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Research Article

Ultrasonic velocity for Binary Liquid Mixtures at different Temperatures

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Abstract Speed of Sound for two binary systems (1-propanol and 2-propanol with n-dodecane were computed at T= (298.15, 308.15, and 318.15) K over the whole composition range at atmospheric pressure by utilizing various theoretical models. Speed of Sound was fitted to Redlich-Kister polynomial equation to estimate the binary coefficients and standard errors. The theoretical models used in the computation were also tested for different systems showing that they provide fair agreement between theory and experiment. A considerable comparison has also been made to study the associational behavior and molecular interactions involved for these systems

Keywords Sound Velocity, Theoretical Models, Binary, Associated, Molecular interactions

1. Introduction

Molecular interactions occurring in a variety of liquid mixtures and solutions can be studied with the help of ultrasonic velocity [1]. Extensive work has been carried out by many workers [2-3] to investigate liquid state through analysis of ultrasonic propagation parameters and to correlate ultrasonic velocity with other physical and thermodynamic parameters. General applicability and comparison merits for the various models in binary solvent mixtures of aprotic protophobic solvent with aprotic protophilic solvents having distinctly different Gutmann donor numbers yield typical interaction gradually varying with nitrogen base size is the major object of the present work. As a part of research concerning the thermo chemical studies on new working fluid pair, we present here some useful data on speed of sound for three binary systems. These data were analyzed in terms of Ramaswamy and Anbananthan (RA) model [4] model suggested by Glinski [5], Prigogine-Flory-Patterson (PFP) model [6]. The first two models, RA and model devised by Glinski (associated) are based on the association constant as adjustable parameters where as PFP and others (non-associated) are based on the additivity of liquids. From these results, deviations in ultrasonic velocity, Δu were calculated and fitted to the Redlich-Kister polynomial equation [7] to derive the binary coefficients and the standard errors. An attempt has also been made to correlate the experimental data with the McAllister multi body interaction model [8] which is based on Eyring's theory of absolute reaction rates.

2. Theoretical

2.1 Ramswamy and Anbananthan Model (RA Model)

Ramswamy and Anbananthan proposed the model based on the assumption of linearity of acoustic impedance with the mole fraction of components. He assumed that when solute is added to solvent the molecules interact according to the equilibrium as:

$$A+B \leftrightarrow AB \tag{1}$$

where [A] is amount of solvent and [B] is amount of solute in the liquid mixture. By applying the condition of linearity in speed of sound with composition and considering the non-associated component present in the liquid mixture, eq takes the form,

$$u_{RA} = [x_A\, u_A + x_B\, u_B + x_{AB}\, u_{AB}] \tag{2}$$

where x_A, x_{AB}, u_A and u_{AB} and u_{obs} are the mole fraction of A, mole fraction of associate AB, ultrasonic velocity of A, ultrasonic velocity of associate AB and observed ultrasonic velocity respectively.

2.2 Model Devised by Glinski

On inspecting the results obtained from Ramaswamy and Anbananthan model, Glisnki suggested the equation assuming additivity with the volume fraction, ϕ of the components, the refined version of Natta and Baccaredda model as,

$$u_{Glinski} = \frac{u_A u_B u_{AB}}{\phi_A u_B u_{AB} + \phi_B u_A u_{AB} + \phi_{AB} u_A u_B} \tag{3}$$

where u_{cal} is theoretical ultrasonic velocity, ϕ_A, ϕ_B are the volume fractions of component A and B and u_A, u_B and u_{AB} are the ultrasonic velocity of components A, B and AB.

2.3 Prigogine-Flory-Patterson Model.

Flory and collaborators used the cell partition function of Hirschfelder and Eyring and a simple Van der Waals energy- volume relation, by putting m=3, n→∞ so that the Flory equations for the mixing functions and partial molar quantities may be obtained from the general corresponding states equations given by making this particular choice of (m,n). Patterson et al have drawn attention to the close connection between the Flory theory and corresponding state theory of Prigogine employing a simple cell model of the liquid state. In order to extend corresponding state theory to deal with the surface tension, Patterson and Rastogi used the reduction parameters as,

$$\sigma^* = k^{1/3} P^{*2/3} T^{*1/3} \tag{4}$$

called the characteristic surface tension of the liquid. Here k is the Boltzmann constant. Paterson and Rastogi extended the simple cell model theory of the surface tension of spherical molecules by Prigogine and Saraga to the case of chain molecules. A segment experiences an increase in the configurational energy equal to $-M\,\tilde{U}\,(\tilde{V})$ due to the loss of a molar fraction, M, of its nearest neighbors at the surface while moving from the bulk phase to the surface phase. Its most suitable value ranges from 0.25 to 0.29. In the present case the value of M is taken as 0.29 throughout the calculation. Thus on the basis of Flory theory, surface tension and speed of sound of liquid mixture are related to the ultrasonic velocity by well-known and well tested relation of Auerbach [9]

$$\sigma = \sigma^* \,\tilde{\sigma}(\tilde{V}) \quad \text{and} \quad u_{PFP} = \left(\frac{\sigma}{6.3 x 10^{-4} \rho}\right)^{2/3} \tag{5}$$

All the notations used in the above equations have their usual significance as detailed out by Flory.

2.4 McAllister – three body model

Taking concept of additivity, McAllister derived an equation for three body interactions as;

$$\ln u = x_1^3 \ln u_1 + 3x_1^2 x_2 \ln u_{12} + 3x_1 x_2 \ln u_{21} \qquad + x_2^3 \ln u_2 - \ln[x_1 + x_2 M_2 / M_1] + 3x_1^2 x_2 \ln[(2 + M_2 / M_1)/3]$$
$$+ 3x_1 x_2^2 \ln[(1 + 2M_2 / M_1)/3] + x_2^3 \ln[M_2 / M_1] \qquad (6)$$

2.5 McAllister –four body model

If there is much difference in size of two molecules, then four body model approaches more nearly a 3-dimensional treatment. Again considering different interactions and their fraction of total occurrences, energy of activation may be written as sum of energy of activations of various interactions

$$\Delta G^* = x_1^4 \Delta G_1^* + 4x_1^3 x_2 \Delta G_{1112}^* + 6x_1^2 x_2^2 \Delta G_{112}^* + 4x_1 x_2^3 \Delta G_{2221}^* + x_2^4 \Delta G_2^* \qquad (7)$$

by techniques entirely analogous to method given above, the following equation is derived;

$$\ln u_{mix} = x_1^4 \ln u_1 + 4x_1^3 x_2 \ln u_{1112} + 6x_1^2 x_2 \ln u_{1122}$$
$$+ 4x_1 x_2^2 \ln u_{222} + x_2^4 \ln u_2 - \ln(x_1 + x_2 M_2 / M_1)$$
$$+ 4x_1^3 x_2 \ln[(3 + M_2 / M_1)/4] + 6x_1^2 x_2^2 \ln[(1 + M_2 / M_1)/2]$$
$$+ 4x_1 x_2^3 \ln[(1 + 3M_2 / M_1)/4] + x_2^4 \ln(M_2 / M_1) \qquad (8)$$

where u,x_1, u_1,M_1,x_2, u_2 and M_2 are the ultrasonic velocity of mixture, mole fraction, ultrasonic velocity and molecular weight of pure component 1 and 2 respectively. McAllister coefficients are adjustable parameters that are characteristic of the system.

3. Results & Discussion

Values of thermal expansion coefficient (α) and isothermal compressibility needed in the PFP model were obtained from the equation which have already been tested in many cases by us [10]. Calculations were performed on the experimental work of Yeh et.al [11].

The mixing function $\Delta\sigma$ can be represented mathematically by Redlich-Kister polynomial equation for correlating the experimental data as;

$$y = x_i (1 - x_1) \sum_{i=0}^{p} A_i (2x_1 - 1)^i \qquad (9)$$

where y refers to deviation in ultrasonic velocity (Δu), x_1 is the mole fraction and A_i is the coefficient.

McAllister coefficients a, b, and c were calculated using the least square procedure and the results of estimated parameters and standard deviation between the calculated and experimental values are presented in Table 2-3.

The absolute average percent deviations (AAPD) in ultrasonic velocity obtained from different models are provided in Table 4. It is observed that associated processes provide fairly good results as compared to non-associated. Higher deviation values in PFP model can be explained as the model was developed for non-electrolyte γ-meric spherical chain molecules and the system under investigation have interacting and associating properties. Moreover, the expression used for the computation of α and β_T are also empirical in nature. Positive deviations in speed of sound are a result of molecular association and complex formation whereas negative deviations are due to molecular dissociation. The actual sign and magnitude of deviations depend upon relative strength of two opposite effect. The lacks of smoothness in deviations are due to the interaction between the components molecules Results of ultrasonic velocity obtained from different models along with percent deviation are reported in Table 4. A careful perusal of the results clearly indicates the close proximity of our results with the experimental findings.

Table 1: Coefficient of Redlich- kister Equation and Standard Deviation for Ultrasonic Velocity of Binary Liquid Mixtures at Various Temperatures

T/K	A0	A1	A2	A3	Std dev	A0	A1	A2	A3	Std dev
	1-Butanol+n-Dodecane					**2-Butanol+n-Dodecane**				
288.15	-5.95	-2.26	-26.04	18.01	0.53	-6.78	0.86	-9.59	15.21	0.38
298.15	-14.41	-3.14	-26.22	14.54	0.45	-14.62	-6.63	-15.15	17.80	0.36
308.15	-22.89	-5.27	-26.97	13.79	0.40	-20.94	-12.52	-21.72	18.11	0.32
318.15	-31.39	-5.20	-22.78	2.65	0.23	-25.24	-15.15	-25.89	10.67	0.24

Table 2: Parameters of McAllister 3 Body Interaction Model and Standard Deviation for Ultrasonic Velocity of Binary Liquid Mixture at Various Temperatures

T/K	a	b	Std dev	a	b	Std dev
	1-Butanol+n-Dodecane			**2-Butanol+n-Dodecane**		
288.15k	709.10	969.36	0.74	700.07	963.29	1.17
298.15k	687.34	939.90	0.68	676.84	934.35	0.97
308.15k	665.82	910.90	0.60	653.99	905.78	0.74
318.15k	644.36	882.82	0.54	631.55	877.78	0.52

Table 3: Parameters of McAllister 4 Body Interaction Model and Standard Deviation for Ultrasonic Velocity of Binary Liquid Mixture at Various Temperatures

T/K	a	b	c	Std dev	a	b	c	Std dev
	1-Butanol+n-Dodecane				**2-Butanol+n-Dodecane**			
288.15k	1334.02	1322.44	1315.44	0.31	1317.00	1305.02	1311.26	0.44
298.15k	1294.01	1282.65	1275.35	0.30	1273.27	1266.25	1270.66	0.48
308.15k	1254.29	1243.67	1235.75	0.30	1229.76	1228.48	1230.41	0.48
318.15k	1215.21	1204.58	1197.64	0.24	1187.17	1190.67	1191.28	1.79

Table 4: Average Percentage Deviation of Ultrasonic velocities from Prigogine-Flory-Patterson (PFP), Ramaswami (RS), Glinski (GLI), Mcallister3body (Mc3) and Mcallister4 body (Mc4) models

T/K	U PFP	U RS	U GLI	U Mc3)	U(Mc4)	U PFP	U RS	U GLI	U(Mc3)	U(Mc4)
1-Butanol+n-Dodecane						**2-Butanol+n-Dodecane**				
288.15	1.07	0.04	0.22	0.05	0.02	1.30	0.20	0.37	0.07	**0.03**
298.15	2.07	0.14	0.36	0.04	0.02	1.83	0.24	0.63	0.06	0.03
308.15	0.29	0.23	0.52	0.04	0.02	0.40	0.26	0.90	0.05	0.03
18.15	1.85	0.15	1.15	0.04	0.01	2.13	0.10	0.82	0.03	0.12

Plots of deviation in speed of sound obtained from various models with mole fractions at various temperatures are presented in figure 1. In all the cases, minimum values of deviations in speed of sound are observed for associated models and maximum deviations are observed for non- associated, PFP model. The model suggested by Glinski provides better results as compared to Ramaswami and Anbananthan. The trend in all the figures is almost similar and negative which indicates stronger interactions between the liquid molecules.
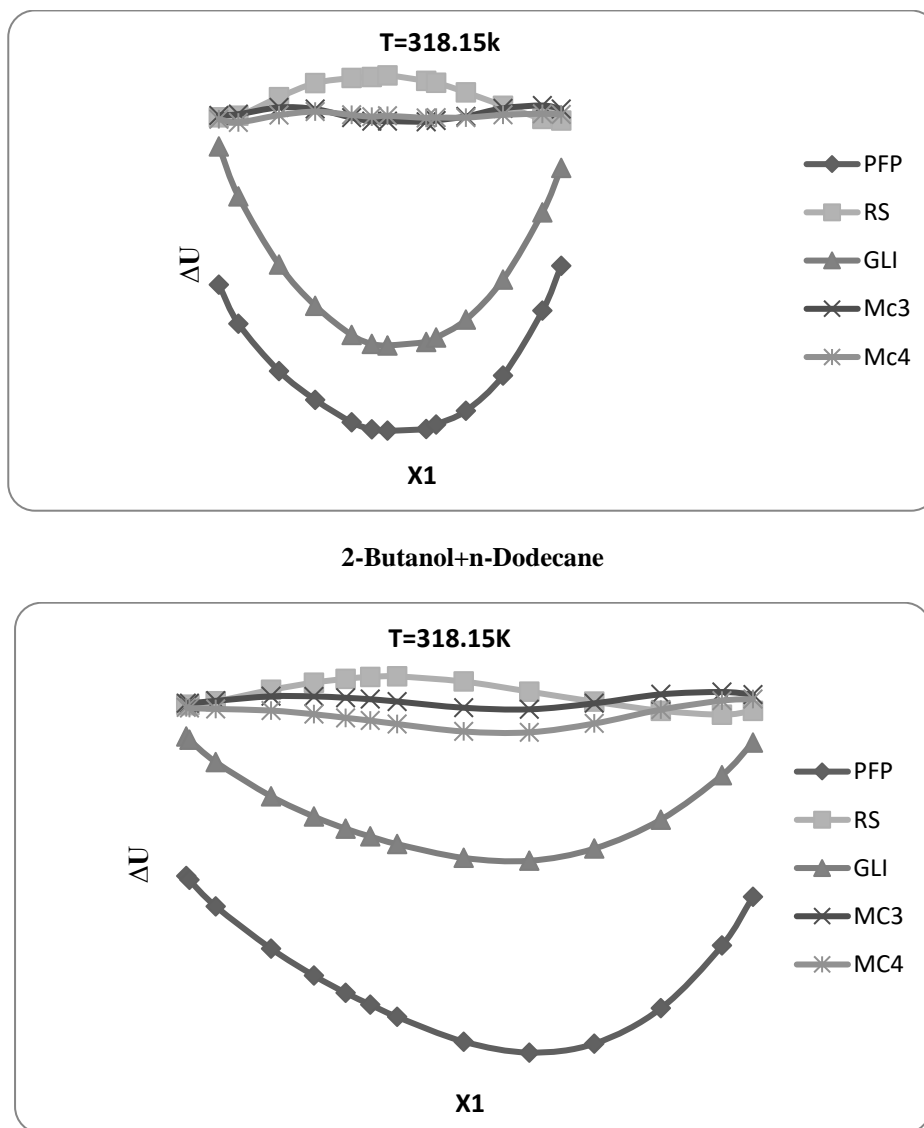
T=318.15k

2-Butanol+n-Dodecane

T=318.15K

Figure 1: Plot of Ultrasonic Velocity deviation ΔU with mole fraction for 1-Butanol + Dodecane and 2-Butanol + Dodecane at 318.15K.

4. Conclusion

Models assuming associated processes give more reliable results as compared to non-associated processes and helpful in deducing the internal structure of associates through the fitted values of ultrasonic velocity in a hypothetical pure associate and observed dependence of concentration on composition of a mixture.

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