

Studies on Molecular Interactions of Bromoform and Ethyl Bromide at Four Different Temperatures

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Abstract: Refractive indices of Bromoform and benzene, Ethyl bromide and benzene with five different concentrations at four different temperatures are measured using Abbe's refractometer. The experimental values are compared with those estimated by the mixing rules Eyring-John (EJ), Gladstone-Dale (G-D), Newton (Nw) and Heller (H) methods. Comparison of various mixing rules has been expressed in terms of root mean square deviation (RMSD).

Keywords: Refractive index, Abbe's refractometer, Benzene, Bromoform, Binary Mixtures, Mixing Rules.

I. Introduction

Dielectric studies of binary mixtures of pure polar liquids at static and optical frequencies can provide information about molecular structure and intermolecular interaction.[1-5]. Many researchers have attempted to get insight into the nature and degree of interactions that are present in polar liquid mixtures using the refractive indices measurements. Benzene evaporates in to air very quickly and dissolves slightly in water. It is highly flammable and is formed from both natural processes and human activities. Benzene is a colourless liquid with a sweet odor. Use benzene, to make other chemicals which are used to make plastics, resins, and nylon and synthetic fibers. Bromoform was used as a solvent, sedative, and flame retardant, but now it is mainly used as a laboratory reagent. Bromoforms high density makes it useful for separation of minerals by density. When two samples are mixed with bromoform and then allowed to settle, the top layer will contain minerals lighter than bromoform, and the bottom layer will contain heavier minerals. Ethyl bromide is used as a solvent, as an anesthetic in medicine, as a refrigerant, as a fumigant. Many researchers have been studied the theoretical refractive index measurements by the refractive index mixing rules [6-8]. In the present study, we report the experimental and theoretical refractive index of binary mixtures, from these the validity of the mixing rules have been analyzed.

II. Experimental Details

Benzene (AR grade), Bromoform (AR grade) and ethyl bromide (AR grade) were commercially obtained from S D fine- Chem Limited (India) and used without further purification. Binary mixtures of bromoform and ethyl bromide with benzene were prepared at five different concentrations by volume. Assuming ideal mixing behaviour the concentration was converted into the mol fraction. The values of refractive indices of pure liquids, and of the binary mixtures have been determined by using Abbe's refractometer at wavelength of sodium D-light. The maximum measurement error in n value is $\pm 0.02\%$. The measurement accuracy in refractive index is 0.3%.

III. Results And Discussion

Measured values of refractive index of bromoform and ethyl bromide with benzene mixtures are presented in TABLE 1.

TABLE 1. Variation of refractive indices (n) at different molefractions of Bromoform (X₂) + Benzene (X₁) and Ethylbromide + benzene at different temperatures

Temperature K	Bromoform + Benzene		Ethyl Bromide + Benzene	
	X ₂	n	X ₂	n
303	0.054	1.502	0.052	1.491
	0.105	1.505	0.100	1.492
	0.155	1.508	0.151	1.488
	0.205	1.513	0.199	1.486
	0.260	1.519	0.246	1.481

308	0.054	1.494	0.052	1.490
	0.105	1.501	0.100	1.489
	0.155	1.506	0.151	1.487
	0.205	1.511	0.199	1.483
	0.260	1.516	0.246	1.476
313	0.054	1.493	0.052	1.487
	0.105	1.497	0.100	1.486
	0.155	1.503	0.151	1.483
	0.205	1.507	0.199	1.479
	0.260	1.513	0.246	1.474
318	0.054	1.490	0.052	1.484
	0.105	1.494	0.100	1.482
	0.155	1.498	0.151	1.478
	0.205	1.504	0.199	1.476
	0.260	1.509	0.246	1.470

3.1 Estimation Models of Refractive Index

Measured experimental refractive index values of the Bromoform+ Benzene and Ethyl bromide+ Benzene binary mixtures were compared to those estimated by four mixing rules which are shown in Table 2 were proposed by

Eyring-John (E-J)[9]

$$n = n_A \phi_A^2 + n_B \phi_B^2 + 2(n_A n_B)^{1/2}$$

Gladstone- Dale (G-D)[10]

$$n - 1 = (n_A - 1)\phi_A + (n_B - 1)\phi_B$$

Newton (Nw)[11]

$$n^2 - 1 = (n_A^2 - 1)\phi_A + (n_B^2 - 1)\phi_B$$

Heller (H)[12]

$$\frac{(n - n_A)}{n_A} = \frac{3}{2} \times \frac{\left(\left(\frac{n_B}{n_A} \right)^2 - 1 \right)}{\left(\left(\frac{n_B}{n_A} \right)^2 + 2 \right)} \phi_B$$

where n , n_A , n_B , ϕ_A , ϕ_B represent refractive index of mixture, bromoform and benzene, ethyl bromide and benzene, volume fraction of bromoform and benzene, ethyl bromide and benzene respectively.

$$R.M.S.D = \left(\frac{1}{m \sum (n_{\text{exp}} - n_{\text{cal}})^2} \right)^{1/2} \quad [13]$$

where m is the number of data points.

TABLE 2. Comparison of Exp Ref Index Data with Theoretical Values of the Binary Mixtures of Bromoform+ Benzene

Mole Fraction	Eyring-John (EJ)				Gladstone-Dale (G-D)				Newton (NW)				Heller(H)			
	303K	308K	313K	318K	303K	308K	313K	318K	303K	308K	313K	318K	303K	308K	313K	318K
0.0539	1.543	1.575	1.507	1.539	1.506	1.483	1.459	1.436	1.506	1.483	1.460	1.436	1.506	1.483	1.459	1.436
0.105	1.514	1.549	1.583	1.517	1.511	1.488	1.464	1.441	1.511	1.488	1.464	1.441	1.511	1.487	1.464	1.441
0.155	1.505	1.541	1.576	1.512	1.516	1.492	1.469	1.445	1.516	1.493	1.469	1.446	1.515	1.492	1.469	1.445
0.205	1.510	1.548	1.585	1.522	1.520	1.497	1.474	1.450	1.521	1.497	1.474	1.451	1.520	1.497	1.473	1.450
0.2595	1.525	1.564	1.503	1.541	1.525	1.502	1.479	1.455	1.526	1.503	1.479	1.456	1.525	1.502	1.478	1.455

TABLE 3. Comparison of Exp Ref Index Data with Theoretical Values of the Binary Mixtures of Ethyl Bromide+ Benzene

Mole Fraction	Eyring-John (EJ)				Gladstone-Dale (G-D)				Newton (NW)				Heller(H)			
	303K	308K	313K	318K	303K	308K	313K	318K	303K	308K	313K	318K	303K	308K	313K	318K
0.0519	1.577	1.522	1.567	1.512	1.497	1.474	1.452	1.429	1.497	1.474	1.452	1.429	1.497	1.474	1.452	1.429
0.1002	1.554	1.501	1.548	1.595	1.493	1.471	1.449	1.427	1.494	1.471	1.449	1.427	1.493	1.471	1.449	1.427
0.151	1.538	1.588	1.537	1.586	1.489	1.468	1.446	1.425	1.490	1.468	1.447	1.425	1.489	1.468	1.446	1.425
0.1989	1.544	1.594	1.545	1.596	1.486	1.465	1.444	1.423	1.486	1.465	1.444	1.423	1.486	1.465	1.444	1.423
0.2461	1.563	1.516	1.568	1.520	1.482	1.462	1.442	1.421	1.482	1.462	1.442	1.421	1.482	1.462	1.441	1.421

A close perusal from the tables shows that all theoretical mixing rules shows good agreement with the experimental values. The average percentage deviation obtained for the binary liquid systems benzene with bromoform shows good agreement than the another liquid systems. All the binary mixtures show better agreement in the lower concentration. This study shows that all the theoretical mixing rules are inter related well within the limits of the experimental error.[14-17].

TABLE 4. Values of Rmsd against Various Mixing Rules of Bromoform-Benzene Mixture

Mixing rules	RMSD			
	303	308	313	318
	Refractive index			
Eyring -John	10.468	3.8302	3.2356	6.6978
Gladstone-Dale	30.455	14.669	5.952	3.73464
Newton	28.798	15.0895	6.020	3.761
Heller	31.262	14.487	5.922	3.722

TABLE 5. Values of Rmsd against Various Mixing Rules of Ethylbromide-Benzene Mixture

Mixing rules	RMSD			
	303	308	313	318
	Refractive index			
Eyring -John	2.9057	2.8188	2.7560	2.1831
Gladstone-Dale	71.082	11.667	5.661	3.765
Newton	68.680	11.786	5.679	3.769
Heller	71.815	11.623	5.654	3.763

The Root Mean Square Deviation (RMSD) values for the Eyring-Johns (E-J), Gladstone-Dale (G-D), Newton (Nw), and Heller (H) are presented in table 3. As RMSD values indicate, refractive index for mixtures under consideration. A close similarity is observed between the E-J and G-D relations. The RMSD values for E-J and G-D relations are found to be identical when volume additivity is assumed. The best predictions are observed for the E-J followed by G-D while the RMSD values predicted by Nw and Heller relations are relatively higher. Since the liquid mixtures of different nature and significantly different molecular sizes are considered, a particular relation provides good agreement at one place and deviates at others. This study indicates that all the theoretical mixing rules are interrelated in a simple quantitative manner and perform well within the limits of experimental error. The applicability of these semi-empirical relations for predicting refractive indices has also been emphasized by others

IV. Conclusions

The refractive indices were reported for the liquid mixtures of benzene with bromoform and ethylbromide at 303K, 308K, 313K and 318K. the variation in refractive index on mixing is calculated shows better agreement with the theoretical mixing rules. For the mixture of benzene and bromoform shows better than benzene- ethylbromide liquid systems. Eyring-John shows good results than the other theoretical relations and Heller shows maximum deviation. These deviations can be minimized to some extent by considering the change in volume of the liquid with refractivity during the mixing.

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