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Study of Molecular Interactions of Binary Mixture of Mandelic Acid in Different Solvents Using Ultrasonic, Acoustical Parameters, Dielectric Constant and FTIR Measurements

S. Usha[1, *], Charles Kanakam Christopher[2], B. Thanuja[1]

[1]Department of chemistry, Sri Sairam Engineering College, Chennai, Tamilnadu, India
[2]Department of chemistry, Presidency College, Chennai, Tamilnadu, India

Email address
usha.che@sairam.edu.in (S. Usha)

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Abstract
Mandelic Acid (MA) is a polar non-centero symmetric chiral molecule, having high polarisability. Solute -solvent interactions of binary liquid mixtures is carried out for MA in different solvents. Polar protic solvent methanol, polar aprotic solvent DMSO and non-polar solvent chloroform are used for the study. Ultrasonic velocity (U), viscosity (η), density (ρ) are measured and theoretical calculations are carried out to determine the adiabatic compressibility (β), relative association (R_A), inter molecular free length (L_f) and acoustic impedance (Z). The excess values are calculated for the above parameters. Compared the solute- solvent interactions in the title compound due to their polarizability behaviour, inter and intra molecular hydrogen bonding in the above solvents, are confirmed by FTIR measurements and their dielectric constant values. The results obtained show the molecular interactions of the title compound with the respective solvents and the nature of hydrogen bonding.

1. Introduction

Mandelic acidis an alpha hydroxy aromatic carboxylic acid, having non-centero symmetric carbon with Polaris ability 14.99.
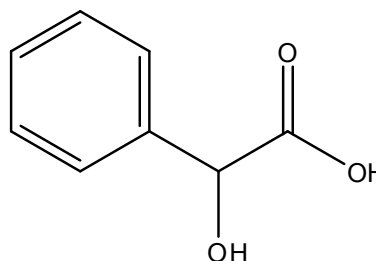
Mandelic acid

The solute - solvent interactions of organic compounds reveal the nature of the compound to undergo hydrogen bonding, dipole change with the type of contributing groups present in the solvent [1-5]. Binary liquid mixtures of organic compounds show

considerable interactions in different types of solvents. The unique property shown by them is responsible for the structural modifications of sample in solution state [6-8]. The polar groups of solvent are responsible for intermolecular hydrogen bonding [9-11] in the title compound. The presence of alpha hydroxy group, carbonyl group of acid and acidic proton are responsible for intra molecular hydrogen bonding in the title compound [12-17]. The intra molecular hydrogen bonding and inter molecular hydrogen bonding exhibited by the title compound with protic polar solvent methanol, aprotic polar solvent DMSO and non- polar solvent chloroform show variations in the measurements of ultrasonic velocity (U), density (ρ), viscosity (η), adiabatic compressibility (β), acoustic impedance (Z), inter molecular free length (L_f) and relative association (R_A) at room temperature. The respective excess acoustic parameters are also calculated. Compared the measured dielectric constant value of the title compound with that of respective solvents literature values.

The title compound is subjected to FTIR analysis for solid and the 5%W/V solution of the above solvents respectively to show the nature of the hydrogen bonding. All the measurements are performed at room temperature.

2. Materials and Methods

MA free from moisture content is purchased from Alfa Aesar (99% pure, dl mixture) and the solvents used are analytical grade. A thermostatic water bath arrangement is made for density, viscosity and ultrasonic velocity measurements. Single crystal ultrasonic interferometer for liquids velocity Model BL-02 working at 2 MHz fixed frequency is used to measure the ultrasonic velocity of the solution.

The title compound is made as solution having different mole % concentration in polar protic solvent methanol, polar aprotic solvent DMSO and non-polar solvent chloroform respectively and measured the ultrasonic velocity.

The density of solution is measured using Pycknometer by relative measurement method. The viscosity of solvent and solution are measured using an Ostwald's Viscometer. The different mole % concentration solutions of the title compound in the above solvents and the parameters are plotted as two dimensional comparative graph and the characteristic interaction of solute and solvent respectively are discussed in this paper. The excess parameter values are calculated respectively and discussed. A programmable automatic RLC bridge model HIOKI 3532-50 Hitester is used to measure the dielectric constant of the title compound.

The title compound is made as 5% W/V solution in the above three solvents and the solid compound are subjected to FTIR analysis respectively. The model FTIR 6300 type A is used for FTIR analysis and the results are discussed in this paper.

3. Theory

The Ultrasonic Velocity (U) of binary liquid have been measured using an Ultrasonic interferometer for liquids Velocity Model BL - 02 working at 2MHz fixed frequency. Ultrasonic Velocity is calculated by,

$$d = n \lambda /2 \qquad (1)$$

where 'd' is the total distance moved by the reflector of the interferometer cell.

From equation (1), wavelength (λ) can be calculated. The frequency (υ) of the interferometer crystal is accurately known as 2 MHz, the ultrasonic velocity (in m/sec) is calculated by the relation, $U = \upsilon \lambda$

The density (ρ) of solution is measured using Pycknometer by relative measurement method .

The viscosity (η) of solvent and solution are measured using a calibrated Ostwald's Viscometer .

Adiabatic compressibility (β) for solvent and solution are calculated using the irrespective density and ultrasonic velocity using the formula, $\beta = 1 / U^2 \rho$

Acoustic impedance (Z) is calculated from the product of density (ρ) and ultrasonic velocity (U) of solvent and solution respectively, $Z = U \rho$

Inter molecular free length (L_f) due to the interaction of solvent with the title compound is calculated using the formula, $L_f = K \beta^{1/2}$, where K is the temperature dependent constant known as Jacobson's constant.

Relative association (R_A) is a function of ultrasonic velocity and is calculated using the formula,
$R_A = \rho_s / \rho_o * (U_0/ U_s)^{1/3}$

The excess parameters (A^E) are calculated by the difference between experimental values and theoretical values of respective parameters.

$$A^E = A_{exp} - A_{theoretical} = A - [X_i A_1 + (1-X_i) A_2]$$

Where, A, A_1 and A_2 are the respective parameter values of solution, solute and solvent respectively.
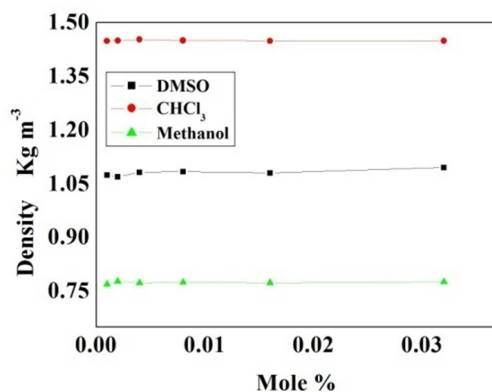
4. Results and Discussion

Fig. 1. *Comparison of density of MA in methanol,DMSO and chloroform.*
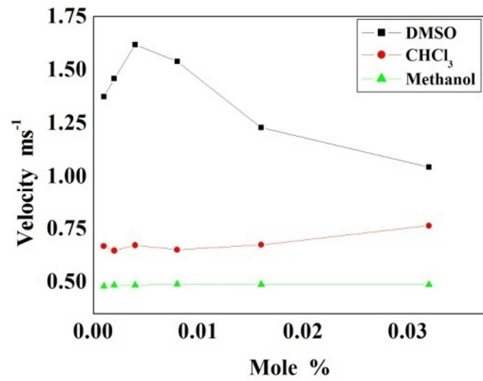
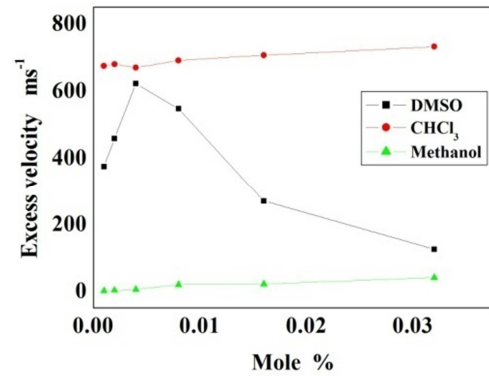*Fig. 2.* Comparison of velocity of MA in methanol, DMSO and chloroform.

Fig. 6. Comparison of excess velocity of MA inmethanol, DMSO and chloroform.
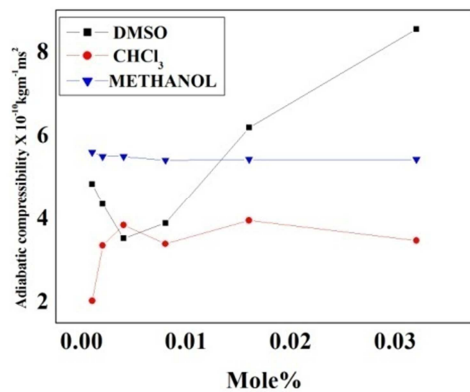

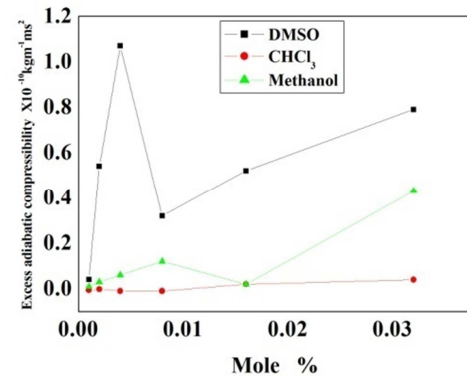*Fig. 3.* Comparison of adiabatic compressibilty of MA in methanol, DMSO and chloroform.

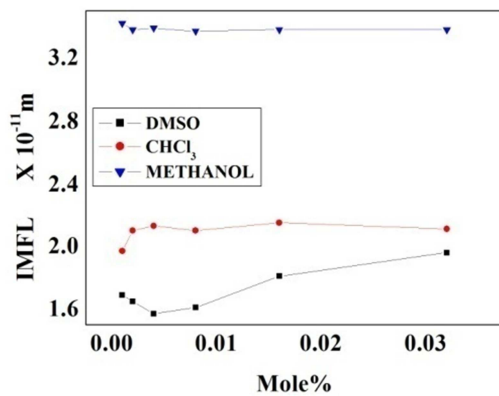*Fig. 7.* Comparison of excess adiabatic compressibility of MA in methanol, DMSO and chloroform.

Fig. 4. Comparison of IMFL of MA inmethanol, DMSOand chloroform.
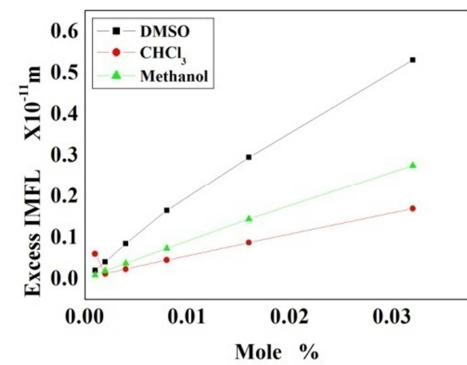

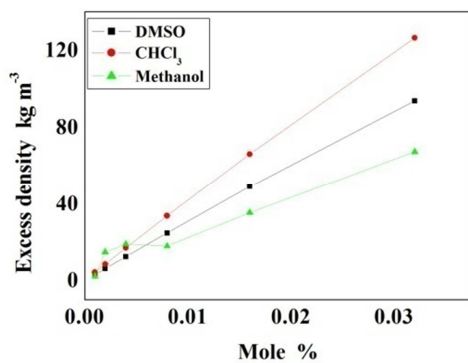*Fig. 8.* Comparison of excess IMFL of MA in methanol, DMSO and chloroform.

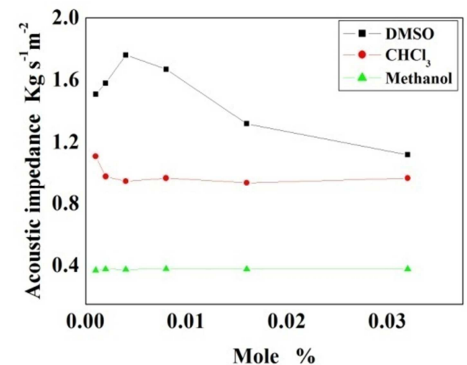*Fig. 5.* Comparison of excess density of MA in methanol, DMSO and chloroform.

Fig. 9. Comparison of acoustic impedance ofMA in methanol, DMSO and chloroform.
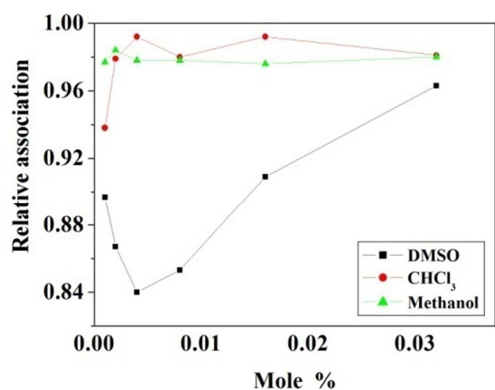
Fig. 10. *Comparison of relative association o fMA in methanol, DMSO and chloroform.*
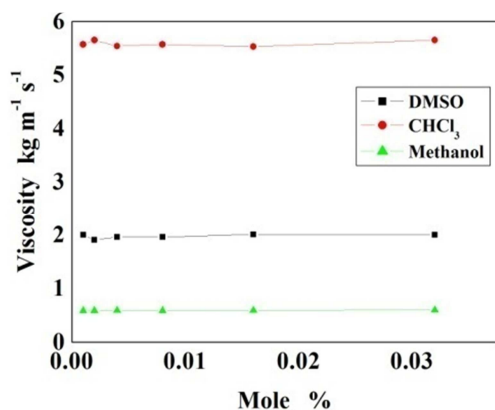

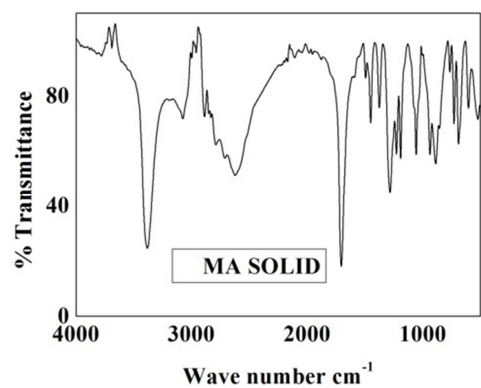**Fig. 11.** *Comparison of viscosity of MA in methanol, DMSO and chloroform.*
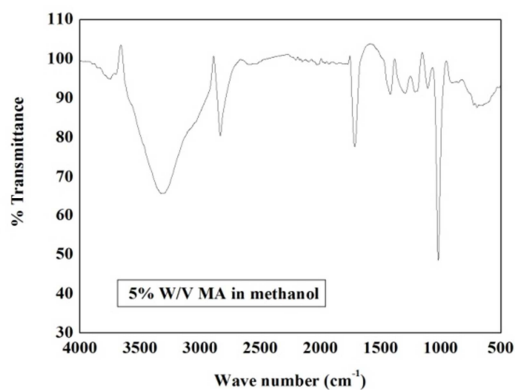

Fig. 12. *FTIR spectrum of solid MA.*

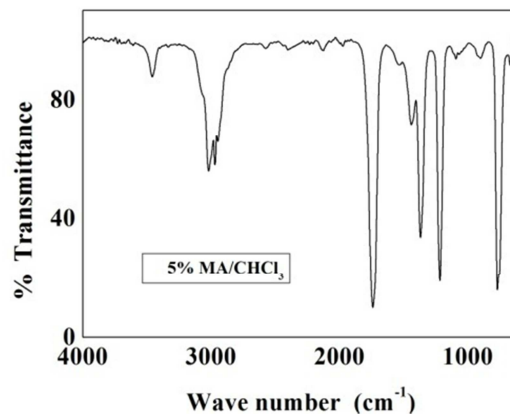**Fig. 13.** *FTIR spectrum of 5%W/V MA in methanol.*

Fig. 14. *FTIR spectrum of 5%W/V MA in chloroform.*
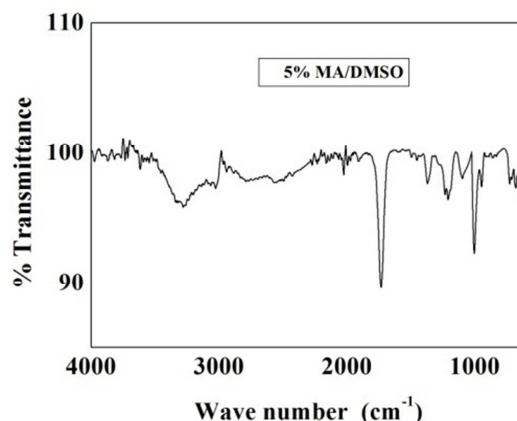
Fig. 15. *FTIR spectrum of 5%W/VMA in DMSO*

Table 1. *Dielectric constant for solvents and MA*

Sample	Dielectric constant
Chloroform	4.81
DMSO	46.7
Methanol	32.7
MA	70.5

Table 2. *Comparison of parameters of MA in different solvents*

Density Kg m^{-3}						
Mole %	0.001	0.002	0.004	0.008	0.016	0.032
DMSO	1.075	1.07	1.083	1.085	1.081	1.096
CHCl3	1.4482	1.4493	1.4523	1.4497	1.4483	1.4484
Methanol	0.7691	0.777	0.7724	0.7742	0.7726	0.7752
Velocity ms^{-1}						
DMSO	1.373	1.458	1.618	1.539	1.229	1.044
CHCl3	0.668	0.647	0.672	0.651	0.674	0.764
Methanol	0.48	0.485	0.485	0.489	0.488	0.487
Adiabatic compressibility *10-10Kgm^{-1}ms^2						
DMSO	4.84	4.35	3.52	3.89	6.19	8.54
CHCl3	2.03	3.35	3.84	3.39	3.95	2.03
Methanol	5.6	5.5	5.5	5.41	5.43	5.43
Intermolecular freelength *10^{-11} m						
DMSO	1.69	1.65	1.57	1.61	1.81	1.96
CHCl3	1.97	2.1	2.13	2.1	2.15	2.11
Methanol	3.42	3.38	3.39	3.37	3.38	3.38
Relative association						

Density Kg m^{-3}						
DMSO	0.897	0.867	0.84	0.853	0.909	0.963
CHCl3	0.938	0.979	0.992	0.98	0.992	0.981
Methanol	0.977	0.984	0.978	0.978	0.976	0.98
Acoustic impedance *106 Kg ms^{-2}/S						
DMSO	1.51	1.58	1.76	1.67	1.32	1.12
CHCl3	1.11	0.98	0.95	0.97	0.94	0.97
Methanol	0.369	0.377	0.375	0.379	0.377	0.378
Excess density Kg m^{-3}						
DMSO	3.1	6.3	12.5	24.8	49.2	93.8
CHCl3	4.3	8.6	17.1	33.8	66.2	126.5
Methanol	2.2	14.9	19	18	35.4	67.4
Excess Velocity ms^{-1}						
DMSO	375.1	458.8	622.2	547.2	270.1	125.5
CHCl3	675	680	670	691.1	706.6	732.3
Methanol	1.35	2.76	5.44	19.8	21.3	40.6
Excess Adiabatic compressibility *10-10Kgm^{-1}ms^2						
DMSO	0.04	0.54	1.07	0.32	0.52	0.79
CHCl3	-0.006	-0.002	-0.01	-0.01	0.02	0.04
Methanol	0.01	0.03	0.06	0.12	0.02	0.43
Excess Intermolecular free length *10^{-11} m						
DMSO	0.02	0.041	0.085	0.165	0.295	0.53
CHCl3	0.06	0.012	0.023	0.045	0.087	0.169
Methanol	0.009	0.019	0.037	0.073	0.144	0.275
Solvent	0.001	0.002	0.004	0.008	0.016	0.032
Viscosity Kg m^{-1}						
DMSO	2	1.91	1.96	1.96	2.01	2
CHCl3	5.57	5.65	5.54	5.57	5.53	5.65
Methanol	0.591	0.59	0.595	0.59	0.595	0.601

The increase in concentration of the solution (0.001-0.032mole%) increases the density of the solution for all the three solvents used from Table.1. The increase in density of solution with concentration in Fig.1.shows the moderate attraction between solute and solvent.

Velocity of title compound increases with concentration in all the solvents shown in Fig.2. indicate the moderate interaction between solute and solvent.

Adiabatic compressibility exhibits reverse trend to that of ultrasonic velocity. Adiabatic compressibility decreases gradually with increase in concentration and frequency - it depends on electron donor and acceptor nature of the title compound in different solvents is shown in Fig.3.

The association of solute and solvent molecules occur resulting in close packing and clinging of molecules due to this, solution become less compressible and hence adiabatic compressibility decreases.

Inter molecular free length depends on adiabatic compressibility and shows similar behaviour to that of adiabatic compressibility and inverse to that of ultrasonic velocity. Inter molecular freelength decreases with increase of velocity - indicates possibility of breaking dipole and gets associated in the structure by electrostriction thus decreasing free space available. Decreased inter molecular free length from Fig.4. indicates structure promoting behaviour of solute molecule.

The excess parameters values indicate the dispersive forces, weak molecular interactions between unlike molecules and dipole induced dipole interactions of the title compound in different polarity solvents is shown by Fig.5. to Fig.8. Acoustic impedance increases with increase in concentration indicates that there is strong interaction between solute and solvent due to hydrogen bonding Fig.9.

Relative association is a parameter used to assesss the association in any solution relative to the association existing in water at 0 ˚C. Relative association of the title compound in different solvents increases with concentration Fig.10. Viscosity is a property arising from collisions between neighboring particles in a fluid that are moving at different velocities. The title compound shows variation of viscosity in different solvents Fig.11.

The solubility of hydrophilic solute increases with increasing dielectric constant of the solvent. The increased dielectric constant of polar solvent methanol increases the interaction of the title compound, the moderate interaction is shown by polar aprotic solvent DMSO and non-polar solvent chloroform with minimum dielectric constant show no interaction with title compound Table-.2. This is confirmed by the FTIR measurement of solid MA and the 5% w/v concentrations of MA in the above solvents Fig.12 to Fig.15.

5. Conclusion

The title compound shows inter and intramolecular hydrogen bonding , dispersive forces due to weak molecular interactions and dipole interactions with polar protic solvent, polar aprotic solvent and non -polar solvent.

Acknowledgement

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