A) Plot of APD as a function of different theoretical refractive index mixture models at 293.15 K.

The predicted and experimentally determined refractive indices of the binary mixtures at different temperatures are compared, and the (average percentage deviation) APD of the results for different models is shown in Fig. 8.6 (A), (B) and (C). Fig. 8.6 reveals that the Gladstone–Dale (G-D) and Arago–Biot (A-B) relations provide identical APD values. The APD values predicted by the Weiner (Wi), Eyring–John (E-J), Gladstone–Dale (G-D), Arago–Biot (A-B), Newton (Nw), Oster (Ost), and Eykman (Eyk) relations are greater than those predicted by Lorentz-Lorentz (L–L), which is the best ft for the studied system (DMF + n-Hexanol) at all different temperatures (293.15 K, 303.15 K and 313.15 K). All theoretical mixture models perform well within the limits of experimental error.

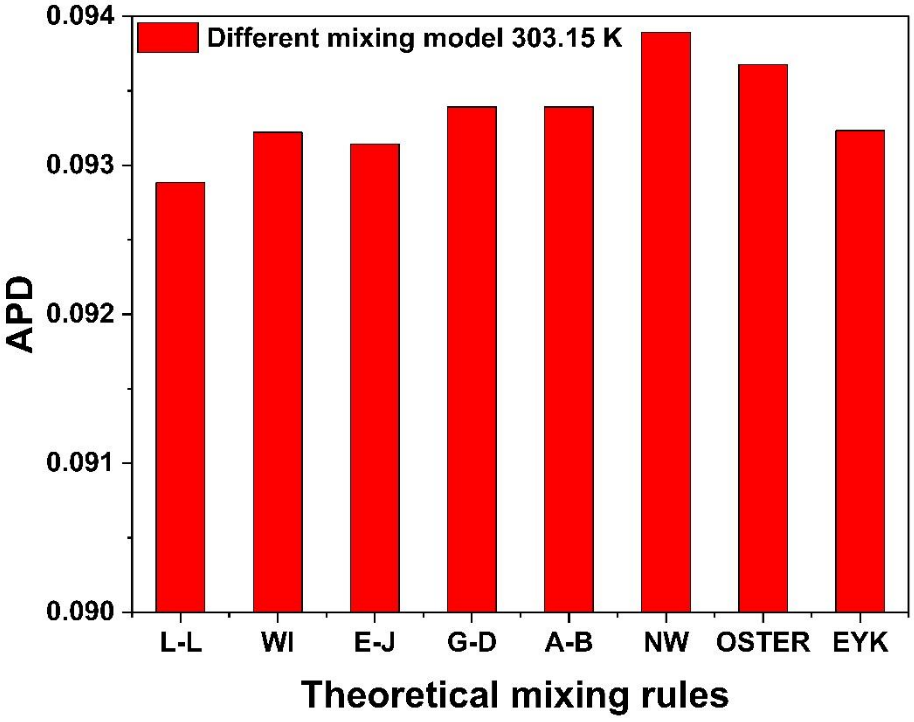

Fig. 8.6 (B) Plot of APD as a function of different theoretical refractive index mixture models at 303.15 K.

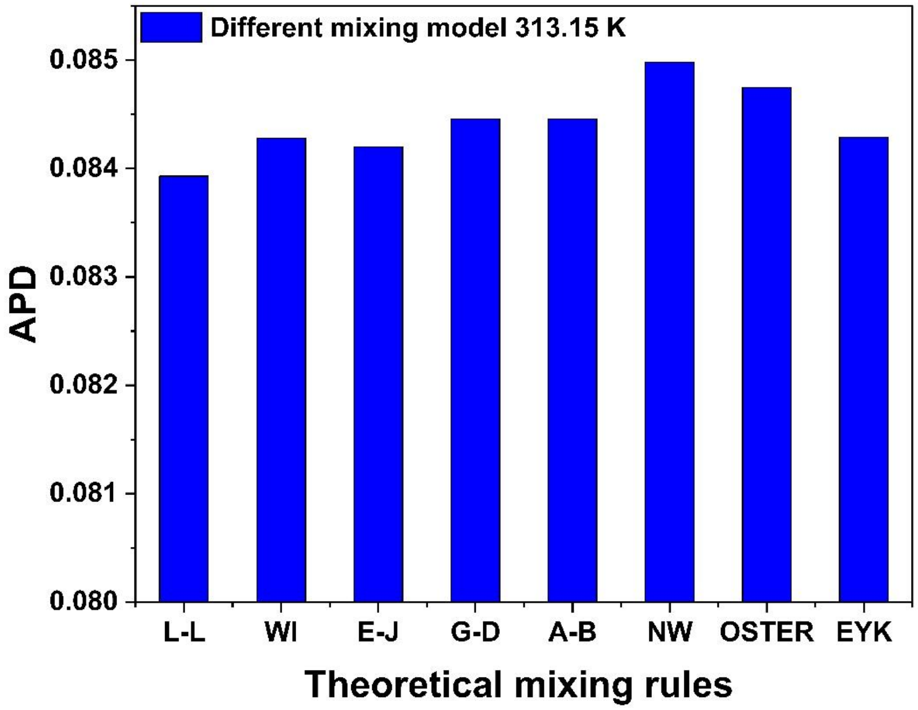

Fig. 8.6 (C) Plot of APD as a function of different theoretical refractive index mixture models at 313.15 K.

8.3.2.2 Validation of different mixing models for static dielectric constant (ε_0)

The relationship between the properties of pure components and the dielectric behavior of their mixtures remains a longstanding challenge. Theoretical and experimental studies on the permittivity of binary systems have emerged as an interdisciplinary and rapidly advancing field of research [57,58]. Such investigations offer critical insights into the potential applications of binary mixtures across various industries, including nuclear, petrochemical, pharmaceutical, and sustainable technologies [59,60]. Static dielectric constant (ε_0) a thermo-physical property, serves as a measurable electrical parameter that reveals valuable information about the intermolecular interactions and structural organization of solution components [61,62]. Due to the high cost of experimental measurements and the need to understand the contributions of molecular interactions, various mixing rules have been developed to predict the permittivity of mixtures. These theoretical approaches estimate the permittivity of mixtures based on the properties of their pure components. Numerous theories have been proposed in the literature to predict the static dielectric constant (ε_0) of binary mixtures. These theories rely on various approaches, including analytical methods, computer simulations, molecular structural parameters, and phenomenological models. However, experimentally determined values of ε_0 often show significant deviations from predictions made by these models. Therefore, it is crucial to evaluate and validate different mixing models or rules to identify the one that best aligns with experimental results for a given binary liquid system (DMF +n-Hexanol and DMF + n-Octanol).

In this present chapter study, we tested twelve mixing models for static dielectric constant (ε_0), including those proposed by Kraszewski [63], Lichtenecker-Rother [64], Brown [65], Peon-Iglesias [66], Looyenga [67], Iglesias [68], Hashin-Shtrikman [69], Bottcher and Bordewijk [70], Oster [71], and Onsager-Bottcher [72].

Kraszewski

$$\varepsilon_{0m}^{1/2} = X_{0A}\varepsilon_{0A}^{1/2} + X_{0B}\varepsilon_{0B}^{1/2} \tag{8.10}$$

Lichenecker -Lother

$$\varepsilon_{0m} = \varepsilon_{0A}^{X_A}\varepsilon_{0B}^{X_B} \tag{8.11}$$

Peon-Iglesias

$$\varepsilon_{0m} = (X_A\varepsilon_{0A} + X_B\varepsilon_{0B})\left(1 - \frac{2}{3}\ln\left(\frac{1+X_A\left(\frac{\varepsilon_{0A}}{\varepsilon_{0B}}-1\right)}{\left(\frac{\varepsilon_{0A}}{\varepsilon_{0B}}\right)^{X_A}}\right)\right) \tag{8.12}$$

Looyenega

$$\varepsilon_{0m} = \left[\varepsilon_{0A}^{1/3} + X_B\left(\varepsilon_{0B}^{1/3} - \varepsilon_{0A}^{1/3}\right)\right]^3 \tag{8.13}$$

Brown

$$\frac{\varepsilon_{0m}}{\varepsilon_{0B}+X_A(\varepsilon_{0A}-\varepsilon_{0B})} = 1 - \frac{1}{3}X_A(1 - X_A)\left\{\frac{(\varepsilon_{0A}-\varepsilon_{0B})}{\varepsilon_{0B}+X_A(\varepsilon_{0A}-\varepsilon_{0B})}\right\}^3 \tag{8.14}$$

Iglesias

$$\frac{\varepsilon_{0m}}{\varepsilon_{0A}+X_A(\varepsilon_{0A}-\varepsilon_{0B})} = \frac{1}{4} + \frac{3}{4} \times \left[1 - \left(\frac{4}{3}\right)^2\left\{\ln[\varepsilon_{0B} + X_A(\varepsilon_{0A} - \varepsilon_{0B})] - \left[\ln\varepsilon_{0B} + X_A\ln\left(\frac{\varepsilon_{0A}}{\varepsilon_{0B}}\right)\right]\right\}\right]^{\frac{1}{2}} \tag{8.15}$$

Hasin-Shtritkman

$$\frac{\varepsilon_{0m}-\varepsilon_{0B}}{\varepsilon_{0m}+2\varepsilon_{0A}} = \frac{X_A(\varepsilon_{0A}-\varepsilon_{0B})}{3\varepsilon_{0A}} \tag{8.16}$$

Bottcher and Brordewijk

$$\frac{3\varepsilon_{0A}}{2\varepsilon_{0m}+\varepsilon_{0A}}X_A + \frac{3\varepsilon_{0B}}{2\varepsilon_{0m}+\varepsilon_{0B}}X_B = 1 \tag{8.17}$$

Oster

$$\frac{(\varepsilon_{0m}-1)(2\varepsilon_{0m}+1)}{\varepsilon_{0m}} = \frac{(\varepsilon_{0A}-1)(2\varepsilon_{0A}+1)}{\varepsilon_{0A}}X_A + \frac{(\varepsilon_{0B}-1)(2\varepsilon_{0B}+1)}{\varepsilon_{0B}}X_B \tag{8.18}$$

Onsager-Bottcher

$$\frac{\varepsilon_{0m}-\varepsilon_{0B}}{3\varepsilon_{0m}}=\frac{X_A(\varepsilon_{0A}-\varepsilon_{0B})}{\varepsilon_{0A}+2\varepsilon_{0m}} \tag{8.19}$$

Wiener

$$\frac{1}{\varepsilon_{0m}}=\frac{X_A}{\varepsilon_{0A}}+\frac{X_B}{\varepsilon_{0B}} \tag{8.20}$$

Ideal

$$\varepsilon_{0m}=\varepsilon_{0A}X_A+\varepsilon_{0B}X_B \tag{8.21}$$

In the formula given, the variables ε_{0m}, ε_{0A}, and ε_{0B} indicate the static dielectric constant (ε_0) of the mixture, the solvent, and the solute, respectively. The variables X_A and X_B denote the volume fractions of the solvent and the solute, respectively.

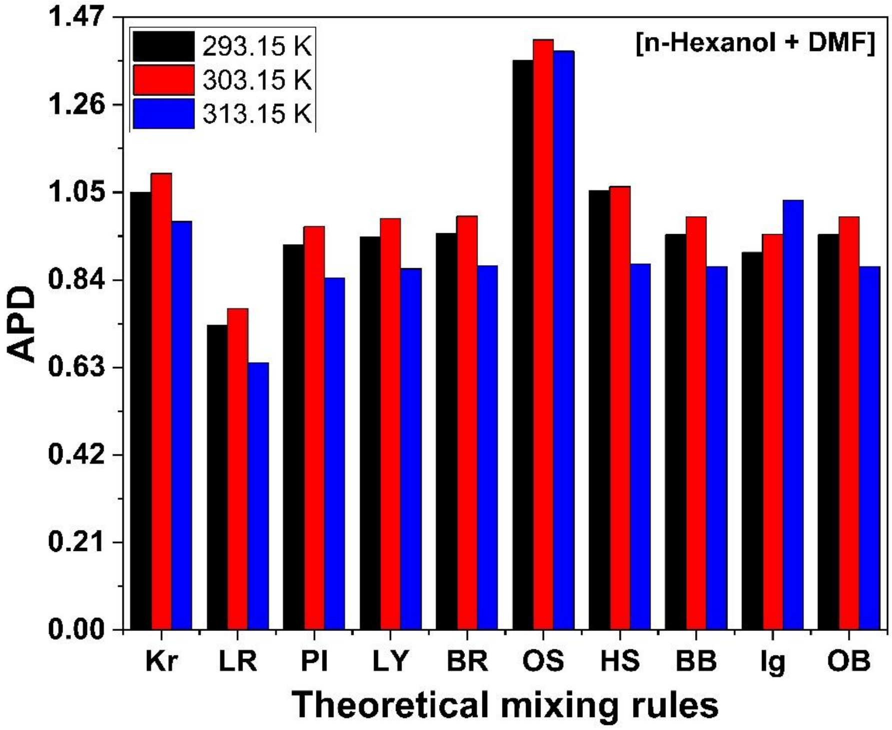

Fig. 8.7 Plot of APD as a function of different theoretical static dielectric constant (ε_0) mixture models for n-Hexanol +DMF system at different temperatures.

The comparison between experimental and predicted static dielectric constant (ε_0) values for the n-Hexanol + DMF system, based on various mixing models, is presented in Fig. 8.7. The Average Percentage Deviation (APD) was calculated for each model at different temperatures [293.15 K, 303.15 K and 313.15 K]. Among the ten models, the Lichtenecker-Rother (LR) model showed the best agreement with the experimental (ε_0) values at all temperatures. Other models exhibited moderate deviations, with intermediate APD values. The Oster model displayed the highest deviation. The APD rankings of the mixing models for predicting ε_0 exhibit a temperature-dependent trend. At 293.15 K, the ranking is as follows: LR < IG < PI < BB = OB < KR < BR < HS < OS. At 303.15 K, the sequence shifts to: LR < IG < PI < LY < BB = OB < BR < KR < HS < OS. At 313.15 K, the order is: LR < LY < BB = OB < BR < HS < KR < IG < OS. These results highlight the varying accuracy of the models in predicting ε_0 across different temperatures.

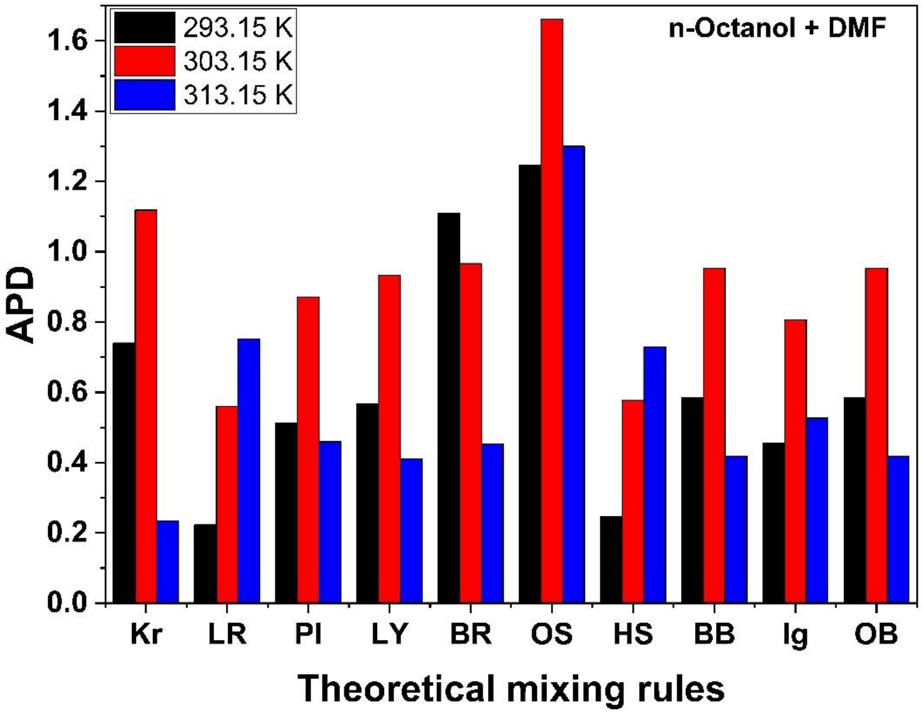

Fig. 8.8 Plot of APD as a function of different theoretical static dielectric constant (ε_0) mixture models for n-Octanol +DMF system at different temperatures.

Figure 8.8 compares the average percentage deviations of various theoretical mixing models for the static dielectric constant of the n-Octanol + DMF system at different temperatures, emphasizing the temperature-dependent accuracy of these models. At 293.15 K, the Oster model shows the highest deviation and the KR model the lowest, with the deviation sequence as LR < HS < Ig < PI < LY < BB = OB < KR < BR < OS. A similar trend is observed at 303.15 K, with the order being LR < HS < Ig < PI < LY < BB = OB < BR < KR < OST. At 313.15 K, the pattern shifts, with the KR model exhibiting the smallest deviation and the Oster model the largest, following the sequence KR < LY < BB = OB < BR < PI < Ig < HS < LR < OST. These results underscore the significant influence of temperature on the predictive performance of the mixing models.

8.3.2.3 Validation of different mixing models for ultrasonic velocity (U)

Ultrasonic velocity and density are key parameters for studying molecular associations and intermolecular interactions in binary liquid mixtures. These properties help to understand the strength, nature, and extent of interactions between the molecules. Experimental ultrasonic velocity measurements in mixtures like n-Hexanol + DMF and n-Octanol + DMF often show deviations from theoretical predictions, reflecting the complex and non-ideal behavior of these systems under different conditions. Many researchers [73-75] have compared experimental data with theoretical models, such as Nomoto's relation [76], Van Dael and Vangeel's model [77], the impedance relation [78], Rao's specific velocity method [79], and Junjie's equation [80], to analyze the molecular interactions in these mixtures. By comparing experimental velocities with theoretical predictions, we gain important insights into the nature and strength of the intermolecular interactions. These theoretical analyses are essential for developing accurate models to describe the behavior of liquid mixtures. As the binary mixtures consist of components from different classes of compounds, leading to different molecular interactions, the applicability of established mixing rules to predict ultrasonic velocity in these systems has been tested. This helps to assess how well these models can describe the ultrasonic behavior of mixtures with varying molecular dynamics.

Nomoto

$$u_{Nom} = \left[\frac{(X_A R_A + X_B R_B)}{(X_A V_A + X_B V_B)}\right]^3 \tag{8.22}$$

VanDael and Vangeel Ideal

$$u_{VDV} = \left[\frac{1}{M_{eff}\left[\left(\frac{X_A}{M_A u_A^2}\right) + \left(\frac{X_2}{M_B u_B^2}\right)\right]}\right]^{1/2} \tag{8.23}$$

Impedance

$$u_{iDR} = \left[\frac{X_A Z_A + X_B Z_B}{X_A \rho_A + X_B \rho_B}\right] \tag{8.24}$$

Junjie's

$$u_{JUN} = \frac{X_A V_A + X_B V_B}{\left[M_{eff}\left\{\frac{(X_A V_A + X_A V_B)}{(X_A \rho_A u_A^2 + X_B \rho_B u_B^2)}\right\}\right]^{1/2}} \tag{8.25}$$

Rao's specific velocity

$$U_R = \left[\left(\frac{X_A}{\rho_A} V_A^{1/3} + \frac{X_B}{\rho_B} V_B^{1/3}\right)\rho_m\right]^3 \tag{8.26}$$

In the formula given, the variables V$_A$, and V$_B$ indicate the molar volume of the mixture, the solvent, and the solute, respectively. The variables X$_A$ and X$_B$ denote the volume fractions of the solvent and the solute, respectively. Further ρ$_A$ and ρ$_B$ denote the density of mixture A and B.

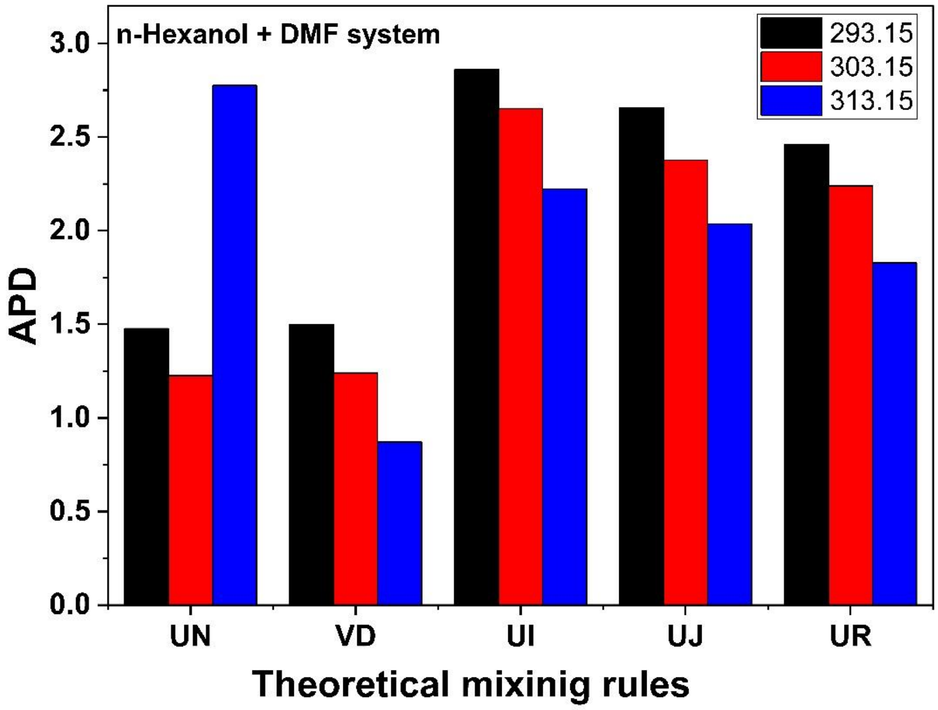

Fig. 8.9 Plot of APD as a function of different theoretical ultrasonic velocity (U) mixture models for n-Hexanol +DMF system at different temperatures.

Figure 8.9 shows the experimental ultrasonic velocities of the n-Hexanol + DMF system alongside theoretical predictions and the corresponding average percentage deviations (APD) for Nomoto's Relation (UN), Van Dael and Vangeel Ideal Mixing Relation (UV), Rao's Specific Sound Speed (UR), Impedance Dependence Relation (UI), and Junjie's Relation (UJ) across different temperatures. At 293.15 K, the APD values follow the order UN < UV < UR < UJ < UI, indicating that Nomoto's Relation exhibits the highest predictive accuracy at this temperature. A similar sequence is observed at 303.15 K: UN < UV < UR < UJ < UI, reaffirming the superior performance of Nomoto's Relation at moderate temperatures. However, at 313.15 K, the sequence changes to UV < UR < UJ < UI < UN, suggesting that Van Dael and Vangeel's model becomes more accurate at elevated temperatures. The observed variations in APD sequences underscore the temperature-dependent reliability of these theoretical models in predicting ultrasonic velocities. Nomoto's Relation performs best at lower and moderate temperatures, while Van Dael and Vangeel's Relation provides the most accurate predictions at higher temperatures. These trends reflect the influence of temperature on the molecular interactions within the n-Hexanol + DMF system and the importance of the need to select appropriate models for specific current conditions to ensure accurate predictions.

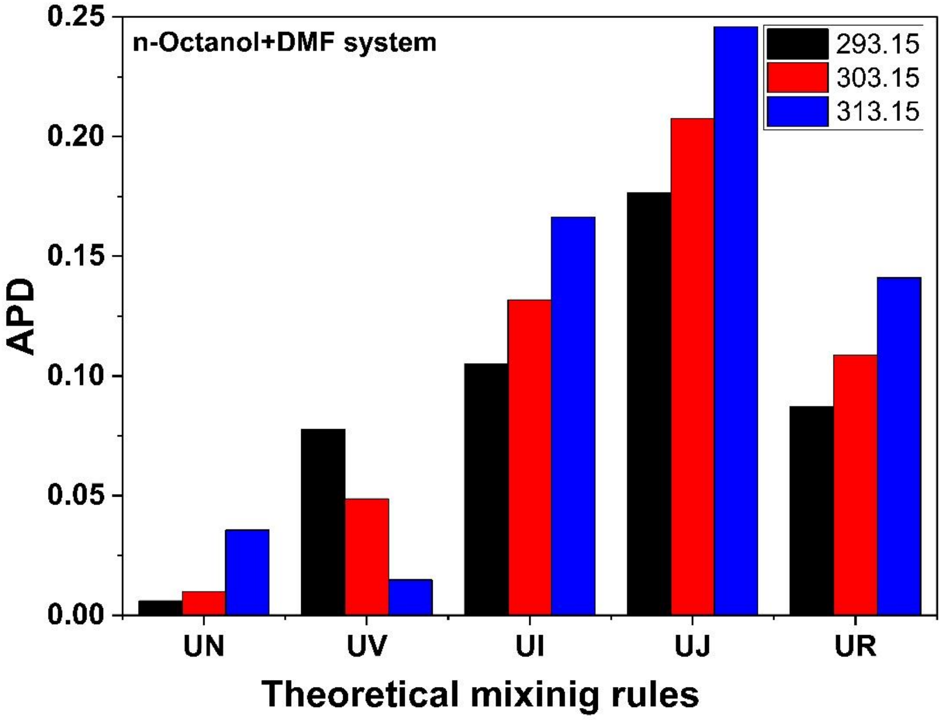

Fig. 8.10 Plot of APD as a function of different theoretical ultrasonic velocity (U) mixture models for n-Octanol+DMF system at different temperatures.

Figure 8.10 shows the average percentage deviation (APD) for ultrasonic velocity predictions using various theoretical mixing models at different temperatures. The experimental ultrasonic speed values for the n-Octanol + DMF system are compared with theoretical predictions from five models: Nomoto's Relation (UN), Van Deal Vangeel Ideal Mixing Relation (UV), Rao's Specific Sound Speed Relation (UR), Impedance Dependence Relation (UI), and Junjie's Relation (UJ). At temperatures of 293.15 K and 303.15 K, the APD trends follow the order UN < UV < UR < UI < UJ, demonstrating that Nomoto's Relation offers the highest accuracy, while Junjie's Relation exhibits the largest deviation. Conversely, at 313.15 K, the order shifts to UV < UN < UR < UI < UJ, indicating that the Van Deal Vangeel model outperforms Nomoto's Relation at elevated temperatures. The predictive accuracy of these models is influenced by temperature. Nomoto's Relation proves to be the most reliable at lower temperatures, whereas the Van Deal Vangeel model demonstrates superior performance at higher temperatures. This variability underscores the need to account for temperature effects when selecting a theoretical model for ultrasonic velocity predictions in binary mixtures.

8.3.2.3 Validation of different mixing models for viscosity (η)

Viscosity is a fundamental transport property that plays a critical role in understanding molecular interactions within binary liquid mixtures and is vital for industrial applications such as fluid flow, mixing, filtration, and heat transfer. Extensive research has been conducted using both experimental methods and theoretical models to study the viscosities of binary mixtures. Among the theoretical approaches, models such as the Bingham relation [81], Kendall-Munroe relation [82], Arrhenius-Eyring relation [83], Hind relation [81], and Gambrill relation [84] are commonly applied to predict viscosities. This study investigates the viscosity of specific binary mixtures using these models, aiming to deepen the understanding of their transport properties while assessing the accuracy and reliability of the predictive models in capturing the behavior of these mixtures. In this chapter, the viscosity of the studied binary liquid mixtures has been calculated using five theoretical models: the Bingham relation, Kendall-Munroe relation, Arrhenius-Eyring relation, Croenaurer-Rothfus-Kermore relation, and Gambrill relation. The results from these models provide a comparative analysis of their predictive accuracy and applicability for the viscosity of binary mixtures.

Bingham relation [BR]

$$\eta_m = \sum X_i \eta_i \tag{8.27}$$

Kendall munroe Relation [KM]

$$\log(\eta_m) = \sum X_i \log(\eta_i) \tag{8.28}$$

Arrhenius Eyring Relation [AE]

$$\log(\eta_m V_m) = \sum X_i \log(V_i \eta_i) \tag{8.29}$$

Gambrill Relation [GR]

$$(\eta_m)^{1/3} = \sum X_i (\eta_i)^{1/3} \tag{8.30}$$

Hind Relation [HR]

$$\eta_m = \sum (X_i)^2 \eta_i + 2X_1X_2\eta_{12} \tag{8.31}$$

Here, ηm and Vm, represent the viscosity and molar volume of the binary mixture, respectively. Similarly, Xi, ηi and Vi denote the mole fraction, viscosity and molar volume of the individual pure components in the mixture.

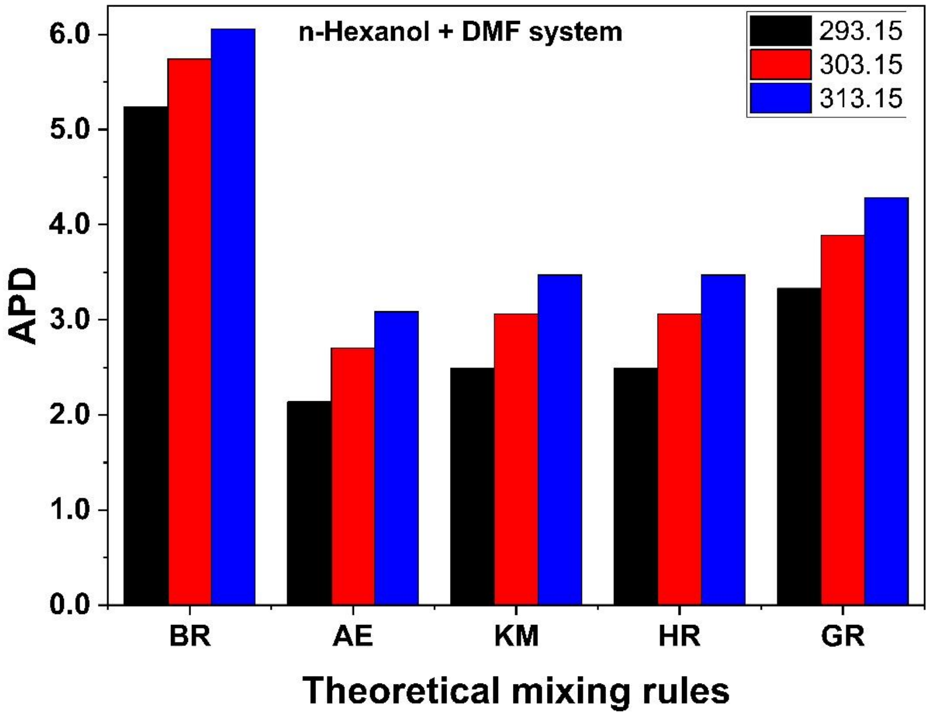

Fig. 8.11 Plot of APD as a function of different theoretical viscosity (η) mixture models n-Hexanol +DMF system at different temperatures.

Figure 8.11 shows the average percentage deviation (APD) for various theoretical viscosity models applied to the n-Hexanol + DMF system at different temperatures. Among the models, the Arrhenius-Eyring relation exhibits the smallest APD values across all studied temperatures, indicating the highest predictive accuracy. In contrast, the Bingham relation shows the largest deviations at all temperatures, suggesting limited applicability for this system. Additionally, the Kendall-Munroe and Hind relations demonstrate consistent agreement in their predictions across the entire temperature range. A similar trend is observed for the n-Octanol + DMF system, as shown in Figure 8.12. The average percentage deviation (APD) values follow the sequence Arrhenius-Eyring Relation (AE) < Kendall-Munroe Relation (KM) = Hind Relation (HR) < Gambrill Relation (GR) < Bingham Relation (NB) across all studied temperatures. This indicates that the Arrhenius-Eyring relation provides the most accurate viscosity predictions, while the Bingham relation shows the largest deviations. The Kendall-Munroe and Hind relations exhibit comparable performance, consistently ranking as intermediate in accuracy, and the Gambrill relation performs slightly better than the Bingham relation.

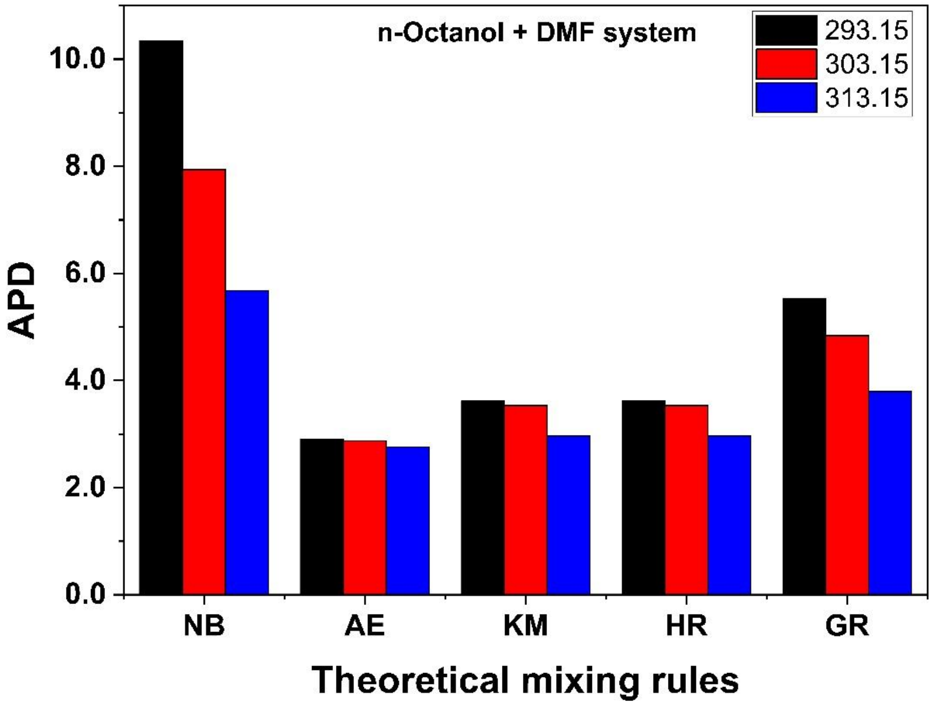

Fig. 8.12 Plot of APD as a function of different theoretical viscosity (η) mixture models n-Octanol +DMF system at different temperatures.

8.4 Conclusions

- In the present study, the density (ρ) and refractive index (n) of binary liquid mixtures throughout the entire mixing composition range (0.0→1.0) for n-Hexanol + DMF system at different temperatures.
- Good agreement was found between the experimental and literature values for the refractive index and density of the n-hexanol and DMF mixture at studied temperatures [293.15 K, 303.15 K and 313.15 K].
- The atomic polarization of the binary mixtures decreased with the decreasing mole fraction of n-hexanol. The molar volume, polarizability, and molecular radii increased with increasing volume fraction of n-hexanol.
- The excess refractive index $(n)^E$ for the n-Hexanol + DMF system shows a negative deviation at all temperatures, with the lowest value around 0.38 mole fraction of n-Hexanol at 303.15 K. This suggests weak molecular interactions between the components, likely due to the disruption of hydrogen bonds when DMF is mixed with n-Hexanol.

- As temperature increases, the negative deviation in excess refractive index and excess molar volume decreases, indicating weaker molecular interactions. The negative excess molar volume suggests that contraction forces, like hydrogen bonding, dominate over expansion forces in the n-Hexanol + DMF mixture.
- The positive excess reduced molar free volume $(V_m/R_m)^E$ indicates weak intermolecular interactions in the n-Hexanol + DMF mixture, with less efficient molecular packing and greater free volume compared to the pure components.
- The negative deviation in internal pressure $(P_{int})^E$ suggests that repulsive forces dominate over attractive forces, indicating weak molecular interactions in the n-Hexanol + DMF mixture.
- The variations in position and intensity of the IR bands related to the functional groups indicated the molecular association in the liquid mixtures.
- The Lorentz-Lorentz (L–L) relation offers the most accurate prediction for the refractive index of the DMF + n-Hexanol system, exhibiting the lowest average percentage deviation (APD) across all temperatures. The Gladstone-Dale (G-D) and Arago-Biot (A-B) relations yield identical APD values, while other models such as Weiner (Wi), Eyring-John (E-J), and Newton (Nw) show higher deviations. All theoretical models provide good predictions within the experimental error limits.
- The ultrasonic velocity predictions for the n-Hexanol + DMF system show that Nomoto’s Relation provides the most accurate results at lower and moderate temperatures (293.15 K and 303.15 K), with the lowest average percentage deviations (APD). However, at higher temperatures (313.15 K), the Van Dael and Vangeel Ideal Mixing Relation becomes the most reliable model.
- The study reveals that Nomoto’s Relation provides the most accurate ultrasonic velocity predictions for the n-Octanol + DMF system at lower temperatures (293.15 K and 303.15 K), while the Van Deal Vangeel Ideal Mixing Relation is more reliable at higher temperatures (313.15 K).
- The Arrhenius-Eyring relation provides the most accurate viscosity predictions for both the n-Hexanol + DMF and n-Octanol + DMF systems, with the lowest deviations. The Bingham relation shows the largest deviations, indicating limited applicability. The Kendall-Munroe and Hind relations perform similarly, with intermediate accuracy, while the Gambrill relation slightly outperforms the Bingham relation.

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