A Brief Study on Molecular Interaction in a Binary Liquid Mixture at 308.15 K and 318.15 K

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Abstract

A study on thermodynamic parameters of liquids plays an important role for chemical engineering field. The thermodynamic and transport properties of acetophenone and nitrobenzene binary mixture were studied for two temperatures 308.15 K and 318.15 K. The density, viscosity, compressibility, molar volume, excess volume etc are calculated and the results are fitted to Redlich- Kister polynomial equation. The molecular interaction for the binary mixture was explained using the calculated data.

Keywords: acetophenone, density, molar volume, nitrobenzene, thermodynamic parameters.

INTRODUCTION

Liquid phase is the intermediate phase between a solid and the gas phase. A solution is a homogeneous mixture of two or more liquids. A liquid mixture is obtained by mixing two, three or four homogeneous liquids called binary, ternary and quaternary liquid mixtures respectively. Based on Raoult's law liquid solutions are classified into two called real and ideal solutions. The interactions occurring between the molecules of liquid mixtures results in deviation from the ideal behaviour of liquid mixture [1]. The thermodynamic properties are useful in understanding the nature of interactions occurring between the molecules in liquid mixtures. Thermodynamic and transport properties of pure liquids as well as liquid mixtures plays vital role in various fields such as textile, oil, pharmaceutical, chemicals etc [2]. The measurements of density, viscosity, ultrasonic velocity and other thermodynamic parameters of liquid mixtures clearly explains the nature of interaction between the like and unlike molecules. The study of nature of interactions in liquid mixtures involving acetophenone with nitrobenzene have been explained by calculating the thermodynamic properties, nature of functional group present and influence of temperature. Acetophenone is an important industrial chemical, widely used as an ingredient for flavors as well as used in agrochemical industry [3]. The ability of the cyclic ethers to act as additives to gasoline due to their octane enhancing and pollution reducing properties makes it an industrial agent. Nitrobenzene is an aromatic hydrocarbon containing NO_2 as a functional group. It is a versatile solvent used in synthetic and electrochemical research. It is an important raw material for the synthesis of explosives. In this paper, the study focuses on the measurement of density, viscosity, ultrasonic velocity [4], Effective molecular weight, free volume, free length, Wada's constant, Rao's constant, molar volume, relative

association for the binary liquid mixture of acetophenone + nitrobenzene at the temperatures of 308.15 and 318.15K. The aim of this work is to provide a set of data in order to catch the influence of the temperature on the molecular interactions between the above specified solvents of binary mixtures and to find out the nature of molecular interactions between these solvents.

MATERIALS AND METHODS

Acetophenone and nitrobenzene used in the present work were of Analar grade (Merck, Mumbai, India and Loba, Mumbai, India), purified as described in the literature [5] The purity of sample was checked by comparing the measurements of density, viscosity and ultrasonic velocity with the available literature data's which are presented in Table-1. Liquid mixtures were prepared by weight by volume in airtight stoppered bottles using an analytical balance with an accuracy of ±0.0001 g. Densities of pure liquids and their mixtures were measured using relative density method. Relative density bottle of 10 ml capacity was cleaned successively with chromic acid, distilled water and acetone and then dried and used for density measurements [6]. The accuracy of the measurement of density in relative density method depends on the accuracy of mass. Density values are accurate to ±0.0002 $kg.cm^{-3}$. Viscosities were measured using Ostwald viscometer. Viscometer was thoroughly cleaned with chromic acid before measurements. The ultrasonic velocity values fir both pure and liquid mixtures were measured using an ultrasonic interferometer (Pico, Chennai, India) with a frequency of 2 MHz was calibrated using water and nitrobenzene. The overall accuracy in the measurement is ±0.2%. All the measurements were made at 308.15 and 318.15K using a digital thermostat with display accuracy ±0.01 K. The details of the methods and techniques of the measurements have been described earlier [8].

RESULTS

Experimental density, viscosity, ultrasonic speeds are compared with literature values and are reported in Table1. The obtained values of density, viscosity, ultrasonic velocity, and other calculated parameters for the binary mixtures are compiled in Table-2.

Table-1: Experimental densities (ρ), viscosities (η) and ultrasonic velocities (U) of pure acetophenone, nitrobenzene and with their literature values

Compounds	T(K)	ρ (kg/cm^{-3})		η (cP)		U (ms^{-1})	
		Exp	Lit	Exp	Lit	Exp	Lit
Acetophenone [9]	308.15	1.0189	1.0194	2.0977	2.0955	1415	-
	318.15	1.0123	-	1.4886	-	1401	-
Nitrobenzene [10]	308.15	1.1877	1.1911	1.5678	1.5543	1375	1379
	318.15	1.1829	1.1859	1.3734	-	1356	1348

Table-2

Thermodynamic transport properties for the binary mixtures of acetophenone + nitrobenzene at 308.15 K

X_1	ρ (kg/ cm^3)	V^E (cm^3 mol^{-1})	Φ_1	ΔK_S (TPa^{-1})	ΔL_f x 10^{-9} ($kg^{-1}K^{-1}$ m^2s)	Ra	α	η (cP)	$\Delta vfx10^{-7}$ (m^3 mol^{-1})	Δη (cP)	V	R	W	τ x10^{-7}
0	1.1877	0	0	0	0	0	0	1.5678	0	0	0	0	0	0
0.1402	1.1641	-0.2554	0.1533	-0.8978	1.2735	1.1892	0.00103	1.5676	1.2552	0.4109	105.3622	52.5841	4.1455	9.4282
0.2392	1.1467	-0.3258	0.2552	-3.4849	1.2779	1.1697	0.00104	1.5492	1.2818	0.3606	106.7095	52.8837	4.1342	9.3774
0.4443	1.1129	-0.5546	0.4551	-4.4800	1.2906	1.1330	0.00104	1.5183	1.3236	0.2636	109.4143	53.4292	4.1086	9.3609
0.4518	1.1129	-0.6817	0.4625	-5.8124	1.2897	1.1328	0.00104	1.5330	1.3055	0.2759	109.3947	53.4388	4.1096	9.4381
0.5717	1.0929	-0.7162	0.5749	-5.8704	1.2973	1.1111	0.00105	1.5151	1.3305	0.2193	111.0771	53.7754	4.0942	9.4307
0.6927	1.0717	-0.5782	0.6867	-3.9026	1.3089	1.0890	0.00105	1.4998	1.3482	0.1650	112.9460	54.1011	4.0747	9.4934
0.7564	1.0597	-0.3856	0.7455	-2.5482	1.3147	1.0763	0.00106	1.5016	1.3455	0.1463	114.0501	54.3026	4.0641	9.5852
0.8165	1.0491	-0.2600	0.8014	-1.0646	1.3188	1.0648	0.00106	1.5004	1.3487	0.1258	115.0357	54.4973	4.0558	9.6330
0.8671	1.0403	-0.1519	0.8489	-0.2003	1.3218	1.0551	0.00106	1.5061	1.3429	0.1156	115.8674	54.6671	4.0492	9.7097
1	1.0189	0	1	0	0	0	0	2.0977	0	0	0	0	0	0

Table-3

Thermodynamic transport properties for the binary mixtures of acetophenone + nitrobenzene at 318.15 K

X_1	ρ (kg/ cm^3)	V^E (cm^3 mol^{-1})	Φ_1	ΔK_S (TPa^{-1})	ΔL_f x 10^{-9} ($kg^{-1}K^{-1}$ m^2s)	Ra	α	η (cP)	$\Delta vfx10^{-7}$ (m^3 mol^{-1})	Δη (cP)	V	R	W	τ x10^{-7}
0	1.16	0	0	0	0	0	0	1.5678	0	0	0	0	0	0
0.1402	1.1575	-0.1239	0.1540	-0.7743	-2.0071	1.1871	0.0010	1.4846	1.3391	0.4620	105.9630	52.4795	4.1250	9.1916
0.2392	1.1404	-0.2401	0.2570	-1.3079	-2.0042	1.1684	0.0010	1.3545	1.5398	0.3029	107.2990	52.7506	4.1124	8.4624
0.4443	1.1054	-0.3875	0.4601	-2.2452	-2.0016	1.1301	0.0011	1.3298	1.5876	0.2181	110.1567	53.3312	4.0864	8.4592
0.4518	1.1061	-0.5870	0.4678	-4.5845	-2.0201	1.1305	0.0011	1.3474	1.5576	0.2335	110.0672	53.3297	4.0881	8.5536
0.5717	1.0868	-0.7124	0.5832	-3.6624	-1.9900	1.1102	0.0011	1.3404	1.5667	0.1914	111.7006	53.6181	4.0709	8.6351
0.6927	1.0644	-0.4653	0.6983	-1.7238	-1.9574	1.0863	0.0011	1.3249	1.5947	0.1404	113.7206	53.9915	4.0518	8.6644
0.7564	1.0526	-0.3003	0.7592	-1.4041	-1.9574	1.0732	0.0011	1.3222	1.6030	0.1191	114.8193	54.2169	4.0431	8.6932
0.8165	1.0416	-0.1366	0.8172	-0.9567	-1.9497	1.0612	0.0011	1.3241	1.6013	0.1034	115.8640	54.4200	4.0343	8.7601
0.8671	1.0331	-0.0669	0.8667	-0.1332	-1.9622	1.0516	0.0011	1.3250	1.6037	0.0895	116.6749	54.5989	4.0289	8.7876
1	1.01	0	1	0	0	0	0	1.3028	0	0	0	0	0	0

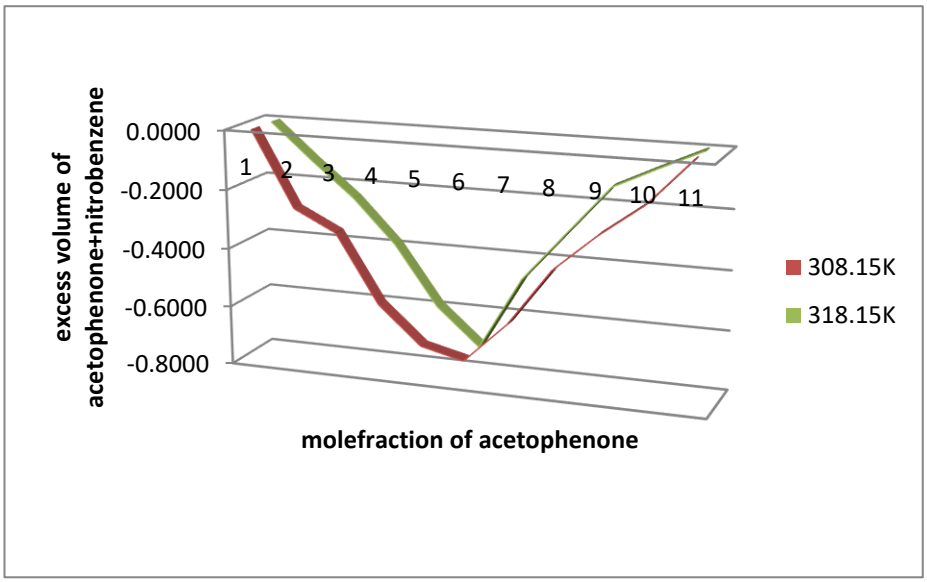

Fig. 1: A plot of mole fraction of acetophenone(x-axis) Vs excess volume of acetophenone + nitrobenxzene (y-axis)

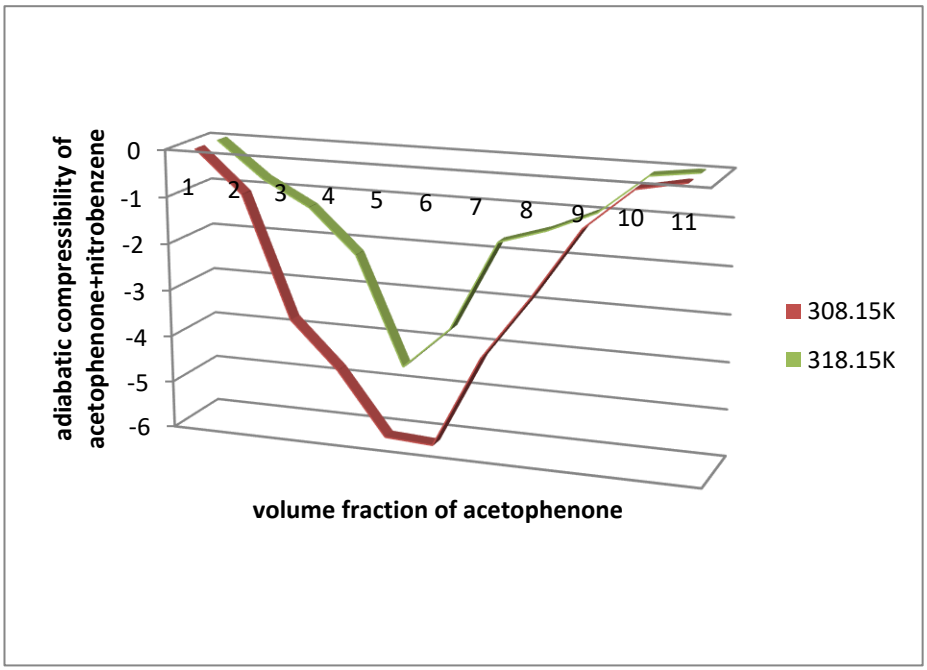

Fig. 2: A plot of volume fraction of acetophenone(x-axis) Vs adiabatic compressibility of acetophenone + nitrobenxzene (y-axis)

The excess volume values for the binary mixtures has been calculated using the relation

$$V^E = ((X_1M_1+X_2M_2)/\rho)-(X_1M_1/\rho_1)-(X_2M_2/\rho_2) \quad ...(1)$$

where X_1,X_2 M_1,M_2 and ρ_1,ρ_2 are the mole fractions, molar mass, densities of pure components 1,2 respectively.

Adiabatic compressibility (Ks) has been calculated from Laplace's equation

$$K_s = 1/\rho U^2 \quad ...(2)$$

where ρ and U are the density and ultrasonic velocity of liquid mixtures. From the above equation excess adiabatic compressibility (ΔKs) has been calculated by [11]

$$\Delta K_s = K_s-(\phi_1 K_{s1} + \phi_2 K_{s2}) \quad ...(3)$$

K_{s1}, K_{s2} are adiabatic compressibility of pure liquids and ϕ_1, ϕ_2 are the volume fractions of pure liquids has been calculated by the relation

$$\phi_1=(X_1M_1/\rho_1)/(X_1M_1/\rho_1+X_2M_2/\rho_2)$$

and $$\phi_2 = 1-\phi_1 \quad ...(4)$$

Viscosity has been calculated using the relation

$$\eta= (At-B/t)\ \rho \quad ...(5)$$

A and B are the constant characteristics of viscometer calculated using the standard liquids water and nitrobenzene, t is the flow time, ρ is the density.

Excess viscosity values are calculated using the following relation

$$\Delta\eta=\eta-((x_1\eta_1)+(x_2\eta_2)) \quad ...(6)$$

Linear Free length has been calculated using Jacobson's relation [12]

$$L_F = K/u\rho^{1/2} \quad ...(7)$$

K is Jacobson's constant which is temperature dependent constant but independent of the nature of the liquid.

Suriyanarayana [13] proposed a relation to calculate free volume

$$V_f = (M_{eff}\ u/K\ \eta)^{3/2} \quad ...(8)$$

K is a temperature independent constant which is equal to $4.28x10^9$ for all the liquids;

M_{eff} is effective molecular weight of the mixture has been calculated using the relation

$$M_{eff} = X_1M_1+X_2M_2 \quad ...(9)$$

where X_1,X_2 and M_1, M_2 are the mole fractions and molar mass of pure components 1,2 respectively.

Acoustic impedence has been calculated using the relation

$$Z = u\rho \quad ...(10)$$

where u is ultrasonic velocity and ρ is density.

Relative association has been calculated using the relation

$$R_a = n\,(\rho/\rho_0)/(u_0/u)^{1/3} \quad ...(11)$$

where u is ultrasonic velocity and ρ is density of the mixture and u_0 and ρ_0 are for the corresponding component unit.

Rao's constant or molar sound velocity can be calculated using the following relation

$$R = Vu^{1/3} \quad ...(12)$$

where u is the ultrasonic velocity and V is the molar volume which has been calculated from the following relation

$$V = X_i M_i/\rho \quad ...(13)$$

where X_i and M_i are mole fraction and molecular weight and ρ is density of the mixture or liquid mixture.

Wada's constant or molar compressibility has been calculated using the relation

$$W = VK_s^{-1/7} \quad ...(14)$$

where V is the molar volume and K_s is adiabatic compressibility.

Excess value parameters are calculated using the relation

$$A^E = A_{exp} - A_{id}$$

$$A_{id} = \Sigma\, X_i A_i \quad ...(15)$$

where Xi and Ai are mole fraction and parameters of the i^{th} component.

All the calculated excess parameters were fitted to Redlich – Kister [14] type polynomial equation

$$A^E = [x_1x_2(a+b(x_1-x_2) + c(x_1-x_2)] \quad ...(16)$$

by the method of least squares to derive the adjustable parameters a, b, c. Using the theoretical values for all excess parameters the standard deviation values were calculated using the relation

$$\sigma = [(A_{exp} - A_{cal})^2/(n-m)]^{1/2} \quad ...(17)$$

n is the number of measurements and m is the number of adjustable parameters.

Table 4:

Adjustable parameters and standard coefficient values for the calculated thermodynamic parameters

Parameters	a	b	C	σ
Acetophenone + nitrobenzene at 308.15K				
V^E ($cm^{3.}mol^{-1}$)	-4.6864	-1.7211	4.2429	0.0011
ΔKs(TPa^{-1})	-18.2290	6.707	-1.793	0.1054
η(cP)	5.9651	-1.4205	11.6002	0.0018
Δη(cP)	1.0995	-2.2882	1.922	$4.08x10^{-5}$
$\Delta L_F x10^{-09}$(m)	4.9740	2.8545	9.7924	0.00165
$\Delta v_F x10^{-07}$($kg^{-1}K^{-1}m^2s$)	4.8050	1.0604	1.0345	0.0032
Acetophenone + nitrobenzene at 318.15K				
V^E (cm^3mol^{-1})	-3.6201	-3.2002	4.1173	0.0025
ΔKs(TPa^{-1})	-1.5100	-5.521	-3.595	0.0452
η(cP)	5.2604	-1.2911	10.1229	0.0015
Δη(cP)	0.9479	-2.0831	1.5452	$4.082x10^{-5}$
$\Delta L_F x10^{-10}$(m)	7.6030	2.912	1.477	0.00023
$\Delta v_F x10^{-07}$ ($kg^{-1}K^{-1}m^2s$)	5.7490	1.328	1.234	0.00029

DISUSSION

The molecular interactions between the molecules are highly influenced by the functional group (substituents) present in the molecule. Molecular interactions refer not only the interactions between the unlike molecules of liquid mixtures but also interactions that occurs between the like molecules, called as self-interactions [15].

The sign of excess volume values depends on either expansion or contraction nature, during the mixing of two liquids. If nature of expansion dominates, it results in positive excess molar volume values and vice versa. Actophenone containing carbonyl group is highly polar and also highly ionic in nature. There is an internal interaction occuring between the negative charge on carbonyl group C=O and electron cloud of benzene ring [16] that is cation – π interaction and anion –π interaction. Similarly, in nitrobenzene, stacking interactions between same molecules of nitrogen containing lone pair and –π electron cloud. Also, there may be an interaction occurring between C=O of the acetophenone and

nitrogen containing lone pair. This may a reason behind the negative excess volume values shows the presence of strong interaction between acetophenone and nitrobenzene. As the temperature raised by 10 degrees the similar negative values results. But the values slightly increase and move towards positive end due to restriction in movement of molecules when temperature increases.

An examination of adiabatic compressibility data's is negative for both the temperature similar to excess volume values [17]. The negative adiabatic compressibility values occur due to change in free volume in the real mixture and presence of π electrons cloud in acetophenone as well as for nitrobenzene leads to the formation of interactions between the molecules similar to excess volume values. The values of deviations in viscosity also rationalize the presence molecular interactions between the acetophenone and nitrobenzene binary mixtures at both the temperatures [18]. The other factors such as thermal expansion coefficient, isothermal compressibility, are also negative support the above factors. Similarly, the positive values of free volume support for the presence of interaction between molecules of binary liquid mixtures.

CONCLUSION

The study spell out the measurements of density, viscosity and ultrasonic measurements for the binary liquid mixture containing acetophenone and nitrobenzene as components. These experiments were carried out at atmospheric pressure and two temperatures of 308.15K and 318.15K. The corresponding excess thermodynamic properties were calculated and fitted to Redlich - Kister polynomial equation to determine the appropriate coefficients. The style in acoustical properties states the presence of possibilities of interactions between molecules.

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