© 2018 IJSRSET | Volume 4 | Issue 1 | Print ISSN: 2395-1990 | Online ISSN : 2394-4099
Themed Section : Engineering and Technology

Acoustic Response in the Binary Liquid Mixtures of an Organophosphoric Compound with Cyclohexane and Dioxane

Ranjeeta Rath[1], Rajeswari Panda[1], Biswajit Dalai[*1], Sarat Kumar Dash[2]
[*1]Department of BSH, Gandhi Institute of Engineering and Technology (GIET), Gunupur,Odisha, India
*biswajit_dalai@rediffmail.com
[2]Department of Physics, Regional Institute of Education (NCERT), Bhubaneswar, Odisha, India
Skdash59@yahoo.com

ABSTRACT

Ultrasonic velocity (*U*) of binary mixtures of an organophosphoric compound (DEHPA) with Cyclohexane and Dioxane including those of pure liquids were measured over entire composition range of DEHPA at 303.15K and 0.1MPa. The theoretical values of ultrasonic velocity have been calculated using various empirical relations and models, viz. Impedance dependence relation, Nomoto's relation, Danusso model, Junjie's relation and Van Dael-Vangeel's ideal mixing relation. The computed values of ultrasonic velocity are compared with the corresponding experimental data by applying Chi-Square test and average percentage error (APE) to assess the validity of all the above theories.

Keywords: Ultrasonic Velocity, Binary Mixtures, Theoretical Models, APE, Chi-Square Test

I. INTRODUCTION

Acoustic properties of binary organic liquid mixtures have been investigated by a number of workers [1-4] over the past several decades. Such studies have great relevance in many areas of applied and theoretical research works. In many industrial applications liquid mixtures are used in processing and product formulations. It also provide a better knowledge in understanding molecular interaction between unlike molecules and strucural behavior of molecules.

The organophosphorous compound Di - (2-ethylhexyl) phosphoric acid (DEHPA) is widely used as an exractant for the extraction of actinides, lanthanides and rare earth metals [5-7]. In continuation of our earlier work [8-10], we propose to extend our investigation to cyclohexane and dioxane if it could be used as better diluent with DEHPA for extraction process. DEHPA is a polar liquid whereas both cyclhexane and dioxane are apolar liquids with cyclic structures. The ultrasonic velocity in binary mixtures of DEHPA with cyclohexane and dioxane were measured at 303.15K over the entire composition range of DEHPA. The experimental velocities have been compared with theoretically computed velocities by using various theoretical relations [11-15], *viz.* Impedance dependence relation, Nomoto's relation, Danusso model, Junjie's relation and Van Dael-Vangeel's ideal mixing relation. The relative merits of these relations have been discussed in terms of Chi-Square test and average percentage error (APE).

II. METHODS AND MATERIAL

All Chemicals, used in this investigation, *viz.* DEHPA ($C_{16}H_{35}O_4P$), Cyclohexane (C_6H_{12}) and Dioxane ($C_4H_8O_2$), are of AR grade. All samples were prepared by weighing liquids in specially designed glass stoppered airtight bottles, taking extreme precautions to avoid evaporation and atmospheric moisture. The mass measurements were performed by using single pan digital balance (Mettler Toledo, AB54-S, Switzerland) with an accuracy of ±0.0001g. The probable error in mole fraction of DEHPA (x_2) was estimated to be less than ± 2 x 10^{-4}. The ultrasonic velocity in pure liquids and binary mixtures were measured by using a single-crystal variable path multi-frequency (ν) ultrasonic interferometer (F-81, Mittal Enterprises, New Delhi) operating at 2 MHz with an accuracy of ± 0.5 ms^{-1}. Ultrasonic velocity (*U*) is the product of wavelength (*λ*) and frequency (ν). The procedure followed to measure the ultrasonic velocity (*U*) is same as explained in our earlier work [8, 9]. The reliability of experimental measurements of ultrasonic data was authenticated by comparing the data available in literature [16]. The temperature of all samples was maintained at 303.15K to an accuracy of ± 0.1K by an electronically controlled thermostatic water bath during measurement of ultrasonic velocity.

III. RESULTS AND DISCUSSION

The experimental values of ultrasonic velocity (*U*) over entire molefraction range of DEHPA (x_2) of two systems at 303.15K are presented in Table 1.

Table 1
Experimentally measured values of ultrasonic Velocity (*U*) at 303.15K

DEHPA + cyclohexane		DEHPA + dioxane	
x_2	U (ms^{-1})	x_2	U (ms^{-1})
0.00	1252	0.00	1345
0.07	1254	0.06	1321
0.14	1256	0.12	1311
0.21	1258	0.23	1305
0.29	1260	0.31	1303
0.37	1263	0.39	1301
0.42	1265	0.46	1300
0.51	1267	0.51	1299
0.59	1270	0.57	1298
0.69	1275	0.61	1297
0.74	1277	0.69	1296
0.81	1281	0.78	1295
0.87	1284	0.85	1294
0.93	1288	0.93	1293
1.00	1293	1.00	1293

These experimental data have been correlated with computed ultrasonic velocities by using different theoretical models such as Impedance dependence relation, Nomoto's relation, Danusso model, Junjie's relation and Van Dael-Vangeel's ideal mixing relation [11-15]. Using the above said theoretical models, values of ultrasonic velocity such as U_{IDR}, U_N, U_D, U_J and U_{IMR} respectively were estimated by using the following relations as given in Equ. 1-5 :

$$U_{IDR} = \sum x_i Z_i / \sum x_i \rho_i \quad (1)$$

$$U_N = \left(\sum x_i R_i / \sum x_i V_{mi}\right)^3 \quad (2)$$

$$U_D = (1/\rho)\left[(1/M_{eff})\sum \left(x_i M_i / \rho_i^2 U_i^2\right)\right]^{-1/2} \quad (3)$$

$$U_J = \sum(x_i V_{mi}) / (M_{eff})^{1/2} \left[\sum(x_i V_{mi} / (\rho_i U_i^2)\right]^{1/2} \quad (4)$$

$$1/U_{IMR}^2 = (M_{eff})\left(\sum\left(x_i / M_i U_i^2\right)\right) \quad (5)$$

where x_i , U_i , ρ_i, Z_i, $R_i = V_{mi} U_i^{1/3}$, V_{mi} and M_i are molefraction, ultrasonic velocity, density, acoustic impedance, molecular sound velocity, molar volume and molecular weight of i^{th} component of the mixture respectively and $M_{eff} = \sum x_i M_i$ is the effective molecular weight of the solution.

The computed values of Ultrasonic velocity are presented in Table 2 and displayed in Fig. 1 and Fig. 2 with a comparision to the experimental value. The average percentage error (APE) and Chi-Square values [17, 18] have been calculated to judge the validity of theoretical models and reported in Table 3.

The average percentage error

$$\text{APE} = \frac{1}{n}\sum \frac{U_{Expt} - U_{Cal}}{U_{Expt}} \times 100\% \quad (6)$$

Chi-Square test

$$\chi^2 = \sum_{i=1}^{n} \frac{(U_{Expt} - U_{Cal})^2}{U_{Cal}} \quad (7)$$

where, n - number of data used,

U_{Expt} - experimental ultrasonic velocity,

$Ucal$ – calculated ultrasonic velocity.

Table 2.
Theoretical values of ultrasonic velocity (SI Unit) with molefraction (x_2) of DEHPA.

Mole fraction (x_2)	U_{IDR}	U_N	U_D	U_J	U_{IMR}
Cyclohexane + DEHPA					
0.00	1252.0	1252.0	1252.0	1252.0	1252.0
0.07	1255.6	1259.6	1256.7	1253.3	1175.3
0.14	1259.0	1265.5	1261.1	1256.2	1120.4
0.21	1262.3	1270.2	1268.1	1259.8	1080.9
0.29	1265.9	1274.6	1271.8	1264.1	1049.9
0.37	1269.4	1278.2	1277.0	1268.4	1030.8
0.42	1271.5	1280.1	1285.2	1270.9	1024.1
0.51	1275.2	1283.1	1283.5	1275.2	1021.4
0.59	1278.4	1285.3	1284.7	1278.8	1029.0
0.69	1282.2	1287.7	1285.9	1282.8	1052.8
0.74	1284.0	1288.7	1287.6	1284.7	1071.6
0.81	1286.6	1290.0	1288.8	1287.2	1107.3
0.87	1288.7	1291.1	1289.1	1289.1	1148.9
0.93	1290.7	1292.0	1290.1	1291.0	1204.1
1.00	1293.0	1293.0	1293.0	1293.0	1293.0
Dioxane + DEHPA					
0.00	1345.0	1345.0	1345.0	1345.0	1345.0
0.06	1342.0	1334.6	1198.4	1333.3	1276.3
0.12	1339.0	1326.8	1216.3	1325.0	1223.9
0.23	1333.6	1316.9	1236.7	1314.9	1157.3
0.31	1329.5	1311.8	1248.6	1310.0	1126.3
0.39	1325.4	1307.8	1257.1	1306.2	1106.5
0.46	1321.8	1305.0	1267.4	1303.6	1097.1
0.51	1319.3	1303.2	1267.6	1302.0	1094.6
0.57	1316.1	1301.4	1271.9	1300.3	1096.1
0.61	1314.0	1300.3	1274.2	1299.3	1099.8
0.69	1309.8	1298.3	1280.0	1297.6	1114.2
0.78	1305.0	1296.5	1284.4	1296.0	1142.7
0.85	1301.2	1295.2	1288.2	1294.9	1175.8
0.93	1296.9	1294.0	1290.7	1293.8	1228.7
1.00	1293.0	1293.0	1293.0	1293.0	1293.0

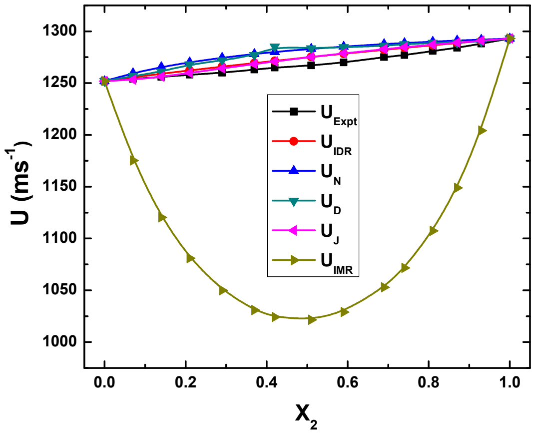

Figure 1. Experimental and theoretical ultrasonic velocity of cyclohexane + DEHPA.

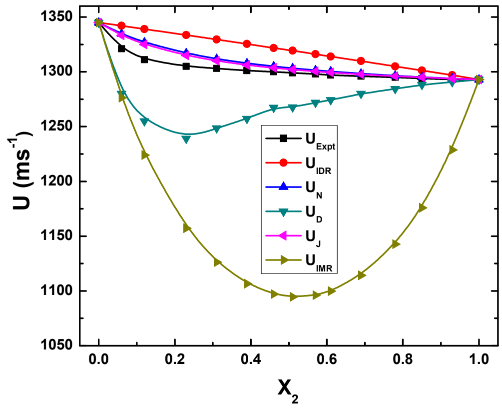

Figure 2. Experimental and theoretical ultrasonic velocity of dioxane + DEHPA.

Table 3.
APE and Chi-Square values of calculated ultrasonic Velocity (U) at 303.15K

U	Cyclohexane + DEHPA		Dioxane + DEHPA	
	APE value	Chi-Square value	APE value	Chi-Square value
U_{IDR}	0.374	0.351	1.212	3.926
U_N	0.771	1.47	0.399	0.586
U_D	0.685	1.316	-2.865	30.458
U_J	0.332	0.33	0.324	0.423
U_{IMR}	-14.893	452.475	-11.673	301.972

The observed modulus of average percentage error (APE) and Chi-Square test of ultrasonic velocity (Table 3), following all relations, illustrate intermolecular interaction between unlike molecules in the liquid mixtures. Among the above mentioned five theoretical relations / models, Junjie's relation exhibits closer data approach to the experimental values (Fig. 1 and Fig. 2).

IV. CONCLUSION

Ultrasonic velocities of the two systems, i.e. DEHPA with cyclohexane and dioxane, have been measured experimentally at 303.15K. The trend of variation of ultrasonic velocity of liquid mixtures over entire composition of DEHPA indicate the presence of molecular interaction between unlike molecules in both systems. Again, ultrasonic velocities have been computed theoretically by using various theoretical relations / models and analysed with those of experimental data in both the binary mixtures. There is a good agreement between experimental and theoretical values of ultrasonic velocity. However, it may be pointed out that Junjie's relation is best suited among the five theoretical models for the calculation of ultrasonic velocity in the present systems.

V. ACKNOWLEDGEMENT

The Authors are grateful to the Chairman, Secretary and Dean of Gandhi Institute of Engineering & Technology (GIET), Gunupur for constant support and thankful to Prof B. B. Swain, Ex-Professor, Khallikote College, Berhampur for valuable discussions.

VI. REFERENCES

[1]. S. Nithiyanantham and L. Palaniappan (2016), Ultrasonic studies on aqueous monosaccharides with enzyme amylase. Journal of Molecular Liquids, 221, 401-407.

[2]. V. P. Stepanov and V. I. Minchenko (2013), Ultrasonic velocity for an equimolar mixture of molten AgI and NaCl in the biphasic region. Journal of Chemical Thermodynamics, 59, 250-253

[3]. M. Oroian, S. Ropciuc, S. Amariei and G. Gutt (2015), Correlations between density, viscosity, surface tension and ultrasonic velocity of different mono- and di-saccharides. Journal of Molecular Liquids, 207, 145-151.

[4]. G. Ravichandran, G. Lakshiminarayanan and D. Ragouraman (2013), Apparent molar volume and ultrasonic studies on some bile salts in water–aprotic solvent mixtures. Fluid Phase Equilibria, 356, 256-263

[5]. S. K. Singh, S. K. Misra, M. Sudersanan and A. Dakshinamoorthy (2009), Studies on the Recovery of Uranium from Phosphoric Acid Medium by D2EHPA/n-Dodecane Supported Liquid Membrane. Separation Science and Technology, 44, 169 - 189.

[6]. M. Mohammadi, K. Forsberg, L. Kloo, J. M. De La Cruz and Å. Rasmuson (2015), Separation of ND(III), DY(III) and Y(III) by solvent extraction using D2EHPA and EHEHPA. Hydrometallurgy, 156, 215-224.

[7]. M. Watanabe et al. (2004), Selective Extraction of Americium(III) over Macroscopic Concentration of Lanthanides(III) by Synergistic System of TPEN and D2EHPA in 1-Octanol. Solvent Extraction and Ion Exchange, 22, 377-390.

[8]. B. Dalai, S. K. Dash , S. K. Singh , N. Swain and B. B. Swain (2016), Ultrasonic and ^{31}P NMR investigations of an acidic nuclear extractant with some monosubstituted benzenes, Journal of Chemical Thermodynamics, 93, 143–150.

[9]. B. Dalai , S. K. Dash, S. K. Singh and B. B. Swain (2015), ^{1}H NMR and acoustic response of binary mixtures of an organophosphorous extractant with 1-alkanols (C_1–C_4, C_8), Journal of Molecular Liquids, 208, 151–159.

[10]. S. Jena, B. Kuanar, B. Dalai, S. K. Dash, N. Swain and S. K. Singh (2018), Validation of Theoretical Approach of Viscosity in Polar-Apolar Liquid Mixtures containing a Nuclear Extractant at 303.15K. International Journal of Scientific Research in Science, Engineering and Technology, 4, 537-540.

[11]. A. Ali, A. K. Nain, V. K. Sharma and S. Ahmad (2004), Study of molecular interaction in ternary mixtures through ultrasonic speed measurements, Physics and Chemistry of Liquids, 42, 375–383

[12]. O. Nomoto (1958), Empirical formula for sound velocity in liquid mixtures, Journal of the Physical Society of Japan, 13, 1528-1532.

[13]. F. Danusso (1951), Ultrasonic velocity and adiabatic compressibility of liquid mixtures, Atti della academia nazionale di lincei. 10, 235-239.

[14]. G. V. Rama Rao, P. B. Sandhya Sri, A. V. Sarma and C. Rambabu (2007), Comparative Study of theoretical ultrasonic velocities of binary mixtures of methanol and pyridine at different temperatures. Indian Journal of Pure and Applied Physics, 45, 135-142.

[15]. S.K. Dash, B. Dalai, S. K. Singh, N. Swain and B.B. Swain (2014), A comparative study of experimental and theoretical values of ultrasonic velocity in binary mixtures of two nuclear extractants. Journal of Pure and Applied Ultrasonic, 36, 60-64,.

[16]. W. M. Haynes (2015-2016), CRC Handbook of Chemistry and Physics, 98th Edition, CRC Press, New York.

[17]. S. C. Gupta and V. K. Kapoor (2002), Fundamentals of Mathematical Statistics (Sultan Chand and Sons Pvt. Ltd.), New Delhi.

[18]. R. L. Plackett (1983), Karl Pearson and the Chi-Squared Test. International Statistical Review. International Statistical Institute. 51 , 59–72.