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A Study of Physio-chemical parameters for Binary Mixtures of Primary Alcohol/Bromoethane

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ABSTRACT:
Background: The binary liquid mixtures of methanol (MeOH) and bromoethane (BR) were analysed across the mixing range (0.0 to 1.0) to determine molecular interactions and structural properties at a constant temperature of 283 K.
Purpose: The ultrasonic speed and refractive index of the binary mixtures were measured at 283.15 K using a DMA 5000M (Anton Paar) and an Abbe refractometer, respectively.
Method: Acoustic parameters such as adiabatic compressibility (β), acoustic impedance (Z), and free length (L_f) were calculated from the ultrasonic velocity data of the binary mixtures. Some refractometric parameters, specifically internal pressure (P_{int}) and molecular radii (r), were assessed applying the measured refractive indices of binary mixtures.
Conclusions: The excess parameters of ultrasonic and refractometric properties were determined and fitted using R. K. polynomial analysis. All these determined parameters have been used to investigate heteromolecular interactions in molecular species.

Keywords: Binary mixtures, Ultrasonic velocity, Refractive index, Molecular Interaction, Structural properties

1. Introduction

The study of dielectric, refractometric, and acoustical quantities for binary liquid have been focused on concentration and temperature dependent measurements, for the last few decades. These studies would have contributed towards the understanding of intermolecular interactions and accompanying structure in liquid mixtures are very critical as these mixtures are used extensively in both basic as well as applied sciences [1–4]. Molecular interactions in liquid Mixtures provide important information with respect to the structural parameters of the component molecules [1–7]. The physicochemical properties of these systems are often determined by the measurement of complex permittivity, optical refractivity, ultrasonic velocity, and density. Rectilinear variations of static dielectric constant, relaxation time, refractive index and ultrasonic velocity in binary mixtures suggest the existence of heteromolecular interactions [8-24]. This paper concerns about the binary mixture of methanol (MeOH) and bromoethane (BR) in the specific concentration range (0.0 to 1.0). MeOH and BR are commonly used solvents in industrial synthesis. The novelty in this study lies in the systematic examination of concentration-dependent refractometric and ultrasonic properties of MeOH–BR mixtures at 283.15 K, and validation of several typical mixing models for the refractive index and ultrasonic velocity in the studied systems.

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2. Materials and sample preparation

Methanol (GC grade) and Bromoethane (Synthesis Grade) were procured from LOBA Chemie, India. Eleven binary solutions with different concentrations (0.0 to 1.0) were prepared by volume concentration [7,15,25]. The volume concentrations were converted into a mole fraction by using following formula,

$$X_{BR} = \frac{\frac{P_{BR}V_{BR}}{R}}{\frac{P_{BR}V_{BR}}{R} + \frac{P_{MeOH}V_{MeOH}}{M_{MeOH}}} \quad (1)$$

Where X, V, M and ρ represents the mole fraction, volume concentration, molecular weight, and density respectively. Suffixes BR and MeOH represent bromoethane and methanol respectively.

3. Experimental methods

Ultrasound velocity and density of binary mixture: The density (ρ) and sound velocity (u) measurements of binary a mixture were carried out by using a density and sound velocity meter (model DSA 5000M, Anton Paar) at 283.15 K. The refractive index of binary mixtures (BR + MeOH) was measured with the and sodium D-line source. For each mixture composition, the refractive index (n) was accurately measured. The values of ρ, u, n for pure MeOH and BR, calculated from Table 1 are consistent with the reported in literatures.

4. Results and discussion

Various acoustic parameters adiabatic compressibility, free length, acoustic impedance, molecular radii and internal pressure were determined for the mixture concentration.

$$\beta = (u^2\rho)^{-1} \quad (2)$$

$$L_f = K_T\beta \quad (3)$$

$$Z = u\rho \quad (4)$$

Where K_T is Jacobson's constant

$$r = \left[\left(\frac{3}{4\pi N}\right)\left(\frac{n^2-1}{n^2+2}\right)Vm\right]^{1/3} \quad (5)$$

$$P_{int} = \frac{2^{1/6}RT}{2^{1/6}V_m - 2rN^{1/3}V_m^{2/3}} \quad (6)$$

Where R is gas constant and V_m represents molar volume.

Table 2 showcase the values of refractive index (n), density (ρ), ultrasonic velocity (u), molecular radii (r), internal pressure (P_{int}), free length (L_f), adiabatic compressibility (β), and acoustic impedance (Z). As the concentration of BR increases, n, ρ, r and Z increases while u, β, (P_{int}) and L_f show opposite trends. The excess parameters such as (β)E, (L_f)E, (Z)E, (n)E, (P_{int})E and (r)E are determined and fitted in R-K polynomial [28]. Figure 1 (a-f) show the variation of excess adiabatic compressibility (β)E, excess free length (L_f)E, excess acoustic impedance (Z)E, excess refractive index (n)E, excess internal pressure (P_{int})E and excess molecular radii (r)E versus the mole fraction of BR. It is realized that (β)E, (L_f)E, (Z)E, (n)E and (r)E show positive deviation over the entire mixing range. This signifies that the physical interaction mostly involves dispersion forces or weak dipole-dipole interactions [29,30]. The negative deviation of (Pint)E over the entire mixing range in Figure 1(e) suggest the dominance of repulsive forces over the attractive forces in the molecular complexes in the binary mixtures ($BR + MeOH$) [31].

The values of the coefficients (a_0, a_1, a_2, a_3, a_4) and correlation constant (γ) are shown in Table 3.

There exist several molecular interactions in binary mixtures since their constituents are composed of different molecular species. In the present study, the experimental values of refractive index and ultrasonic velocity of binary mixture are fitted in various mixing models and validated in terms of average percentage deviation (APD).

We examined five mixing models for ultrasonic velocity: Nomoto (N), VanDael and Vangeel Ideal (VV), impedance dependent (IM), Jungie (J), and Rao's specific sound speed (R).

For Refractive index, we investigated nine mixing models: Lorentz-Lorentz (LL), Arago-Biot (AB), Newton (N), Wiener (W), Eykman (EY), Oster (O), Gladstone-Dale (GD), Eyring-John (EJ), and Heller (H). Their equations are presented in literature [5]. From the figure 2, Jungie's relation (J) is the most accurate estimate of ultrasonic velocity; on the other side

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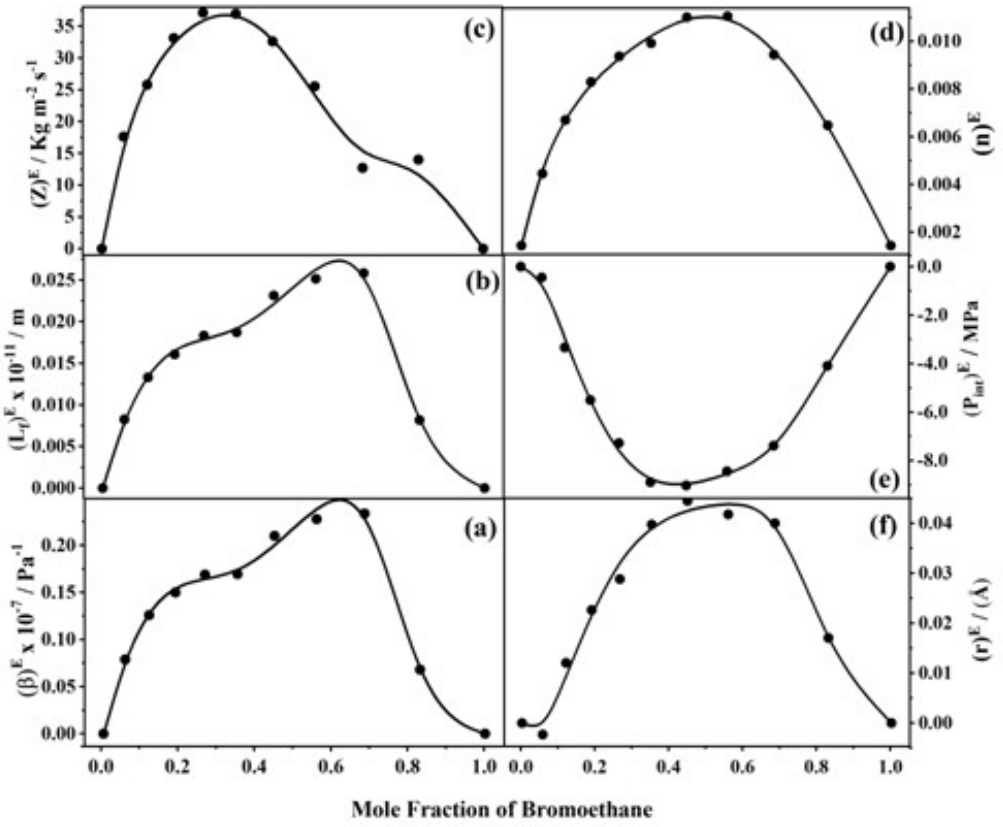


Figure 1: 1a-1f, Excess Acoustic and excess refractometric parameters

Table 1: Analysis of Experimental and Literature (Reported) values for absolute liquids.

Pure Compound	Density (ρ)(Kg/m^3)		Ultrasonic velocity(u) (m/s)		Refractive index (n)	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
MeOH	800.93	800.70 [26]	1154.20	1152.66 [26]	1.3326	1.3328[26]
BR	1471.50	1480 [27]	927.07	935.00 [27]	1.4322	—

experimental data on ultrasonic velocity demonstrate a significant difference with Rao's specific sound speed (R).

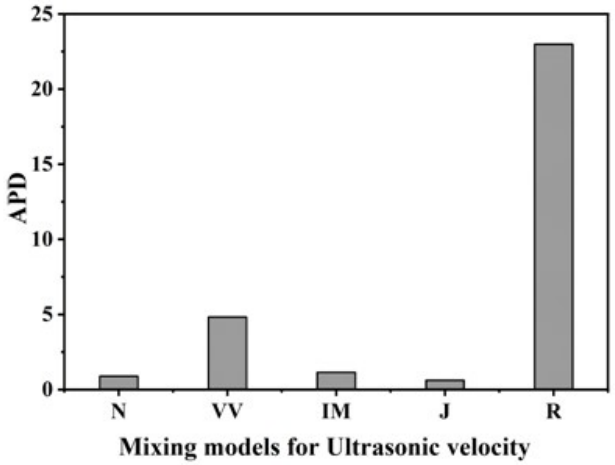


Figure 2: APD values for different mixing model of ultrasonic velocity

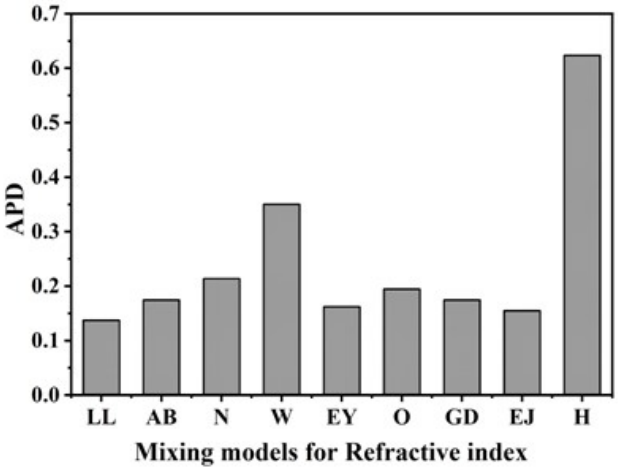


Figure 3: APD values for different mixing model of Refractive index

5. Conclusion

The ultrasonic parameters and refractometric parameters have been studied for ($MeOH$ + BR) binary

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Table 2: Values of experimental (n, u, and ρ) and envaulted parameters (r, P_{int}, β , L_f, and Z) against mole fraction BR.

X_{BR}	n	u (m s^{-1})	ρ (kg m^{-3})	r (Å)	P_{int} (MPa)	β (10^{-7} Pa^{-1})	L_f (10^{-11} m)	Z (kg m^{-2} s^{-1})
0.0000	1.3326	1154.20	800.90	1.48	169.27	9.37	6.12	924.43
0.0568	1.3417	1103.90	876.00	1.56	151.62	9.36	6.12	967.00
0.1192	1.3505	1069.71	937.30	1.63	137.95	9.32	6.11	1002.67
0.1884	1.3592	1039.50	1000.90	1.69	128.61	9.24	6.08	1040.42
0.2653	1.3681	1013.38	1064.00	1.74	121.77	9.15	6.05	1078.18
0.3513	1.3773	992.76	1124.00	1.79	116.37	9.02	6.01	1115.86
0.4482	1.3882	970.74	1188.90	1.83	112.99	8.92	5.98	1154.15
0.5582	1.3992	952.49	1255.10	1.87	110.58	8.78	5.93	1195.47
0.6842	1.4099	938.88	1318.60	1.91	108.50	8.60	5.87	1238.00
0.8298	1.4210	932.91	1397.10	1.94	108.15	8.22	5.74	1303.35
1.0000	1.4322	927.07	1471.50	1.97	107.80	7.90	5.63	1364.19

Table 3: Values of coefficients of the Redlich–Kister polynomial with correlation constant for $MeOH + BR$ binary mixture.

Coefficients	$(\beta)^E$	$(L_f)^E$	$(Z)^E$	$(n)^E$	$(P_{\text{int}})^E$	$(r)^E$
a_0	54.4861	-109.7456	21.4437	-0.0192	-93.7602	25.2103
a_1	33.8573	-137.6197	-3.2047	0.0017	40.4895	-5.1660
a_2	75.6052	-194.9195	2.8375	0.0266	-25.5164	10.5666
a_3	-28.8282	22.9343	2.5292	-0.0079	3.0984	-0.3209
a_4	-99.3726	307.0526	-7.5848	-0.0247	14.9057	-13.1623
γ	0.9966	0.9946	0.9992	0.9969	0.9998	0.9997

mixtures at temperature 283.15 K. The calculated ultrasonic parameters such as adiabatic compressibility (β), acoustic impedance (Z), and free length (Lf) as well as refractometric parameters named internal pressure (Pint) and molecular radii (r) of binary mixtures. Several excess parameters for acoustic and refractometric quantities were computed and fitted to the R-K type polynomial equation. A negative deviation is observed for the behaviour of excess internal pressure. For entire concentration range excess free length, excess adiabatic compressibility, excess refractive index, excess molecular radii and excess acoustic impedance exhibited a positive deviation from ideal behaviour. In conclusion, of the nine mixing relations examined for the refractive index, Lorentz-Lorentz (LL) mixing relations provide the most accurate fit to the experimental values. In the context of ultrasonic speed, Nomoto's theoretical mixing relationship provides favourable results among five examined options.

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