Study of intermolecular interactions in binary mixtures of 2′-chloro-4-methoxy-3-nitro benzil in various solvents and at different concentrations by the measurement of acoustic properties

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ABSTRACT

Density (ρ), ultrasonic velocity (u), adiabatic compressibility (β), apparent molar volume ($\text{\O}$), acoustic impedance (Z), intermolecular free length (L_f), relative association (RA) of binary mixtures of 2′-chloro-4-methoxy-3-nitro benzil (abbreviated as 2CBe) in ethanol, acetonitrile, chloroform, dioxane and benzene were measured at different concentrations at 298 K. Several useful parameters such as excess density, excess ultrasonic velocity, excess adiabatic compressibility, excess apparent molar volume, excess acoustic impedance and excess intermolecular free length have been calculated. These parameters are used to explain the nature of intermolecular interactions taking place in the binary mixture. The above study is useful in understanding the solute – solvent interactions occurring in different concentrations at room temperature.

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 rate 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 2′-chloro-4-methoxy-3-nitro benzil with various solvents of different concentration at room temperature.

From this, ultrasonic parameters like adiabatic compressibility, apparent molar volume, acoustic impedance, intermolecular free length were calculated using standard formulae [7]. Excess functions such as excess density, excess viscosity, excess ultrasonic velocity, excess adiabatic compressibility, excess apparent molar volume, excess acoustic impedance and excess intermolecular free length were also calculated. The values are plotted against concentration and ultrasonic parameter at 298 K. 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 nature of solvents at different concentrations.

2. Experimental

2CBe was synthesised in two steps by crossed benzoin condensation followed by oxidation with conc.HNO₃. The structure of the compound was studied by IR, PMR, CMR and mass spectra. The molecular conformation was confirmed by single crystal XRD studies (Fig. 1). The crystal structure of the compound 2CBe was also published [8]. Solvents like ethanol, acetonitrile, chloroform, benzene and 1,4-dioxane (S.D. Fine, India, AR) were dried over molecular sieves. All the binary mixtures were prepared by mass in a dry box and were kept in special air tight bottles. Solutions of 2′-chloro-4-methoxy-3-nitro benzil in the concentration range of 0.00125–0.018 mol percent with different solvents were prepared at room temperature. The densities of pure liquids and binary mixtures were measured using a simple capillary pycnometer of bulb capacity 8×10^{-6} m³ with a graduated stem width of 5×10^{-8} m³ divisions (Systronies India Ltd.). The marks on the capillary were calibrated using known densities of double distilled water. The accuracy of the density measurement was found to be ±0.001 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

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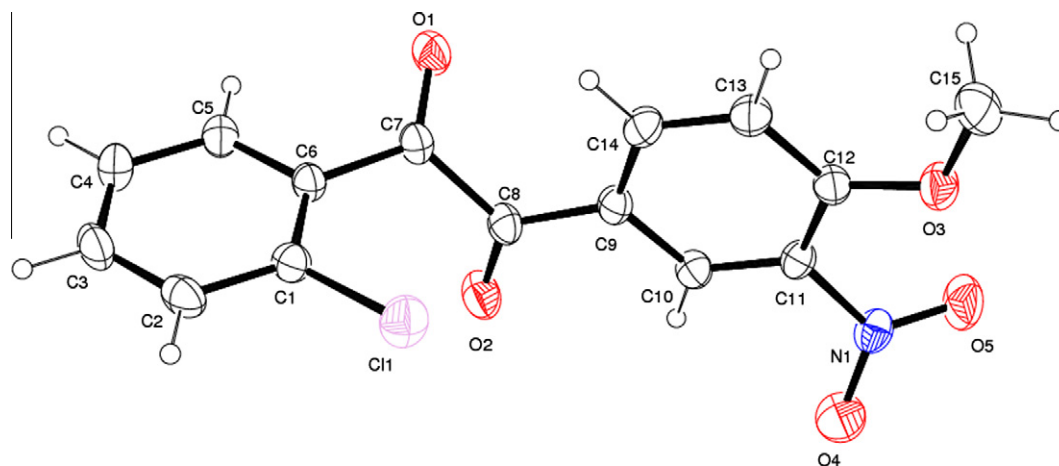   E-mail address: nithyaranju@gmail.com (G. Nithya).

Fig. 1. Single XRD of 2'-chloro-4-methoxy-3-nitro benzil.

was found to be +0.05%. The temperature of the test liquids and their binary mixtures was maintained to an accuracy of ±0.02 in an electrically controlled thermostatic water bath.

From the measured values of density ρ, viscosity η and ultrasonic velocity U, the adiabatic compressibility β or K_s, intermolecular free length L_f, relative association RA and acoustic impedance Z, have been calculated using the following standard relations (9–11).

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

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

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

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

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 ^{o}, , 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:

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

$$E_{ideal} = [(x)y1 + (1-x)y2]$$

where, $y1$ and $y2$ are the ultrasonic parameters of pure solvent and solution respectively. The values of , u, K_s, and L_f as a function of mole fraction x of various solvents (ethanol, acetonitrile, chloroform, benzene, dioxane) at 298 K are presented in the Table 1.

3. Result and discussion

From the variation of densities, viscosities and ultrasonic parameters with different solvents and concentration, a qualitative interpretation of the intermolecular interactions in the above binary mixtures can be proposed. A decrease in the density of the solution with dilution is the expected trend [9,10]. The ideal graph for all solvents are in the same trend. For the system of 2'-chloro-4-methoxy-3-nitro benzil with highly polar solvents like ethanol and acetonitrile there is an initial steep decrease in the density (Fig. 2) in the concentration range 0.005625–0.0025 mol%. This can be attributed to the breaking of intermolecular interactions between the solvent molecules by the addition of the solute which reaches

a minimum. Beyond this point there is an increase in the density with concentration 0.0025 mol%, which can be attributed to the formation of clusters of the solute molecules with solvent molecules. An increase in the concentration allows for a closer approach of solvent and solute molecules and stronger association between solute and solvent molecules [2,4]. This leads to the decrease in the volume and increase in the density of the solution. Beyond the concentration 0.005 mol%, a decrease in density is observed with an increase in concentration. This can be explained by an increase in induced dipole solvent/solute interactions. For the non polar solvents there is a decrease in density with increase in concentration due to the increase in solute solvent interactions. At lower concentration increase in density can be attributed to the ionic interactions between solute and solvent which replace solvent–solvent interactions that already exist in the pure solvent. At higher concentrations the solute–solvent interactions are slowly replaced by the solute–solute interactions.

The ultrasonic velocity is found to be the lowest at very low concentration and the increase in ultrasonic velocity with increase in concentration is the expected trend [11]. For polar solvents there is a sharp increase in velocity, reaching a maximum followed by a decrease. The increase in ultrasonic velocity indicates formation of induced dipole interaction (Fig. 3). An opposite trend is observed in the adiabatic compressibility. A similar explanation for the decrease in compressibility with concentration of the liquid mixtures has been suggested by Fok and Moore [12]. The decrease in ultrasonic velocity indicates that the interaction between ion and solvent is becoming less dominant. This is due to the replacement of stronger intermolecular interactions between solvent molecules by the weaker intermolecular interactions. For non polar solvents there is an increase in velocity by increasing the concentration due to strong solvent solute interactions.

The adiabatic compressibility generally decreases with increase in concentration [11]. A high value of adiabatic compressibility for low concentration 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 (Fig. 4). 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 0.009 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 of the solute molecules in

Table 1

Values of density, ρ; ultrasonic velocity, u; adiabatic compressibility, β; intermolecular freelength, L_f; relative association, RA; and excess functions of binary mixtures as a function of concentration (mole percent) using various solvents.

Solvents	Concentration for various ultrasonic parameters					
	Velocity ms^{-1}					
Non-ideal (NI)	0.000562	0.001125	0.00225	0.0045	0.09	0.018
Ethanol	1392	1211.1	1089.6	1398.4	1292.8	
Chloroform	1404.1	1036.8	1043.2	971.2	1249.6	985.6
Acetonitrile	1233.6	1260.8	1312	1232	1280	1257.6
Benzene	1331.2	1281.6	1248	1268.8	1273.6	1305.6
1,4-dioxane	1350.4	1480	1203.2	1328	1321.6	1138
Non-ideal (NI)	*Density kg m^{-3}*					
Ethanol	767	667	768	773	772	
Chloroform	1440	1443	1445	1455	1453	1447
Acetonitrile	762	761	758	761	760	761
Benzene	864	858	864	858	868	860
1,4-dioxane	1000	1001	1000	1016	1022	1025
Non-ideal (NI)	*Adiabatic compressibility kg^{-1}ms^2*					
Ethanol	6.7286	10.2198	10.9674	6.6154	7.7503	
Chloroform	3.5224	6.4467	6.3591	7.2865	4.4075	7.1142
Acetonitrile	8.6237	8.2665	7.6641	8.6575	8.0309	8.3086
Benzene	6.5313	7.0959	7.4311	7.2397	7.1025	6.8215
1,4-dioxane	5.4837	4.5608	6.9075	5.5809	5.6020	7.5334
Non-ideal (NI)	*Intermolecular freelength A^0*					
Ethanol	5.3338	6.5735	6.8097	5.2887	5.7244	
Chloroform	3.8591	5.2209	5.1853	5.5505	4.3169	5.4845
Acetonitrile	6.0384	5.9120	6.6925	6.0502	5.8271	5.9270
Benzene	5.2550	5.4774	5.6053	5.5327	5.4800	5.3705
1,4-dioxane	4.8151	4.3913	5.4042	4.8577	4.8668	5.6438
Non-ideal(NI)	*Relative association (RA)*					
Ethanol	0.85249	0.77654	0.92622	0.85785	0.87946	
Chloroform	0.87985	0.97547	0.97483	1.00524	0.92297	0.99483
Acetonitrile	1.01158	1.00292	0.98580	1.01069	0.99658	1.00378
Benzene	0.99816	1.00385	1.01987	1.00722	1.01768	1.00000
1,4-dioxane	0.98676	0.95802	1.02546	1.00815	1.01574	1.07080
Excess velocity						
Ethanol	292.2047	112.8571	−5.6944	305.5139	209.7306	
Chloroform	440.3054	73.7220	83.3723	18.9047	302.9520	72.4298
Acetonitrile	−16.8550	11.8226	65.7826	−7.7188	51.8909	52.3799
Benzene	25.8609	−23.4575	−56.4881	−34.6120	−27.6467	8.4706
1,4-dioxane	−11.7200	120.0469	−148.8048	−15.3045	−1.2651	−133.45
Excess density						
Ethanol	−63.8891	−162.5264	−59.5638	−50.2209	−42.5970	
Chloroform	2.6911	5.3654	10.6756	21.0485	41.5452	83.0922
Acetonitrile	−4.0854	5.8307	4.6672	11.2702	17.4202	32.2616
Benzene	4.1745	−1.6483	4.6984	−0.5949	10.7732	5.5796
1,4-dioxane	−14.9907	−11.9930	−9.0092	14.6130	35.6030	67.1758
Excess adiabatic compressibility						
Ethanol	−3.1739	0.3248	1.0925	−3.2382	−1.9326	
Chloroform	−3.8666	−0.9357	−0.9883	−0.0129	−2.7014	0.1372
Acetonitrile	0.2063	−0.1400	−0.7187	0.3092	−0.2277	0.2019
Benzene	−0.2888	0.2770	0.6146	0.4286	0.3022	0.0442
1,4-dioxane	0.2147	−0.6947	1.6596	0.3784	0.4730	2.4319
Excess intermolecular free length						
Ethanol	−1.13364	0.11242	−0.36321	−1.11267	−0.61145	
Chloroform	−1.72458	−0.35424	−0.36911	0.03598	−1.08155	0.20809
Acetonitrile	0.07644	−0.04139	−0.24650	0.13775	−0.02531	0.18332
Benzene	−0.11442	0.10904	0.23899	0.17068	0.12662	0.03484
1,4-dioxane	0.09980	−0.31338	0.71115	0.20381	0.28105	1.14264
Excess acoustic impedance						
Ethanol	0.15274	−0.10545	−0.07412	0.17249	0.09844	
Chloroform	0.62688	0.10446	0.12047	0.03550	0.44747	0.10652
Acetonitrile	−0.00659	0.01397	0.05110	−0.00096	0.04268	0.04449
Benzene	−0.000005	−0.02275	−0.04359	−0.03230	−0.01362	0.00728
1,4-dioxane	−0.03483	0.09849	−0.17264	−0.01687	0.00577	−0.1196

solution, leading to weaker intermolecular interaction. This is attributed to the steric requirement of arranging an increasing number of larger molecules. In this situation, the steric factor takes predominance over intermolecular interactions.

Intermolecular free length and adiabatic compressibility are directly related to each other [13,14]. Hence, the adiabatic compressibility increases with an increase in intermolecular free length (Fig. 5). The stronger intermolecular interactions results in a tightly packed liquid structure, and, as such, the adiabatic compressibility and intermolecular free length decreases. The formation of weaker intermolecular interaction leads to an increase in adiabatic compressibility and intermolecular free length. The intermolecular free
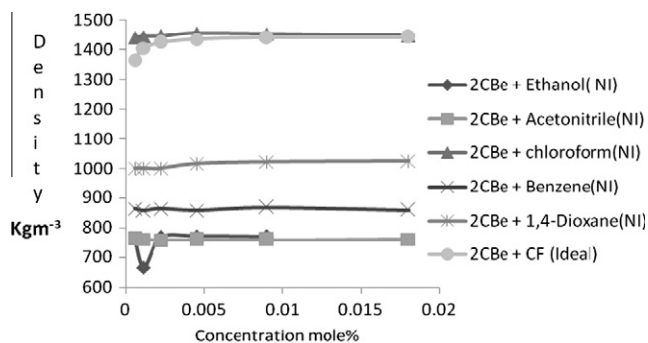
Fig. 2. Density (kg m^{-3}) vs. concentration (mol%). NI: non-ideal; CF: chloroform; 2CBe: 2′-chloro-4-methoxy-3-nitro benzil.

Fig. 3. Velocity (ms^{-1}) vs. concentration (mol%). NI: non-ideal; AN: acetonitrile; CF: chloroform; 2CBe: 2′-chloro-4-methoxy-3-nitro benzil.
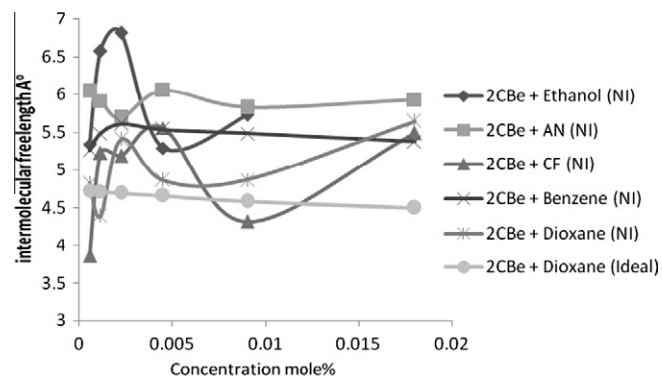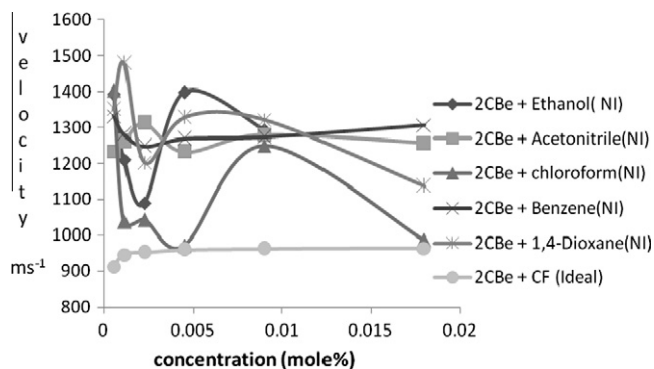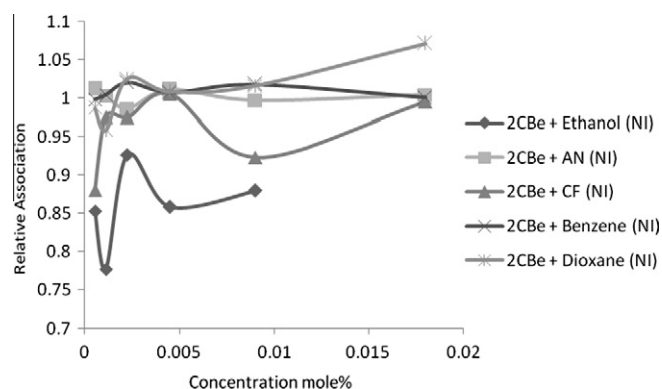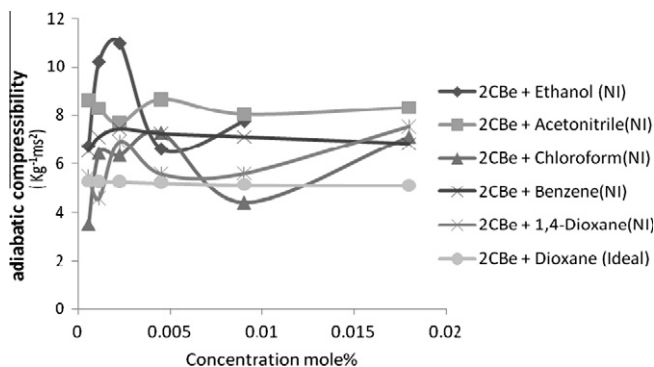

Fig. 4. Adiabatic compressibility (kg^{-1} ms^2) vs. concentration (mol%). NI: non-ideal; AN: acetonitrile; CF: chloroform; 2CBe: 2′-chloro-4-methoxy-3-nitro benzil.

Fig. 5. Intermolecular freelength (10^{-11} m) vs. concentration (mol%). NI: non-ideal; AN: acetonitrile; CF: chloroform; 2CBe: 2′-chloro-4-methoxy-3-nitro benzil.

Fig. 6. Relative association vs. concentration (mol%). NI: non-ideal; AN: acetonitrile; CF: chloroform; 2CBe: 2′-chloro-4-methoxy-3-nitro benzil.

association, breaking up of hydrogen bonds and differences in the size and shapes of molecules in the liquid mixtures [16,17].

The relative association, RA, is directly proportional to $\rho_u^{1/3}$. 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 0.001125 mol% for polar solvent (Fig. 6). Beyond this concentration, the RA values increases, reaching a maximum at 0.018 mol% The maxima and minima are shifted to low concentration regions of 0.018 and 0.001125 mol%, respectively. Further, the addition of 2CBe does not affect the existing intermolecular interactions significantly. This trend can be explained that at low concentration, the solvent/solvent interactions break down to give way to solvent/solute (Fig. 8) interactions. In the concentration range of 0.0025–0.009 mol%., there is a sharp decrease in apparent molar volume for polar solvent 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. As the polarity of the solvent decreases, there is a slight increase in apparent molar volume from concentration 0.009 mol%. This is explained as increase in concentration allows for close approach of solvent and solute molecules and stronger association between solute and solvent molecules. This leads to decrease in volume and an increase in the density of the solution.
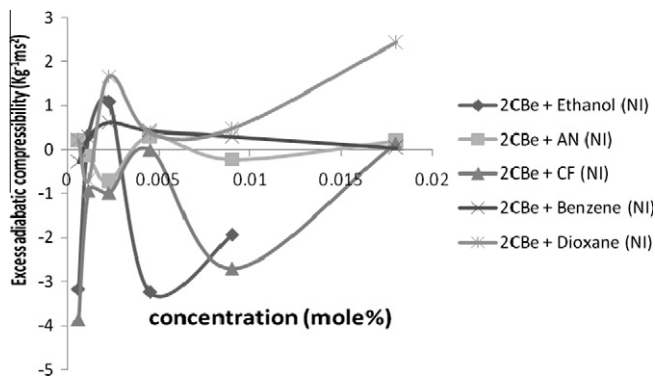
length and ultrasonic velocity are inversely related to each other [9,10]. The ultrasonic velocity increases with a decrease in the intermolecular free length. There is an initial increase in intermolecular free length in the low concentration region, followed by a steady decrease with an increase of concentration. The decrease of intermolecular free length with increase in concentration is a normal trend [15]. 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

Fig. 7. Excess adiabatic compressibility (kg^{-1} ms^2) vs. concentration (mol%). AN: acetonitrile; CF: chloroform; 2CBe: 2′-chloro-4-methoxy-3-nitro benzil.
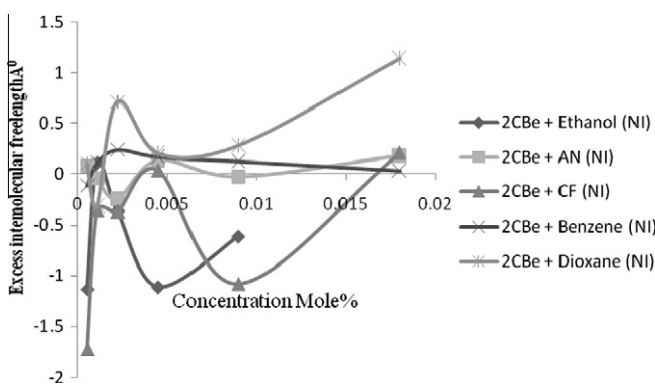

Fig. 8. Excess intermolecular freelength A^0 vs. concentration (mol%). AN: acetonitrile; CF: chloroform; 2CBe: 2′-chloro-4-methoxy-3-nitro benzil.
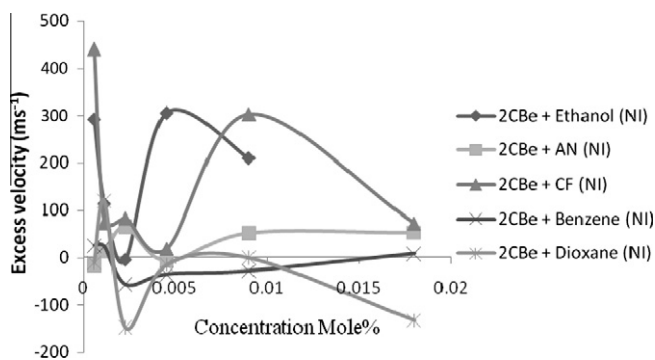

Fig. 9. Excess velocity ms^{-1} vs. concentration (mol%). AN: acetonitrile; CF: chloroform; 2CBe: 2′-chloro-4-methoxy-3-nitro benzil.

The strength of interaction between component molecules is well reflected in deviations observed in K_s, , 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. Conclusion

In polar hydroxylic solvents, molecules are held together by comparatively strong hydrogen bonds forming a network. Polar solvent is capable of taking part in dipole–dipole, induced dipole and intermolecular hydrogen bonding interactions which are being slowly replaced by solvent–solute interaction. This leads to the solvation of the solute particles resulting in an increase in volume and a decrease in density of the mixture. In non-polar solvents, at higher concentration the dipole induced dipole interaction increases leading to decrease in volume. The study of ultrasonic parameters and excess functions for the binary mixture of 2CBe with different solvents at various concentrations indicate that there are intermolecular interactions such as dipole–dipole, dipole induced dipole and hydrogen bonding interactions between the solute and solvent. The type and the magnitude of interaction depend on the polarity of the solvent and concentration of the solute.

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 ideal values is significant. Excess functions were calculated using the general formula [14]. For ideal binary mixtures:

$$Y^{EXC} = Y^{Exp} - Y^I = 0$$

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

In general for non-ideal mixtures

$$Y^{EXC} = Y^{Exp} - Y^I$$

$$Y^I = (1 - x)Y_0 + (X)Y_s$$

Y^{Exc} = Excess function

Y^{Exp} = Experimental value

Y^I = Ideal value

x = mole fraction of solute

Y_o = value for pure solvent

Y_s = 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 were calculated by following the reported procedures [18–22].The negative values of excess adiabatic compressibility and excess inter molecular free length (Figs. 7 and 8), in the concentration range of 0.001125–0.009 mol% for polar solvents and a positive excess velocity at higher concentration for polar solvent and non-polar solvent suggest that either a strong intermolecular interaction or a change in conformation or orientation of molecules are taking place in solution. This results 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,
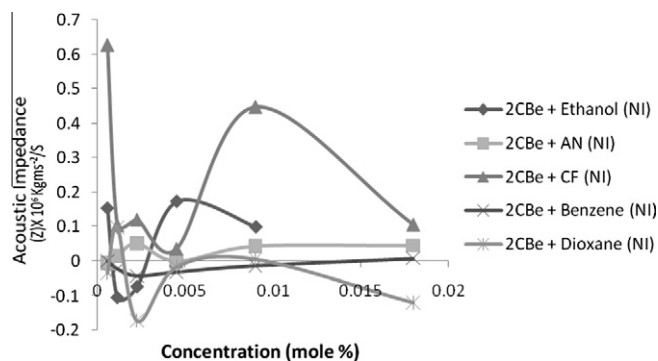
Fig. 10. Excess acoustic impedance ($Z \times 10^6$ kg ms^{-2}/S) vs. concentration (mol%). NI: non-ideal; AN: acetonitrile; CF: chloroform; 2CBe: 2′-chloro-4-methoxy-3-nitro benzil.
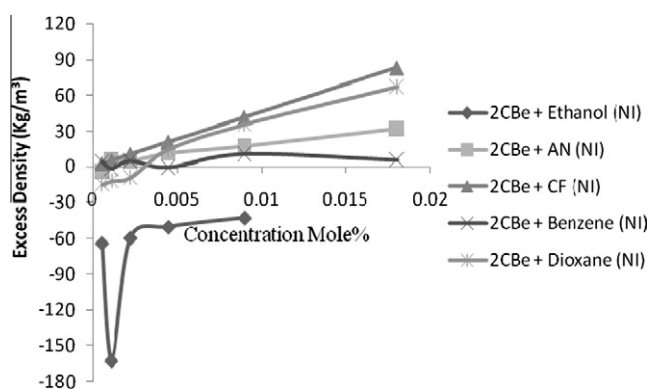

Fig. 11. Excess density (kg/m^3) vs. concentration (mol%). AN: acetonitrile; CF: chloroform; 2CBe: 2′-chloro-4-methoxy-3-nitro benzil.

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 0.0045–0.018 mol% for polar solvents and 0.0045, 0.009, 0.018 mol% for non-polar solvents that 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 0.001125–0.0045 mol% for polar solvents and 0.00125–0.009 mol% for non polar solvents. The rate of disruption of intermolecular interaction between solvent molecules is increased as the polarity of the solvent is increased. This results in an increase in the negative excess volume and a decrease in the excess density of the solution (Fig. 11). At a concentration of 0.018 mol% a maximum for excess density for polar solvents indicates that solvent–solvent interactions are replaced by solvent–solute interactions. Thus, the positive excess velocity, acoustic impedance (Figs. 9 and 10), 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 Desai [23,24] attributed the positive excess $K_{s\ and}\ L_f$ 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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