Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2016, 8(7):49-53

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Ultrasonic velocity, density and viscosity studies of the binary mixtures of ethyl acetate with hexane

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ABSTRACT

Density, viscosity and ultrasonic velocity in binary mixtures of ethyl acetate and hexane has been calculated at temperature 292 K and frequency 2 MHz. Using experimental values various acoustical parameters such as adiabatic compressibility, intermolecular free length, acoustic impedance, ultrasonic attenuation, available volume, free volume, internal pressure, Gibb's free energy and enthalpy has been calculated. Theoretical values of ultrasonic velocity has also been computed using various models such as impedance relation, Nomoto's relation, Junjie's equation and Van-Deal and Vangeel. To check the validity of theoretical models with experimental values, percentage error has been calculated. Further the chi-square test has also been applied to check the relation between theoretical and experimental data. The non-linear variation in acoustical parameters shows that there is a complex formation and the deviation in experimental values from theoretical models proves the strong molecular interaction in the binary mixture.

Keywords: Theoretical ultrasonic velocity, Binary mixture, intermolecular interaction, acoustical parameters.

INTRODUCTION

Ultrasonic, volumetric and viscometric study of liquid mixtures is of substantial importance to understand the physico-chemical behaviour of a liquid mixture.[1-4]The physical properties of liquid mixtures forms the basis to evaluate various thermo-acoustical functions.It has gained much attention in both practical and theoretical point of views.[7, 8]The pure liquids and liquid mixtures find a wide applications in leather, textile, chemical and pharmaceutical industries. [10-14]

Ethyl acetate is an organic compound, a product of esterification reaction between ethyl alcohol and acetic acid. It is currently classified as an eye irritant and can cause drowsiness and dizziness if high concentrations of vapours are inhaled. It is used as a processing solvent for the manufacture of other chemicals and in solvent based coatings, adhesives and links used in industry and by professional workers.

Hexane is an alkane of six carbon atoms used in industries as an ingredient in glues for manufacturing shoes and leather bags. It is also used to extract cooking oils from seeds and in laboratory, for extracting oil and grease contaminants from water and soil.

In the present study, attempt has been made to calculate ultrasonic velocity, density and viscosity of a binary system, namely ethyl acetate + hexane and to derive thermo-acoustical properties for the study of molecular interactions at

temperature 292 K. For further verification of the experimental results, theoretical ultrasonic velocity is also calculated by using various theoretical models.

EXPERIMENTAL SECTION

Chemicals used in the present investigation are ethyl acetate and hexane having molecular weight 88.11 g/mol and 86.05 g/mol respectively of 99% AR grade. The ultrasonic velocity is measured at temperature 292 K using Mittal Enterprises ultrasonic interferometer at frequency of 2 MHz with an accuracy of ±0.1m/s. Specific gravity bottle is used to measure density of pure components and liquid mixtures at temperature 292 K with an accuracy of ±0.01 mg. To calculate viscosity of liquid systems Oswald's viscometer is used with uncertainty in accuracy of ± 0.001 s. The **derived parameters**[27-29]namely Acoustic impedance (Z), Adiabatic compressibility (β), Intermolecular free length (L_f), Ultrasonic Attenuation (α/f^2), Relaxation Time (τ), Effective Molecular Weight (M_{eff}), Free Volume (V_f), Wada's Constant (W), Rao's Constant (R), Molar Volume (V_m), Vander Waal's Constant (b), Internal Pressure (π_i), Available Volume (V_a), Gibb's Free Energy (ΔG) and Enthalpy (H) are calculated by using following relations:

$Z = \rho \times U$ $\beta = 1/(U^2 \times \rho)$ $L_f = K_T \times \beta^{1/2}$ $\alpha/f^2 = 8\pi^2\eta/3\rho U^3$

$\tau = 4\beta\eta/3$ $M_{eff} = X_1M_1 + X_2M_2$ $V_f = [M_{eff}\, U / K\eta]^{3/2}$ $W = (\beta)^{-1/7}M_{eff}/\rho$

$R = U^{1/3}M_{eff}/\rho$ $V_m = M_{eff}/\rho$ $b = V_m[1-(RT/MU^2)\{(1 + (MU^2/3RT))^{1/2} - 1\}]$

$\Pi_i = bRT[(k\eta/U)^{1/2}(\rho^{2/3}/M^{7/6})]$ $H = V_m \times \pi_i$ $V_a = M/\rho(1 - U/U_\infty)$ $\Delta G = K_B T \ln(K_B T \tau/h)$

To calculate **theoretical ultrasonic velocity** following relations has been used:

Nomoto's Relation of sound velocity[5]:

$$U_{NOM} = [(X_1R_1+X_2R_2)/(X_1V_1+X_2V_2)]^3$$

Impedance dependent relation:

$$U_{IMP} = (X_1Z_1 + X_2Z_2)/X_1\rho_1 + X_2\rho_2$$

Van-Dael and Vangeel Ideal mixing relation[6]:

$$U_{VDV} = [(X_1/M_1U_1^2 + X_2/M_2U_2^2)(X_1M_1+X_2M_2)]^{-1/2}$$

Junjie equation[9]:

$$U_{JUN} = [(X_1M_1/\rho_1 + X_2M_2/\rho_2)/(X_1M_1+X_2M_2)^{1/2}][\{X_1M_1/\rho_1U_1^2+X_2M_2/\rho_2U_2^2\}]^{-1/2}$$

Percentage deviation in ultrasonic velocity:

$$(\Delta U/U)\,\% = ((U_{EXP}-U_{THEORY})/(U_{EXP}))\,x100$$

Chi-square test for goodness of fit: According to Karl Pearson, the Chi-square value is calculated by using the following formula:

$$(x^2) = \sum \frac{(U_{mix(\exp)}-U_{mix(cal)})^2}{U_{mix(cal)}}$$

Average Percentage Error (APE): Average percentage error has been calculated using following formula:

$$APE = \frac{1}{n}\sum \frac{U_{mix(\exp)}-U_{mix(cal)}}{U_{mix(exp)}}\, x\, 100$$

RESULTS AND DISCUSSION

The experimental values and the values from literature of ultrasonic velocity, density and viscosity of pure components are given in **Table 1.**The experimentally measured values along with calculated values of derived acoustical parameters: adiabatic compressibility, intermolecular free length, relaxation time, acoustic impedance, ultrasonic attenuation and molar volume of binary mixtures at different compositions of ethyl acetate and hexane at 292 K are presented in **Table 2,** then in **Table 3**free volume, available volume, Wada's constant, Rao's constant, Vander Waal's constant, enthalpy, Gibb's free energy and internal pressure are listed, and the corresponding graphs are shown in **Figures 1-6.**

Table 1: Ultrasonic velocity, density and viscosity of pure compounds as well as comparison with literature data

Compounds	U_{exp} (m s^{-1})	U_{ref} (m s^{-1})	ρ_{exp} (Kg m^{-3})	ρ_{ref} (Kg m^{-3})	η_{exp} (m Pa-s)	η_{ref} (m Pa-s)
Ethyl acetate	1160.0	1160.2[26]	893.196	894.600[15]	0.4994	0.4991[26]
Hexane	1080.0	1079.8[18,21]	655.036	655.072[18]	0.3131	0.3130[18]

Table 2: Ultrasonic velocity (U), density (ρ), viscosity (η), adiabatic compressibility (β), intermolecular free length (L_f), relaxation time (τ), acoustic impedance (Z), ultrasonic attenuation (α/f^2) and molar volume (V_m) for binary system of ethyl acetate and hexane at 292 K

X_1	U m/s	ρ Kg/m^3	η x10^{-3} mPa-s	β×10^{-10} Kg$m^{-1}s^2$	L_f×10^{-5} A^0	τ ×10^{-12} s	Z x 10^5 kg$m^{-2}s^{-1}$	α/f^2×10^{-14} s^2m^{-1}	V_mx$10^{-2}$$m^3$$mol^{-1}$
0.9	1088.0	908.500	0.8360	9.2983	6.3929	1.0364	9.8844	1.8784	09.6642
0.8	1105.2	898.503	0.7888	9.1115	6.3284	0.9583	9.9302	1.7098	09.7495
0.7	1090.4	877.863	0.7966	9.5806	6.4892	1.0176	9.5722	1.8402	09.9559
0.6	1113.6	867.540	0.7073	9.2957	6.3917	0.8765	9.6609	1.5521	10.0514
0.5	1064.0	846.760	0.7399	1.0432	6.7713	1.0291	9.0095	1.9073	10.2744
0.4	1084.0	784.203	0.7392	1.0850	6.9063	1.0695	8.5007	1.9455	11.0685
0.3	1044.0	813.080	0.7726	1.1289	7.0425	1.1624	8.4885	2.1955	10.6508
0.2	1092.6	799.314	0.6346	1.0488	6.7869	0.8867	8.7333	1.6002	10.8092
0.1	1060.8	783.920	0.7062	1.1334	7.0587	1.0673	8.3158	1.9840	10.9960

Table3: Free volume, Wada's constant, Rao's constant, effective mass, enthalpy, Gibb's free energy, available volume, Vander Waal's constant and internal pressure for binary system of ethyl acetate and hexane at 292 K

X_1	V_f x 10^{-3} m^3/mol	W m^3/mol (pa)$^{1/7}$	R m^3/mol(m/s)$^{1/3}$	M_{eff} gm	H x 10^4 J/mol	(ΔG) × 10^{-21} KJmol^{-1}	V_ax 10^{-2} m^3 mol^{-1}	b x 10^{-2} m^3 mol^{-2}	π_i × 10^5N/m^2
0.9	4.3625	1.8853	0.9939	87.8	1.3638	7.5372	3.0925	09.63754	1.4113
0.8	4.8564	1.9075	1.0080	87.6	1.3198	7.6875	3.0150	09.72296	1.3537
0.7	4.6733	1.9339	1.0247	87.4	1.3462	7.1027	3.1709	09.92843	1.3522
0.6	5.7455	1.9609	1.0418	87.2	1.2606	7.3448	3.0556	10.02414	1.2542
0.5	4.9975	1.9717	1.0489	87.0	1.3303	6.7433	3.4419	10.24526	1.2948
0.4	5.1292	2.1121	1.1370	86.8	1.3520	7.3903	3.5696	11.03764	1.2215
0.3	4.5210	2.0211	1.0804	86.6	1.3921	7.5454	3.7011	10.61994	1.3071
0.2	6.4803	2.0730	1.1133	86.4	1.2407	7.8811	3.4278	10.77924	1.1479
0.1	5.2624	2.0853	1.1214	86.2	1.3375	6.7896	3.7056	10.96453	1.2164

Ultrasonic velocity, density and viscosity are found to increase but nonlinearly with increasing concentration of ethyl acetate. This non-linear variation in ultrasonic velocity is due to the change in intermolecular free length of the components of mixture. Increase in density indicates the presence of more number of molecules with increasing concentration of ethyl acetate. Further non-linear increase in viscosity suggests more connotation between solute and solvent molecules. Adiabatic compressibility, intermolecular free length and relaxation timeare calculated from velocity data and are found to show opposite trend as compared to ultrasonic velocity which is further signifying that there is an interaction between the molecules.[16, 17]

The non-linear variation in acoustic impedance, attenuation, enthalpy, Gibb's free energy and internal pressure exhibits the strong hydrogen bonding between solute and solvent molecules.[19, 20] Moreover, according to mathematical relation of acoustic impedance and adiabatic compressibility, they must show the opposite trend whereas intermolecular free length and adiabatic compressibility must follow the same behavior which is in perfect aggreement with experimental results.

The effective mass is found to be linearly increasing with the increasing concentration of ethyl acetate which proves that there is a strong molecular interaction among the molecules of the mixture. Non-linear trend shown by Wada's constant, Rao's constant and Vander Waal's constant suggests the complex formation in the mixture. The observed decreasing trend of molar volume, available volume and free volume indicates the close association between solute and solvent molecules.

The experimental ultrasonic velocity along with theoretical ultrasonic velocity which is computed by using theoretical models namely Nomoto's relation, impedance relation, Van-Deal and Vangeel**'s** equation and Junjie's equation are given in **Table 3.**The percentage deviation in experimental and theoretical data is calculated and is given in **Table 4.**To check the validity of theoretical models average percentage error is computed and chi-square test has been applied.

Table4: Experimental and theoretical ultrasonic velocities in the liquid mixtures of ethyl acetate and hexane at temperature 292 K and frequency 2 MHz

Mole Fraction		U_{EXP}	U_{NOM}	U_{IMP}	U_{VDV}	U_{JUN}
X_1	X_2	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}
1.0	0.0	1160.00	1159.98	1160.00	1160.00	1159.95
0.9	0.1	1088.00	1150.60	1153.23	1150.97	1146.07
0.8	0.2	1105.20	1141.58	1146.23	1142.19	1134.00
0.7	0.3	1090.40	1132.91	1138.98	1133.66	1123.51
0.6	0.4	1113.60	1124.56	1131.47	1125.36	1114.36
0.5	0.5	1064.00	1116.52	1123.68	1117.29	1106.40
0.4	0.6	1084.00	1108.77	1115.59	1109.44	1099.48
0.3	0.7	1044.00	1101.29	1107.21	1101.79	1093.47
0.2	0.8	1092.60	1094.07	1098.49	1094.34	1088.27
0.1	0.9	1060.80	1087.10	1089.42	1087.08	1083.79
0.0	1.0	1080.00	1080.36	1080.00	1080.00	1079.97

It can be clearly observed from Table 3 that there is a deviation of experimental ultrasonic velocity from theoretical data. The accuracy of predictive data given by theoretical models depends upon the type of interaction present in the liquid system. These models generally be unsuccessful to foretell accurate data where there is a strong molecular interaction existing in the liquid mixture.

Further, Table 4 shows that average percentage error and the value of chi square test is minimum for Junjie's equation as compared to other theories. The main reason for deviation from theoretical data is that interaction among the molecules of the liquid is not considered in these models. As soon as two liquids are mixed together, there are certain forces like hydrogen bonding, charge transfer, dispersive force, dipole-dipole and dipole-induced dipole which comes into play due to which interaction between the molecules occurs. Therefore, these deviations from experimental data evidences the presence of strong molecular interaction in the mixture. Similar kind of results were obtained by earlier workers.[22-25]

Table5: Percentage deviations between experimental and theoretical ultrasonic velocities and chi square test in the liquid mixtures of ethyl acetate and hexane at temperature 292 K and frequency 2 MHz

Mole Fraction		$\%U_{NOM}$	$\%U_{IMP}$	$\%U_{VDV}$	$\%U_{JUN}$
X_1	X_2				
1.0	0.0	0.0019	0.0000	0.0000	0.0039
0.9	0.1	-5.7536	-5.9957	-5.7875	-5.3371
0.8	0.2	-3.2921	-3.7126	-3.3471	-2.6062
0.7	0.3	-3.8986	-4.4553	-3.9675	-3.0361
0.6	0.4	-0.9844	-1.6045	-1.0565	-0.0684
0.5	0.5	-4.9360	-5.6089	-5.0088	-3.9850
0.4	0.6	-2.2847	-2.9149	-2.3466	-1.4277
0.3	0.7	-5.4873	-6.0544	-5.5353	-4.7382
0.2	0.8	-0.1345	-0.5392	-0.1589	0.3964
0.1	0.9	-2.4791	-2.6988	-2.4770	-2.1677
0.0	1.0	-0.0335	0.0000	0.0000	0.0028
APE		-2.6620	-3.0531	-2.6987	-2.0876
Chi Square		117.3573	145.1799	120.1010	83.9590

CONCLUSION

The density, ultrasonic velocity and viscosity of binary liquid mixture has been measured experimentally and are used to calculate various parameters. The variations in the derived acoustical parameters indicates the presence of strong molecular interaction in the mixture. The non-linear behaviour shown by Wada's constant, Vander Waal's constant and Rao's constant suggests the presence of complex formation in the mixture. The experimental ultrasonic velocity is compared with the theoretical velocity data obtained by Nomoto's relation, impedance dependent relation, ideal mixture relation and Junjie's equation. It is found that Junjie's method is the best suitable model to predict ultrasonic velocity. In addition to this the deviation of experimental values from theoretical data confirms the presence of strong molecular interaction in the mixture.

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