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Refractive Properties of Binary Liquid Mixtures Containing Cyclic Ether + 1-Alkanols at 298.15K

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Abstract: ***Refractive indices for all binary mixtures dicyclic ether with 1-alkanols at T = 298.15K are determined. From these measurements, deviation in refractive indices were calculated. The deviation in refractive indices, found to be negative, were analyzed in correlation with excess molar volumes. Redlich-Kister polynomial equation is used to get the flexible parameters and standard deviations between the deliberate and fitted qualities, separately. The results obtained have been discussed based on specific intermolecular interactions between different species.***

Keywords: 1,3-dioxolane, molar volume, excess refractive indices, density, hydrogen bonding, molecular interaction

1. Introduction

The study of refractive indices in binary liquid mixtures provide a very good information about the molecular interaction in liquid and liquid mixtures.

Since the early nineteenth century, the refractive index of binary mixtures has been measured and interpreted, making it one of the most well-established optical properties. The thermophysical property of binary mixtures, particularly those involving polar liquids offers valuable insights into inter molecular interactions and geometrical changes during the liquid mixing process. This knowledge is crucial for designing, that incorporate polar liquids, which have recently gained attention as 'tunable solvents' due to their unique physicochemical properties.[1-7] The refractive index is medium polarity[8,9], and free volume, as described through molar refraction. Therefore, studying it is essential for gaining deeper insights into the structural and interactional aspects of binary liquid mixtures. In particular, excess thermodynamic properties offer significant insights into the structural changes occurring within these systems[10]. In this study, 1,3-dioxolane is selected as a solvent due to its diverse applications. Alcohols are crucial in many chemical reactions, primarily because of their ability to undergo self-association through hydrogen bonding[11].

Several studies suggest that deviations between theoretical and experimental refractive index values minimized by incorporating the concept of deviation in volume. The ratio between the speed of light in medium to speed in a vacuum is the refractive index. When light travels in a medium other than the vacuum, the atoms of that medium continually absorb and re-emit the particles of light, slowing down the speed light. In this article, let us discuss the refractive index of water and various mediums[12-14]. This thermodynamic property is influenced by temperature, pressure, and wavelength[15].

2. Experimental Procedure

Chemicals 1,3-Dioxolane (dicyclic ether), pentanol, hexanol, heptanol, octanol, nonanol, and decanol were purchased from CDH Ltd., New Delhi, India. All chemicals were of analytical reagent (AR) grade and purified by standard methods. It sounds like you're ensuring the reliability of your experimental data by comparing the density and refractive index of the studied chemicals with literature values [16-23]**.** This verification process is crucial for validating the purity of the chemicals and the accuracy of the measurements**.**

Table 1: Comparison of refractive index (n) and density (ρ) of pure liquid and their literature values at T = 298.15K.

Compound	Density ρ (g.cm^{-3})		Refractive index (n)	
	Experimental	Literature Values	Experimental	Literature Values
1,3-Dioxolane	1.0616	1.0577[18]	1.402	1.3905[22]
		1.0586[19]		1.3979[22]
Pentanol	0.8124	0.8108[16]	1.4042	1.4053[20]
		0.8107[16]		1.4081[20]
Hexanol	0.8176	0.8187[16]	1.4155	1.4154[21]
		0.8152[17]		1.4161[21]
Heptanol	0.8196	0.8187[16]	1.4267	1.4226[20]
		0.8197[19]		1.4224[21]
Octanol	0.8236	0.8216[16]	1.4357	1.4283[20]
		0.8218[16]		1.4264[20]
Nonanol	0.8248	0.8244[17]	1.4368	1.4319[21]
		0.824224[17]		1.4318[20]
Decanol	0.8292	0.8267[17]	1.4398	1.4346[23]
		0.8264[19]		1.4358[21]

Apparatus and Procedure: All binary liquid mixtures were prepared by accurately weighing appropriate amounts of pure liquids using an electronic balance (Citizen Scale (I) PVT. LTD., Mumbai, India). The mixtures were thoroughly stirred to ensure homogeneity before conducting any measurements, using a digital electronic balance. All prepared solutions were prepared based on mass ratios.

Measurements

Density The density (ρ) of the liquid mixture was determined using a 25-mL specific gravity bottle. The bottle containing the liquid mixture was immersed in a temperature-controlled water bath to maintain a constant temperature during the measurements. The density of liquid and liquid mixtures was determined using the given formula

$$\rho = M / V \quad (1)$$

where ρ is density, *M* is mass, and *V* is volume.

Refractive index

The refractive indices of the liquids and of the mixtures were determined using Abbe's refractometer (Model R-8, M/S Mittal Enterprises, New Delhi) which has the least number of moving parts; thus the chances of error arising due to strain are also minimal. Refractive indices of pure liquids such as double distilled water were measured to ascertain the accuracy of the results. Measurements were taken after the samples reached thermal equilibrium. For each sample, an average of five measurements was recorded to ensure accuracy. Good agreement was found between measured and literature values.

Theoretical The density (ρ) and refractive index (n) were utilized to calculate parameters, including volume (V_m), using equations. These parameters provide insights into molecular interactions, structural variations, and deviations from ideal mixing behavior in binary liquid mixtures.

The molar volume (V_m) determined by:

$$V_m = \frac{(X_1M_1 + X_2M_2)}{\rho} \quad (1)$$

The excess refractive index (Δn or n^E) has been determined as:

$$\Delta n = n_{mix} - n_{ideal} \quad (2)$$

Here, n_{mix} is represent the refractive indices and the n_{ideal}, ideal refractive indices of binary mixture, respectively.

$$n_{ideal} = X_1 n_1 + X_2 n_2 \quad (3)$$

Here, X_1, X_2 represent the mole fractions, while n_1, n_2 is the refractive indices of chemical 1 and 2.

To calculate the excess parameters of all acoustical properties were computed using the relation:

$$A^E = A_{exp.} - (X_1 A_1 + X_2 A_2) \quad (4)$$

where $A_{ideal} = (X_1 A_1 + X_2 A_2)$, A is any acoustical parameter and X_1 and X_2 are the mole fractions of the liquid 1 and 2, respectively.

3. Results and Discussion

Excess Molar Volume (V_m^E)

Calculation of molar volume (V_m) and deviation in molar volume (V_m^E) for binary mixtures of dicyclic ether (1,3-Dioxolane) with n-alcohols at 298.15 K using experimental density values **(ρ).** These values reported in figure 1. As the mole fraction of dicyclic ether (X_1) increases, molar volume (Vm**)** decreases for all binary mixtures. This suggests that 1,3-Dioxolane molecules may be filling the voids between alcohol molecules, leading to more efficient packing.

Excess molar volumes are valuable in understanding molecular interactions in liquid and liquid binary mixtures.

Additionally, (V_m^E) data play a crucial role in designing technological processes, predicting vapor-liquid equilibria using appropriate equation-of-state models, and providing reliable insights into molecular interactions in liquid and liquid mixtures. The measurement of molar volume in binary liquid mixtures provides valuable insights into molecular interactions. A perusal of graph-1 indicates that the excess molar volume (V_m^E) values for the binary mixtures are consistently positive. These values, presented in graph-1, remain positive across the hole composition range at 298.15 K. The order of the positive deviation in molar volume follows the trend:

Pentanol < Hexanol < Heptanol < Octanol < Nonanol < Decanol.

This suggests that the power of interactions between two molecules (1,3-Dioxolane and alkanols) is greater than that between like molecules. The larger positive values of (V_m^E) for these binary mixtures have also been reported in previous studies. Furthermore, it is observed that the hydrogen bonding present between 1,3-Dioxolane and alkanol molecule.

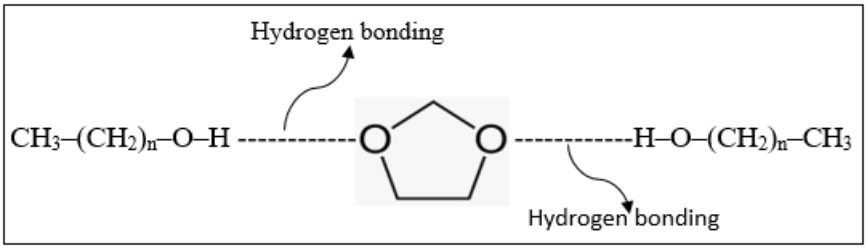

Figure: Hydrogen bonding present in Dicyclic ether n-Alkanols**.**

It looks like about to list the order in which the deviation in molar volume (V_m^E) values change for binary liquid mixtures. Based on your previous statements, the trend likely follows:

Pentanol < Hexanol < Heptanol < Octanol < Nonanol < Decanol

This order suggests that the carbon chain length of the alkanol molecule increases, the deviation in molar volume also increases. This is likely due to the reduced proton-donating ability of longer-chain alcohols, leading to weaker hetero-association between 1,3-dioxolane and alkanols.

Excess Refractive Index

It looks like you're discussing the impact of molecular interactions on the excess refractive index (n^E) and how deviations from ideal behaviour are influenced by intermolecular forces. The excess refractive index is negative in six binary mixtures studied, which suggests that the molecular interactions between two molecules lead to a decrease in refractive index relative to an ideal mixture.

We explanation about dipole-dipole and hydrogen bonding effects is well-grounded. The negative values of (n^E) could be due to:

1) **Destruction of hydrogen bonds in pure alkanols**: When mixed with 1,3-dioxolane, the self-associated hydrogen-bonded structures of alcohols break apart.
2) **Formation of weaker intermolecular interactions**: The new interactions between 1,3-dioxolane and alkanols might not compensate for the strength of the original hydrogen bonds.
3) **Structural changes and packing efficiency**: If the components mix in a way that increases free volume or disrupts molecular packing, the refractive index can decrease.

Dipole-dipole [24-25] interactions between two molecules in the mixture lead to negative. The experimental data for refractive index and density at the temperature 298.15K are summarized in figure -2. Negative excess refractive index (n^E), Implies weaker interactions. Suggests disruption of alcohol-alcohol hydrogen bonding by 1,3-dioxolane molecules. [26-29].

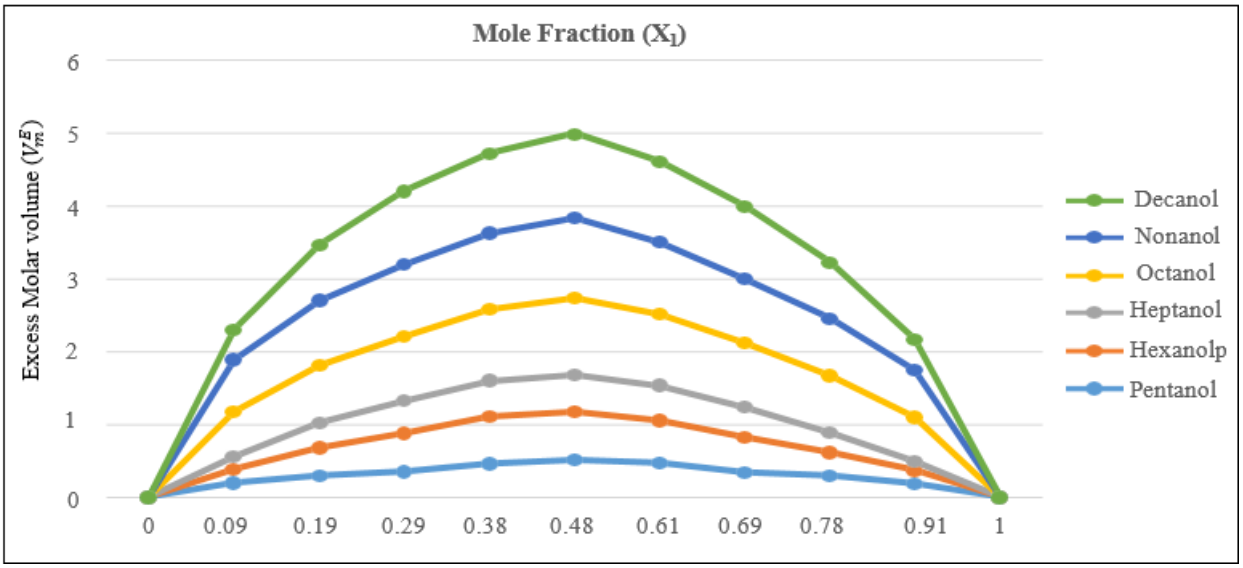

Figure 1: Variation of deviation in excess molar volume (V_m^E) versus mole fraction (X_1) of the binary mixtures of dicyclic ether with alkanols

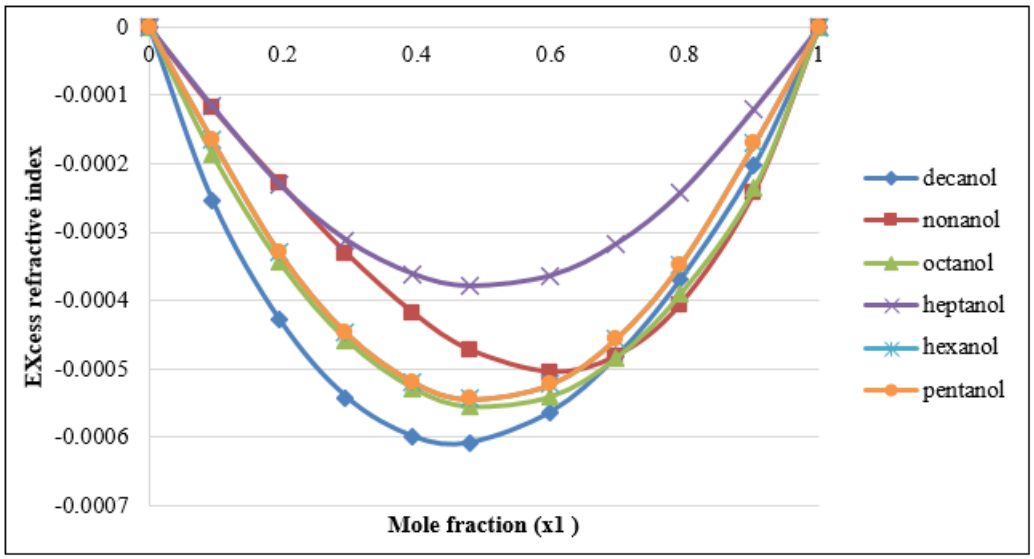

Figure 2: Variation of deviation in excess refractive index (n^E) versus mole fraction (X_1) of the binary mixtures of dicyclic ether with alkanols.

4. Conclusion

The present investigations suggest that dicyclic ether and alkanols is the dominant interaction, surpassing hydrogen bonding. This means that the molecular structure and packing efficiency of the binary mixtures significantly influence their thermodynamic and optical properties.

We concluded that the excess refractive index (n^E) values are negative across all studied binary mixtures indicates non-ideal mixing behaviour. This suggests that molecular interactions between 1,3-dioxolane and alcohols lead to structural rearrangements, affecting the overall refractive index. The idea that hydrogen bonding strength and steric effects influence the refractive index deviations. Would you like to explore correlating these trends with density variations or excess molar volume (V_m^E) data for a more comprehensive interpretation.

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