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THEORETICAL EVALUATION OF SOUND VELOCITY, VISCOSITY IN BINARY LIQUID SYSTEM

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ABSTRACT

Ultrasonic velocity, density and viscosity have been measured using the standard techniques in the binary mixtures of m-cresol with carbon tetrachloride. The study of ultrasonic waves through the solution is used for knowing the nature and strength of the intermolecular forces and their interactions in pure liquids and their mixtures. The theoretical ultrasonic velocity in binary mixtures computed using theoretical models of liquid mixtures such as Nomoto's relation, Ideal mixture relation, Impedance relation, Rao's specific velocity relation, Junjie's relation and Danusso model. The validity of the theories was interpreted in terms of average percentage error (APE). Further, the theoretical values of viscosity for the binary mixtures were calculated using different empirical relations and theories. The relative merits of these relations were discussed.

Key words: Binary liquid mixtures, Ultrasonic velocity, Theoretical models, Viscosity empirical relations, APE.

INTRODUCTION

Thermodynamic properties derived from the measurement of ultrasonic velocities, densities and viscosities for binary mixtures are useful in understanding the nature and type of intermolecular interactions present between the component molecules. 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 ultrasonic velocity, density and viscosity find extensive application in solution theory and molecular dynamics. The classification of mixtures through their thermodynamic and transport properties is important from the major viewpoint of understand their mixing behavior. The practical need

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for thermodynamic data for investigation and research as well as for design and set up of industrial processes continue to drive research in the study of multicomponent systems.

The impetus of the present investigation is to compare the experimentally determined ultrasonic velocity in binary liquid mixture with the computed ultrasonic velocity using different theoretical relations like Nomoto, Van Dael and Vangael, Impedance relation, Rao's specific velocity, Junjie's relation and Danusso relation[1-8]. Further, the theoretical values of viscosity for the binary mixtures were calculated using different empirical relations and theories such as the Kendall-Monroe, Arrhenius, Grunberg-Nissan, Katti-Chaudhri, Hind-Ubbelohde and Wijk[9-13].

EXPERIMENTAL

Material and methods

M-cresol used in present work is procured from Merck, Mumbai with assay greater than 99% and Carbon tetrachloride from Sdfine Chemical limited, Mumbai with assay of 99.8%. All compounds were of AR/GR grade, used without further purification. The ultrasonic velocities in pure and binary mixtures were measured using the single-crystal variable-path ultrasonic interferometer operating at 2MHz.The densities of pure and binary mixture were measured using the pre-calibrated standard 10ml specific gravity bottle with Teflon stopper and digital weighing balance with accuracy of ± 0.1 mg. Viscosity measurements were made by a pre-calibrated Ostwald's viscometer, using the method based on the measurement of flow time of the liquid. An electronic digital stop watch with reliability of ± 0.01 sec was used for flow time measurements. The measurement of flow time of the solution between the two points on the viscometer was performed at least five times for each solution and the result was averaged.

Theory and calculations

The adiabatic compressibility is computed using the following relation.

$$\beta_s = 1/U^2\rho$$

The linear free length given by the relation.

$$L_f = K/\sqrt{\rho U}$$

Where K is the temperature independent Jacobson's constant

$$K = (93.875 + 0.375\ T) \times 10^{-8}$$

The acoustic impedance (Z) computed by the relation

$Z = \rho U$

The molar volume (V_m) computed by the relation.

$V_m = M_{eff}/\rho$

$M_{eff} = \sum_i x_i M_i$

The available volume (V_a) computed by the relation.

$$V_a = V_m \left(1 - \frac{U_{exp}}{U_\infty}\right)$$

Where $U_\infty = 1600$ m/s

The comparison of theoretical values of ultrasonic velocity in binary mixture those obtained from the experimentally in the binary mixture is expected to interpretation the nature of interaction between components molecules. Such theoretical study is useful in the wide-ranging theoretical model for the liquid mixtures.

Van Dael & Vangel ideal mix relation

The ideal mixing theory innovative by Van Deal and Vangael [4] suggested the sound velocity in binary mixture with following relation.

$$U_{VV} = \sum_i x_i/m_i \; u_i^2 \times \sum_i 1/x_i \; m_i$$

Where x_i is mole fraction, m_i is molecular weight, and u_i is ultrasonic velocity of i^{th} components, respectively.

Impedance relation

The impedance relation[5] based on the interaction molecules based on the forces of resistance for sound velocity is given by –

$$U_{IMP} = \sum_i x_i z_i / \sum_i x_i \rho_i$$

Where x_i is mole fraction, z_i is the acoustic impedance and ρ_i is the density of the i^{th} components, respectively

Nomoto's relation

The additivity of molar sound velocity R and no volume change on mixing, Nomoto established [6] the following relation for the sound velocity of binary liquid mixture is –

$$U_{NOM} = \left(\frac{\Sigma_i R_i}{\Sigma_i V_i} \right)^3$$

$$R_i = m_i/\rho_i \times u_i^{1/3}$$

$$V_i = m_i/\rho_i$$

Where m_i is molecular weight, ρ_i is the density and u_i is ultrasonic velocity of i^{th} components, respectively.

Jungie's relation

Jungie has suggested [7] an equation for the determine the velocity of sound in liquid mixtures given as follows:

$$U_{JR} = \left[\frac{\Sigma_i x_i V_i}{\Sigma_i x_i m_i^{1/2}} \right] \times \left[\frac{\Sigma_i x_i V_i}{\Sigma_i \rho_i U_i^2} \right]^{-1/2}$$

Where x_i is mole fraction, V_i is molar volume, m_i is molecular weight, ρ_i is the density and u_i is ultrasonic velocity of i^{th} components respectively.

Rao's specific velocity

The Rao's specific sound velocity[7] in liquid mixture is given by –

$$U_R = \sum_i (x_i r_i \rho_i)^3$$

Where x_i is mole fraction, ρ_i is the density of i^{th} component and r_i is the Rao's specific sound velocity $r_i = U_i^{1/3}/Z_i$ and Z_i is acoustic impedance.

Danusso model

Danussomodel[8] of velocity of sound velocity in liquid mixture is given by –

$$U_D = \left(1/\rho_{mix}\right)\left(1/M_{eff} \times \sum_i x_i m_i/\rho_i^2 U_i^2 \right)$$

$$M_{eff} = x_i M_i$$

Where M_{eff} is the effective molecular weight of the solute and solvent, x_i is mole fraction, m_i is molecular weight of i^{th} component.

Molecular association

The degree of intermolecular interaction or molecular association is given by –

$$\alpha = (U_{exp} - U_{comp}) - 1$$

Viscosity deviation

The viscosity deviation evaluated from following relation,

$$\Delta\eta = \eta_m - \sum_i x_i \eta_i$$

Where η_m is the viscosity of the mixture and x_i is mole fraction, η_i is viscosity of i^{th} component.

Kendall and Monroe

Kendall and Monroe[9] derived the following equations for analyzing the viscosity of binary liquid mixtures based on zero adjustable parameter.

$$\eta_m = (x_1 \eta_1^{1/3} + x_2 \eta_2^{1/3})^3$$

Modified Kendall-Monroe equation

$$E\eta_m = x_1 x_2 (x_1 \eta_1^{1/3} + x_2 \eta_2^{1/3})^3$$

Where x_1, x_2 and η_1, η_1 are the mole fraction and viscosity of pure component, respectively.

Arrhenius

Arrhenius [9] derived the following equations for viscosity of liquid mixtures based on zero adjustable parameter.

$$\log n_m = x_1 \log \eta_1 + x_2 \log \eta_2$$

Where x_1, x_2 and η_1, η_1 are the mole fraction and viscosity of pure component respectively.

Grunberg–Nissan

A commonly used and suggested liquid mixture viscosity correlation is the Grunberg–Nissan [10] approach is given by –

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d_{12}$$

Where d_{12} is the Grunberg-Nissan interaction parameter and others were usual meaning.

Katti and Chaudhri

The Katti-Choudhari[11] viscosity relation for binary liquid mixtures is given by –

$$\ln \eta V = x_1 \ln V_1 \eta_1 + x_2 \ln V_2 \eta_2 + x_1 x_2 W_{vis}/RT$$

Where W_{vis} represents the interaction energy between the components, V is the molar volume and others were usual meaning.

Hind-Ubbelohde

Molecular interactions may also be interpreted by the following viscosity model of Hind-Ubbelohde [12].

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

Where H_{12} is Hind interaction parameter, it is attributed to unlike pair interactionand others were usual meaning.

Wijk

The Wijk[13] viscosity relation for binaryliquid mixtures is given by –

$$\lg \eta = x_1^2 \lg \eta_1 + x_2^2 \lg \eta_2 + 2x_1 x_2 \lg \eta_{12}$$

Where η_{12} interaction parameter and others were usual meaning.

Percentage error

The percentage deviation in ultrasonic velocity between experimental and computed values can be calculated as –

Percentage deviation $AU/U\% = [(U_{exp} - U_{comp})/U_{exp}] \times 100\%$

The measured physical parameters such as ultrasonic velocity, density, viscosities data are recorded sequential in Microsoft Excel 2010 and the various acoustical, thermodynamical, viscosity parameters are computed using the user friendly developed package in VB.NET language running under 64-bit Windows 8 platform.

RESULTS AND DISCUSSION

The experimental values of ultrasonic velocity U, density ρ and viscosity η of binary mixtures of m-cresol with carbon tetrachloride and over the entire composition range (0.0 to 1.0) expressed in terms of mole fraction x_1 are listed in Table 1.

Table 1: Experimental value of ultrasonic velocity U, density ρ and viscosity η of m-cresol with carbon tetra chloride

Mole fraction m-cresol x_1	Velocity U	Density ρ	Viscosity η
	m/s	Kg/m^3	$x\ 10^{-3}\ Ns/m^2$
0.0000	980.80	1626	0.9894
0.0947	939.20	1578	1.1714
0.1906	968.00	1518	1.2490
0.2876	1048.00	1466	1.6166
0.3857	1052.80	1412	1.9247
0.4851	1190.40	1347	2.2874
0.5856	1246.40	1294	3.2243
0.6873	1160.00	1236	3.9952
0.7902	1313.60	1180	5.3534
0.8945	1380.80	1121	7.2343
1.000	1456.00	1069	9.0758

The computed acoustical, thermodynamical parameters listed in Table 2 and Table 3. The change in ultrasonic velocity shows the association between solute and solvent molecules. The decrease in density with increase in mole fraction of component x_1 indicates formation of intermolecular forces between the binary mixtures. Also, the variation of compressibility β form-cresol with CCl_4 indicates the molecular association and hydrogen bond formation between unlike molecules.

Table 2: Computed acoustical thermo dynamical parameters of m-Cresol with carbon tetra chloride

Mole fraction m-cresol x_1	Compressibility β	Linear free length L_f	Acoustic impedance Z
	x 10^{-10} $kg^{-1}ms^{-2}$	x 10^{-10} m	x 10^5 kg/m^2s
0.0000	6.39320	5.2371	15.9478
0.0947	7.18417	5.5516	14.8205
0.1906	7.03036	5.4919	14.6942
0.2876	6.21074	5.1618	15.3636
0.3857	6.38960	5.2356	14.8655
0.4851	5.23898	4.7408	16.0346
0.5856	4.97452	4.6196	16.1284
0.6873	6.01264	5.0788	14.3376
0.7902	4.91125	4.5902	15.5004
0.8945	4.67878	4.4802	15.4787
1.000	4.41265	4.3509	15.5646

Table 3: Computed acoustical thermo dynamical parameters of m-cresol with carbon tetra chloride

Mole fraction m-cresol x_1	Molar volume V_m	Available volume V_f
	x 10_{-2} m_3	x $10_{-3}m_3$
0.0000	9.4600	6.7239
0.0947	6.9953	2.9737
0.1906	7.4376	2.9232
0.2876	7.8949	2.3211
0.3857	8.4250	1.8746
0.4851	9.1056	1.8213
0.5856	9.8087	1.2274
0.6873	10.6737	0.8466

Cont…

Mole fraction m-cresol x_1	Molar volume V_m	Available volume V_f
	x 10_{-2} m_3	x $10_{-3}m_3$
0.7902	11.6832	0.7026
0.8945	12.9366	0.5200
1.000	10.1159	0.2580

The deviation of intermolecular free length L_f decreasing trend with increasing in mole fraction of component x_1 suggests that the specific interaction between the components of two system binary mixture molecules. According to Eyring and Kincaid[14], the ultrasonic velocity increases, if the L_f decreases and vice-versa in a result of mixing components. The decrease or increase in values of L_f can be explained on the basis of interactions between the solute and solvent molecules.

The nonlinear variation of acoustic impedance Z exposes that presence of specific interaction and cluster formation between the mixing components. The molar volume V_m changes in increasing trend and available volume V_a changes non-linearly with concentration of solutions.

Table 4: Experimental velocities and computed theoretical velocities for m-cresol with carbon tetra chloridebinary system in m/s

Mole fraction m-cresol x_1	U_{EXP}	U_{NOM}	U_{JR}	U_{VV}	U_R	U_{IMP}	U_D
0.0947	939.20	1023.089	1014.101	1012.046	1020.574	1011.399	1008.912
0.1906	968.00	1066.511	1049.692	1045.760	1061.893	1044.519	1046.880
0.2876	1048.00	1111.077	1087.817	1082.248	1104.819	1080.485	1081.900
0.3857	1052.80	1156.797	1128.756	1121.869	1149.414	1119.680	1120.924
0.4851	1190.40	1203.684	1172.835	1165.044	1195.747	1162.560	1172.366
0.5856	1246.40	1251.749	1220.429	1212.279	1243.886	1209.669	1217.415
0.6873	1160.00	1301.003	1271.979	1264.177	1293.904	1261.668	1271.185
0.7902	1313.60	1351.455	1327.997	1321.466	1345.875	1319.355	1327.701
0.8945	1380.80	1403.117	1389.096	1385.041	1399.880	1383.723	1393.219

Table 5: Percentage deviation for m-cresol with carbon tetra chloride binary system

Mole fraction m-cresol x_1	$\%U_{NOM}$	$\%U_{JR}$	$\%U_{VV}$	$\%U_R$	$\%U_{IMP}$	$\%U_D$	α
0.1926	-8.9319	-7.9750	-7.7561	-8.6641	-7.6872	-7.4224	-0.1387
0.3493	-10.1767	-8.4392	-8.0330	-9.6996	-7.9048	-8.1488	-0.1431
0.4792	-6.0187	-3.7992	-3.2679	-5.4216	-3.0997	-3.2347	-0.0622
0.5887	-9.8781	-7.2146	-6.5604	-9.1769	-6.3526	-6.4707	-0.1193
0.6822	-1.1159	1.4755	2.1300	-0.4491	2.3387	1.5149	0.0440
0.7631	-0.4291	2.0836	2.7375	0.2017	2.9469	2.3255	0.0570
0.8336	-12.1554	-9.6533	-8.9807	-11.5434	-8.7644	-9.5849	-0.1580
0.8957	-2.8817	-1.0960	-0.5988	-2.4569	-0.4381	-1.0735	-0.0118
0.9508	-1.6162	-0.6008	-0.3071	-1.3818	-0.2116	-0.8994	-0.0061

From the various computed acoustical, thermodynamical parameters for the binary mixtures imply that the specific chemical interactions directed towards the weak molecular interaction prevailing in the present systems of the binary mixtures. Such interactions are due to weak dipole-dipole and dipole-induced dipole forces. Dispersive forces are also found to exist between the components of the mixtures[15-18].

The computed theoretical ultrasonic theoretical velocities are listed in Table 4 for the binary system m-cresol with carbon tetra chloride, the corresponding percentage of deviation and interaction parameters (α) are listed in Table 5.

The observed deviations of the theoretical ultrasonic velocity from the experimental values are attributed to the presence of intermolecular interactions between the component molecules of the mixture. The observed deviations following all theories illustrate molecular interaction between unlike molecules in the liquid mixtures. The suitability of these theories based on percentage deviation. The overall comparison of percentage deviation of this system shows the following trend.

$$U_{IMP} < U_{VV} < U_D < U_{JR} < U_R < U_{NOM}$$

The viscometric information includes viscosity as a function of composition on the bases of weight, volume, and mole fraction, comparison of experimental viscosities with those calculated with several different equations. Viscosity itself is consequently not a simple additive property. The computed Viscosity interaction parameters and Computed theoretical viscosities are listed in Table 6, Table 7 and Table 8, respectively.

Table 6: Computed viscosity interaction parameters for m-cresol with carbon tetra chloride binary system.

Mole fraction m-cresol x_1	Grunberg Nissan	Katti and Chaudhri	Hind	Wijk
	D_{12}	W_{vis}	H_{12}	H_{12}
0.1926	-0.4806	-1351.2398	0.0016	0.0024
0.3493	-1.2286	-3122.7800	0.0009	0.0016
0.4792	-0.7152	-1857.0419	0.0009	0.0021
0.5887	-0.8003	-2077.5433	0.0004	0.0020
0.6822	-0.9492	-2381.8127	-0.0002	0.0019
0.7631	-0.4803	-1225.8607	-0.0001	0.0024
0.8336	-0.5938	-1492.5988	-0.0009	0.0022
0.8957	-0.3809	-954.3393	-0.0011	0.0025
0.9508	0.0743	271.0371	-0.0002	0.0031

Table 7: Experimental viscosity, viscosity deviation and computed theoretical viscosities for m-cresol with carbon tetra chloride binary system

Mole fraction m-cresol x_1	Experimental Viscosity	Viscosity Deviation	Grunberg Nissan	Katti and Chaudhri	Hind	Wijk
	η	Δη	GNη	KCη	Hη	Wη
	$x10^{-3}$ Ns/m^2	$x10^{-3}$	$x10^{-3}$ Ns/m^2	$x10^{-3}$Ns/m^2	$x10^{-3}$ Ns/m^2	$x10^{-3}$ Ns/m^2
0.1926	1.1714	-0.5843	1.1714	1.1714	1.1714	1.1714
0.3493	1.2490	-1.2820	1.2490	1.2490	1.2490	1.2490
0.4792	1.6166	-1.6988	1.6166	1.6166	1.6166	1.6166
0.5887	1.9247	-2.1844	1.9247	1.9247	1.9247	1.9247
0.6822	2.2874	-2.6248	2.2874	2.2874	2.2874	2.2874
0.7631	3.2243	-2.5007	3.2243	3.2243	3.2243	3.2243
0.8336	3.9952	-2.5523	3.9952	3.9952	3.9952	3.9952
0.8957	5.3534	-2.0267	5.3534	5.3534	5.3534	5.3534
0.9508	7.2343	-0.9884	7.2343	7.2343	7.2343	7.2343

Table 8: Computedtheoretical Viscosities for m-cresol with carbon tetra chloride binary system

Kendall-Monroe	Modified Kendall-Monroe	Arrhenius
KMη	MKMη	Arη
$x10^{-3}$ Ns/m^2	$x10^{-3}$ Ns/m^2	$x10^{-3}$ Ns/m^2
7.0221	0.6023	1.2207
9.6520	1.4892	1.5097
11.649	2.3869	1.8718
13.237	3.1366	2.3266
14.485	3.6181	2.8994
15.402	3.7376	3.6228
15.949	3.4276	4.5389
16.013	2.6539	5.7023
15.265	1.4405	7.1837

All the values of Δη were negative, indicating that dispersion forces are primarily responsible for interaction. The viscosity of a mixture [9-13] depends on the molecular interactions between the components mixture with strong interactions between different molecules show positive viscosity deviations, while for mixtures absence of specific interactions, viscosity deviations are negative. The negative viscosity deviation in the present investigation suggests that without specific interactions between component molecules over the entire composition range in all the binary mixtures. The measured experimental viscosity excellent agreement with Grunberg Nissan, Katti and Chaudhri, Hind and Wijk theoretical approaches, whereas, Kendall-Monroe, Modified Kendall-Monroe, Arrhenius shows significant deviations between theoretical and experimental values of viscosities.

CONCLUSION

In the present work, the investigational densities, viscosities and ultrasonic velocities of binary mixtures for the m-cresol with carbon tetra chloride determined as function of composition at temperature 302.15K. Using these data, various acoustical and thermodynamical parameters were computed with the standard relations obtained from the literature survey. All these parameters indicate the presence of specific interactions between

the subjected system components of molecules. Again, the computed ultrasonic velocities and viscosity for binary mixture from different theories and various relations have been correlated with the experimentally measured values. Viscosity of all semi-empirical relations used to predict the viscosities of the present binary mixture provided a better representation of viscosity data. Thus, the present study further supports the effectiveness of a sample.

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