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## Selection of Organic Solvents for Microencapsulation Technique Among Chlorobenzene, 1,4-Dioxane and Benzaldehyde with Water

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Surface tension, density, ultrasonic velocity, viscosity and refractive index values have been determined at temperatures 313.15 K for the whole compositions for the binary liquid mixtures of chlorobenzene, 1,4-dioxane and benzaldehyde with water at atmospheric pressure. These experimental values have been used to estimate the respective excess properties along with some acoustic properties namely, excess molar volume ( $V^E$ ), viscosity deviation ( $\Delta\eta$ ), deviation in refractive index ( $\Delta n_D$ ), deviation in ultrasonic velocity ( $\Delta u$ ), isentropic compressibility ( $\beta$ ), intermolecular free length ( $L_f$ ), acoustic impedance ( $Z$ ), deviation in acoustic impedance ( $\Delta Z$ ), degree of intermolecular attraction ( $\delta$ ), relaxation time ( $\tau$ ), free volume ( $V_f$ ), absorption coefficient ( $\alpha$ ), deviation in surface tension ( $\Delta\sigma$ ), Gibbs free energy ( $\Delta G^E$ ) and internal pressures ( $\pi_i$ ). The excess values of these parameters are also evaluated over the different mole fraction range. The result is interpreted in terms of molecular interaction such as dipole-dipole interaction through hydrogen bonding between components of mixtures. The dependence of excess properties of mixtures on compositions were compared and discussed in terms of the intermolecular free length and other factors affecting the solvation and self-association effect. The excess values of these indicate the complexity of dipole-induced interaction in the binary liquid mixtures and also discussed selection of organic solvent for microencapsulation techniques. Also the new model equations have been developed by using Design Expert program for viscosity, ultrasonic velocity, refractive index, surface tension and density.

**Keywords:** Acoustical properties, Molecular interactions, Microencapsulation, Thermodynamic properties, Dipole-dipole interactions.

### INTRODUCTION

Surface tension, density, viscosity, refractive index and ultrasonic velocity is a flexible non-destructive properties and helpful for measurement of different properties like excess molar volume ( $V^E$ ), viscosity deviation ( $\Delta\eta$ ), deviation in refractive index ( $\Delta n_D$ ), deviation in ultrasonic velocity ( $\Delta u$ ), isentropic compressibility ( $\beta$ ), intermolecular free length ( $L_f$ ), acoustic impedance ( $Z$ ), deviation in acoustic impedance ( $\Delta Z$ ), degree of intermolecular attraction ( $\delta$ ), relaxation time ( $\tau$ ), free volume ( $V_f$ ), absorption coefficient ( $\alpha$ ), deviation in surface tension ( $\Delta\sigma$ ) and Gibbs free energy ( $\Delta G^E$ ), internal pressures ( $\pi_i$ ) at 313.15 K. The study of molecular interaction plays a vital role in the development of molecular science and selection of organic solvent for microencapsulation technique. Molecular interactions and structural behaviour of molecules and their mixtures can be identified using surface tension and ultrasonic studies. Late advancements have discovered utilization of surface tension in medication, building and farming [1-4]. The practical application of mixed solvents, rather than single solvent, in industrial and biological processes

has been recognized all over the world, as they provide a wide choice of solvent mixtures with appropriate properties [5,6]. Ultrasonic velocity and surface tension together with density and viscosity information outfit excess of data about the association between particles, dipoles, hydrogen bonding, multi-polar and dispersive forces [7-10]. We focus in this paper the selection of organic solvent for microencapsulation techniques and also results of surface tension, refractive index, density, viscosity and ultrasonic studies of binary mixtures of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water. As a result, best organic solvent are identified for microencapsulation techniques and significant interaction through hydrogen bonding between unlike molecules in these binary mixtures is expected. Also, it is worthwhile examining the effect of intermolecular interaction between chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water. We report here the results of surface tension of molecular interactions of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water at 313.15 K. Various acoustical properties have been useful in understanding the molecular interaction and microencapsulation techniques. The excess property study has been

used for the design of equipment in heat transfer, fluid mechanics, process calculation, bioprocess technology, fermentation technology, biochemical engineering, drying, process control and microencapsulation technique.

Literature survey shows that the work reported on thermo physical, thermo acoustical and thermodynamic properties of the binary mixtures is scanty. Hence in the present study an attempt is made to find out the above properties for the system acetone-water. The objective of the present work is to provide new experimental data on the density, viscosity, refractive index, ultrasonic velocity and surface tension of organic solvent with water mixture and to estimate excess volumes and derived thermodynamic properties such as excess molar volume ( $V^E$ ), viscosity deviation ( $\Delta\eta$ ), refractive index deviation ( $\Delta n_D$ ), deviations in ultrasonic velocity ( $\Delta u$ ), adiabatic compressibility ( $\beta$ ), acoustic impedance ( $Z$ ) using different correlations and a well known equation of state and also the new model equations have been developed by using Design Expert program for viscosity, ultrasonic velocity, refractive index, surface tension and density and then finally best organic solvent is identified for microencapsulation technique.

## EXPERIMENTAL

The blends of different fixations in mole division were readied by taking systematic reagent grade and spectroscopic reagent grade chemicals with purity of 99.9 % and got from E. Merck Ltd (India). In every one of the blends, the mole part of the blend is changed from 0 to 1.0, so as to have the blend of distinctive focus. The density, viscosity, surface tension, refractive index and ultrasonic velocity were measured as an element of grouping of the parallel fluid blend at temperature of  $T = 313.15$  K.

The densities of the blend were measured using a 25 mL specific gravity bottle with an accuracy of  $\pm 0.01$  kg/m<sup>3</sup>. An Ostwald viscometer (10 mL) with an accuracy of  $\pm 0.001$  mPa.s was utilized for the viscosity estimation. Refractive indexes were measured utilizing thermostatically controlled Abbe refractometer (Atago 3T) with accuracy under 0.001 units. Ultrasonic velocity estimations were made by an ultrasonic interferometer (Model M-84, supplied by M/s Mittal Enterprises, New Delhi), with the exactness of  $\pm 0.1$  m/s. Surface tension was resolved utilizing drop volume tensiometer and the precision of the surface tension estimation was evaluated to be 0.1 mN m<sup>-1</sup>.

**Theoretical aspect:** The following thermodynamic parameters were calculated:

Excess molar volume ( $V^E$ ) has been calculated from the density ( $\rho$ ) of the medium using the following equation:

$$V^E = \left( \frac{x_1 M_1 + x_2 M_2}{\rho_m} \right) - \left( \frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad (1)$$

where  $x_1$  and  $x_2$  refer to the mole fraction of components **1** and **2**.  $\rho_1$ ,  $\rho_2$  and  $\rho_m$  refer to the density of components **1** and **2** and the density of the mixture, respectively.

Viscosity deviation ( $\Delta\eta$ ) has been determined as follows:

$$\Delta\eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \quad (2)$$

where  $\eta$ ,  $\eta_1$ ,  $\eta_2$  are the viscosity of the mixture and the viscosity of pure components **1** and **2**, respectively. The uncertainty in the calculation of  $\Delta\eta$  from viscosity measurements was estimated to be  $\pm 0.0001$ .

Refractive index deviation ( $\Delta n_D$ ) from linear additive value of the mole fraction is obtained by

$$\Delta n_D = n_D - (x_1 n_{D1} + x_2 n_{D2}) \quad (3)$$

where  $n_D$ ,  $n_{D1}$ ,  $n_{D2}$  are the refractive index of the mixture and the refractive index of pure components **1** and **2**, respectively.

Ultrasonic velocity deviations ( $\Delta u$ ) has been determined as follows:

$$\Delta u = u - (x_1 u_1 + x_2 u_2) \quad (4)$$

where  $u$ ,  $u_1$ ,  $u_2$  are the ultrasonic velocity of the mixture and the ultrasonic velocity of pure components **1** and **2**, respectively.

Isentropic compressibility ( $\beta$ ) has been calculated from the ultrasonic velocity ( $u$ ) and the density ( $\rho$ ) of the medium using the Newton-Laplace equation [11] as follows:

$$\beta = \frac{1}{\rho u^2} \quad (5)$$

Intermolecular free length ( $L_f$ ) has been determined as follows [12]:

$$L_f = K_T \beta^{\frac{1}{2}} \quad (6)$$

where  $K_T$  is the temperature-dependent constant known as Jacobson's constant ( $K_T = 2.131 \times 10^{-6}$  at 313 K) and  $\beta$  is the isentropic compressibility.

Acoustic impedance ( $Z$ ) has been determined as follows:

$$Z = \rho u \quad (7)$$

where  $\rho$  is the density of mixture and  $u$  is the ultrasonic velocity of the mixture.

Deviation in acoustic impedance ( $\Delta Z$ ) has been determined as follows:

$$\Delta Z = Z - (x_1 Z_1 - x_2 Z_2) \quad (8)$$

where  $Z$ ,  $Z_1$  and  $Z_2$  are the acoustic impedance of the mixture and the acoustic impedance of pure components **1** and **2**, respectively.

Degree of intermolecular attraction ( $\delta$ ) was calculated by the equation:

$$\delta = \left( \frac{u^2}{u_{im}^2} \right) - 1 \quad (9)$$

$$\text{where, } u_{im}^2 = \frac{1}{(x_1 M_1 + x_2 M_2) \left( \frac{x_1}{M_1 u_1^2} + \frac{x_2}{M_2 u_2^2} \right)}$$

Relaxation time ( $\tau$ ) in terms of adiabatic compressibility ( $\beta$ ) and viscosity ( $\eta$ ) of the liquid is as follows:

$$\tau = \frac{4}{3} (\beta \eta) \quad (10)$$

where  $\beta$  is the adiabatic compressibility and  $\eta$  is the viscosity of the mixture.

Free volume ( $V_f$ ) in terms of ultrasonic velocity ( $u$ ) and the viscosity ( $\eta$ ) of liquid is [13] as follows:

$$V_f = \left( \frac{M_{\text{eff}} u}{k\eta} \right)^{\frac{2}{3}} \quad (11)$$

where  $M_{\text{eff}}$  is the effective molecular weight of the mixture ( $M_{\text{eff}} = \sum m_i x_i$ , where  $m_i$  and  $x_i$  are the molecular weight and mole fraction of individual constituents, respectively),  $k$  is a temperature independent constant which is equal to  $4.281 \times 10^9$  for all liquids.

Absorption coefficient ( $\alpha$ ) or attenuation coefficient is a characteristic of the medium and it depends on the external condition like temperature, pressure and frequency of measurement. It is given by the following [14]:

$$\alpha = \frac{8\pi^2 \eta f^2}{3\rho u^2} \quad (12)$$

where  $f$  is the frequency of ultrasonic wave.

**Internal pressure:** The equation for the evaluation of internal pressure is:

$$\pi_i = bRT \left( \frac{K\eta}{u} \right) \left[ \frac{\rho^{\frac{2}{3}}}{M_{\text{eff}}^{\frac{7}{6}}} \right] \quad (13)$$

where  $K$  is a constant,  $T$  the absolute temperature,  $\eta$ , the viscosity in cs,  $u$ , the ultrasonic velocity in  $m/s$ ,  $\rho$ , the density in  $g/cc$  of the liquid.

**Gibb's free energy:**

$$\Delta G^* = KT \log \left( \frac{h}{KT\tau} \right) \quad (14)$$

where  $K$  is the Boltzmann constant and  $h$  is Plank's constant.

## RESULTS AND DISCUSSION

Density ( $\rho$ ), viscosity ( $\eta$ ), ultrasonic velocity ( $u$ ), refractive index ( $n_D$ ) and surface tension ( $\sigma$ ) for the three systems are given in Table-1 and the other parameters, such as excess molar volume ( $V^E$ ), viscosity deviation ( $\Delta\eta$ ), refractive index deviation ( $\Delta n_D$ ), deviations in ultrasonic velocity ( $\Delta u$ ), adiabatic compressibility ( $\beta$ ), intermolecular free length ( $L_f$ ), acoustic impedance ( $Z$ ), deviation in acoustic impedance ( $\Delta Z$ ), degree of intermolecular attraction ( $\delta$ ), relaxation time ( $\tau$ ), free volume ( $V_f$ ), absorption coefficient ( $\alpha$ ), internal pressure ( $\pi_i$ ) and Gibb's free energy ( $\Delta G^*$ ) for the three binary mixtures chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water at 313.15 K have been calculated.

Table-1 shows that the density decreases from 0.9995 to 0.8736  $g/cc$  with increase of concentration of chlorobenzene in the mixture from 0 to 1.0 mole fraction where as it increases from 0.9995 to 1.0222  $g/cc$  in the case of 1,4-dioxane-water mixture and from 0.9995 to 1.0428  $g/cc$  in the case of benzaldehyde-water mixture. Increase in density indicates that minimum interaction between unlike molecules [15]. In our analysis density of chlorobenzene-water mixture decreases with increases in composition of the binary system due to strong interaction between the unlike molecules and the density of 1,4-dioxane-water and benzaldehyde-water mixtures density increases with increase in composition of binary systems due strong interaction between the like molecules and less

interaction between the unlike molecules, so based on this analysis the best organic solvent for microencapsulation technique is benzaldehyde-water mixture.

The equation generated for density of chlorobenzene-water mixture in terms of coded factor has been given as:

$$\rho = 0.0491x^2 - 0.1869x + 1.0154 \quad (15)$$

$$R^2 = 0.9343$$

The equation generated for density of 1,4-dioxane-water mixture in terms of coded factor has been given as:

$$\rho = 0.0445x^2 - 0.0056x + 0.9994 \quad (16)$$

$$R^2 = 0.9718$$

The equation generated for density of benzaldehyde-water mixture in terms of coded factor has been given as:

$$\rho = 0.0496x^2 - 0.0084x + 0.9996 \quad (17)$$

$$R^2 = 0.9910$$

From the eqns 15, 16 and 17 the  $R^2$  values it has been seen that the predicted values of density is a linear, function of actual one having intercept 0 and of slope 1, so benzaldehyde-water mixture is the best fitting binary mixture compared to remaining two binary mixtures. Then the best organic solvent for microencapsulation technique is benzaldehyde-water mixture.

Table-1 indicates that the viscosity decreases from 0.6553 to 0.5354 CP with increases in concentration of chlorobenzene-water in the mixture from 0 to 1.0 mole fraction where as it increases from 0.6553 to 1.0943 CP in the case of 1,4-dioxane-water mixture and the increases still more from 0.6563 to 1.3356 CP in the case of benzene-water mixture. An increasing viscosity indicates the closer approach of unlike molecules is due to hydrogen bonding [16]. In the present analysis viscosity of chlorobenzene-water mixture decreases due to large dipole-induced interaction between the mixture and the 1,4-dioxane-water, benzaldehyde-water mixtures viscosity increases due to dipole-dipole interaction between the binary systems, so here best organic solvent for microencapsulation technique is benzaldehyde-water mixture.

The equation generated for viscosity of chlorobenzene-water mixture in terms of coded factor has been given as:

$$\eta = 0.0124x^2 - 0.1275x + 0.6539 \quad (18)$$

$$R^2 = 0.9874$$

The equation generated for viscosity of 1,4-dioxane-water mixture in terms of coded factor has been given as:

$$\eta = -0.5043x^2 + 0.917x + 0.6662 \quad (19)$$

$$R^2 = 0.9896$$

The equation generated for viscosity of benzaldehyde-water mixture in terms of coded factor has been given as:

$$\eta = -0.7283x^2 + 1.3703x + 0.6735 \quad (20)$$

$$R^2 = 0.9908$$

From the eqns. 18, 19 and 20 the  $R^2$  values it has been seen that the predicted values of density is a linear, function of actual one having intercept 0 and of slope 1, so benzaldehyde-water mixture is the best fitting binary mixture compared to remaining two binary mixtures. Then the best organic solvent for microencapsulation technique is benzaldehyde-water mixture.

TABLE-1  
THERMO PHYSICAL, THERMO ACOUSTICAL AND THERMODYNAMIC PROPERTIES OF  
CHLOROBENZENE, 1,4-DIOXANE, BENZALDEHYDE WITH WATER SYSTEM AT 313.15 K

Chlorobenzene-Water						
X <sub>1</sub>	X <sub>2</sub>	ρ	η	n <sub>D</sub>	u	σ
0	1.0000	0.9995	0.6553	1.2933	156	21.6987
0.1728	0.8272	0.9983	0.6341	1.3222	296	22.9417
0.2155	0.7845	0.9979	0.6191	1.3384	350	23.6512
0.3441	0.6559	0.9581	0.6162	1.3699	489	24.1236
0.4945	0.5055	0.9172	0.5968	1.4001	657	25.6984
0.5566	0.4434	0.9139	0.5827	1.4191	789	26.0154
0.6872	0.3128	0.9098	0.5772	1.4492	1007	26.6541
0.7446	0.2554	0.9061	0.5639	1.4566	1064	26.9564
0.8639	0.1361	0.9024	0.5497	1.4889	1155	27.1254
0.9981	0.0019	0.8781	0.5441	1.5178	1268	28.9542
1.0000	0	0.8736	0.5354	1.5248	1270	29.5987
1,4-Dioxane-Water						
X <sub>1</sub>	X <sub>2</sub>	ρ (g/cc)	η (CP)	n <sub>D</sub>	U (m/s)	σ (dyne/cm)
0	1.0000	0.9995	0.6553	1.2933	156	21.6987
0.1828	0.8172	1.0004	0.7113	1.3722	856	22.8417
0.2355	0.7645	1.0008	0.7773	1.3884	1195	23.7512
0.3641	0.6359	1.0012	0.9526	1.4299	1314	24.5236
0.4845	0.5155	1.0016	0.9999	1.4601	1425	25.7984
0.5666	0.4334	1.0024	1.0162	1.4791	1444	27.0154
0.6972	0.3028	1.0069	1.0449	1.5092	1489	28.6541
0.7546	0.2454	1.0123	1.0599	1.5196	1498	29.9564
0.8739	0.1261	1.0168	1.0701	1.5389	1587	30.1254
0.9881	0.0119	1.0189	1.0854	1.5478	1610	32.9542
1.0000	0	1.0222	1.0943	1.5591	1614	33.6015
Benzaldehyde-Water						
X <sub>1</sub>	X <sub>2</sub>	ρ (g/cc)	η (CP)	n <sub>D</sub>	U (m/s)	σ (dyne/cm)
0	1.0000	0.9995	0.6553	1.2933	156	21.6987
0.1928	0.8072	1.0008	0.8843	1.4202	714	22.8417
0.2855	0.7145	1.0012	0.9563	1.4644	905	23.7512
0.3741	0.6259	1.0016	1.0999	1.4999	1050	24.9236
0.4945	0.5055	1.0065	1.1241	1.5501	1195	25.9984
0.5766	0.4234	1.0111	1.1564	1.5691	1294	26.8154
0.6072	0.3928	1.0156	1.2355	1.5792	1297	27.7541
0.7246	0.2754	1.0201	1.2509	1.5999	1310	28.9564
0.8839	0.1161	1.0291	1.2613	1.6169	1311	30.1254
0.9981	0.0019	1.0394	1.2771	1.6178	1314	31.9542
1.0000	0	1.0428	1.3356	1.6248	1316	32.5987

Refractive index increases from 1.2933 to 1.5248 with increase of concentration of chlorobenzene-water in the mixture from 0 to 1.0 mole fraction and from 1.2933 to 1.5591 in the case of 1,4-dioxane-water where as it increases from 1.2933 to 1.6248 in the case of benzaldehyde-water mixture. The refractive index increases with the increase in composition. An increasing refractive index suggests that the weak interaction between unlike molecules due to hydrogen bonding [17]. In the present analysis all three systems refractive index increases due to strong interaction between the organic solvents with water mixtures so here highest refractive index is benzaldehyde-water mixture then best organic solvent for microencapsulation technique is benzaldehyde as shown in Table-1. The equation generated for refractive index of chlorobenzene-water mixture in terms of coded factor has been given as:

$$\eta_D = 0.0124x^2 + 0.2187x + 1.2905 \quad (21)$$

$$R^2 = 0.9982$$

The equation generated for refractive index of 1,4-dioxane-water mixture in terms of coded factor has been given as:

$$\eta_D = -0.1621x^2 + 0.4184x + 1.297 \quad (22)$$

$$R^2 = 0.9986$$

The equation generated for refractive index of benzaldehyde-water mixture in terms of coded factor has been given as:

$$\eta_D = -0.3622x^2 + 0.6852x + 1.296 \quad (23)$$

$$R^2 = 0.9990$$

From the eqns. 21, 22 and 23 the R<sup>2</sup> values it has been seen that the predicted values of density is a linear, function of actual one having intercept 0 and of slope 1, so benzaldehyde-water mixture is the best fitting binary mixture compared to remaining two binary mixtures. Then the best organic solvent for microencapsulation technique is benzaldehyde-water mixture.

Ultrasonic velocity increases from 156 to 1270 m/s with increase of concentration of chlorobenzene-water mixture from

0 to 1.0 mole fraction and from 156 to 1614  $m/s$  in the case of 1,4-dioxane-water where as it increases from 156 to 1316  $m/s$  in the case of benzaldehyde-water mixture. The ultrasonic velocity increases due to hetero-and homomolecular groups were the first to bring up the ultrasonic velocity approach for subjective estimation of the binary mixtures in fluids [18,19]. The result shows that ultrasonic velocity is not depending either on entropy or enthalpy. Thus the ultrasonic velocity between organic components-water mixtures do not rely upon atomic interactions and also size and state of the particles as shown in Table-1.

The equation generated for ultrasonic velocity of chlorobenzene-water mixture in terms of coded factor has been given as:

$$u = -50.03x^2 + 1241.9x + 107.24 \quad (24)$$

$$R^2 = 0.9891$$

The equation generated for ultrasonic velocity of 1,4-dioxane-water mixture in terms of coded factor has been given as:

$$u = -2065.7x^2 + 3299x + 304.9 \quad (25)$$

$$R^2 = 0.9356$$

The equation generated for ultrasonic velocity of benzaldehyde-water mixture in terms of coded factor has been given as:

$$u = -1867x^2 + 2969.8x + 186.31 \quad (26)$$

$$R^2 = 0.9942$$

From the eqns. 24, 25 and 26 the  $R^2$  values it has been seen that the predicted values of density is a linear, function of actual one having intercept 0 and of slope 1, so benzaldehyde-water mixture is the best fitting binary mixture compared to remaining two binary mixtures. Then the best organic solvent for microencapsulation technique is benzaldehyde-water mixture.

Surface tension increases from 21.6987 to 29.5987 dyne/cm with increase of concentration of chlorobenzene in the mixture from 0 to 1.0 mole fraction and from 21.6987 to 32.9915 dyne/cm in the case of 1,4-dioxane-water mixture where as it increases from 21.6987 to 33.5987 dyne/cm in the case of benzaldehyde. An increasing surface tension suggests that the liquid structure and enthalpy increases between unlike molecules due to hydrogen bonding [20]. In the present result shows that the all three binary systems surface tension increases due to strong interaction between like molecules then best organic solvent for microencapsulation technique is benzaldehyde-water mixture. The equation generated for surface tension of chlorobenzene-water mixture in terms of coded factor has been given as:

$$\sigma = 0.1243x^2 + 7.0083x + 21.842 \quad (27)$$

$$R^2 = 0.9754$$

The equation generated for surface tension of 1,4-dioxane-water mixture in terms of coded factor has been given as:

$$\sigma = 5.303x^2 + 6.1557x + 21.712 \quad (28)$$

$$R^2 = 0.9894$$

The equation generated for surface tension of benzaldehyde-water mixture in terms of coded factor has been given as:

$$\sigma = 2.929x^2 + 7.7714x + 21.502 \quad (29)$$

$$R^2 = 0.9926$$

From the eqns. 27, 28 and 29 the  $R^2$  values it has been seen that the predicted values of density is a linear, function of actual one having intercept 0 and of slope 1, so benzaldehyde-water mixture is the best fitting binary mixture compared to remaining two binary mixtures. Then the best organic solvent for microencapsulation technique is benzaldehyde-water mixture.

Fig. 1 shows that the excess molar volumes 1,4-dioxane-water and benzaldehyde-water mixtures are always positive and chlorobenzene-water mixtures are negative for all the studied temperatures. Treszczanowicz *et al.* [21] and Roux and Desnoyers [22] suggested that excess molar is the resultant contribution from several opposing effects. These may be divided arbitrarily into three types, namely chemical, physical and structural. A physical contribution, that is specific interactions between the real species present in the mixture, contribute a negative term to excess molar volume. The chemical or specific intermolecular interactions result in a volume decrease and these include charge transfer type forces and other complex forming interactions. This effect contributes negative values to excess molar volume. The structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes of free volume. In other words, structural contributions arising from geometrical fitting of one component into the other due to the differences in the free volume and molar volume between components lead to a negative contribution to excess molar volume. But in our 1,4-dioxane-water and benzaldehyde-water systems are positive excess molar volume indicate that the presence of specific interactions between 1,4-dioxane, benzaldehyde and water molecules. The positive excess molar volume values are attributed to strong dipole-dipole interactions between like molecules in the mixtures. Excess molar volume values are more positive for benzaldehyde-water. So the best organic solvent for microencapsulation technique is benzaldehyde-water mixture.

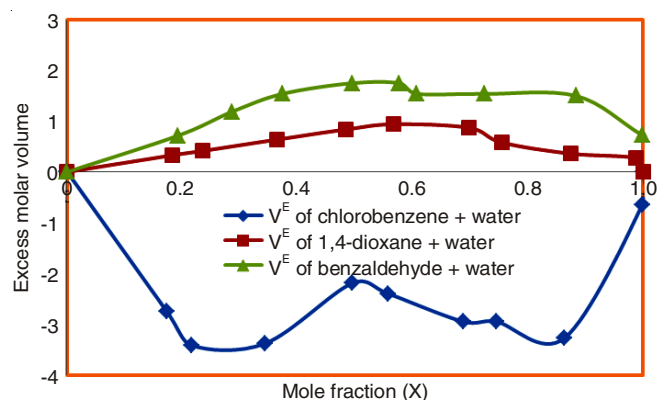


Fig. 1. Excess molar volume of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water at 313.15 K

Viscosity values are positive for the all three binary mixtures at the temperature of 313.15 K as shown in Table-1. The variation of viscosity deviations, with the mole fraction of binary systems are shown in Fig. 2 and the data shows that

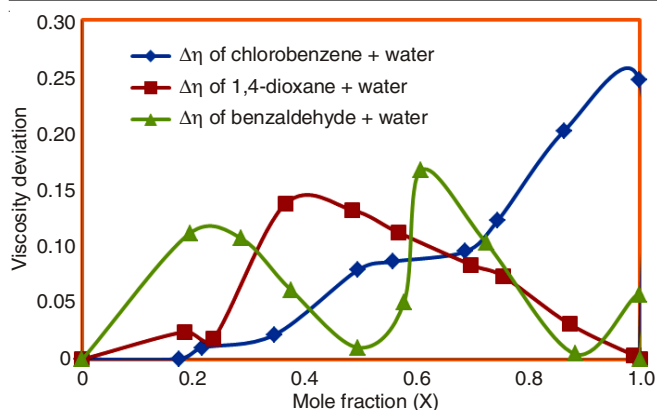


Fig. 2. Viscosity deviation of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water at 313.15 K

the viscosity deviations are positive for all the three binary systems, indicating that interaction between binary mixtures is strong. The positive viscosity deviation indicates that the interaction between binary mixtures is strong and it is observed in the systems diethyl carbonate with alcohols, diacetone alcohol + benzene or chlorobenzene, methanol, ethanol, *n*-propanol and *n*-butanol with pyridine [23-25]. The viscosity of binary mixture highly depends on entropy of mixture, which is related with liquid's structure and enthalpy. Therefore the viscosity deviation depends on molecular interactions as well as on the size and shape of the molecules and also the negative  $V^E$  shows strong complex formation due to charge transfer between the liquids. So the best organic solvent for micro-encapsulation technique is benzaldehyde-water mixture.

The results of refractive index deviation *versus* mole fraction at 313.15 K for the systems of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water are shown in Fig. 3. Here all the three binary systems exhibit a positive deviation at the studied temperature. It has also been observed that the refractive index deviation shows positive values for the entire mole fraction. It may be noted that such values are due to the electronic perturbation of the individual molecules during mixing and therefore depend very much on the nature of the mixing molecules [26].

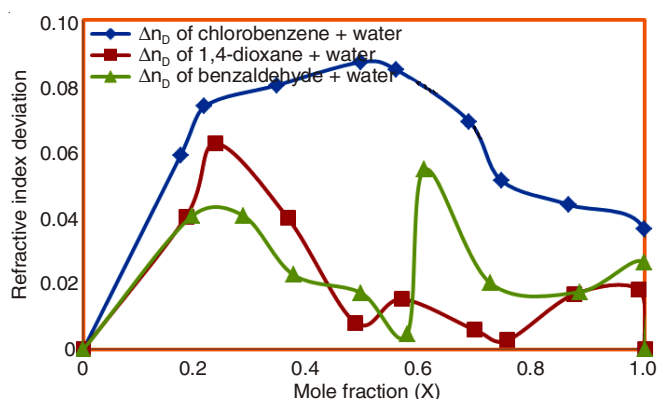


Fig. 3. Refractive index deviation of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water at 313.15 K

The values of adiabatic compressibility are positive for all the three binary systems at the temperature of 313.15 K and it is also reported similar results for the system acetophenone-

methyl acetate [27]. The values of adiabatic compressibility become negative, the weak structure making interactions at elevated temperatures due to enhanced thermal motion. In the present systems the values of adiabatic compressibility become highly positive. This may be indicated that the strong structure making interactions at temperatures due to dipole-dipole interaction as shown in Fig. 4.

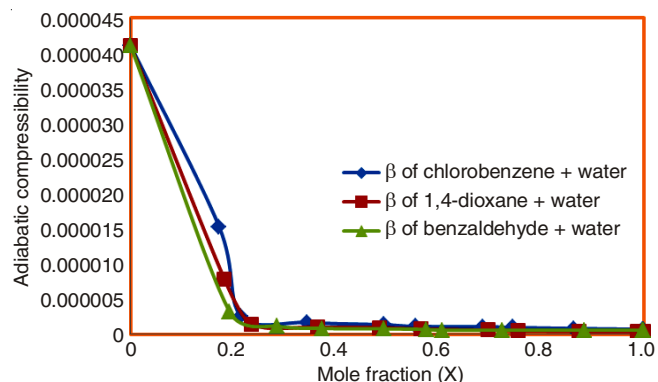


Fig. 4. Adiabatic compressibility of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water at 313.15 K

The intermolecular free length is positive over the whole mole fraction range for all binary mixtures at temperature of 313.15 K (Fig. 5). This shows that the structural adjustment in the liquid mixtures towards high compressible phase of fluid. For the system 1,4-dioxane with nitrobenzene [28,29] the negative adiabatic compressibility is observed. Fig. 6 shows that the ultrasonic velocity deviations of all three systems are positive at the temperature of 313.15 K. In our analysis chlorobenzene-water, dioxane-water and benzaldehyde-water mixtures not depends on the entropy, the positive ultrasonic velocity deviation is depends only on the liquid structure and enthalpy of a binary mixtures.

The surface tension deviation is negative over the whole mole fraction range for all binary mixtures at temperature of 313.15 K. The positive surface tension deviation between benzylparaben with benzene does not depend on molecular interactions as well as on the size and shape of the molecules [30]. Fig. 7 shows that the negative surface tension over the whole mole fraction range for all binary mixtures, so in all three systems the deviation in surface tension ( $\Delta\sigma$ ) strongly depends on the entropy, liquid structure and enthalpy of a

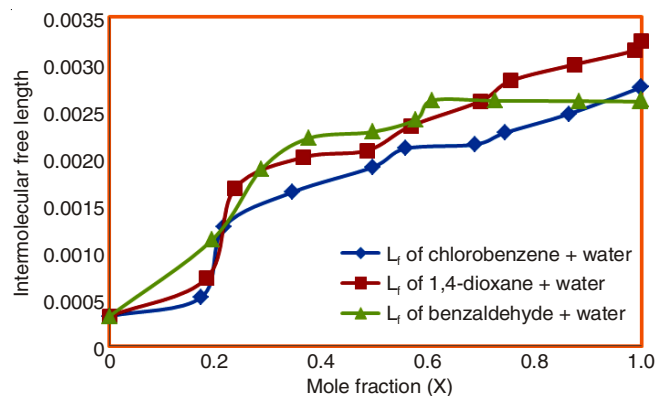


Fig. 5. Intermolecular free length of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water at 313.15 K

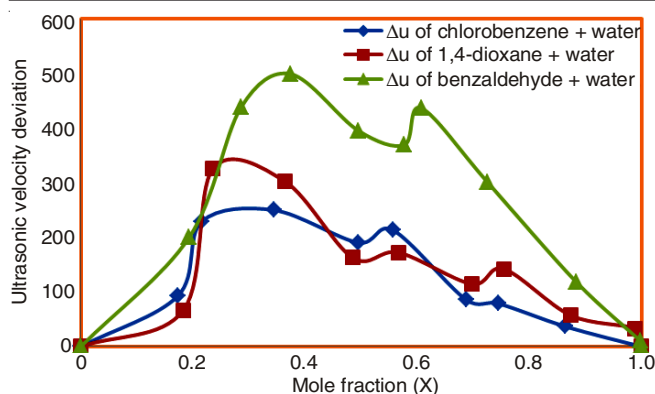


Fig. 6. Ultrasonic velocity deviation of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water at 313.15 K

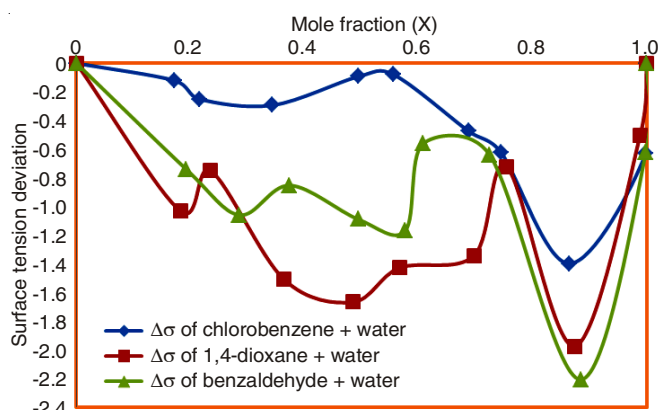


Fig. 7. Surface tension deviation of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water at 313.15 K

binary mixtures so the benzaldehyde-water mixture molecular interactions are very high compared to chlorobenzene-water and dioxane-water mixtures then the best organic solvent for microencapsulation technique is benzaldehyde-water mixture.

The values of acoustic impedance deviation ( $\Delta Z$ ) (Fig. 8) were positive over the entire range of mole fraction for all binary mixtures at temperature of 313.15 K. Based on the above results benzaldehyde-water mixture is the best solvents for microencapsulation technique.

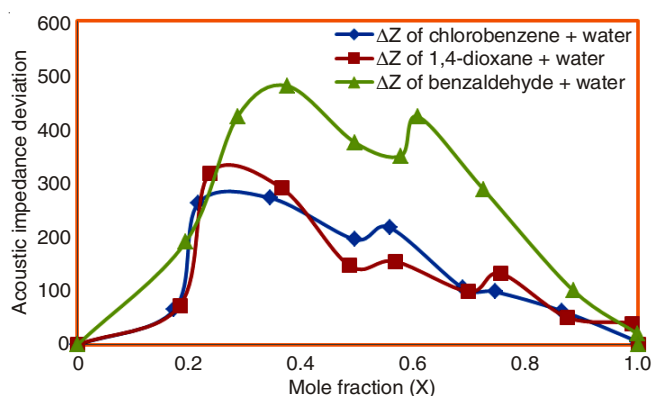


Fig. 8. Acoustic impedance deviation of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water at 313.15 K

The degree of intermolecular attraction ( $\delta$ ) has also been evaluated to study the structural variations and the nature of interaction occurs in the system, benzylparaben with benzene [30].

Fig. 9 shows that the positive value of degree of intermolecular attraction ( $\delta$ ) over the entire mole fraction of all binary systems at the studied temperature. It has been observed that the maximum value of  $\delta$  (1.0956) occurs at nearly mole fraction of chlorobenzene with water is 0.4945, mole fraction of dioxane with water is 0.4845 and the reference  $\delta$  is 0.7726 and the mole fraction of benzaldehyde with water is 0.4945 and the reference  $\delta$  is 1.0145. This suggests that the high intermolecular interaction occurs within the system *i.e.* benzaldehyde-water mixture.

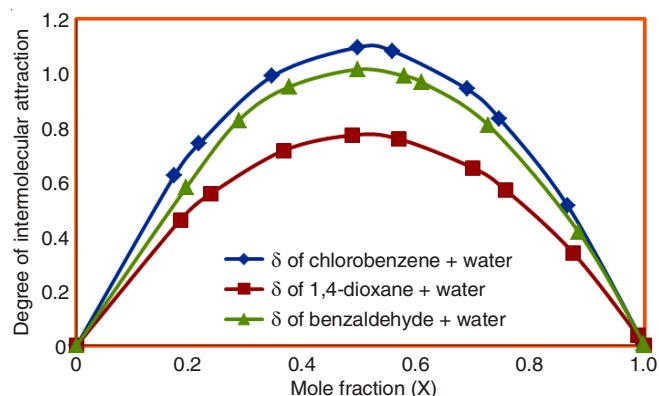


Fig. 9. Degree of intermolecular attraction of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water at 313.15 K

The relaxation time which is in the order of  $10^{-12}$  sec is due to structural relaxation process [26] and in such a situation it is suggested that the molecules get rearranged due to co-operative process [27].

Fig. 10 indicates that the positive relaxation time over the entire mole fraction of binary systems at the studied temperature, so the high relaxation time is benzaldehyde-water system.

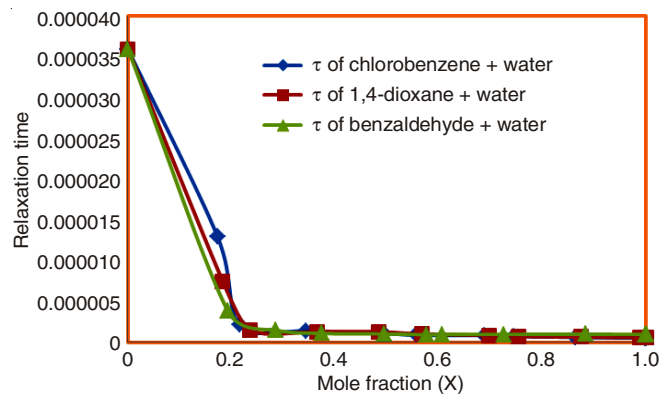


Fig. 10. Relaxation time of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water at 313.15 K

The plot of Gibbs free energy *versus* mole fraction at 313.15 K for chlorobenzene + water, dioxane-water and benzaldehyde-water are presented in Fig. 11. Excess properties provide information about the molecular interactions and macroscopic behaviour of binary mixtures which can be used to test and improve thermodynamic models for calculating and predicting fluid phase equilibrium [28]. The magnitude of Gibbs free energy represents the strength of interaction between unlike molecules [28,29]. Excess Gibbs free energy of activation of viscous flow was found to be negative for all binary systems.

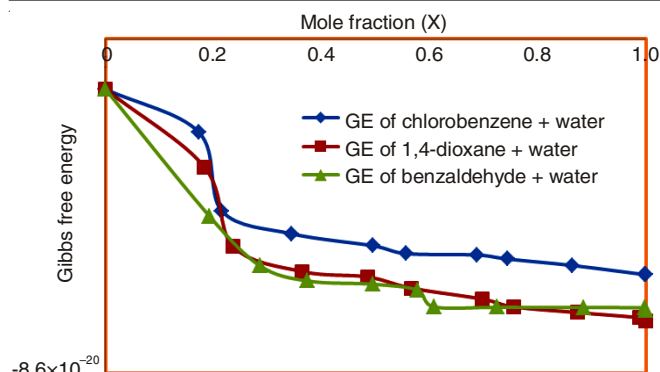


Fig. 11. Gibbs free energy (GE) of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water at 313.15 K

In Fig. 11 less Gibb's free energy in benzaldehyde with water mixture. So the best organic solvent for microencapsulation technique is benzaldehyde with water.

Fig. 12 indicates that the absorption coefficient decreases as it is proportional to the square of the frequency is 10. The absorption coefficient decreases with increasing mole fraction of binary systems that shows a high absorption capacity between the mixtures. So here high absorption capacity is benzaldehyde-water mixture.

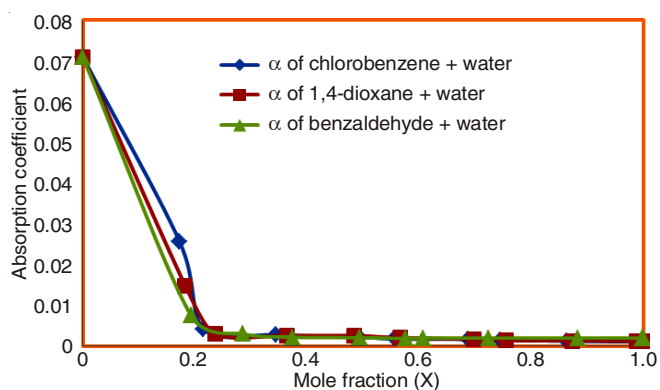


Fig. 12. Absorption coefficient of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water at 313.15 K

The internal pressure (Fig. 13) of the liquid mixtures decreases and free volume values increase with increase in mole fraction. At temperature of 313.15 K, Brownian moment is less. However, decrease in internal pressure and increase in free volume (Fig. 14) is due to destruction of association at temperature 313.15 K. Similar observations are reported earlier by Shafiq *et al.* [27], the internal pressure decreases while free volume increases.

Acoustic impedance increases with increase in mole fraction of all the three systems at studied temperature. Acoustic impedance increases with the increase in composition. This supports the possibility of strong interaction between like molecules. Acoustic impedance is also given by the product of the ultrasonic velocity and density  $Z = \text{ultrasonic velocity} \times \text{density}$  of binary mixtures and is used for assessing the absorption of sound in a medium, benzylparaben with benzene [30]. So here our analysis also acoustic impedance positive over the entire range of mole fraction, The strong interaction between the binary systems is benzaldehyde-water mixture. Benzaldehyde-water mixture is best solvent for microencapsulation technique as shown in Fig. 15.

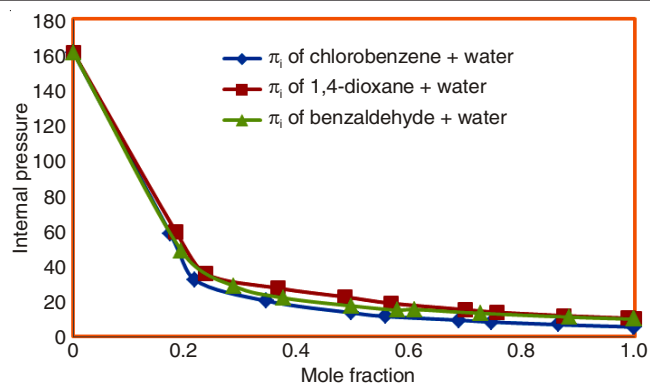


Fig. 13. Internal pressure of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water at 313.15 K

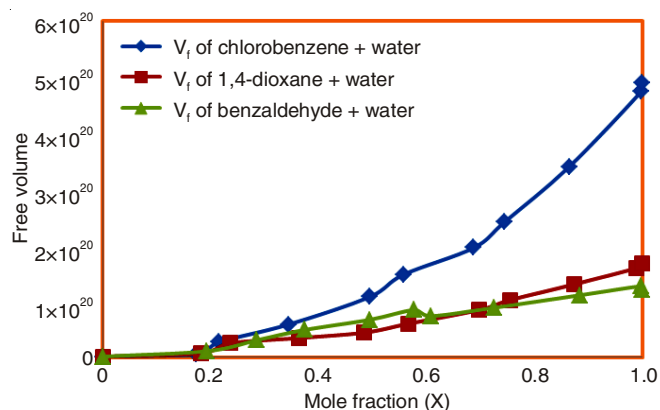


Fig. 14. Internal pressure of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water at 313.15 K

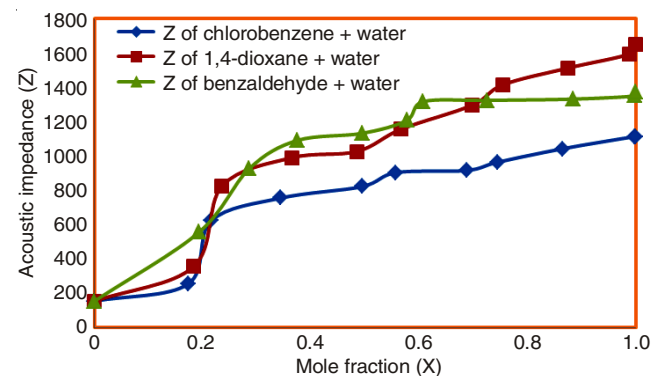


Fig. 15. Acoustic impedance of chlorobenzene-water, 1,4-dioxane-water and benzaldehyde-water at 313.15 K

## Conclusion

The systems chlorobenzene, 1,4-dioxane, benzaldehyde with water has been studied by measuring density, viscosity, ultrasonic velocity, refractive index and surface tension at the temperature of 313.15 K. These experimental data and the derived properties have been analyzed in terms of specific interaction and molecular interaction due to electron donor-accepter complex between the component molecules and also determined best organic solvent for microencapsulation technique. The important fact is that the new equations developed for density, viscosity, refractive index, ultrasonic velocity and surface tension has been found to fit well as compared to the existing equations. So based on the above results, the best organic solvent for microencapsulation technique is benzaldehyde-water mixture.

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