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Acoustical and optical properties of binary liquid mixtures: A comparative study

Ranjan Dey*, Praveen Rangnath P, Kartikeya Tiwari & Aditya P Pandey

Department of Chemistry, Goa Campus, BITS Pilani, Zuarinagar, Goa, 403 726, India

Email: ranjandey@goa.bits-pilani.ac.in

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Ultrasonic velocity in conjunction with density plays a major role in determining a number of key thermophysical parameters which are used in multifarious industrial applications. In the present investigation, a comparative study has been carried out employing a number of predictive approaches for evaluating ultrasonic velocity for 82 binary systems and refractive index for 76 binary systems, taking AAPD as the criterion for their predictive capability. Some very important findings emerge which will be beneficial to researchers in this, and allied fields of work.

Keywords: Solution chemistry, Acoustical properties, Optical properties, Ultrasonic velocities, Refractive indices, Binary systems, Density

Knowledge of acoustical, transport and specially optical properties, plays a vital role in multifarious engineering applications. This has evoked considerable interest among researchers from various disciplines in the past few decades as is evident from literature[1-6]. A number of correlative, empirical, semi-empirical and statistical-mechanical approaches are being used by researchers for evaluation of ultrasonic velocity (u) and refractive index (n) of binary liquid mixtures comprising of components of varying sizes, shapes and orientations[7-12]. Density values coupled with ultrasonic velocity lead to the evaluation of several significant thermodynamic properties, viz., compressibility, expansivity, etc. Knowledge of the thermodynamic parameters in conjunction with transport properties, helps in getting a deeper and better insight of the different types of intermolecular interactions occurring in these mixtures under different physicochemical conditions[12-17].

In the present investigation, a very comprehensive study has been carried out for testing the merits/demerits of various existing approaches for evaluating ultrasonic velocity and refractive index of binary liquid mixtures. Fourteen approaches have been employed[7-9,12,18] which include Danusso (Dan), Van Dael and Vangeel (VD), Nomoto (Nom), Junjie (Jun) and Collision Factor Theory (CFT) approaches for the evaluation of ultrasonic velocity. In case of refractive index, nine mixing rules[12,18,19] viz., Gladstone-Dale[12] (GD), Wiener[12] (W) , Arago–Biot[18] (AB), Heller[19] (H), Newton[19] (Nn), Lorentz-Lorentz[18] (LL), Eyring & John[20] (EJ), Eykman[12] (Eyk) and Oster[18] (Os) relations have been employed. The findings have been used to carry out a comparative study of these mixing rules by considering the Absolute Average Percentage Deviation (AAPD) as the criterion for ascertaining their predictive capabilities.

Theoretical

Sound velocity measurement serves as a vital tool for interpreting the extent and nature of intermolecular interactions present in a system, as it helps in the determination of some important thermodynamic parameters of liquids which are not obtained easily[21-24]. Thus the theoretical prediction of ultrasonic velocity assumes considerable significance and has been successfully employed by several workers[7-9,12,25]. In the present investigation, ultrasonic velocities of 82 binary mixtures have been evaluated by fourteen different approaches.

Equation proposed by Van Dael and Vangeel[7] based on the ideal mixing approach is given by:

$$\frac{1}{(x_1M_1+x_2M_2)U_m^2} = \left[\left(\frac{x_1}{M_1U_1^2}\right) + \left(\frac{x_2}{M_2U_2^2}\right)\right] \quad \ldots (1)$$

The Nomoto[7] approach based on the linearity of the molar sound velocity and molar volumes of the compounds constituting the binary mixtures is given as:

$$U_m = \left(\frac{x_1R_1+x_2R_2}{x_1V_1+x_2V_2}\right)^3 \quad \ldots (2)$$

where the molar sound velocity is given as : $R = U^{\frac{1}{3}}V$

The Junjie[7] and Danusso[7,9] relations for evaluating the ultrasonic velocity of the liquid mixtures are also included in this investigation.

Based on the collision factor theory, the relation proposed by Nutsch-Kunkies[9], an extension of Schaff's theory, is given as:

$$U_m = \frac{U_\infty}{V_m}(x_1S_1 + x_2S_2)(x_1B_1 + x_2B_2) \quad \ldots (3)$$

where S and B represent the collision factor and the actual volume of the molecule/mole of the pure components constituting the mixtures and can be computed as,

$$S = \frac{UV}{U_\infty B} \quad \text{and} \quad B = \frac{4}{3}\pi r^3 N_0$$

where U_∞= 1600 m/s and r is the molecular radius.

The molecular radius can be calculated using several different approaches[26],

CP-FCC: $r = \frac{1}{2}\sqrt[3]{\frac{M\sqrt{2}}{\rho N}}$ … (4)

Schaff's relation: $r = \sqrt[3]{\frac{M}{\rho N}}\sqrt[3]{\frac{3}{16\pi}\left[1 - \frac{\gamma RT}{Mu^2}\left(\sqrt{1 + \frac{Mu^2}{3\gamma RT}} - 1\right)\right]}$ … (5)

Rao's relation: $r = \sqrt[3]{\frac{M}{\rho N}}\sqrt[3]{\frac{3}{16\pi}\left[1 - \frac{\gamma RT}{Mu^2}\left(\sqrt{1 + \frac{Mu^2}{\gamma RT}} - 1\right)\right]}$ … (6)

Eyring's relation:

$$r = \sqrt[3]{\frac{M}{\rho N}}\frac{1}{2}\sqrt[3]{\left[1 - \left(1 - \frac{1}{u}\sqrt{\frac{\gamma RT}{M}}\right)^3\right]\sqrt{2}} \quad \ldots (7)$$

Kittel's relation: $r = \sqrt[3]{\frac{M}{\rho N}}\frac{1}{2}\sqrt[3]{\left[\left(1 - \frac{1}{u}\sqrt{\frac{3\gamma RT}{M}}\right)\right]\sqrt{2}}$ … (8)

where $\gamma = \frac{\beta_t}{\beta_s}$; $\beta_t = \frac{1.71*10^{-3}}{\rho^{\frac{4}{3}}u^2T^{\frac{4}{9}}}$ and $\beta_s = \frac{1}{u^2\rho}$,

M is the molar mass, ρ the density, N the Avogadro's number, T the temperature in Kelvin and β_T and β_S are isothermal and adiabatic compressiblities respectively.

The ultrasonic velocities have also been evaluated by neglecting the γ parameter in the Schaffs (SCH), Rao, Eyring (EYR) and Kittel's (KITT) expressions (Eqs 7-10). In the graphical representations and in further discussions, the AAPDs of these approaches have been represented as Schaff-1, Rao-1, Eyring-1 and Kittel-1 respectively.

Gladstone-Dale[7] proposed the following relation for computing the refractive index for binary liquid mixtures:

$$n_m - 1 = \varphi_1(n_1 - 1) + \varphi_2(n_2 - 1) \quad \ldots (9)$$

Wiener's relation[19] for evaluating the refractive index of binary liquid mixtures is given as:

$$\left(\frac{n_m^2 - n_1^2}{n_m^2 + 2n_1^2}\right) = \left(\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}\right)\varphi_2 \quad \ldots (10)$$

The following equation was proposed by Newton for calculating the refractive index of binary liquid mixtures:

$$n_m^2 - 1 = \varphi_1(n_1^2 - 1) + \varphi_2(n_2^2 - 1) \quad \ldots (11)$$

Eyring & John's[20] relation is given as:

$$n_m = n_1\varphi_1^2 + 2(\varphi_1\varphi_2)^{1/2} + n_2\varphi_2^2 \quad \ldots (12)$$

where n is the refractive index of the pure component and φ is the volume fraction.

Oster's relation[18], Eykman's relation[18], L-L relation[18] and Heller's relation[18] for the evaluation of refractive index are also included in the present investigation.

The absolute average percentage deviations (AAPD) by the different approaches have been computed using the expression:

$$\text{AAPD} = \frac{1}{n}\sum\frac{|Y_{experimental} - Y_{theoretical}|}{Y_{experimental}} \times 100 \quad \ldots (13)$$

where Y denotes the property, viz., ultrasonic velocity and refractive index.

Results and discussion

Ultrasonic velocity has been evaluated for 82 binary liquid mixtures, including mixtures containing ionic liquid as one of the components. Ten different approaches have been employed for the evaluation of ultrasonic velocity. Furthermore, four more CFT approaches have been utilized without employing γ, and the corresponding values obtained have been compared with those employing γ. A compilation of the Absolute Average Percentage deviation (AAPD) values of ultrasonic velocity using various approaches at different temperatures for all the systems taken into consideration in the present investigation, is given in Table S1 (Supplementary data). A comparative study has been carried out taking the AAPDs as the criterion for their predictive capability. The experimental data for the systems under consideration have been taken from literature[27-45].

The ultrasonic velocity of 13 binary mixtures could not be evaluated by the CFT approach due to the lack of requisite literature data of pure components (Table S1).

The graphical representation of AAPD values for the evaluation of ultrasonic velocity through fourteen different approaches for seven binary liquid mixtures at 298 K is shown in Fig. 1. The binary mixtures under consideration include organic liquids of diverse nature, comprising alkanes, alcohols, amines, esters and common solvents such as DMF and 1,4-Dioxane. It is clearly seen from the figure that the Nomoto approach gives ultrasonic velocity values closest to that of experimental findings for all the systems under consideration.

For the 1-butyl-3-methylimidazolium tetrafluoro borate+N-vinyl-2-pyrrolidinone system at six different temperatures in the range of 298 K to 303 K, it is seen that the AAPD values of Nomoto approach show the least deviation, while the Van Deal approach gives the highest deviation (Fig. 2). Furthermore, Danusso and Van Dael approaches show a steady increase in AAPD values as the temperature increases, whereas Junjie and CP-FCC approaches show a comparatively moderate increase for the same. It is pertinent to note that Nomoto and CFT approaches show consistency with minute changes in AAPD values, 0.60 (298 K)–0.68 (323 K) and 2.06 (298 K)–2.02 (323 K) respectively (Table S1). It is evident from the above graph that Nomoto approach predicts the ultrasonic velocity more accurately than other approaches, which is also reflected in earlier investigations[7].

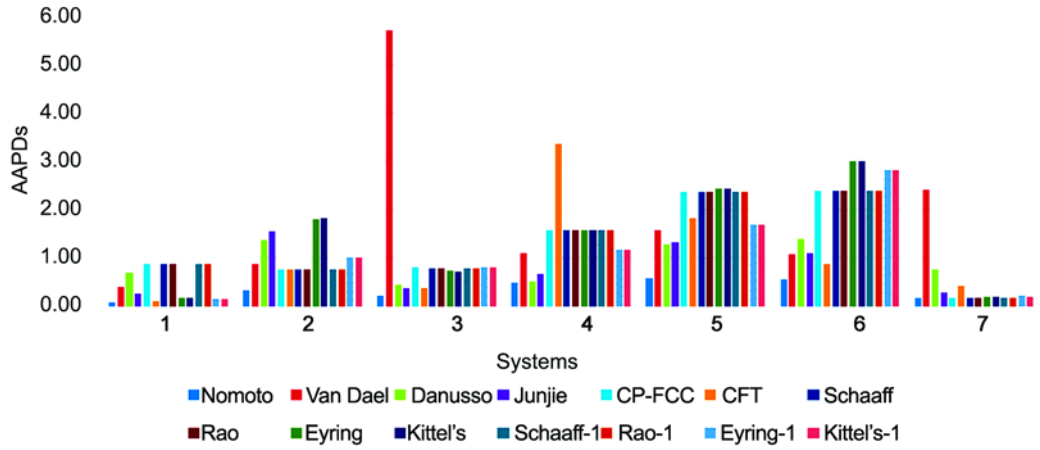

Fig. 1 — Comparison of AAPD values of various approaches for evaluation of ultrasonic velocity of binary mixtures at 298.15 K. [1: ethenylbenzene+DMF; 2: 2-chloroethanol+pentan-1-ol; 3: tri-*n*-butylamine+trimethylamine; 4: ethenylbenzene+decane; 5: 2-chloroethanol+butylacetate; 6: 1,4-dioxane+ethanediol; 7: ethenylbenzene+THF].

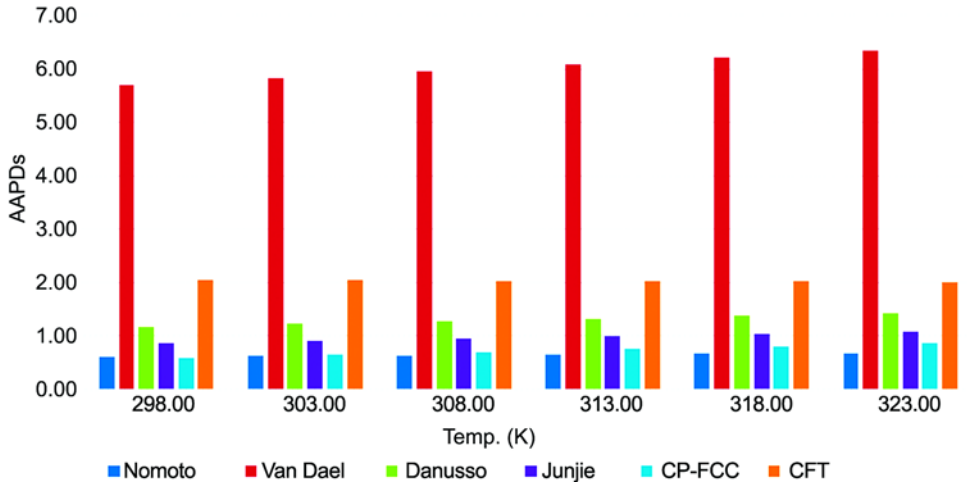

Fig. 2 — Comparison of AAPD values of various approaches for evaluation of ultrasonic velocity for the system, 1-butyl-3-methylimidazolium tetrafluoroborate+N-vinyl-2-pyrrolidinone in the temperature range of 298–323 K.

Comparison of AAPD values of various approaches for evaluation of ultrasonic velocity at 303.15 K, for the five systems, viz., pyridine+octanol, acetophenone+ethylchloroacetate, acetophenone+ methyl acetate, γ-butyrolactone+1-butanol, pyridine+ decanol shows that the Nomoto equation gives the least AAPD values for all the systems. It is also seen that the Van Dael approach gives the highest AAPD values for most of the systems, suggesting that these systems are far from ideality (Table S1 and Fig. S1).

Comparison of AAPD values of various approaches for evaluation of ultrasonic velocity of binary mixtures, viz., 2-chloroethanol+ethanol, tri-*n*-butylamine+trimethylamine, dimethylcarbonate+ methanol, γ-butyrolactone+methanol, 2-chloroethanol +methanol at 298.15 K, shows that the Nomoto relation gives the least deviation from the experimental ultrasonic velocity for all the systems under consideration, whereas Van Dael gives the highest deviation for most of the systems. It is also observed that Junjie and Danusso approaches give similar results as seen from the proximal AAPD values, and a similar trend is seen with respect to the CFT and CP-FCC approaches (Table S1 and Fig. S2).

A compilation of the Absolute Average Percentage deviation (AAPD) values of refractive index using various approaches at different temperatures for all the 76 systems taken into consideration in the present investigation is given as Table S2 (Supplementary data). The experimental data for the systems under consideration have been taken from literature[27-45].

Refractive index values for binary mixtures have been evaluated by using nine different approaches at various temperatures. These include[23,24] Gladstone-Dale (GD) relation, Arago–Biot (AB) relation, Heller's (H) relation, Wiener's (W) relation, Lorentz–Lorenz (LL) relation, Newton's (Nn) relation, Eykman's (Eyk) relation, Eyring and Oster's (Os) relation. A comparative study of the results obtained by the various approaches in terms of the AAPD values for all the nine approaches considered for the present investigation have been reported in Table S2.

Comparison of AAPD values of various approaches of refractive index of six binary systems, viz., ethenylbenzene+bromoform, 2-chloroethanol +ethanol, 1,4-dioxane+diethyl phthalate, tri-*n*-butylamine+tetrachloroethylene, ethylchloroacetate +*p*-xylene, 2-chloroethanol+butyl acetate at 298.15 K, shows that all the approaches give an AAPD value of less than 0.1 for the systems. This indicates that all the equations perform well in the prediction of refractive index. For all the systems under consideration, the AAPD values from all the equations (Eqs 9-12) are in close proximity to one another (Table S2 and Fig. S3).

Comparison of AAPD values of various approaches of refractive index of binary systems viz., 2-chloroethanol+ethylacetate, ethenylbenzene+dodecane, dimethyl carbonate+methanol, 2-chloroethanol +1-hexanol, ethenylbenzene+DMSO at 298.15 K shows that for all the systems taken into consideration, the AAPD values generated by all the approaches are very close to each other and the difference in AAPD values of any two approaches is less than 0.1. The above statement is also an indication that all the approaches evaluate the refractive index values to a close agreement with the experimental refractive index values (Table S2 and Fig. S4).

A perusal of Figs 3 and 4 clearly indicates that for the binary systems, ethyl chloroacetate+benzyl

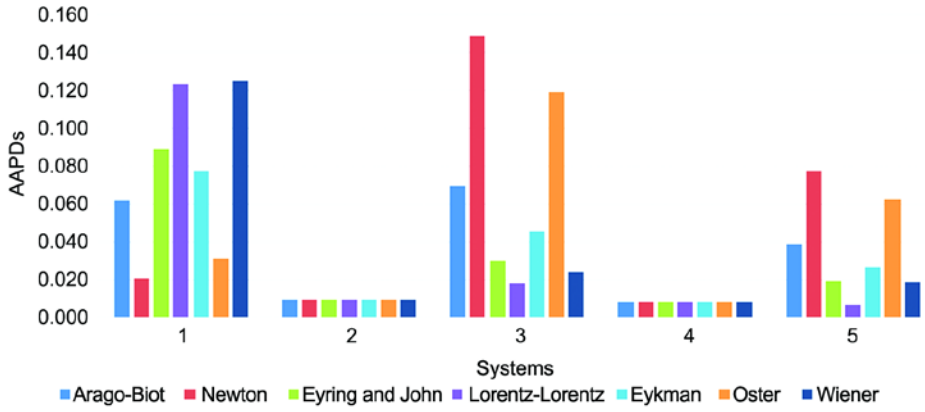

Fig. 3 — Comparison of AAPD values of various approaches of refractive index of binary systems at 298.15 K. [1: ethylchloroacetate+ benzylalcohol; 2: 1,4-dioxane+diethyloxalate; 3: ethylchloroacetate+bromobenzene; 4: 1,4-dioxane+ethylacetoacetate; 5: ethylchloroacetate+anisole].

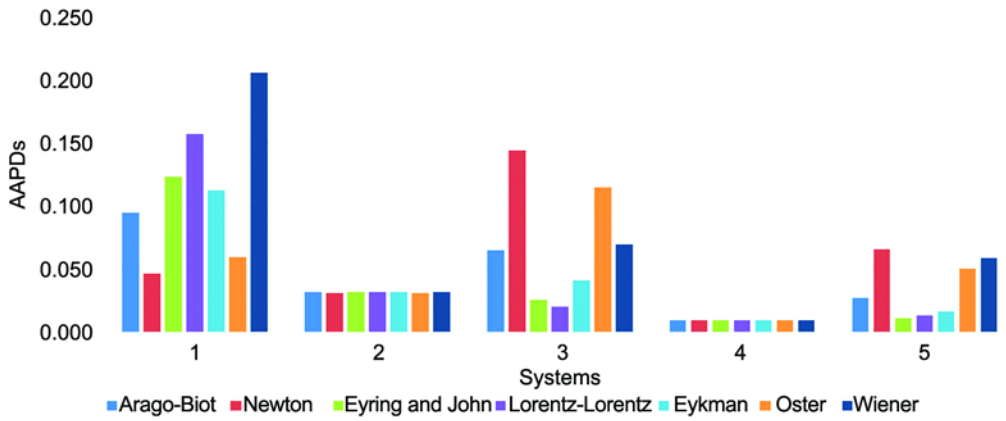

Fig. 4 — Comparison of AAPD values of various approaches of refractive index of binary systems at 308.15 K. [1: ethylchloroacetate+ benzylalcohol; 2: 1,4-dioxane+diethyloxalate; 3: ethylchloroacetate+bromobenzene; 4: 1,4-dioxane+ethylacetoacetate; 5: ethylchloroacetate+anisole]

Table 1 — Grand AAPD values for ultrasonic velocities for 82 binary systems

Approaches	Grand AAPD
NOM	1.49
VD	4.60
DAN	2.31
JUN	2.14
CPF	1.73
CFT	1.92
SCH	1.72
RAO	1.72
EYR	4.03
KITT	4.04
SCH-1	1.62
RAO-1	1.61
EYR-1	3.63
KITT-1	3.64

alcohol, 1, 4-dioxane+diethyl oxalate, and 1, 4-dioxane+ethyl acetoacetate, the AAPD values for the Arago-Biot, Newton, Eyring, Eykman and Oster approaches show an increase, as the temperature increases from 298 K to 308 K whereas they show a decrease for the other two systems for the same temperature change. It is also observed that the Lorentz-Lorentz equation and the Wiener relation shows an increase in AAPD values for all the systems as the temperature increases.

A perusal of Grand AAPD values recorded in Table 1, shows that the Nomoto approach is superior to all other approaches for predicting the ultrasonic velocity of binary liquid mixtures. The grand AAPD values also suggest that the CFT approaches, viz., Schaaffs, Rao, Kittel and Eyring exhibit lower AAPD values when employed excluding the parameter gamma (γ) as compared to the AAPDs obtained during their evaluation with inclusion of gamma (γ). Further scrutiny of Table 1 and S1, reveals that the Schaff and Rao approaches give identical AAPD values for all the systems under consideration. It is pertinent to point out that Kittel and Eyring approaches also exhibit identical AAPD values.

Table 2 — Grand AAPD values for refractive indices for 76 binary systems

Approaches	Grand AAPD
AB	0.11
GD	0.11
Nn	0.12
EJ	0.11
LL	0.12
H	0.12
Eyk	0.11
W	0.12
Os	0.12

The grand AAPD values from Table 2, indicate that all the approaches for the evaluation of refractive indices perform well as they give low grand AAPD values with the values not differing from each other across all the approaches used for investigation.

In summary, the study shows that while carrying out comparative studies for predictive capabilities of various approaches for the evaluation of ultrasonic velocities, either of Rao or Schaaff, and, similarly either of Eyring or Kittel approaches should be employed, since each pair gives identical AAPD values. The AAPD values also clearly indicate that

the Nomoto approach gives the values closest to experimental findings. Another significant finding is that, the AAPD values indicate that the predictive capabilities of the CFT approaches for ultrasonic velocity, show a marked improvement when used excluding the parameter γ, than when used including γ (Eqs 5-8). A perusal of Table 2 and Table S2, indicates that all the approaches exhibit very good agreement with experimental findings with almost identical grand AAPD values, suggesting that all the approaches are equally effective in predicting the refractive index.

Supplementary data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_57A(07)920-925_SupplData.pdf.

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926