



## Study of Intermolecular Interactions of Binary Liquid Mixtures by Measuring Intensive Macroscopic Properties at (303.15, 313.15 and 323.15) K and at Ambient Pressure

T.R Kubendran (corresponding author)

Department of Chemical Engineering

Alagappa College of Technology

Anna University, Chennai-600025, India

E-mail: trkubendran@yahoo.co.in

R. Baskaran

Department of chemical engineering

St. Joseph's college of Engineering, Chennai-119, India

E-mail: rbaskaran2000@yahoo.com

### Abstract

Measurements of thermodynamic and transport properties have been adequately employed in understanding the nature of molecular systems and physico-chemical behavior in liquid mixtures. These properties are important from practical and theoretical point of view to understand liquid theory. In the present study density ( $\rho$ ) and viscosity ( $\eta$ ), have been measured for a binary liquid mixture of Diacetone alcohol with benzene and chlorobenzene, over the entire composition range at 303.15 K, 313.15 K and 323.15 K and the evaluation of different excess properties. The viscosity values and excess values were fitted to respective models. It was found that in all cases, the data obtained fitted with the values correlated by the corresponding models very well. The molecular interactions existing between the components and comparison of liquid mixtures were also discussed.

**Keywords:** Binary mixture, Diacetone alcohol, Benzene, Chlorobenzene, Density, Viscosity

### 1. Introduction

Binary liquid mixtures due to their unusual behavior have attracted considerable attention Ewing et al. (1970). In chemical process industries materials are normally handled in fluid form and as a consequence, the physical, chemical, and transport properties of fluids assume importance. Thus data on some of the properties associated with the liquids and liquid mixtures like Density, and viscosity, find extensive application in solution theory and molecular dynamics Mchaweh et al. (2004). Such results are necessary for interpretation of data obtained from thermo chemical, electrochemical, biochemical and kinetic studies "Kenart, (2000)". Diacetone alcohol is used as coating solvent. Diacetone alcohol + benzene mixture is used in the preparation of tetramethyl oxopiperidine and also acts as pigments. Diacetone alcohol + chlorobenzene mixture is used in the preparation of polymeric photonic crystals which is used for producing switches. In the present paper, we have reported density ( $\rho$ ) and viscosity ( $\eta$ ) of pure diacetone alcohol with benzene and chlorobenzene as well as for the binary system constituted by these chemicals at temperatures of 303.15 K, 313.15 K and 323.15 K. The viscosity values have been fitted to "McAllister, (1960)" model. The deviation values have been fitted to "Redlich-Kister, (1948)" equation. Literature survey showed that no measurements have been previously reported for the mixture studied in this paper.

### 2. Materials and methods

The chemicals used were of analytical reagent grade obtained from loba chemicals. All were dried over anhydrous calcium chloride and fractionally distilled "Oswal and Patel,(1995)". All the weighing measurements were done with Shimadzu Corporation Japan Type BL 2205 electronic balance accurate to 0.01 g. The possible uncertainty in the mole fraction was estimated to be less than  $\pm 0.0001$ . All the measurements described below were performed at least three times and the results were averaged to give the final values.

### 2.1 Density

The densities were determined by using bicapillary pycnometer as described by Arun et al.(1995) and calibrated with deionized double distilled water with  $0.9960 \times 10^3 \text{ Kg.m}^{-3}$  as its density at temperature 303.15 K. The positions of the liquid level in the two arms were recorded with a help of traveling microscope which could read to 0.01mm. The precision density measurements were within  $\pm 0.0003 \text{ g.cm}^{-3}$ . The excess volumes can be computed from experimental density data using the relationship

$$V^E = (x_1 M_1 + x_2 M_2) / \rho_m - (x_1 M_1 / \rho_1 + x_2 M_2 / \rho_2) \quad (1)$$

Where  $x_1$  and  $x_2$  refers to the mole fraction of components 1 and 2.  $\rho_1$  and  $\rho_2$  refers to the density of components 1 and 2.  $\rho_m$  is the density of mixture.

### 2.2 Kinematic viscosity

The Kinematic viscosities were measured as described by Kubendran et al. (2004) at the desired temperature using Ostwald viscometer. The viscometer was calibrated using water. The flow measurements were made with an electronic stopwatch with a precision of 0.01sec. In the calculation of viscosity, two constants a and b of the viscometer in the relation  $v = (at) - (b/t)$  were obtained by measuring the flow time with high purity benzene at the working temperature. The calculated viscosities were fitted in Eq. (2) and constants were determined. The kinematic viscosity were correlated by means of McAllister model considering three-body interaction, which for a two component mixture gives

$$\ln v = x_1^3 \ln v_1 + 3 x_1^2 x_2 \ln v_{12} + 3 x_1 x_2^2 \ln v_{21} + x_2^3 \ln v_2 - \ln(x_1 + x_2 M_2 / M_1) + 3 x_1^2 x_2 \ln ((2 + M_2 / M_1) / 3) + x_2^3 \ln (M_2 / M_1) + 3 x_1 x_2^2 \ln ((1 + 2 M_2 / M_1) / 3) \quad (2)$$

Where  $v$  refers to the kinematic viscosity of the mixture of components 1 and 2 having mole fractions  $x_1$  and  $x_2$  respectively.  $v_1$  and  $v_2$  refers to the kinematic viscosity of pure liquids 1 and 2 respectively.  $v_{12}$  and  $v_{21}$  represent the interaction parameters obtained by multiple regression analysis.  $M_1$  and  $M_2$  refer to the molecular weight of the two components respectively. The viscosity deviations can be calculated as

$$\Delta \eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \quad (3)$$

where  $\eta$ ,  $\eta_1$ , and  $\eta_2$  are the dynamic viscosities of the mixture and those of the pure components 1 and 2 respectively. The experimentally determined excess volume and viscosity deviation data for the binary system of this investigation have been correlated using Redlich Kister equation by the method of least square.

$$V^E \text{ or } \eta = x_1 x_2 \sum a_i (x_1 - x_2)^i \quad (4)$$

### 3. Results and discussion

“Table 1-3” summarizes experimentally determined densities ( $\rho$ ) and viscosities ( $\eta$ ) of Diacetone alcohol with benzene and chlorobenzene mixtures at 303.15 K, 313.15 K and 323.15 K. “Table 4” represents Redlich-Kister Constants for excess volume, viscosity deviation and McAllister constants for the viscosity of mixtures at 303.15 K, 313.15K, and 323.15 K. Excess volume and viscosity deviation of the mixtures were plotted in Fig.1-4. As seen in Fig.1&2 the excess molar volume values of the mixtures are negative and increases when temperature increases. It can be summarized that excess values may be affected by three factors. The first factor is the specific forces between molecules, such as hydrogen bonds, charge transfer complexes, breaking of hydrogen bonds and complexes bringing negative excess values Changsheng wang et al. (2006). The second factor is the physical intermolecular forces, including electrostatic forces between charged particles and between a permanent dipole and so on induction forces between a permanent dipole and an induced dipole, and forces of attraction (dispersion forces) and repulsion between non polar molecules. Physical intermolecular forces are weak and the sign of excess value may be positive or negative, but the absolute values are small. Third factor is the structural characteristics of the component arising from geometrical fitting of one component in to other structure due to the differences in shape and size of the components and free volume. The negative  $V^E$  values in the mixtures under study indicate that interactions between molecules of the mixtures are stronger than interactions between molecules in the pure liquids and that associative force dominate the behavior of the solution Rena et al. (2006). There fore in this system, compression in free volume is considered to occur, making the mixture more compressible than the ideal mixture which ultimately culminates into negative values of  $V^E$ . In Fig. 3&4, the deviations in viscosity for the mixtures are positive for all the mole fractions and increases when temperature increases. The viscosity of the mixture strongly depends on the entropy of mixture, which is related with liquid’s structure and enthalpy Kauzman et al. (1940), consequently with molecular interactions between the components of the mixture. Therefore the viscosity deviation depends on molecular interactions as well as on the size and shape of the molecules. For negative deviations of Raoult’s law and with strong specific interactions, the viscosity deviations are positive.

#### 4. Conclusion

It may be concluded that the interactions resulting in the interstitial accommodation of benzene, and chloro in to diacetone alcohol are the predominant factor over dipole – dipole and dipole induced–dipole interaction. The intermolecular interaction of the mixtures leads to specific type. The excess values of the mixtures show a systematic change with increasing temperature. With an increase in temperature the intermolecular interactions between molecules become weak. At 323.15 K the intermolecular interaction become weak compared with 303.15 K and 313.15 K. It is clear from standard deviation values that McAllister equation can represent the viscosity values, and Redlich Kister equation can represent the excess volume and viscosity deviation values very well. It has been observed that the intermolecular interaction was more with chlorobenzene than with benzene. The algebraic values of excess values fall in the order reflecting an easier flow of the mixture at the direction of decreasing molecular weight of arylhalides.

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Table 1. Diacetone alcohol, benzene and chlorobenzene mixtures at 303.15 K

Diacetone alcohol + benzene			Diacetone alcohol + chlorobenzene		
$x_1$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mpa}\cdot\text{s}$	$x_1$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mpa}\cdot\text{s}$
0.0000	0.8720	0.6905	0.0000	1.1020	0.7705
0.1225	0.8825	0.9699	0.1268	1.0790	1.0555
0.2525	0.8927	1.2658	0.2462	1.0568	1.3221
0.3224	0.8979	1.4200	0.3454	1.0395	1.5440
0.4218	0.9047	1.6482	0.4991	1.0135	1.8770
0.5045	0.9111	1.8400	0.5214	1.0100	1.9331
0.6112	0.9164	2.0800	0.6119	0.9961	2.1331
0.7123	0.9221	2.2828	0.7214	0.9785	2.3441
0.8191	0.9275	2.5151	0.8585	0.9580	2.6221
0.9337	0.9331	2.7600	0.9141	0.9490	2.7224
1.0000	0.9360	2.8900	1.0000	0.9360	2.8900

Molefraction, density and viscosity of diacetone alcohol+ benzene and diacetone alcohol + chlorobenzene mixture at 303.15 K.

Table 2. Diacetone alcohol, benzene and chlorobenzene mixtures at 313.15 K

Diacetone alcohol + benzene			Diacetone alcohol + chlorobenzene		
$x_1$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mpa}\cdot\text{s}$	$x_1$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mpa}\cdot\text{s}$
0.0000	0.8450	0.6780	0.0000	1.0800	0.6914
0.1225	0.8559	0.9378	0.1268	1.0565	0.9771
0.2525	0.8665	1.2250	0.2462	1.0338	1.2210
0.3224	0.8719	1.3710	0.3454	1.0163	1.4661
0.4218	0.8791	1.5810	0.4991	0.9899	1.7994
0.5045	0.8846	1.7700	0.5214	0.9864	1.8551
0.6112	0.8912	2.0000	0.6119	0.9721	2.0661
0.7123	0.8970	2.2130	0.7214	0.9546	2.2662
0.8191	0.9029	2.4210	0.8585	0.9335	2.5444
0.9337	0.9088	2.6600	0.9141	0.9251	2.6331
1.0000	0.9121	2.7910	1.0000	0.9121	2.7910

Molefraction, density and viscosity of diacetone alcohol+ benzene and diacetone alcohol + chlorobenzene mixtures at 313.15 K.

Table 3. Diacetone alcohol, benzene and chlorobenzene mixtures at 323.15 K

Diacetone alcohol + benzene			Diacetone alcohol + chlorobenzene		
$x_1$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mpa}\cdot\text{s}$	$x_1$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mpa}\cdot\text{s}$
0.0000	0.8280	0.6600	0.0000	1.0674	0.5543
0.1225	0.8398	0.9180	0.1268	1.0435	0.8551
0.2525	0.8512	1.2000	0.2462	1.0215	1.1224
0.3224	0.8570	1.3400	0.3454	1.0041	1.3445
0.4218	0.8647	1.5400	0.4991	0.9780	1.6775
0.5045	0.8708	0.8708	0.5214	0.9745	1.7338
0.6112	0.8781	1.9311	0.6119	0.9604	1.9358
0.7123	0.8846	2.1441	0.7214	0.9431	2.1446
0.8191	0.8911	2.3314	0.8585	0.9220	2.4339
0.9337	0.8975	2.5524	0.9141	0.9138	2.5227
1.0000	0.9010	2.6700	1.0000	0.9010	2.6700

Molefraction, density and viscosity of diacetone alcohol+ benzene and diacetone alcohol + chlorobenzene mixture at 323.15 K.

Table 4. Parameters of Redlich and McAllister

Redlich kister constants								McAllister constants		
$V^E / \text{cm}^3/\text{mole}^{-1}$				$\Delta\eta / \text{mpa}\cdot\text{s}$				$v / \text{mpa}\cdot\text{s}$		
$A_0$	$A_1$	$A_2$	S	$A_0$	$A_1$	$A_2$	S	$v_{12}$	$v_{21}$	S
Diacetone alcohol – benzene										
303.15 K										
-0.2576	-0.1427	0.3333	0.80	0.0689	0.0235	-0.0549	3.12	2.2082	1.8540	1.40
313.15 K										
-0.1557	-0.0611	0.0261	4.18	0.1316	0.0578	-0.1348	2.15	2.1415	1.7558	1.01
323.15 K										
-0.1280	-0.0226	0.0528	3.12	0.0559	0.1583	-0.1308	1.09	2.1633	1.6717	0.42
Diacetone alcohol – chloro benzene										
303.15 K										
-1.3946	-0.4311	0.9939	0.47	0.1793	0.0582	-0.1343	1.73	2.2738	1.8748	0.70
313.15 K										
-1.2565	-0.2556	0.5894	1.32	0.2402	0.1011	-0.2332	1.02	2.1240	1.7048	2.60
323.15 K										
-1.1253	-0.3754	0.8656	0.45	0.2906	0.1594	-0.3676	0.59	2.0150	1.6312	1.51

Redlich kister and McAllister constants for the diacetone alcohol+ benzene and diacetone alcohol + chlorobenzene mixture at 303.15 K, 313.15 K, 323.15 K.

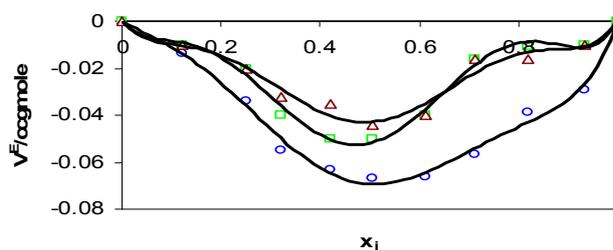


Figure 1. Plot of  $V^E$  against  $x_1$  of Diacetone alcohol + benzene at 303.15 K ( $\square$ ), 313.15 K ( $\square$ ) and 323.15 K ( $\Delta$ )

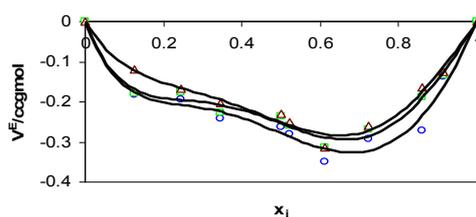


Figure 2. Plot of  $V^E$  against  $x_1$  of Diacetone alcohol + chloro benzene at 303.15 K ( $\square$ ), 313.15 K ( $\square$ ) and 323.15 K ( $\Delta$ )

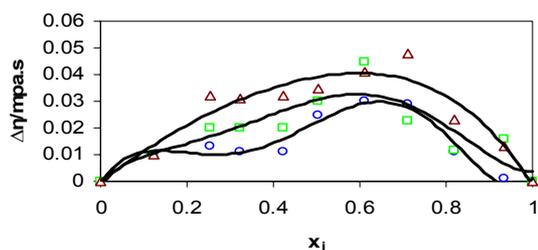


Figure 3. Plot of  $\Delta\eta$  against  $x_1$  of Diacetone alcohol + benzene at 303.15 K ( $\square$ ), 313.15 K ( $\square$ ) and 323.15 K ( $\Delta$ )

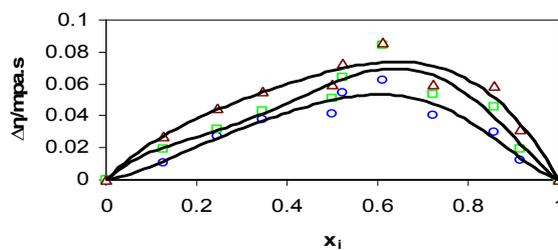


Figure 4. Plot of  $\Delta\eta$  against  $x_1$  of Diacetone alcohol + chlorobenzene at 303.15 K ( $\square$ ), 313.15 K ( $\square$ ) and 323.15 K ( $\Delta$ )