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# Ultrasonic investigations of the water, carbontetrachloride and methanol ternary mixture at its miscibility point

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**Abstract** : Using experimentally measured ultrasound velocity and density data, an investigation in the ultrasound response of a ternary mixture (of water, carbontetrachloride and methanol) is done, at its miscibility point Several acoustical and thermodynamical parameters of the mixture are evaluated at 308 K. The physico-chemical behaviour of the ternary system is explained on the basis of obtained results.

**Keywords** : Ultrasound velocity, thermodynamical parameters, miscibility point.

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The non-linear behaviour of acoustical parameters in multicomponent liquid systems is related to the nature and strength of the interactions between molecules. To understand these interactions, some acoustical parameters have been used by different researchers [1–3]. These include molar sound velocity, molar adiabatic compressibility, acoustic impedance, free length, ralative association, free volume, available volume and Van der Waals constant. Excess values of these parameters give an idea of the complex formation. All these parameters and their excess values are evaluated here for water-carbon tetrachloride-methanol ternary mixture at 308 K. The measured ultrasound velocity ($u$) data (at 5 MHZ) and densities of the mixture reported by Krishnamoorthy *et al* [4,5] have been used in these calculations.

The expressions for the various parameters, such as the adiabatic compressibility ($K_s$), molar sound velocity ($R$), molar adiabatic compressibility ($W$), acoustic impedance ($Z$), intermolecular free lengths ($L_f$, thermodynamic approach; $L_f'$, Jacobson's approach),

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relative association ($RA$), available volume ($V_a$), free volume ($V_f$) and van der Waals constant ($b$), are taken from literature [6–8]. The excess values of the acoustical and thermodynamical parameters ($P$) studied here are obtained from $\Delta P = P_{am} - P_{im} = P_{am} - \sum x_i P_i$ where $\Delta P$ is excess value, $P_{am}$ is the experimental value and $P_{im}$ is the ideal mixture value of the parameter ($P$). Here, $x_i$ and $P_i$ are the molar fraction and parameter ($P$)'s value for $i$-th component of the mixture.

**Table 1.** Some acoustic parameters of $H_2O(x_1) + CCl_4(x_2) + CH_3OH(x_3)$ ternary mixture at 308 K (S.I. Units).

| $x_1$ | $x_2$ | $u$ | $V \times 10^6$ | $K_s \times 10^{11}$ | $R \times 10^6$ | $W \times 10^6$ | $Z \times 10^{-3}$ | $b \times 10^6$ |
|---|---|---|---|---|---|---|---|---|
| | | | | Pure Liquids | | | | |
| 1.0000 | 0.0000 | 1469 | 18.12 | 46.62 | 206 | 390 | 1460 | 15.41 |
| 0.0000 | 1.0000 | 849 | 96.86 | 88.48 | 917 | 1907 | 1331 | 84.23 |
| 0.0000 | 0.0000 | 1051 | 40.75 | 115.18 | 414 | 771 | 826 | 34.60 |
| | | | | Top Layer | | | | |
| 0.7095 | 0.1327 | 1481 | 40 07 | 48.09 | 457 | 856 | 1404 | 34.61 |
| 0.6128 | 0.1146 | 1436 | 40.28 | 52.54 | 454 | 850 | 1325 | 34 72 |
| 0.4816 | 0.0901 | 1356 | 42.24 | 63.68 | 468 | 867 | 1158 | 34.29 |
| 0.3966 | 0.0742 | 1215 | 38.86 | 74 44 | 415 | 780 | 1106 | 33.22 |
| | | | | Bottom Layer | | | | |
| 0.7095 | 0.1327 | 850.6 | 24.40 | 88.77 | 226 | 478 | 1324 | 20 64 |
| 0.6128 | 0.1146 | 842.6 | 23.99 | 90.87 | 227 | 468 | 1306 | 20.28 |
| 0.4816 | 0.0901 | 853.3 | 24.41 | 92.92 | 231 | 475 | 1261 | 20.64 |
| 0.3966 | 0.0742 | 866.0 | 22.89 | 86.30 | 218 | 450 | 1338 | 19.35 |
| | | | | Ternary Mixture | | | | |
| 0.4160 | 0.0255 | 1294 | 32.27 | 65.88 | 352 | 661 | 1173 | 27.55 |
| 0.3639 | 0.0401 | 1215 | 34.97 | 73.65 | 373 | 705 | 1118 | 29.84 |
| 0.3000 | 0.0551 | 1116 | 36.68 | 85.53 | 380 | 724 | 1048 | 31.25 |
| 0.2655 | 0.0813 | 1078 | 39.00 | 88.22 | 400 | 767 | 1051 | 33.24 |
| 0.2158 | 0.1189 | 1065 | 42.50 | 86.61 | 434 | 838 | 1081 | 36.28 |

$x_3 = 1.000 - (x_1 + x_2)$

**Table 2.** Some acoustic and thermodynamic parameters of $H_2O(x_1) + CCl_4(x_2) + CH_3OH(x_3)$ mixture at 308 K (S.I. Units).

| $x_1$ | $x_2$ | $V_0 \times 10^6$ | $V_a \times 10^6$ | $L_f \times 10^{12}$ | $L_f' \times 10^{12}$ | R.A. | $\Delta V_f \times 10^6$ | $\Delta V_a \times 10^6$ | $\Delta L_f \times 10^{12}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Pure Liquids | | | | |
| 1.0000 | 0.0000 | 14.92 | 3.19 | 25.59 | 43.40 | 4.88 | 2.71 | | |
| 0.0000 | 1.0000 | 76.04 | 20.81 | 56.28 | 59.79 | 1.20 | 12.62 | | |
| 0.0000 | 0.0000 | 30.93 | 9.81 | 48.40 | 68.21 | 2.80 | 6.15 | | |

**Table 2.** *(Cont'd.)*

| $x_1$ | $x_2$ | $V_0 \times 10^6$ | $V_a \times 10^6$ | $L_f \times 10^{12}$ | $L_f' \times 10^{12}$ | R.A. | $\Delta V_f \times 10^6$ | $\Delta V_a \times 10^6$ | $\Delta L_f \times 10^{12}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Top Layer | | | | |
| 0.7095 | 0.1327 | 25.56 | 14.51 | 84.24 | 44.08 | 0.16 | 5.47 | 7.93 | 47.46 |
| 0.6128 | 0.1146 | 26.30 | 13.98 | 76.84 | 46.07 | 0.21 | 5.56 | 6.97 | 41.06 |
| 0.4816 | 0.0901 | 27.29 | 14.95 | 80.17 | 50.72 | 0.25 | 5.95 | 7.34 | 41.58 |
| 0.3966 | 0.0742 | 27.93 | 10.93 | 57.67 | 54.84 | 0.86 | 5.64 | 2.92 | 17.54 |
| | | | | | Bottom Layer | | | | |
| 0.7095 | 0.1327 | 15.57 | 8.83 | 68.78 | 59.89 | 0.66 | 3.76 | 2.25 | 43.34 |
| 0.6128 | 0.1146 | 15.31 | 8.68 | 68.40 | 60.59 | 0.70 | 3.70 | 1.66 | 36.23 |
| 0.4816 | 0.0901 | 15.58 | 7.31 | 54.94 | 61.27 | 1.25 | 3.77 | –0.31 | 21.56 |
| 0.3966 | 0.0742 | 14.61 | 8.28 | 67.34 | 59.05 | 0.67 | 3.53 | 0.28 | 1.89 |
| | | | | | Ternary Mixture | | | | |
| 0.4160 | 0.0255 | 25.43 | 6.84 | 38.47 | 51.59 | 2.41 | 4.72 | –0.49 | 3.46 |
| 0.3639 | 0.0401 | 27.33 | 7.63 | 40.88 | 54.55 | 3.12 | 5.13 | –0.34 | 3.40 |
| 0.3000 | 0.0551 | 28.63 | 8.06 | 41.84 | 58.78 | 2.77 | 5.44 | –0.38 | 2.79 |
| 0.2655 | 0.0813 | 30.34 | 8.66 | 43.24 | 59.70 | 2.63 | 5.76 | –0.29 | 2.88 |
| 0.2158 | 0.1189 | 32.85 | 9.64 | 45.69 | 59.15 | 2.17 | 6.21 | –0.05 | 3.36 |

$x_3 = 1.000 - (x_1 + x_2)$

**Table 3.** Some excess parameters of $H_2O(x_1)$ + $CCl_4(x_2)$ + $CH_3OH(x_3)$ mixture at 308 K (S.I. Units).

| $x_1$ | $x_2$ | $\Delta u$ | $\Delta d$ | $\Delta V \times 10^6$ | $\Delta K_s \times 10^{11}$ | $\Delta R \times 10^6$ | $\Delta W \times 10^6$ | $\Delta Z \times 10^{-3}$ |
|---|---|---|---|---|---|---|---|---|
| | | | | | Top Layer | | | |
| 0.7095 | 0.1327 | 160.2 | –89.37 | 7.93 | –14.90 | 123 | 207 | 60.95 |
| 0.6128 | 0.1146 | 152.0 | –80.12 | 6.97 | –17.56 | 110 | 185 | 52.83 |
| 0.4816 | 0.0901 | 121.9 | –102.63 | 7.34 | –16.07 | 108 | 180 | –18.94 |
| 0.3966 | 0.0742 | 13.2 | –16.52 | 2.92 | –11.56 | 46 | 78 | –9.43 |
| | | | | | Bottom Layer | | | |
| 0.7095 | 0.1327 | –470.2 | 519.6 | –7.74 | 25.78 | –107 | –171 | –18.65 |
| 0.6128 | 0.1146 | –441.4 | 546.9 | –9.33 | 20.77 | –118 | –197 | 33.43 |
| 0.4816 | 0.0901 | –380.8 | 521.4 | –10.50 | 13.17 | –127 | –213 | 84.21 |
| 0.3966 | 0.0742 | –335.8 | 618.5 | –13.05 | 0.30 | –151 | –252 | 222.89 |
| | | | | | Ternary Layer | | | |
| 0.4160 | 0.0255 | 74.26 | 14.03 | –0.49 | –20.09 | 11 | 20 | 79.26 |
| 0.3639 | 0.0401 | 5.91 | 16.21 | –0.34 | –17.06 | 9 | 17 | 24.40 |
| 0.3000 | 0.0551 | –49.58 | 46.97 | –0.37 | –7.64 | 1 | 5 | 3.19 |
| 0.2655 | 0.0813 | –67.35 | 76.89 | –0.29 | –6.56 | 0 | 4 | 16.14 |
| 0.2158 | 0.1189 | –52.50 | 93.90 | –0.05 | –10.64 | 5 | 13 | 60.93 |

$x_3 = 1.000 - (x_1 + x_2)$

The results obtained (in S.I. units) for the ternary mixture under study, are presented in Tables 1 to 3. In this system, water ($H_2O$) and carbontetrachloride ($CCl_4$) are the two immiscible components and methanol (which is freely miscible with each of them) is the third component. It is expected that the added methanol ($CH_3OH$) will distribute between water and carbon-tetrachloride. But, it is noted that as more and more methanol is added more $CCl_4$ is being extracted into the top layer, as is obvious from decreasing values of $u$ (Table 1, column 3). An examination of the bottom layer, indicates the presence of a single component ($CCl_4$), irrespective of the amount of methanol added. This is indicated by almost constant $u$ values for the bottom layer (Table 1, column 3). The added third component seems to modify the properties of only one layer (top layer) and the binary mixture extracts the second immiscible layer (bottom layer) into it.

It is interesting to note for the ternary system that as the mole fraction $x_2$ of the $CCl_4$ increases, the quantity of the methanol (*i.e.* $x_3$) required for homogenizing the layers, also increases till it reaches a maximum for a similar (*i.e.* maximum) mole fraction of the $CCl_4$. It is found that as $x_1$ (mole fraction of $H_2O$) is decreased such that $x_2$ is increased, the $u$ decreases (Table 1, column 3) and the $K_s$ (Table 1, column 5) increases. This is likely due to the replacement of highly associated $H_2O$ molecules (Dipole moment = 1.87 D) by unassociated molecules of $CCl_4$ (Dipole moment = 0D) and less associated molecules of $CH_3OH$ (Dipole moment = 1.70 D). The $V$, $R$, $W$, $Z$ and $b$ values vary erratically with rise in $x_3$ in the top layer (Table 1), whereas these parameters report an almost constant behaviour with such a change in bottom layer. In the ternary system, there is a regular increase in the values of $V$, $K$, $R$, $W$ and $b$, with rise in $x_3$. However, behaviour of $Z$ is opposite to that reported for $V$ and $K_s$ *etc.* for this system. This trend of variation of the acoustical parameters can be understood as follows.

Composition changes (with addition of large sized molecules of $CCl_4$ and $CH_3OH$, as compared to $H_2O$ molecules) in a ternary system, enhances the dispersion forces in it, leading to an increase in its molar volume ($V$). The increase in $V$ affects the $K_s$, $R$ and $W$. The presence of strongly hydrogen bonded molecules of $H_2O$ and $CH_3OH$ contributes to attractive interactions in the system. In the ternary system, $L_f$, $L_f'$ and $V_f$ show a steady increase in their values with rise in $CCl_4$ contents. While these parameters report an almost constant behaviour for bottom layer, their variation for top layer is erratic (Table 2). In the present ternary mixture, the relative association (RA) is found to be high (around 2.8) as compared to RA values for top and bottom layers. It points to the dominance of attractive interactions over the dispersive forces in the ternary system, as compared to the magnitude of such forces in the top and bottom layers. For the ternary mixture, the rise in $x_2$ causes expansion, increasing $V$, $K_s$, $b$, $V_a$, $V_a$, $L_f$ and $L_f'$. The $L_f$ and $L_f'$ increase due to looser packing of molecules. Obviously, the intermolecular cohesion present in the system weakens with rise in content of $CCl_4$. This trend is confirmed by the slight decrease reported in RA values for the system (Table 2). As a measure of van der Waals interactions in the system, the co-volume '$b$' is determined.

It registers a steady rise from $27.55 \times 10^{-6}$ to $36.28 \times 10^{-6}$ $m^3$/mole for the mixture whereas it reports an almost constant behaviour for top layer and bottom layer of the mixture (Table 1).

The molecules in a solution interact with each other to form new complex species making the solution non-ideal. The negative deviations from ideality of $K_s$, in the binary/ternary mixtures are mainly due to formation of complexes and molecular association by weak bonds [8–10]. However, if the deviations are positive, they may be attributed to molecular dissociation of an associated species caused by addition of a component leading to weak interactions mainly due to dispersion forces [10].

Excess molar volume ($\Delta V$), excess available volume ($\Delta V_a$), excess adiabatic compressibility ($\Delta K_s$) are negative over the entire range of compositions investigated for the ternary system. Excess density ($\Delta d$) and ($\Delta K_s$) show a similar change for top layer, while excess molar sound velocity ($\Delta R$), excess molar adiabatic compressibility ($\Delta W$), excess ultrasound velocity ($\Delta u$) and ($\Delta V$) show a similar variation for bottom layer (Table 3). From Tables 2 and 3, it is obvious that for the ternary mixture, the additivity rule is obeyed in case of $V_a$, $L_f$, $V$, $R$ and $W$ in a better way than in case with $K_s$, whereas this is not so in case of top layer and bottom layer mixtures. However, the analysis of the trend of variations of excess parameters points to the existence of only weak interactions (of the van der Waals type) due to the presence of non-polar $CCl_4$ molecules in the bottom layer, whereas relatively stronger attractive interactions exist due to the presence of hydrogen bonded molecules of $H_2O$ and $CH_3OH$ in the top layer. The behaviour of the ternary mixture $H_2O$–$CCl_4$–$CH_3OH$ is intermediate of the two extremes, in general. It is pointed out that for $H_2O$ + $CCl_4$ inhomogeneous mixture, on addition of the methanol, there is a progressive variation in the acoustic and thermodynamic response of the two layers, due to the distribution of the third component between them.

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