



Studies on intermolecular interaction on binary mixtures of methyl orange–water system: Excess molar functions of ultrasonic parameters at different concentrations and at different temperatures

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ABSTRACT

Density (ρ), viscosity (η) and ultrasonic velocity (u) of binary mixtures of methyl orange and water were measured at different concentrations and at different temperatures; several useful parameters such as excess volume, excess velocity, and excess adiabatic compressibility have been calculated. These parameters are used to explain the nature of intermolecular interactions taking place in the binary mixture. The above study is helpful in understanding the dye/solvent interaction at different concentration and temperatures.

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1. Introduction

Intermolecular interactions play a very important role in binary and ternary liquid mixtures [1,2]. They influence the arrangement, orientation and conformations of molecules in solution. Ultrasonic velocity of the liquid mixtures have been used for the qualitative determination of the degree of association in liquid mixtures [3,4]. The practical application of using mixed solvents rather than single solvents in industrial and biological processes is such that it provides a wide choice of solvents or solvent mixtures with desirable properties [5,6]. The rates of reactions and the stability of the intermediates formed depend on the intermolecular interactions of the medium. Density, viscosity and ultrasonic velocity were experimentally determined for methyl orange–water systems of different concentrations at different temperatures (see Fig. 1).

From this, ultrasonic parameters like adiabatic compressibility, intermolecular free length and apparent molar volume were calculated using standard formulae. Excess functions such as excess adiabatic compressibility, excess velocity, excess intermolecular free length, excess acoustic impedance, and excess apparent molar vol-

ume were also calculated. The values are plotted against concentration and temperature. The graphs obtained are explained on the basis of the various intermolecular interactions present in the system and how the interactions are affected by the change of temperature and concentration.

2. Experimental

Water was purified by double distillation. Solutions of methyl orange in water, of different mole percent are prepared at room temperature. All of them are allowed to attain constant temperature in a constant temperature bath, before carrying out the experiment. The densities of solutions were measured using a pycnometer of bulb capacity $8 \times 10^{-6} \text{ m}^3$ with a graduated stem with of $5 \times 10^{-8} \text{ m}^3$ divisions (Systronics India, Ltd.). The marks on the stem were calibrated using known densities of double-distilled water. The accuracy of density was found to be $\pm 0.001 \text{ g/cc}$. The viscosities of the binary mixtures were determined using an Ostwald Viscometer (Sigma Chemicals Instruments). The ultrasonic velocities of pure solvent and the binary mixtures were measured using a single crystal variable path interferometer at 2 MHz (Mittal Enterprises, New Delhi). The accuracy in ultrasonic velocity was found to be $\pm 0.05\%$.

The temperature of the test liquids was maintained to an accuracy of ± 0.02 in an electrically controlled thermostatic water bath.

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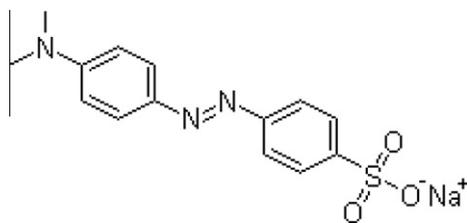


Fig. 1. Methyl orange structure. Ion–ion interaction-concentrated solution. Ion–dipole interaction-dilute solution. Ion–solvent hydrogen bonding interaction-very dilute solution. Solvent–solvent hydrogen bonding interaction in pure solvent.

From the measured density, viscosity and ultrasonic velocity u , the adiabatic compressibility, β or K_s , intermolecular free length L_f , relative association RA and acoustic impedance Z , were calculated using the following relations.

$$\beta = K_s = 1/u^2\rho \quad (1)$$

$$L_f = K/u\rho^{1/2} \quad (2)$$

$$RA = (\rho/\rho^o) \times (u^o/u)^{1/3} \quad (3)$$

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

where K is a temperature-dependent constant $(93.875 + 0.375 \times T) \times 10^{-8}$, T is the absolute temperature, Z is the acoustic impedance, K_s the adiabatic compressibility, L_f the intermolecular free length, RA is the relative association, and ρ^o , ρ , u^o , and u are the densities and ultrasonic velocities of the solvent and solution respectively. The excess functions for each of the ultrasonic parameter were calculated using the following formula.

$$E_f = E_{\text{expt}} - E_{\text{ideal}}$$

$$E_{\text{ideal}} = [xy^1 + (1-x)y^2]$$

where y^1 and y^2 are the ultrasonic parameters of pure solvent and solution respectively. The values of ρ , u , K_s , and L_f as a function of

concentration of methyl orange and temperatures (303, 308, 313, 318 K) are presented in the Table A1.

3. Results and discussion

From the variation of densities, viscosities and ultrasonic parameters with concentration and temperature, a qualitative interpretation of the intermolecular interactions in the above binary mixtures can be proposed. A decrease in the density of a solution with dilution is the expected trend [17,18]. For the system of methyl orange and water under study, there is a decrease in density in the low concentration region. From the concentration of 0.5% onwards, the decrease in density is insignificant. At the higher temperatures (313 and 318 K) and in the low concentration region, there is a sharp decrease in density. Beyond the concentration of 0.1 mol.% the density increases with concentration up to 0.5 mol.%. The sharp decrease in density at the concentration of 0.1 mol.% is also reflected in the abnormal values of all the other ultrasonic parameters. The sharp decrease in density can be explained on the basis of a sudden increase in the volume of the solution with the addition of methyl orange. Water is associated in the pure state through intermolecular hydrogen bonding. Addition of methyl orange leads to the breakdown of the hydrogen bonds, releasing the dipoles of water. As a result, the free dipoles of water interact with methyl orange molecules, forming intermolecular hydrogen bonds. Incorporation of large solute molecules in the solvent leads to an increase in the volume of solution. The increase in volume can be attributed to the ion/molecule interactions between solute and solvent which replace solvent/solvent interactions that already exists in the pure solvent. At higher concentrations, the solute–solvent interactions are slowly replaced by the solute/solute interactions.

The variation of density with temperature almost follows the expected trend of a decrease in density with an increase in temperature (Fig. 3). Deviation from ideal behavior is noticed for the solution with a concentration of 0.1 mol.%. At the higher temperature the breaking of hydrogen bonds in the solvents is facilitated. In addition to this, the inclusion of larger solute molecules in the

Table A1

Values of density, ρ , ultrasonic velocity, u , adiabatic compressibility, β , intermolecular free length, L_f of binary mixtures as a function of concentration (mol.%) at different temperatures (K).

Temperatures (K)	Concentration for various ultrasonic parameters				
	0.05	0.1	0.5	1	2
<i>Velocity (ms⁻¹)</i>					
303	1513.2	1550.4	1624.8	1542.4	1492
308	1534.4	1520.8	1600	1540.8	1518
313	1539.6	1619.2	1520.8	1547.2	1536
318	1532.8	1604	1551.2	1560	1537
Ideal at 303 K	1480.001	1480.004	1480.019	1480.096	1480.006
<i>Density (kg m⁻³)</i>					
303	1098	1097	1096	1095	1093
308	1095	1094	1093	1093	1091
313	1094	1089	1092	1091	1089
318	1091	1086	1090	1089	1087
Ideal at 303 K	997.9733	997.4672	997.86	997.73	997.998
<i>Adiabatic compressibility (kg⁻¹ ms²)</i>					
303	3.8344	3.7323	3.4562	3.9	4.1102
308	3.8789	3.9521	3.8538	3.8573	3.9776
313	3.9069	3.5024	3.9594	3.8289	3.9374
318	3.9165	3.6675	3.8127	3.7733	3.9395
Ideal at 303 K	4.5315	4.63154	4.63136	4.63134	4.63137
<i>Intermolecular free length (10⁻¹¹ m)</i>					
303	2.0719	2.1472	1.9543	1.7256	2.1312
308	2.1073	2.1272	2.0189	2.1015	2.134
313	2.1519	2.0376	2.1664	2.1304	2.1479
318	2.18748	2.0952	2.1625	2.1513	2.1855
Ideal at 303 K	2.2483	2.24827	2.24835	2.24825	2.24832

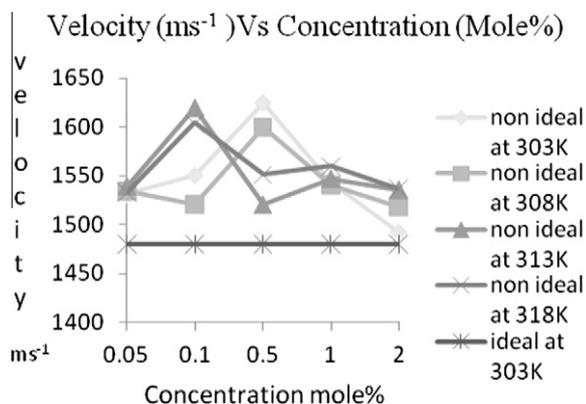


Fig. 2. Velocity (ms^{-1}) Vs various concentration (mol.%) and different temperatures (K) for methyl orange–water system.

liquid structure also enhances the volume of the solution. This is reflected in a decrease in density. At this stage, an increase in concentration allows for a closer approach of solvent and solute molecules, and stronger association between solute and solvent molecules [2,4]. This leads to a decrease in the volume and an increase in the density of the solution. Beyond the concentration of 0.5 mol.%, a decrease in density is observed with an increase in concentration. This can be explained by an increase in weaker ion/dipole solvent/solute interactions.

The ultrasonic velocity is found to be lowest at very low concentration and the increase in ultrasonic velocity with increase in concentration is an expected trend [19]. Beginning with a concentration of 0.1 mol.%, there is sharp increase in velocity, reaching a maximum and then followed by a decrease (Fig. 2). The increase of ultrasonic velocity from 0.1 mol.% concentration indicates the formation of strong hydrogen bonds of the solvent molecules with the larger dye molecules. An opposite trend is observed in the adiabatic compressibility (Fig. 4). A similar explanation for the decrease in compressibility with concentration of the liquid mixtures has been suggested by Fork and Moore [7]. The maximum in ultrasonic velocity is observed at 0.5 mol.% concentration and at low temperatures (Fig. 2). The decrease in ultrasonic velocity indicates that the interaction between ion (ionized dye molecule) and solvent is becoming less dominant. This is due to the replacement of strong intermolecular attraction between solvent molecules by the weaker intermolecular interactions. At higher temperature this behavior occurs at the low concentration of 0.1 mol.%.

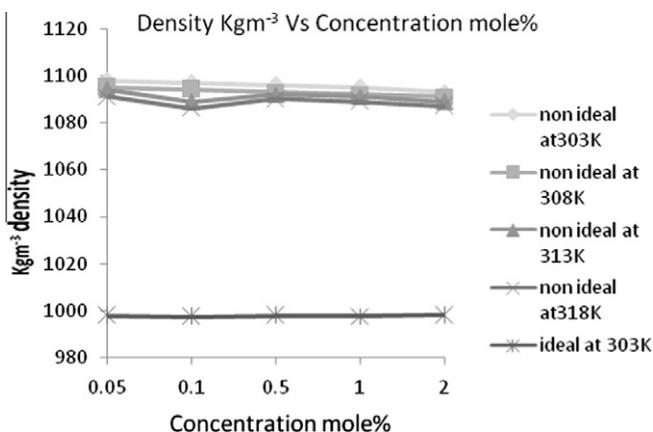


Fig. 3. Density (kg m^{-3}) Vs various concentration (mol.%) and different temperatures (K) for methyl orange–water system.

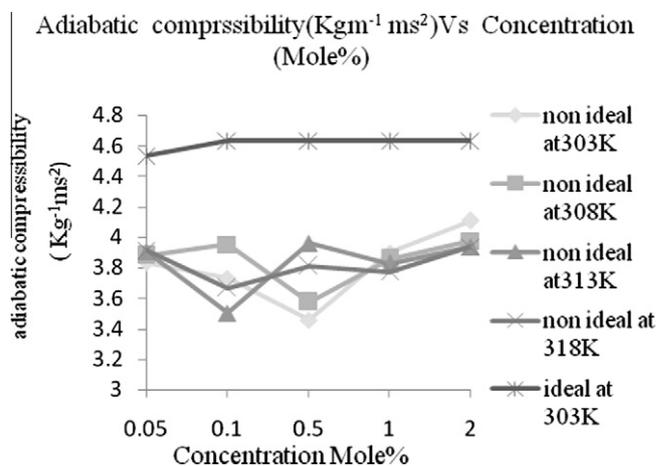


Fig. 4. Adiabatic compressibility ($\text{kg m}^{-1} \text{ms}^{-2}$) Vs various concentration (mol.%) and different temperatures (K) for methyl orange–water system.

This indicates that the solvent–solvent interaction is replaced by solute–solvent interaction even at the low concentration of 0.1 mol.% at high temperature. Generally, adiabatic compressibility decreases with increase in concentration [19]. A high value of adiabatic compressibility for the low concentration (0.1 mol.%) indicates a positive ion–solvent interaction, and at the same time the network of hydrogen bonding formed by the solvent molecules is not much disturbed. The decrease in adiabatic compressibility with further increase in concentration indicates the breakdown of the network formed by the solvent molecules. Adiabatic compressibility reaches a minimum at 0.5 mol.% concentration. Beyond this concentration there is an increase in the adiabatic compressibility with an increase in concentration. This indicates that the ion/solvent interaction is replaced by comparatively stronger interaction between solute molecules, releasing the solvent molecules. Further increase in adiabatic compressibility indicates a change in the conformation/orientation of the solute molecules in solution, leading to weaker inter-molecular interaction. This is attributed to the steric requirement of arranging an increasing number of larger molecules. In this situation, there steric factor takes predominance over intermolecular interactions. The same trend is observed for the system at higher temperatures (313 and 318 K). The minimum observed at 0.5 mol.% (at 303 and 308 K) is shifted at 0.1 mol.% to higher temperatures (313 and 318 K). An increase of temperature leads to the breakdown of intermolecular hydrogen bonds between solvent molecules. The changes in acoustic impedance are expected to be similar to those of ultrasonic velocity. At temperatures (303 and 308 K) there is a maximum at 0.5 mol.% and a minimum at 1 mol.%. The maximum is shifted from 0.5 to 0.1 mol.% at higher temperatures (313 and 318 K). An increase in adiabatic compressibility indicates a change in the orientation of the solvent molecules around the ionized dye molecule, which may be due to the influence of electrostatic fields around the ionized solute molecules. This means that the solution becomes less compressible. It also indicates the associating tendency of the dye molecules in solution.

Intermolecular free length and adiabatic compressibility are directly related to each other [8,9]. Hence, the adiabatic compressibility increases with an increase in intermolecular free length. The stronger intermolecular interactions results in a tightly packed liquid structure, and, as such, the adiabatic compressibility and intermolecular free length decrease. The formation of weaker intermolecular interaction leads to an increase in adiabatic compressibility and intermolecular free length. The intermolecular free length and ultrasonic velocity are inversely related to each other

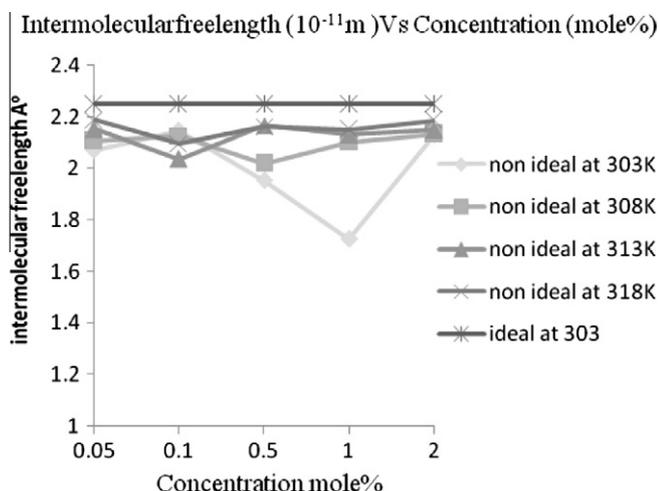


Fig. 5. Intermolecular free length (\AA) Vs various concentration (mol.%) and different temperatures (K) for methyl orange–water system.

[17,18]. The ultrasonic velocity increases with a decrease in the intermolecular free length. There is an initial increase in intermolecular free length in the low concentration region, followed by a steady decrease with an increase of concentration (Fig. 5). The decrease of intermolecular free length with increase in concentration is a normal trend [20]. But the initial rise in intermolecular free length indicates that weak forces are acting between solute and solvent molecules, forming loosely held aggregates. The decrease in free length can be attributed to an increase in the stronger forces of cohesion between solute and solvent. The initial increase of free length with an increase in molar concentration shows the reduction in the degree of association among solvent molecules. This is due to the loss of dipolar association; breaking up of hydrogen bonds and differences in the size and shapes of molecules in the liquid mixtures [13,14].

The behavior at temperatures 303 and 308 K resemble each other, while the behavior at 313 K resembles that at 318 K. The relative association, RA, is directly proportional to $\rho/V^{1/3}$. This is influenced by two factors:

- (i) The breaking up of solvent/solvent interaction on addition of solute indicates higher value of RA.
- (ii) Solvation of solute indicates a lower value of RA^{*10} .

Relative association is found to have an initial minimum value at 0.5 mol.% for all temperatures 303 and 308 K. Beyond this concentration, the RA values increases, reaching a maximum at 1 mol.%. The maxima and minima are shifted to low concentration regions of 0.5 and 0 mol.%, respectively, for higher temperatures 313 and 318 K. Further, the addition of methyl orange does not affect the existing intermolecular interactions significantly. This trend can be explained in that at low concentration, ionization and formation of ions from methyl orange is highly favored, with the result being that the solvent/solvent interactions break down to give way to solvent/solute (ionized dye) interactions. In the concentration range of 0.1–0.5 mol.%, there is a sharp decrease in apparent molar volume as the concentration increases. This clearly shows that within the concentration range a significant solute–solvent interaction is taking place. Beyond this concentration range, the decrease in molar volume is not very significant.

The strength of interaction between component molecules is well reflected in deviations observed in K_s , ρ , u , and L_f from the expected trend. The excess parameters are found to be more sensitive towards intermolecular interactions in the binary mixture.

4. Conclusions

In water, molecules are held together by comparatively strong hydrogen bonds forming a network. Water, being a polar molecule, is capable of taking part in dipole–dipole, ion–dipole and intermolecular hydrogen bonding interactions with the solute molecules, which are being slowly replaced by solvent–solute interaction. This leads to solvation of the solute particles, resulting in an increase in volume and a decrease in the density of the mixture. Increasing the temperature results in an increase in the total volume of solution, because of the weakening of intermolecular interactions. Due to solvation effects, the particles in solution become larger in size. The study of ultrasonic parameters and excess functions for the binary mixture of methyl orange and water at various concentrations and temperatures indicate that there are intermolecular interactions such as dipole–dipole, ion–dipole and hydrogen bonding between the solute and solvent. The type and the magnitude of interaction depend on the concentration and temperature.

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Appendix A. Excess functions

An ideal solution should be considered as non-associated and for an ideal mixture the values of excess property is zero. For non-ideal mixtures, the difference between experimental values and the ideal values is significant. Excess functions were calculated using the general formula [16]. For ideal binary mixtures:

$$Y^{\text{Exc}} = Y^{\text{Exp}} - Y^{\text{I}} = 0$$

$$Y^{\text{I}} = Y^{\text{Exp}}$$

In general for non-ideal mixtures

$$Y^{\text{Exc}} = Y^{\text{Exp}} - Y^{\text{I}}$$

$$Y^{\text{I}} = (1 - x)Y_o + (x)Y_s$$

$$Y^{\text{Exc}} = \text{Excess function}$$

$$Y^{\text{Exp}} = \text{Experimental value}$$

$$Y^{\text{I}} = \text{Ideal value}$$

$$x = \text{Mole fraction of solute}$$

$$Y_o = \text{Value for pure solvent}$$

$$Y_s = \text{Value for solution}$$

For non-ideal mixtures, depending upon the magnitude and type of intermolecular interactions or changes in concentration and orientation of solute molecules in solution, the magnitude and the sign of the excess values also change.

Excess functions are calculated by following the literature procedures reported [9–12]. The negative values of excess adiabatic compressibility and excess inter molecular free length, and a positive excess velocity suggest that either a strong intermolecular interaction or a change in conformation or orientation of molecules taking place in solution, resulting in the formation of a more compact structure due to hydrogen bonding between unlike molecules.

The positive values of excess adiabatic compressibility, excess intermolecular free length, and negative excess velocity, indicate weaker interactions between solute and solvent molecules, resulting from the disruption of molecular association. When excess volumes are negative for all concentrations, the existence of interactions between solute and solvent molecules is apparent. A positive excess acoustic impedance value indicates that over the concentration range of 0.1–0.5 mol.% significant interaction between solute and solvent is present. The negative excess adiabatic compressibility and excess intermolecular free length are attributed to the presence of intermolecular interaction between solute and solvent. This is especially true for solutions of concentration 0.1 and 0.5 mol.% at 303 and 308 K and, for the low concentration region (0.1 mol.%) the same trend is observed at high temperatures (313 and 318 K). The rate of disruption of intermolecular interaction between solvent molecules is increased as the temperature is increased. This results in an increase in the negative excess volume and a decrease in the excess density of the solution. At a concentration of 0.5 mol.%, a minimum is observed for excess volume and maximum for excess density. This indicates that solvent–solvent interactions are replaced by solvent–solute interactions. Thus, the positive excess velocity, acoustic impedance, and negative excess K_s and L_f may be attributed to specific, strong interactions like hydrogen bonding and dipole–dipole interactions, while the negative deviations may be ascribed to weak dispersion forces in the system. Oswal and Desaihs [15,16] attributed the positive excess of K_s and L_f values to the large size of the solute molecules and

weaker cohesive forces between unlike components of the solution, as in the present system.

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