



## Investigation on molecular interaction of 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone in ethanol with reference to volumetric compressibility and viscometric measurements

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Received 15 December 2014,

Accepted 15 February 2015.

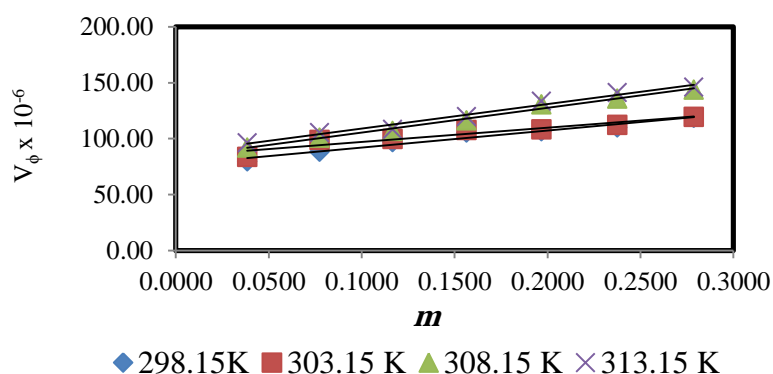
### • Novelty and Highlights:

1–Density, ultrasonic velocity and viscosity measurements of 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone in ethanol solution.

2 – Investigation of structure maker/breaker behaviour of solute through thermodynamic parameters.

### • Graphical Abstract:

The limiting apparent molar volume ( $V_\phi^0$ ), limiting apparent molar expansivity ( $\phi_0^E$ ), second derivative of infinite dilution of partial molar volume with temperature  $(\partial^2 V_\phi^0 / \partial T^2)_p$  have been determined and also viscosity  $B$ -coefficient, variation of  $B$  with temperature  $dB/dT$  were evaluated. From these results shows that of 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone are structure maker in the ethanol solution.





## Investigation on molecular interaction of 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone in ethanol with reference to volumetric, compressibility and viscometric measurements

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**Abstract:** Apparent molar volumes ( $V_\phi$ ), apparent molar compressibility ( $K_{s,\phi}$ ) and viscosity  $B$  coefficients for 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone (0.03-0.21) mol·kg<sup>-1</sup> in ethanol solutions were determined from the density, ultrasonic velocity and viscosity measurements at (298.15, 303.15, 308.15, and 318.15) K. The data ( $V_\phi$ ) and ( $K_{s,\phi}$ ) were utilized to estimate the limiting values of apparent partial molar properties ( $V_\phi^0$ ,  $K_{s,\phi}^0$ ) and experimental slopes ( $S_v$ ,  $S_k$ ). The structure-making or structure-breaking ability of the solutes have also been discussed in terms of the sign of  $(\partial^2 V_\phi^0 / \partial T^2)_p$ . The free energy of activation of viscous flow per mole of the solvent  $\Delta\mu_1^{0\#}$  and the solute  $\Delta\mu_2^{0\#}$  for the solutions were also explained in terms of transition state theory.

**Keywords:** Density · Acetophenones · Apparent molar volume · B-coefficient · Molecular interactions

### Introduction

Ultrasonic technique has become an influential tool in providing information regarding the molecular behaviour of liquids owing to its ability of characterizing physicochemical behaviour of the medium. The study of intermolecular interaction plays an imperative role in the development of molecular sciences consequently; it is emerging in the field of forensic sciences, space research and also in wars. The ultrasonic investigations of pure liquids consisting polar components are substantial significance in analyzing intermolecular interaction between component molecules. These studies find several applications in industries and such studies as variations in concentrations and temperatures are helpful in giving insight in to structure and various bonding of associated molecular complexes and other related molecular processes. The measurement of speed of sound, density and viscosity in liquids and their mixtures is useful in determining the thermodynamic and acoustical properties that are very sensitive to molecular interactions. Also such measurements are useful to study the strength of molecular interactions occurring among the component molecules besides finding extensive applications in several industrial and technological processes [1-4]. Thermodynamics studies of binary mixtures have attracted much attention of scientists. The measurement of ultrasonic speed enables us to the

accurate measurement of some useful acoustic and thermodynamic parameters.

The study of molecular association in binary liquid mixture having alcohol as one of component is of particular interest since alcohols are strongly self-associated liquids having three dimensional network of hydrogen bonding and can be associate with any other group having some degree of polar attraction. Several researchers [5-11] have measured the density, viscosity, and speed of sound for a wide range of liquid solutions containing alcohols as one of the components. Even though considerable work has been reported on alcohols as one of the component in binary and ternary mixtures, the data on liquid solution of alcohols with acetophenones is scanty. In order to have clear understanding of intermolecular interaction, an attempt has been made to study the ultrasonic behaviors of dihydroxyl substituted acetophenones in ethanol at different temperatures.

### Experimental

**Materials** Acetophenones 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone with a mass fraction purity >99% obtained from S.D.'s Fine Chemicals Mumbai, India. These were used without further purification, however all the chemicals were vacuum

dried and stored in desiccators over  $P_2O_5$  for at least two days before their use. Ethanol was distilled prior to use according to standard procedure [12]. The solutions were made afresh in distilled ethanol, all necessary precautions were taken during the preparation of solutions to avoid moisture contamination and evaporation.

**Method, Density measurements** the density of pure solvent and solutions were measured by using pre-calibrated bicapillary pycnometer made of borosilicate glass having a bulb capacity of 10 mL was used to measure the density. The pycnometer was calibrated at four experimental temperatures (298.15-313.15) K with doubly distilled water. The pycnometer with the test solution was equilibrated in a thermostatic water bath maintained within  $\pm 0.1$ K of the desired temperatures. Requisite precautions were taken to avoid evaporation losses while actual measurements. An average of triplicate measurements was taken into an account. Accuracy of the density measurements was up to  $\pm 0.0001$  g  $cm^3$ .

**Speed of sound measurements** the speed of sound was measured with the help of multifrequency ultrasonic interferometer (M-81, Mittal Enterprises New Delhi, India) at 2 MHz. The interferometer was calibrated by measuring speed of sound in freshly prepared double distilled water. The uncertainty in measured value of ultrasonic velocity was  $\pm 0.1$ ms $^{-1}$ .

**Viscosity measurements** the viscosity measurements were performed with Ostwald's type viscometer. The viscometer was calibrated at four working temperatures against liquids of known viscosities. The uncertainty in the viscosity measurements was  $\pm 0.002$  mPas. During the measurements temperature of the test solution was maintained with electronically controlled thermostatic water bath (Yorco-YSI 413) with an uncertainty of  $\pm 0.1$  K.

## Results and discussion

The experimental values of density, speed of sound and viscosity of binary systems of (2,4-dihydroxyacetophenone + ethanol) and (2,6-dihydroxyacetophenone + ethanol) at T = (298.15-313.15) K are listed in Table 1.

**Volumetric study** it can be observed from the Table 1 that density of solution increases linearly with the increase in concentration of solute in the solution and decreases slightly with increase in the temperature for both the studied systems. The most important thermodynamic property used to obtain the information regarding the nature of solute-solvent interaction is the apparent molar volume ( $V_\phi$ ) of solute. The apparent molar volumes of solute in ethanol solution at different temperatures were

calculated from experimentally measured densities by using the relation:

$$V_\phi = \frac{\rho^* - \rho}{m \cdot \rho \cdot \rho^*} + \frac{M}{\rho} \dots\dots\dots (1)$$

Where  $\rho^*$  and  $\rho$  are density of solvent and solution, respectively, m is the molality of the solution, M is the molecular mass of solute. The limiting apparent molar volume  $V_\phi^0$  at infinite dilution for both the acetophenones was evaluated by using following equation:

$$V_\phi = V_\phi^0 + S_v m \dots\dots\dots (2)$$

Where  $V_\phi^0$  represents limiting values of apparent partial molal property (equal to the infinite dilution partial molar property) and  $S_v$  is experimental slope.

It is evident from the Table 2 that the values of apparent molar volume are positive and increase linearly with addition of solute for both the solutes. These clearly specify that there is strong interaction between solute-solvent molecules. The  $V_\phi^0$  is a measure of solute-solvent interactions, whereas, experimental slope ( $S_v$ ) provides the quantitative estimates of solute-solute interactions. It also reveals that  $V_\phi^0$  values are positive for both the solutes studied in the present work and increase with an increase in temperatures. This indicates the presence of strong solute-solvent interactions, and these interactions are further strengthened at higher temperatures. Table 3 also indicates that  $S_v$  values are positive for both the solutions and it is decreases as the temperatures of the solution increases. Since  $S_v$  is a measure of solute-solute interactions, the results indicate the presence of weak solute-solute interactions at all experimental temperatures. A quantitative comparison of the magnitude of  $S_v$  values shows much greater in magnitude than  $V_\phi^0$  values but it is lowering with temperatures although the  $V_\phi^0$  value increases with temperature. This suggests that solute-solvent interactions dominate over solute-solute interactions.

The limiting apparent molar expansivity ( $\phi_0^E$ ) of solutes at infinite dilution in ethanol have been obtained at T = (298.15- 313.15) K by using the following relation:

$$\phi_0^E = \left( \frac{\partial V_\phi^0}{\partial T} \right)_p = a_1 + 2a_2 T \dots\dots\dots (3)$$

Values of limiting apparent molar expansibility  $(\partial V_{\phi}^0 / \partial T)_p$  for 2,4-DHAP and 2,6-DHAP are listed in Table 4. It can be observed that  $(\partial V_{\phi}^0 / \partial T)_p$  are increases with increasing temperatures. This indicates that the

interaction of molecules of 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone molecules of solvent increases with increasing temperature.

Table 1 Density, speed of sound and viscosity, of 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone in ethanol solution at different temperatures 298.15-313.15 K.

m	T/K			
mol.kg <sup>-1</sup>	298.15	303.15	308.15	313.15
<b>2,4-dihydroxyacetophenone <math>\rho \times 10^3 \text{ kg m}^{-3}</math></b>				
0.0384	0.7882	0.7836	0.7790	0.7748
0.0773	0.7905	0.7859	0.7809	0.7767
0.1166	0.7924	0.7878	0.7830	0.7787
0.1564	0.7939	0.7892	0.7845	0.7799
0.1967	0.7959	0.7912	0.7861	0.7817
0.2374	0.7975	0.7927	0.7876	0.7830
0.2787	0.7981	0.7935	0.7888	0.7843
<b>(u) m s<sup>-1</sup></b>				
0.0384	1158.41	1137.85	1121.82	1107.00
0.0773	1162.99	1141.98	1126.21	1110.87
0.1166	1168.47	1145.81	1128.00	1113.12
0.1564	1169.25	1148.73	1129.21	1114.69
0.1967	1172.72	1151.89	1131.88	1115.34
0.2374	1175.78	1152.41	1132.23	1117.17
0.2787	1177.65	1154.27	1135.39	1120.00
<b><math>\eta</math>, (mPa's)</b>				
0.0384	1.0967	0.9895	0.8762	0.8344
0.0773	1.1500	0.9991	0.8873	0.8491
0.1166	1.2100	1.0721	0.8905	0.8597
0.1564	1.3083	1.1645	0.9011	0.8606
0.1967	1.4603	1.2421	0.9221	0.8616
0.2374	1.5259	1.2932	0.9502	0.8773
0.2787	1.6867	1.3643	0.9999	0.8801
<b>2,6-dihydroxyacetophenone <math>\rho \times 10^3 \text{ kg m}^{-3}</math></b>				
0.0384	0.7883	0.7837	0.7791	0.7748
0.0773	0.7905	0.7859	0.7811	0.7768
0.1166	0.7925	0.7879	0.7831	0.7789
0.1564	0.7940	0.7893	0.7847	0.7801
0.1967	0.7963	0.7913	0.7862	0.7819
0.2374	0.7980	0.7933	0.7880	0.7832
0.2787	0.7993	0.7942	0.7891	0.7845
<b>(u) m s<sup>-1</sup></b>				
0.0384	1160.21	1139.05	1123.11	1107.12
0.0773	1164.38	1143.87	1127.21	1111.87
0.1166	1170.47	1146.81	1130.32	1113.98

0.1564	1173.05	1149.03	1132.31	1116.19
0.1967	1175.62	1152.90	1133.98	1118.34
0.2374	1178.78	1154.12	1134.23	1120.77
0.2787	1180.32	1156.22	1136.09	1123.40
<b><math>\eta_r</math> (mPa's)</b>				
0.0384	1.0969	0.9896	0.8765	0.8348
0.0773	1.1501	0.9992	0.8876	0.8497
0.1166	1.2202	1.0723	0.8910	0.8617
0.1564	1.3184	1.1647	0.9013	0.8630
0.1967	1.4606	1.2424	0.9225	0.8646
0.2374	1.5260	1.2935	0.9506	0.8780
0.2787	1.6868	1.3649	1.0081	0.8820

Table 2 Apparent molar volume and apparent molar compressibility of 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone in ethanol solution at different temperatures 298.15-313.15 K.

<b>m</b>	<b>T/K</b>			
<b>mol.kg-1</b>	<b>298.15</b>	<b>303.15</b>	<b>308.15</b>	<b>313.15</b>
<b>2,4-dihydroxyacetophenone <math>V_\phi \times 10^{-6} \text{m}^3 \text{mol}^{-1}</math></b>				
0.0384	79.51	83.58	87.73	91.98
0.0773	88.28	90.30	100.90	103.10
0.1166	96.95	98.35	102.60	105.60
0.1564	105.50	107.70	110.00	115.50
0.1967	106.60	108.40	113.60	116.32
0.2374	110.10	112.34	116.70	120.50
0.2787	118.52	119.37	120.83	123.51
<b><math>K_{s,\phi} \times 10^{-13} \text{m}^3 \text{mol}^{-1} \text{Pa}^{-1}</math></b>				
0.0384	-3.999	-3.685	-3.049	-2.916
0.0773	-3.209	-3.014	-2.674	-2.510
0.1166	-2.976	-2.602	-2.069	-2.047
0.1564	-2.157	-2.156	-1.546	-1.523
0.1967	-2.016	-2.005	-1.417	-1.198
0.2374	-1.830	-1.592	-1.087	-1.026



0.2787	-1.502	-1.320	-1.047	-0.988
<b>2,6-dihydroxyacetophenone <math>V_{\phi} \times 10^{-6} \text{m}^3 \text{mol}^{-1}</math></b>				
0.0384	75.09	79.31	83.41	91.98
0.0773	88.28	90.30	96.65	100.98
0.1166	95.17	96.94	101.21	102.69
0.1564	102.49	106.68	107.85	113.33
0.1967	103.28	107.54	112.74	114.61
0.2374	106.68	108.18	113.93	119.08
0.2787	111.48	115.21	119.03	122.29
<b><math>K_{s,\phi} \times 10^{-13} \text{m}^3 \text{mol}^{-1} \text{Pa}^{-1}</math></b>				
0.0384	-5.053	-4.463	-3.924	-2.994
0.0773	-3.579	-3.550	-3.061	-2.872
0.1166	-3.350	-2.816	-2.557	-2.286
0.1564	-2.668	-2.218	-2.045	-1.801
0.1967	-2.373	-2.131	-1.679	-1.603
0.2374	-2.145	-1.826	-1.337	-1.422
0.2787	-1.820	-1.550	-1.140	-1.306

Table 3 Limiting values of apparent molar volume and apparent molar compressibility with their slopes for 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone in ethanol solution at different temperatures 298.15-313.15 K.

T/K	$V_{\phi}^0 \times 10^{-6}$	$S_v \times 10^{-6}$	$K_{s,\phi}^0 \times 10^{-13}$	$S_k \times 10^{-13}$
	$\text{m}^3/\text{mol}$	$\text{m}^3/\text{mol kg}$	$\text{m}^3/\text{mol/Pa}$	$\text{m}^3/\text{mol kg/Pa}$
<b>2,4-dihydroxyacetophenone</b>				
298.15	76.91	151.6	-4.09	11.88
	( $\pm 2.586$ )	( $\pm 14.646$ )	( $\pm 0.203$ )	( $\pm 1.155$ )
303.15	80.22	143.8	-3.81	11.18
	( $\pm 2.280$ )	( $\pm 12.914$ )	( $\pm 0.131$ )	( $\pm 0.747$ )
308.15	87.60	126.3	-3.21	10.42

	(±2.578)	(±14.601)	(±0.180)	(±1.023)
313.15	91.30	124.6	-3.08	10.18
	(±2.649)	(±15.004)	(±0.170)	(±0.966)
<b>2,6-dihydroxyacetophenone</b>				
298.15	75.93	137.0	-4.89	12.04
	(±3.487)	(±19.749)	(±0.330)	(±1.870)
303.15	79.03	137.0	-4.45	11.45
	(±3.447)	(±19.523)	(±0.285)	(±1.617)
308.15	83.56	136.1	-4.02	11.28
	(±2.965)	(±16.794)	(±0.194)	(±1.100)
313.15	89.79	123.8	-3.25	7.70
	(±2.148)	(±12.169)	(±0.154)	(±0.873)

(Parentheses indicate standard errors.)

This phenomenon can be interpreted by the following reasons. The molecular thermal motion intensified with increasing temperature, and the interaction between molecules corresponding stronger. Another useful parameter called the Hepler constant [13], to consider the behaviour of the second order derivatives of partial volume of solute at infinite dilution with respect to temperature, was calculated by the following relation:

$$\left(\frac{\partial \phi_0^E}{\partial T}\right)_p = \left(\frac{\partial^2 V_0^\phi}{\partial T^2}\right)_p = 2a_2 \dots\dots\dots (4)$$

For determining "structure-making" or "structure-breaking" capacities of solute in solvent Hepler equation was used. The values of term  $\left(\partial^2 V_0^\phi / \partial T^2\right)_p$  are summarized in Table 4. According to Hepler criterion, structure-making solutes should have positive values and structure-breaking solutes, negative values. From Table 4  $\left(\partial^2 V_0^\phi / \partial T^2\right)_p$  are positive for 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone in ethanol solvent indicating structure-making tendency of solutes in the present systems. Similar type of result has been reported by Rajagopal et al [14] for 4-aminobutyric acid in aqueous solutions of salbutamol sulphate.

3.2 Ultrasonic study the speed of sound is considered as a thermodynamic property. It increases with temperature as well as with concentration as represented in Table 1 and this was used to calculate apparent molar compressibility. The apparent molar compressibility ( $K_{s,\phi}$ ) of the solute in ethanol solutions at different temperatures has been computed using following expression:

$$K_{s,\phi} = \frac{\beta_s - \beta_s^*}{m \cdot \rho^*} + V_\phi \beta_s \dots\dots\dots (5)$$

Where  $\rho^*$  density of solvent, m is the molality of the solution.  $\beta_s$  and  $\beta_0$  represent the values of adiabatic compressibility of solution and pure solvent, respectively. The calculated values of  $K_{s,\phi}$  for both the solutes at T = (298.15 - 313.15) K are given in Table 2. The apparent molar adiabatic compressibility of solutes ( $K_{s,\phi}$ ) which shows the negative values indicate the loss of structural compressibility of solvent molecules and the solution is incompressible due to complex formation between solute and solvent molecule. The concentration dependence of apparent molar compressibility has been used to obtain the limiting molar compressibility values.

The limiting apparent molar adiabatic compressibility of the solutes in ethanol has been obtained by relation

$$K_{s,\phi} = K_{s,\phi}^0 + S_k m \dots\dots\dots (6)$$

The partial molar compressibility  $K_{s,\phi}^0$ , is obtained graphically by  $K_{s,\phi}$  against m. Here m is molality and  $S_k$  is experimental slope. The values of apparent molar compressibility  $K_{s,\phi}^0$  and its limiting values i.e.  $S_k$  are also summarized in Table 3. The  $K_{s,\phi}^0$  and  $S_k$  values are measure of the solute-solvent and solute-solute interactions, respectively. From close study of Table 3 it observed that the  $K_{s,\phi}^0$  values are in good agreement with those drawn from the values of  $V_\phi^0$ .

Viscometric study the relative viscosity  $\eta_r$  of ethanol solutions for both the systems at T = (298.15- 313.15) K has been calculated by using the following formula:

$$\eta_r = n / n_0 = t\rho / t_0\rho_0 \dots\dots\dots (7)$$

where  $\eta$ ,  $t$ ,  $\rho$  are the coefficient of viscosity, time flow, and density of solution and  $\eta_0$ ;  $t_0$ ;  $\rho_0$  are the coefficient of viscosity, time flow and density of solvent, respectively.

The viscosity data for this system has been analyzed by Jones-Dole [15] equation

$$\eta_r = \frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \dots\dots\dots (8)$$

Where  $\eta_r$  is relative viscosity of solution,  $\eta$  and  $\eta_0$  are the viscosities of solution and solvent respectively. The A coefficient signifies the inter-ionic forces, and Jones-Dole B coefficient is a measure of solute-solvent interactions. In the case of non-electrolyte, A is zero[16]. The values of B- coefficient have been obtained from the intercepts and slopes of the plots of  $\eta_r - 1 / m^{1/2}$  against  $m^{1/2}$ . The intermolecular interaction can be discussed through the change of a dynamic property such as viscosity. The viscosity B-coefficient is another avenue into the effects of solute-solvent interactions on the solution viscosity and thereby provides valuable information regarding solvation of solutes and their effect on the solvent in the vicinity of the solute molecule. The values of B-coefficient obtained from experimental data by least-squares analysis are presented in Table 5. According to the data presented in Table 5 the B-coefficients are positive. The values B-coefficient decreases with increase of temperature, therefore, the values of  $dB/dT$  are negative for both the solutes. Generally, the  $dB/dT$  was known to be a sole criterion for determining the structure-making and structure breaking nature of any solute, and for structure-making solute, the values are negative and for structure breaking, it is positive. Here in studied systems the negative value of  $dB/dT$  indicates that 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone behaves as structure maker.

*Activation parameters of viscous flow* The viscosity data have been analysed on the basis of Eyring transition state theory. The free energy of activation per mole of solute and per mole of solvent has been evaluated by using Feakins et al. [17]. Activation free energies of solvent  $\Delta\mu_1^{0\#}$  are calculated from the relation:

$$\Delta\mu_1^{0\#} = RT \ln(\eta_0 \bar{V}_1^0 / hN_A) \dots\dots\dots (9)$$

where, h is the Planck constant,  $N_A$  is the Avogadro number and  $\eta_0$  is viscosity of solvent.

According to this theory, the Jones Dole viscosity B-coefficient is given by the relation:

$$\Delta\mu_2^{0\#} = \Delta\mu_1^{0\#} + (RT / \bar{V}_1^0) [1000B - (\bar{V}_1^0 - \bar{V}_2^0)] \dots\dots (10)$$

where  $\Delta\mu_2^{0\#}$  is the contribution per mole of solute to the free energy of activation for viscous flow of solution and  $\Delta\mu_1^{0\#}$  is the free energy of activation per mole of the solvent. The  $\bar{V}_1^0 = M/\rho_0$  is the molar volume of the solvent, M is the molar mass of solvent and  $\rho_0$  is density of the solvent and  $\bar{V}_2^0 = V_\phi^0$  is the limiting partial molar volume of solute.

Feakins and co-workers applied transition state treatment for relative viscosity of solution. It is evident from the data in Table 5 that the  $\Delta\mu_2^{0\#}$  values are positive and larger than the  $\Delta\mu_1^{0\#}$  values. This may be due to the fact that 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone in ethanol interaction in the ground state is stronger than in the transition state. In other words, the solvation of solute in the transition state is unfavourable in terms of free energy. Furthermore, as  $\Delta\mu_2^{0\#} > \Delta\mu_1^{0\#}$ , then according to the Feakins model, the solute behaves as structure-maker. This again supports the behaviour of  $dB/dT$  for both the solutes in ethanol. Similar results were also reported for amino acids/glycylglycine in aqueous D-galactose solutions [18]. The  $\Delta\mu_2^{0\#}$  values follow the order, 2,4-dihydroxyacetophenone > 2,6-dihydroxyacetophenone. According to Feakins et al. [19], the greater the value of  $\Delta\mu_2^{0\#}$  the greater is the structure-making ability of the solute. Therefore, both solutes are act as structure-makers in ethanol solution. This again supports the behaviour of the properties discussed earlier. Structure making behaviour may be occurred because of electron donating (-OH) group present in both the solutes systems.

### Conclusions

On the bases of experimental data, it is concluded that in the studied systems, solute-solvent interactions predominates. The limiting apparent molar volume ( $V_\phi^0$ ), limiting apparent molar expansivity ( $\phi_0^E$ ), second derivative of infinite dilution of partial molar volume with temperature  $(\partial^2 V_\phi^0 / \partial T^2)_p$  were determined. These results shows that of 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone are structure maker in the





ethanol solution. Viscosity  $B$ -coefficient, variation of  $B$  with temperature  $dB/dT$ , free energy of activation per mole of solute  $\Delta\mu_2^{0\ddagger}$  values were calculated. These results also confirm the same structure maker behavior of both the solutes in ethanol solution.

### Acknowledgements

The authors are thankful to the University authorities for providing laboratory facilities.

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Table 4 The partial molar expansibility ( $\phi_E^0$ ) and  $(\partial\phi_E^0/\partial T)_p$  of 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone in ethanol solution at different temperatures.

T/K	$\phi_E^0 / (\text{m}^3 \text{mol}^{-1} \text{K}^{-1})$	$(\partial\phi_E^0 / \partial T)_p / (\text{m}^3 \text{mol}^{-1} \text{K}^{-2})$
<b>2,4-dihydroxyacetophenone</b>		
298.15	0.953	<b>0.0078</b>
303.15	0.992	
308.15	1.031	
313.15	1.070	
<b>2,6-dihydroxyacetophenone</b>		
298.15	-15.886	<b>0.0078</b>
303.15	-15.847	
308.15	-15.808	
313.15	-15.769	

Table 5 values of B-coefficient, activation free energies of solvent  $\Delta\mu_1^{0\#}$  and solute  $\Delta\mu_2^{0\#}$  along with values of  $dB/dT$  of 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone in ethanol solution at different temperatures 298.15-313.15 K.

B-coefficient	T/K				dB/dT
	298.15	303.15	308.15	313.15	
<b>2,4-dihydroxyacetophenone</b>					
$B \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	2.5016(±0.3514)	2.4760(±0.2034)	1.7570(±0.1042)	1.7360(±0.2490)	<b>-0.060</b>
$\Delta\mu_1^{0\#} / \text{kJmol}^{-1}$	6.3965	6.4790	6.5559	6.6484	
$\Delta\mu_2^{0\#} / \text{kJmol}^{-1}$	16.1252	16.1903	11.7118	11.7598	
<b>2,6-dihydroxyacetophenone</b>					
$B \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	2.4900 (±0.3137)	2.4774(±0.2035)	1.7806(±0.1096)	1.7410(±0.2529)	<b>-0.058</b>
$\Delta\mu_1^{0\#} / \text{kJmol}^{-1}$	6.3965	6.479	6.5559	6.6484	
$\Delta\mu_2^{0\#} / \text{kJmol}^{-1}$	16.0485	16.1890	11.7062	11.7430	

(Parentheses indicate standard errors.)