

Comments on “Acoustic and Thermodynamic Properties of Binary Liquid Mixtures of Benzaldehyde in Hexane and Cyclohexane” by S. Azhagiri, S. Jayakumar, R. Padmanaban, S. Gunasekaran, and S. Srinivasan

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In a recent paper, S. Azhagiri et al. [1] reported the acoustic and thermodynamic properties of binary liquid mixtures of benzaldehyde with hexane and with cyclohexane at 303.15 K. These authors calculated so-called excess adiabatic compressibility (κ_S^E), intermolecular free length (L_f^E), acoustic impedance (Z^E), and ultrasonic velocity (U^E) from the equation $Y^E = Y - [(1-x)Y_1 + xY_2]$, where Y denotes κ_S , L_f , Z or U of the mixtures; x is the mole fraction of benzaldehyde (the solute) and subscripts 1 refers to benzaldehyde (solute) and 2 refers to hexane or cyclohexane (solvent). The results were reported in their Table 4. The variation of κ_S , L_f , Z or U and κ_S^E , L_f^E , Z^E and U^E were discussed in terms of molecular interactions. I have several comments to make concerning this paper.

Their calculation [1] of κ_S^E , L_f^E , Z^E , and U^E is wrong and erroneous, and thus the calculated values κ_S^E , L_f^E , Z^E , and U^E are not the claimed excess properties. The reported experimental density and ultrasonic velocity data for the pure components are also quite different from reliable literature values, and their interpretation of the reported results is unrealistic.

First, values of κ_S^E , L_f^E , Z^E , and U^E , their so-called excess properties (in fact they are actually deviations from mole fraction averages: $\Delta\kappa_S$, ΔL_f , ΔZ or ΔU) when $x = 0$ or 1 unexpectedly have significant finite values, whereas, in fact they should be zero. I recalculated and analyzed the data looking for the error. It became clear that the authors have made a gross error in using the equation $Y^E = Y - [(1-x)Y_1 + xY_2]$, their Eq. 6. In fact, this equation should actually be

$$\Delta Y = Y - [xY_1 + (1-x)Y_2] \quad (1)$$

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Table 1 Values of deviations in the ultrasonic velocity, adiabatic compressibility, acoustic impedance, and intermolecular free length of binary systems at (303.15 ± 0.05) K

x_1	ΔU m·s ⁻¹	$(\Delta\kappa_S) \times 10^9$ m ² ·N ⁻¹	$(\Delta Z) \times 10^{-6}$ kg·m ⁻² ·s ⁻¹	$(\Delta L_f) \times 10^{10}$ m
Benzaldehyde (1) + hexane (2)				
0.0	0.0	0.0000	0.0000	0.0000
0.1	-29.9	0.0351	-0.0587	0.0164
0.2	-45.8	0.0188	-0.0906	0.0167
0.3	-39.7	-0.0341	-0.0977	0.0038
0.4	-40.6	-0.0721	-0.0893	-0.0070
0.5	-33.5	-0.0887	-0.0862	-0.0127
0.6	-34.4	-0.0913	-0.0714	-0.0153
0.7	7.7	-0.1226	-0.0054	-0.0323
0.8	-10.2	-0.0689	-0.0362	-0.0150
0.9	-9.1	-0.0328	-0.0302	-0.0061
1.0	0.0	0.0000	0.0000	0.0000
Benzaldehyde (1) + cyclohexane (2)				
0.0	0.0	0.0000	0.0000	0.0000
0.1	-16.2	0.0116	-0.0313	0.0065
0.2	-8.4	-0.0184	-0.0264	-0.0026
0.3	27.4	-0.0725	0.0086	-0.0225
0.4	19.2	-0.0638	-0.0052	-0.0187
0.5	27.0	-0.0760	0.0154	-0.0242
0.6	10.8	-0.0535	-0.0066	-0.0155
0.7	0.6	-0.0403	-0.0085	-0.0111
0.8	25.4	-0.0487	0.0243	-0.0172
0.9	10.2	-0.0262	0.0187	-0.0094
1.0	0.0	0.0000	0.0000	0.0000

In place of x , they have wrongly used $(1 - x)$ and vice versa. To emphasize the point, recalculated results using Eq. 1 are reported in Table 1. Unlike the authors' reported values, there is a regular variation in ΔU , $\Delta\kappa_S$, ΔZ , or ΔL_f as the mole fraction composition x is varied. Further, it seems that the values of ultrasonic velocity at $x = 0.7$ are in error for benzaldehyde + hexane. The values of κ_S^E , L_f^E , Z^E , and U^E obtained by Azhagiri et al. [1] are unreliable, and are therefore inappropriate for interpretation. By implication, the discussion of the authors' values for κ_S^E , L_f^E , Z^E , and U^E is also inappropriate. If one wants to calculate true excess functions Y^E , then the following expressions should be used

$$Y^E = Y - Y^{id} \tag{2}$$

where Y is either κ_S , L_f or U .

Values of κ_S^{id} , U^{id} and L_f^{id} for an ideal mixture were calculated from the relations recommended by Bertrand and Smith [2], Benson and Kiyohara [3], and Douheret et al. [4, 5]:

$$\kappa_S^{id} = \sum \phi_i \{ \kappa_{S,i}^o + T V_i^o (\alpha_i^o)^2 / C_{p,i}^o \} - T (\sum x_i V_i^o) (\sum \phi_i \alpha_i^o)^2 / \sum x_i C_{p,i}^o \tag{3}$$

Table 2 Values of the excess ultrasonic velocity, adiabatic compressibility, and intermolecular free length of binary system at (303.15 ± 0.05) K

x_1	U^E m·s ⁻¹	$(\kappa_S^E) \times 10^9$ m ² ·N ⁻¹	$(L_f^E) \times 10^{10}$ m
Benzaldehyde (1) + hexane (2)			
0.1	6	0.013	0.0101
0.2	23	-0.021	0.0059
0.3	57	-0.088	-0.0100
0.4	80	-0.135	-0.0227
0.5	105	-0.156	-0.0293
0.6	114	-0.157	-0.0314
0.7	154	-0.182	-0.0461
0.8	118	-0.116	-0.0261
0.9	76	-0.060	-0.0126
Benzaldehyde (1) + cyclohexane (2)			
0.1	3	0.005	0.0055
0.2	27	-0.030	-0.0038
0.3	76	-0.087	-0.0234
0.4	77	-0.081	-0.0201
0.5	91	-0.093	-0.0255
0.6	76	-0.070	-0.0171
0.7	62	-0.055	-0.0126
0.8	75	-0.060	-0.0180
0.9	41	-0.032	-0.0099

$$U^{\text{id}} = (\sum_i \phi_i \rho_i^0) \kappa_S^{\text{id}})^{-1/2} \quad (4)$$

$$L_f^{\text{id}} = \sum_i \phi_i L_{f,i} \quad (5)$$

in which V_i^0 , ρ_i^0 , α_i^0 , $C_{p,i}^0$, and $L_{f,i}$ are, respectively, the molar volume, density, isobaric thermal expansion coefficient, molar isobaric heat capacity, and intermolecular free length of pure component i , and $\phi_i = x_i V_i / \sum x_j V_j$ is the volume fraction of i in the mixtures calculated in terms of the unmixed pure components. The excess properties κ_S^E , U^E and L_f^E calculated from Eqs. 2 to 5 are reported in Table 2, for comparison with $\Delta\kappa_S$, ΔU and ΔL_f and to show the difference between the two sets of quantities. It is obvious that both sets of parameters have significant differences; therefore, the estimation of intermolecular interactions from deviations calculated by Eq. 1 seems to be unjustified and the conclusions are rather misleading.

Second, the interpretation provided throughout their paper [1] seems to be totally out of place, unrealistic and misleading. The interpretation by the authors that “the decrease of κ_S and L_f , and also the increase in R_a and Z , with increasing mole fraction of benzaldehyde in both liquid systems indicates the presence of molecular interactions between unlike molecules” does not seem right. It is well known that when two liquid components having largely different properties are mixed, significant variation in the properties is bound to occur, either a decrease or an increase, depending upon the properties of the individ-

Table 3 Comparison of the reported experimental values of the ultrasonic velocity and density of pure liquids with literature values at 303.15 K

Liquid	Ultrasonic velocity (U), $\text{m}\cdot\text{s}^{-1}$		Density (ρ), $\text{kg}\cdot\text{m}^{-3}$	
	Reference [1]	Literature	Reference [1]	Literature
Benzaldehyde	1464	1447 [6]	1049	1035.6 [7]
Hexane	1075	1053.7 [8]	675	650.56 [10]
		1054 [9]		650.18 [7]
Cyclohexane	1202	1229.1 [11]	790	769.04 [10]
		1230 [12]		768.45 [7]

ual components. In this particular case, when benzaldehyde having a low compressibility ($0.445 \times 10^{-9} \text{ m}^2\cdot\text{N}^{-1}$ or 445 TPa^{-1}) is added to a component having a higher compressibility, cyclohexane ($0.876 \times 10^{-9} \text{ m}^2\cdot\text{N}^{-1}$ or 876 TPa^{-1}) or hexane ($1.283 \times 10^{-9} \text{ m}^2\cdot\text{N}^{-1}$ or 1283 TPa^{-1}), then the values of κ_S of the mixture should decrease. To analyze the molecular interactions, it is important to know the size of these decreases. In other words, how large is the deviation from its reference state (ideal values from Eq. 2, combined with Eqs. 3–5) or from mole fraction or volume fraction averages. Because the calculation of their so-called excess properties through Eq. 6 of the original paper [1] (in fact these are normally called deviations from mole fraction additivity or averages) was incorrect, the discussion and interpretation by the authors is incorrect.

Also, it is worth pointing out that authors made statements about weak and strong dipole–dipole interaction and H-bonding [1]. The authors should remember that neither cyclohexane nor hexane has a dipole moment. Similarly, there is no hydrogen bond in benzaldehyde molecules, and neither cyclohexane nor hexane can form H-bonds with benzaldehyde. In fact, it is dispersion interactions and/or breaking of dipolar order in benzaldehyde that is responsible for most of the interactions in these types of mixtures. In that case, the values of κ_S^E should have been positive.

Third, the reported ultrasonic velocity and density data of the pure components (see Table 3) are quite different from reliable literature data. The values of U differ by 17 to $28 \text{ m}\cdot\text{s}^{-1}$ and densities by 13 to $24 \text{ kg}\cdot\text{m}^{-3}$, which will add substantial uncertainty to the final calculated results.

Fourth, the authors have stated [1] that the use of their Eqs. 7 to 9 provide theoretical estimates of the ultrasonic velocity of mixtures. In fact, all three relations are empirical rather than theoretical. Therefore, it will be more correct to write that the ultrasonic velocity was estimated from empirical relations.

Finally, it is proper to emphasize here that, once the correct expression for calculating the ideal isentropic compressibility is known, one should use only that expression to derive the excess isentropic compressibility and hence the correct excess ultrasonic velocity, rather than using the approximate mole fraction or volume fraction averages. Recently, many authors [13–18] have continued to predict molecular interactions from the deviations calculated using mole fraction or volume fraction averages rather than using the correct equations described herein.

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