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Study of Molecular Interactions in Binary Liquid Mixtures of Acetophenone with Benzyl Acetate using Volumetric and Viscometric Properties.

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ABSTRACT

Densities and viscosities of the binary mixtures of acetophenone with benzyl acetate have been measured over the entire mole fractions at (303.15, 308.15, 313.15, 318.15 and 323.15) K. From these experimental results, excess molar volume V^E and viscosity deviation $\Delta\eta$ are calculated. The viscosity data have been correlated with the equations of Grunberg and Nissan, Hind et al., Tamura and Kurata, Katti and Chaudri, Sedgwick, Krishnan- Laddha and McAllister. The thermo physical properties under study were fit to the Jouyban - Acree model. The excess values were correlated using Redlich-Kister polynomial equation to obtain their coefficients and standard deviations. It was found that in all cases, the data obtained fitted with the values correlated by the corresponding models very well. The results are interpreted in terms of molecular interactions occurring in the solution.

Keywords: Viscosity; Density; Molecular interactions; Excess volumes; Viscosity deviations

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INTRODUCTION

The thermodynamic, acoustic and transport properties of liquids and liquid mixtures[1] are used to study the molecular interactions between the various components of the mixtures and also to understand engineering applications concerning heat transfer, mass transfer, and fluid flow. 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 [2]. Such results are necessary for interpretation of data obtained from thermo chemical, electrochemical, biochemical and kinetic studies [3]. Acetophenone is an important industrial chemical widely used as an ingredient of flavor and fragrance in soaps, detergents, cosmetics and perfumes. It has also been used as an important intermediate for pharmaceuticals and agrochemicals. The acetates are commonly used as solvents in the production of lacquers and other products and also as synthetic fruit flavorings in food. Benzyl acetate is used as a solvent in inks for coatings, cosmetics and personal-care products, intermediate for pharmaceuticals & agrochemicals, flexographic and rotogravure printing. In our earlier paper, we had studied the transport properties of binary liquid mixtures [4, 5]. In continuation of this research, we have reported density (ρ) and viscosity (η) of pure acetophenone and benzyl acetate as well as for the binary system constituted by these two chemicals at temperatures of (303.15, 308.15, 313.15, 318.15 and 323.15 K). The viscosity values have been fitted to Grunberg and Nissan [6], Hind et al. [7], Tamura and Kurata [8], Katti and Chaudri [9], Sedgwick [10], McAllister [11] and Krishnan and Laddha model [12]. The Jouyban –Acree model [13] has also been extended to density and viscosity of binary mixtures. The deviation values have been fitted to Redlich-Kister type [14] equation. Literature survey showed that no measurements have been previously reported for the mixture studied in this paper.

EXPERIMENTAL SECTION

Materials and Methods

All the chemicals used in this study were of analytical grade and obtained from Lobo Chemicals, India. The claimed mass fraction purity for the chemicals was ≥0.998. These chemicals were dried over molecular sieves and partially degassed prior to use [15, 16]. The purity of these experimental chemicals was checked by comparing the observed densities and viscosities with those reported in the literature. The measured values are included in Table 1 along with the available literature values. Binary mixtures are prepared by mixing appropriate volumes of the liquid components in the specially designed glass bottles with air tight Teflon coated caps and mass measurements performed on a Shimadzu Corporation Japan type BL 2205 electronic balance, with a precision of ±0.01 mg. The required properties are measured on the same day immediately after preparing each composition. The uncertainty of the mole fraction is ±0.0001. For all measurements, temperatures were controlled by circulating the water through a thermostat (Technico, Madras) keeping temperature fluctuation within ±0.03K.

Table 1. Comparison of experimental density and viscosity of pure liquids with literature values at 303.15 K

Pure liquids	ρ / g·cm$^{-3.}$		η/(mPa · s)	
	lit.	Exp	lit	Exp
Acetophenone	1.0194[20]	1.0199	----------	
	1.0164[21]		1.455[21]	1.4553
	1.0476[22]		--------	
	1.0482[9]		1.838[23]	
Benzyl acetate	1.04817[23]	1.04817		1.8382

Density

Densities were determined by using a 25 cm^3 bicapillary pycnometer and calibrated with deionized double distilled water with a density of 996.0 kg m^{-3} at a temperature of 303.15 K. The pycnometer was thermostatted in a transparent walled water bath (maintained constant to ± 0.01 K) for 15 min to attain thermal equilibrium, and the liquid level in the two arms was obtained with a traveling microscope which could read to 0.01 mm. The precision of the density measurements was estimated to be ± 0.0003 g·cm$^{-3.}$

Kinematic viscosity

The kinematic viscosities were measured with Ostwald viscometer previously calibrated using water. The time was measured with a precision of 0.01 s, and the uncertainty in the viscosity was estimated to be less than 0.003 mPa·s. The kinematic viscosity was obtained from the working equation

$$v = at - b / t \qquad (1)$$

where the two constants a and b were obtained by measuring the flow time t of benzene. The viscosities of mixtures of acetophenone and benzyl acetate have been correlated with the model proposed by Mc Allister [11] for a two-component mixture considering three body interactions.

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

In equation 2, v_1 and v_2 refer to the kinematic viscosity of pure liquids 1 and 2 having mole fractions x_1 and x_2, respectively. The parameters v_{12} and v_{21} represent the interaction parameters obtained by multiple regression analysis, while M_1 and M_2 are the molar mass of the components.

The kinematic viscosity was correlated by means of the Krishnan and Laddha model [12] for a two component mixture, which gives

$$\ln v = x_1 \ln v_1 + x_2 \ln v_2 + x_1 \ln M_1 + x_2 \ln M_2 + \ln(x_1 M_1 + x_2 M_2 - 2.30 x_1 x_2 (B + C(x_1 - x_2)...)) \qquad (3)$$

Where B and C are interaction parameters. The Grunberg –Nissan [6] phenomenological equation reads

$$\eta = \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12}) \tag{4}$$

where G_{12} is a parameter proportional to the interchange energy and has been regarded as indicator for the nonideal behavior of binary mixtures. A semiemprical equation due to Tamura and Kurata [8] is

$$\eta = x_1 V_1 \eta_1 + x_2 V_2 \eta_2 + 2(x_1 x_2 V_1 V_2)^{1/2} T_{12} \tag{5}$$

Hind et al [7]., have proposed the following equation

$$\eta = x_1{}^2 \eta_1 + x_2{}^2 \eta_2 + 2 x_1 x_2 H_{12} \tag{6}$$

where H_{12} is attributed to unlike pair interactions. Katti and chaudri [9] derived the following equation

$$\ln \eta V = x_1 \ln V_1 \eta_1 + x_2 \ln V_2 \eta_2 + x_1 x_2 K_{12} \tag{7}$$

where K_{12} is an interaction parameter. The Sedgwick [10] model of mixture viscosity is

$$\eta^2 = x_1{}^2 \eta_1{}^2 + x_2{}^2 \eta_2{}^2 + 2 x_1 x_2 C^2 \tag{8}$$

where C is an interaction parameter. Jouyban et.al [13] proposed a model for correlating the thermal properties of liquid mixtures at various temperatures

$$\ln Y_{m,T} = f_1 \ln y_1 + f_2 \ln y_2 + f_1 f_2 \Sigma[A_J(f_1 - f_2)^J / T] \tag{9}$$

where $Y_{m,T}$, $y_{1,T}$, and $y_{2,T}$ are the viscosity of the mixture and solvents 1 and 2 at temperature T, respectively. A_J is the model constant.

RESULTS AND DISCUSSION

Measured values of densities and viscosities of acetophenone with benzyl acetate at temperatures of (303.15, 308.15, 313.15, 318.15 and 323.15) K are listed in Table 2. The density values have been used to calculate excess molar volumes V^E using the following equation

$$V^E = (x_1 M_1 + x_2 M_2) / \rho_m - (x_1 M_1 / \rho_1 + x_2 M_2 / \rho_2) \tag{10}$$

where x_1 and x_2 refer to the mole fraction of components 1 and 2. ρ_1, ρ_2, and ρ_m refer to the density of components 1 and 2 and the density of the mixture, respectively. The viscosity deviations $\Delta\eta$ were calculated from the viscosity values using

$$\Delta\eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \tag{11}$$

where η, η$_1$, and η$_2$ are the viscosity of the mixture and the viscosity of pure components 1 and 2, respectively. The uncertainty in the calculation of Δ*η* from viscosity measurements was estimated to be ±0.0001.

Table 2. Densities ρ and viscosities η for the acetophenone (1) + benzyl acetate (2) mixture at *T*= (303.15, 308.15, 313.15, 318.15 and 323.15) K

Acetophenone (1) + benzyl acetate (2)										
	ρ g·cm^{-3}					η/ (mPa·s)				
X$_1$	303.15	308.15	313.15	318.15	323.15	303.15	308.15	313.15	318.15	323.15
0.0000	1.04817	1.04439	1.04141	1.03703	1.03465	1.8382	1.7034	1.5872	1.4327	1.2304
0.1087	1.04555	1.04178	1.03860	1.03408	1.03136	1.8033	1.6742	1.5544	1.4067	1.2165
0.2132	1.04294	1.03918	1.03580	1.03113	1.02808	1.7685	1.6452	1.5219	1.3807	1.2019
0.3137	1.04033	1.03657	1.03299	1.02818	1.02480	1.7337	1.6158	1.4894	1.3547	1.1871
0.4106	1.03771	1.03397	1.03018	1.02523	1.02152	1.6989	1.5865	1.4570	1.3287	1.1721
0.5039	1.03510	1.03136	1.02738	1.02228	1.01825	1.6641	1.5570	1.4246	1.3027	1.1573
0.5940	1.03248	1.02876	1.02458	1.01934	1.01498	1.6293	1.5274	1.3925	1.2768	1.1420
0.6809	1.02987	1.02615	1.02177	1.01640	1.01172	1.5945	1.4977	1.3604	1.2508	1.1260
0.7648	1.02725	1.02354	1.01897	1.01346	.00846	1.5597	1.4679	1.3283	1.2248	1.1101
0.8458	1.02463	1.02094	1.01617	1.01052	1.00520	1.5249	1.4381	1.2965	1.1988	1.0937
0.9242	1.02202	1.01833	1.01337	1.00758	1.00195	1.4901	1.4082	1.2646	1.1728	1.0773
1.0000	1.01941	1.01573	1.01058	1.00465	0.99871	1.4553	1.3782	1.2329	1.1469	1.0609

Excess molar volumes and deviations of viscosity were fitted to a Redlich–Kister [14] equation of the type

$$Y= x_1 \, x_2 \, \Sigma \, A_i(x_1- x_2)^i \qquad\qquad (12)$$

where *Y* is either V^E or Δη and *n* is the degree of polynomial. Coefficients Ai were obtained by fitting equation 12 to experimental results using a least-squares regression method. In each case, the optimum number of coefficients is ascertained from an examination of the variation in standard deviation (*S*). *S* was calculated using the relation

$$S(Y)=[\Sigma(A_{exp}-A_{cal})^2 \, / \, (N-n)]^{\frac{1}{2}} \qquad\qquad (13)$$

Where *N* is the number of data points and *n* is the number of coefficients. The calculated values of coefficients along with the standard deviation (*S*) are given in Table 3. Interaction parameters and standard deviations of the McAllister model [11] and Krishnan and Laddha [12] model for the viscosity of acetophenone and benzyl acetate mixture at (303.15, 308.15, 313.15, 318.15 and 323.15) K are presented in Table 4 and 5. Constants and standard deviations of the Jouban-Acree model [13] of the acetophenone and benzyl acetate are presented in Table 6.

Excess molar volumes with the mole fraction (x_1) of acetophenone and benzyl acetate at (303.15, 308.15, 313.15, 318.15 and 323.15) K are represented in figure1. This shows that the excess molar volumes are always negative for all the studied temperatures. Treszczanowicz et al. [17] and Roux and Desnoyers [18] suggested that V^E 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

V^E. 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 V^E. 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 V^E.

Table 3. Parameters and standard deviations (*S*) of Redlich–Kister Equation for acetophenone (1) + benzyl acetate (2) *T* = (303.15, 308.15, 313.15, 318.15 and 323.15) K

Functions	A0	A1	A2	A3	S
303.15K					
V^E/cm^{3}mol^{-1}	-0.0102	0.0064	0.0116	0.0031	0.0001
Δη/ mPa·s	-0.0568	-0.1648	0.0636	0.1006	0.0015
308.15 K					
V^E/cm^{3}mol^{-1}	-0.0062	0.0103	0.0067	-0.0002	0.0002
Δη/ mPa·s	-0.0549	-0.1518	0.0621	0.0923	0.0020
313.15K					
V^E/cm^{3}mol^{-1}	-0.0064	0.016	0.0072	-0.0052	0.00005
Δη/ mPa·s	-0.0477	-0.1397	0.0542	0.0851	0.0012
318.15 K					
V^E/cm^{3}mol^{-1}	-0.0042	0.0213	0.0051	-0.01	0.00027
Δη/ mPa·s	-0.0374	-0.1229	0.0415	0.0749	0.0023
323.15K					
V^E/cm^{3}mol^{-1}	-0.0032	0.0302	0.0035	-0.0188	0.0001
Δη/ mPa·s	-0.0165	-0.1052	0.0145	0.0637	0.00100

Table 4. Parameters of the McAllister model and Standard deviation for the kinematic viscosity acetophenone (1) + benzyl acetate (2) mixture

Temperature	Mc Allister constants		
T/K	A	B	S
303.15	1.62374	1.73926	0.00004
308.15	1.52325	1.62123	0.00037
313.15	1.38654	1.49417	0.00080
318.15	1.27240	1.35902	0.00057
323.15	1.14152	1.19147	0.00064

Table 5. Parameters of the   Krishnan – Laddha model and standard deviation for the kinematic viscosity acetophenone (1) + benzyl acetate (2) mixture

Temperature	Krishnan – Laddha Constants				
T/K	A_0	A_1	A_2	A_3	S
303.15	-0.04236	-0.0060	-0.0008	-0.0002	0.0003
308.15	-0.04008	-0.0053	-0.0005	-0.0007	0.0001
313.15	-0.04423	-0.0061	-0.0007	-0.0003	0.0001
318.15	-0.04034	-0.0057	-0.0007	0.0005	0.0009
323.15	-0.03389	-0.0055	-0.0004	0.0034	0.0048
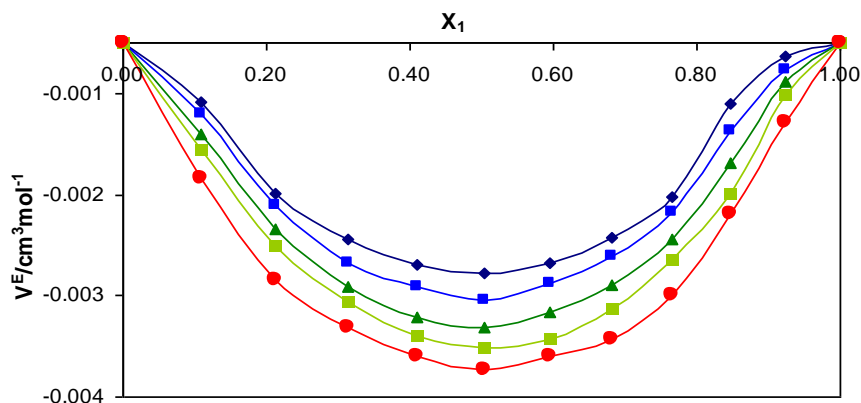
Fig.1 Excess molar volume for [Acetophenone (1) + Benzyl acetate (2)]: ♦ T=303.15 K; ■ T=308.15 K; ▲ T=313.15K;× T=318.15 K;●T=323.15K

Table 6. Parameters and standard deviations of Jouyban- Acree model for Acetophenone (1) + benzyl acetate (2) mixture

Properties	T/K	A0	A1	A2	A3	S
ρ / g·cm$^{-3.}$	303.15	41.031	-5.50518	-39.919	-14.446	0.0011
	308.15	3.0375	-0.0359	-2.7709	-0.9381	0.00008
	313.15	13.272	-0.532	-12.351	-5.2151	0.03320
	318.15	41.031	-5.50518	-39.919	-14.446	0.0011
	323.15	79.947	-8.7436	-76.941	-60.423	0.0018
η/ mPa·s	303.15	2.7273	-0.0357	-2.2016	0.5171	0.00005
	308.15	-1.587	0.0072	1.3252	0.2613	0.00003
	313.15	-1.587	0.0072	1.3252	0.2613	0.00003
	318.15	2.363	0.0046	-1.6297	-0.702	0.00007
	323.15	-1.6796	0.0089	1.7603	0.2385	0.00003

Viscosity deviations with the mole fraction of component 1 were presented in figure 2. Viscosity values are positive for the acetophenone and benzyl acetate mixture at all the studied temperatures. Fig.2 shows that the viscosity deviations are positive [19], indicates that the interaction between binary mixtures is strong. The negative viscosity deviations may be attributed to the existence of dispersion and dipolar forces between unlike molecules and related to the difference in size and shape of the unlike molecules. Experimental values of mixture viscosities and the viscosities of their components are used in Eqs.(4),(5),(6),(7), and (8) to evaluate $G_{12},T_{12},H_{12},K_{12}$ and C .These values for the system studied are recorded in table.7.

Table.7. Interaction parameters (G_{12}), (T_{12}), (H_{12}), (C) and (K_{12}) for acetophenone with benzyl acetate at (303.15, 308.15, 313.15, 318.15 and 323.15) K

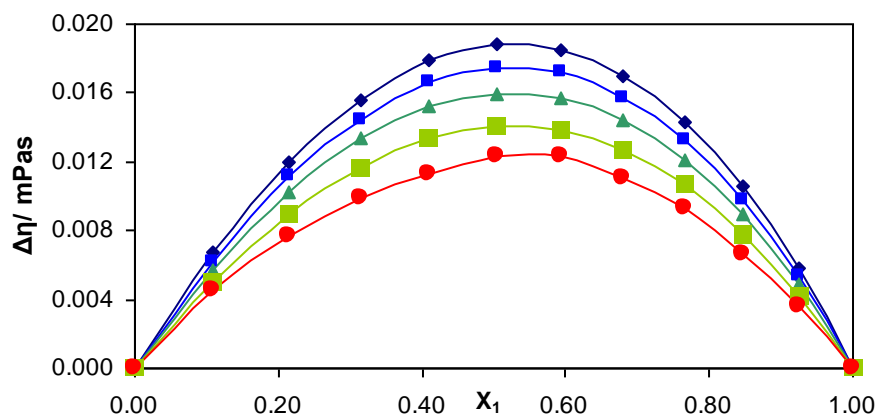| T/K	G_{12}	S	T_{12}	S	H_{12}	S	C	S	K_{12}	S
303.15	0.2078	0.023	-1.3708	0.006	1.0503	0.005	0.0255	0.001	-0.0566	0.003
313.15	0.1354	0.001	-1.2008	0.005	0.8166	0.007	0.0210	0.001	-0.0385	0.009
323.15	0.2246	0.003	-1.0160	0.016	0.9518	0.006	0.0341	0.005	-0.0331	0.005

Fig.2 Viscosity deviations for [Acetophenone (1) + Benzyl acetate (2)]:♦ T=303.15 K; ■ T=308.15 K; ▲ T=313.15K;× T=318.15 K;●T=323.15K

CONCLUSIONS

Densities and viscosities for binary mixtures have been measured. Excess molar volumes and viscosity deviations of acetophenone and benzyl acetate were obtained from the experimental results and fitted by the Redlich-Kister equations. The results are analyzed in the light of molecular interactions between the components. The viscosity data are correlated with the Grunberg and Nissan, Hind, Tamura and Kurata, Katti and Chaudri, Sedgwick, Krishnan- Laddha and McAllister.   It has been concluded that the Jouyban - Acree model is very well suited for correlating the thermo physical properties of the binary mixture studied.

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REFERENCES

[1]   Kim E S, Marsh K N. J Chem Eng Data 1988;33: 288-292.
[2]   Mchaweh A, Alsaygh A, Mosh-Feghian M A. Fluid Phase Equilib 2004;224: 157-167.
[3]   Kenart C M, Kenart W. Phys Chem Liq 2000;38: 155-180.
[4]   Baskaran R, Kubendran T R. J Chem Eng Data 2008;53: 978-982.
[5]   Baskaran R, Kubendran T R. J Chem Eng Data 2008; 53: 1956-1961.
[6]   Grunberg L, Nissan A. Mixture law of viscosity. Nature, 1949, 164:799-800.
[7]   Hind R K, Mclaughlin E, Ubbelohde A R. Trans Faraday Soc 1960;56:328-334.
[8]   Tamura M, Kurata M. Bull Chem Soc Jpn 1952;25:32-37.
[9]   Katti P K, Chaudhari M M. J Chem Eng Data 1964;9: 442–443.
[10]   Sedgwick TO. The viscosity and thermal conductivity of liquid mixtures, Ph.D thesis Brooklyn Polytechnic Institute (Department of Physics and Chemistry) (1962).
[11]   McAllister R A. Viscosity of liquid mixtures. A I C H E Journal, 1960, 6:427-431.
[12]   Krishnan M R V, Laddha G S. Ind Chem Eng Trans 1963:57.

[13]   Jouyban A, Khoubnasabjafari M, Vaezgharamaleki Z, Fekari Z, Jr Acree W E. Chem Pharm Bull 2005;53: 519-523.

[14]   Redlich O, Kister A T. Ind Eng Chem 1948;40:345-353.

[15]   Perrin D D, Armerego W L F. Purification of Laboratory chemistry, 3[ed]. Pergamon press, Oxford 1988.

[16]   Riddick J A, Bunger W B, Sakano T K. 4th ed.; Wiley-Interscience: New York, 1986.

[17]   Treszczanowicz A J, Kiyohara O, Benson G C. J Chem Thermodyn 1981;13:253-260.

[18]   Roux A, Desnoyers J. J Proc Chem Soc 1978;78: 435-439.

[19]   Fort R J, Moore W R. Trans Faraday Soc 1966;62:1112-1119.

[20]   Syamala V, Venkateshwarlu P, Sivakumar K. J Chem Eng Data 2006;51:928-934.

[21]   Iloukhani H, Rostami Z. J Chem Eng Data 2007;52:921-928.

[22]   Rathnam M V, Sudhir Mohite, Kumar M S S. J Solution Chem 2010;39:1735-1748

[23]   Nani Indraswati, Mudjijati, Filicia Wicaksana, Herman Hindarso, Suryadi Ismadji. J Chem Eng Data 2001;46:696-702.