

Acoustical Properties of Ternary Mixtures of Di-(2ethyl-hexyl)phosphoric Acid, Benzene and *m*-Xylene at Different Temperatures

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Abstract: Ultrasonic velocity (U) and density (ρ) of the ternary mixtures of di-(2-ethylhexyl) phosphoric acid (DEHPA), benzene and *m*-xylene were measured at atmospheric pressure and temperatures from 298.15K to 313.15K at an interval of 5K. The experimental data have been used to calculate adiabatic compressibility (K_s), intermolecular free length (L_f), acoustic impedance (Z), surface tension (σ), molar volume (V_m) and Wada's constant (W). From the data, the deviations in adiabatic compressibility (ΔK_s), ultrasonic velocity (ΔU), intermolecular free length (ΔL_f) and acoustic impedance (ΔZ) were calculated. The results are discussed in terms of molecular interaction among components of the ternary mixture. The theoretical values of ultrasonic velocity have been calculated using various empirical relations and are compared with the corresponding experimental data by calculating percentage deviation.

Keywords: DEHPA, Ternary mixture, Ultrasonic studies, Molecular interaction

Introduction

Molecular interaction study¹⁻³ plays an important role in understanding the structure and properties of liquids. A large number of studies have been made on the interaction in liquid mixture by various methods like dielectric relaxation, Infrared spectroscopy, nuclear magnetic resonance spectroscopy *etc.* have become powerful tools to provide information regarding the physical and chemical properties of liquid system. The method of studying the molecular interaction from the knowledge of variation of thermodynamic parameters with

composition and temperature gives an insight into the molecular process. Industry demands reliable data on the physical and chemical properties of a wide variety of liquid mixtures. DEHPA is one of the most widely used and characterized extractant⁴ in the atomic energy industry. Increasing use of DEHPA, benzene and m-xylene in many industrial process have greatly stimulated the need for extensive information on the acoustic and transport properties of these liquids and their mixtures. DEHPA is a polar liquid and the dipolar association of DEHPA molecules decreases when they are mixed with non-polar aromatic hydrocarbons, viz. benzene and m-xylene due to some specific intermolecular interaction between DEHPA molecules and aromatic hydrocarbons.

In the present study, ultrasonic velocities in the ternary mixtures have been estimated using impedance dependence relation⁵, Nomoto's relation⁶, and Rao's specific sound velocity relation⁷. The validity of these formulations for describing the ultrasonic response in this present study has been compared with experimental values by calculating percentage deviation. Such comparisons help to understand the thermodynamics of the mixtures.

Experimental

All chemicals are of AR grade (E. Merck, India) and the purity of the sample was checked by comparing the experimental data of density and ultrasonic velocity with the values available in the literature⁸⁻¹¹. The ternary liquid mixture of DEHPA, benzene and m-xylene were prepared by volume. Nine mixtures were prepared in air tight bottles. The mass measurements were performed on a digital top loading balance with a precision of 0.0001g. Density of pure liquids and their mixtures were determined with a specific gravity bottle of 25 mL capacity calibrated at four different temperatures from 298.15K to 313.15K. The increment in temperature was kept regular at 5 K, with a view to ensuring measurable effects of temperature change on experimental observations. The maximum error in the density measurement was found to be $\pm 0.01 \text{ kg m}^{-3}$. The ultrasonic velocity was determined by using a single crystal variable path ultrasonic interferometer (F-81, Mittal Enterprises, New Delhi) working at 2 MHz with an accuracy of 0.5 ms^{-1} . The working principle used in the measurement of speed of sound through the sample was based on the accurate determination of the wavelengths of ultrasonic waves of known frequency produced by quartz crystal in the measuring cell. The temperature of the sample was controlled by circulating water at a desired temperature through a steel jacket of double walled cell. The temperature of the sample was maintained to a precision of $\pm 0.1 \text{ K}$ in an electronically digital operated water bath for measurement of all the physical properties.

Theoretical

The experimental values of U and ρ were taken to calculate the various thermo-acoustic parameters, viz. adiabatic compressibility (K_s), intermolecular free length (L_f), acoustic impedance (Z), surface tension (σ), molar volume (V_m) and Wada's constant (W), using following relations¹¹⁻¹³ and are presented in Table 1.

$$K_s = \frac{1}{\rho U^2} \quad (1)$$

$$L_f = k K_s^{1/2} \quad (2)$$

Where $k = (93.875 \pm 0.375T) \times 10^{-8}$ is the Jacobson temperature dependent constant.

$$Z = \rho U \quad (3)$$

$$\sigma = 6.3 \times 10^{-4} \rho U^2 \quad (4)$$

$$V_m = \sum_{i=1}^3 x_i M_i / \rho \quad (5)$$

$$W = V_m K_s^{-1/7} \quad (6)$$

The excess function (ΔY) such as ΔU , ΔZ , ΔK_s and ΔL_f have been computed using the following expression.

$$\Delta Y = Y_{\text{exp}} - Y_{\text{ideal}} = Y_m - (x_1 Y_1 + x_2 Y_2 + x_3 Y_3) \quad (7)$$

Where Y_m represents the parameters Z , K_s , L_f , V_m of ternary mixtures, x is the mole fraction, and subscripts 1, 2 and 3 refer to components of ternary mixture. Using Impedance dependence relation⁵, Nomoto's relation⁶ and Rao's specific sound velocity relation⁷, theoretical values of ultrasonic velocity such as U_{IDR} , U_N and U_R respectively were estimated (Table 3) by the following relations and models as given by :

$$U_{IDR} = \sum x_i Z_i / \sum x_i \rho_i \quad (8)$$

$$U_N = \left(\sum x_i R_i / \sum x_i V_{mi} \right)^3 \quad (9)$$

$$U_R = \left(\sum x_i r_i \rho \right)^3 \quad (10)$$

Where x_i , ρ_i , Z_i , $R_i = V_{mi} U_i^{1/3}$, $r_i = U_i^{1/3} / \rho_i$ and V_{mi} are mole fraction, density, acoustic impedance, molecular sound velocity, Rao's specific sound velocity and molar volume of i^{th} component of the mixture, respectively. The percentage deviation in ultrasonic velocity between experimental and computed values can be calculated as

$$\left(\frac{\Delta U}{U} \right) \% = \left(\frac{U_{\text{exp}} - U_{\text{th}}}{U_{\text{exp}}} \right) \times 100 \quad (11)$$

Results and Discussion

The comparison between experimental and literature values of density (ρ) and ultrasonic velocity (U) of pure liquids are given in the Table 1.

Table 1. Density (ρ) and ultrasonic velocity (U) of pure liquids at different temperatures

Pure Liquid	T, K	ρ , kgm ⁻³		U, ms ⁻¹	
		Expt.	Lit. [Ref]	Expt.	Lit. [Ref]
DEPHA	298.15	975.0	-	1344	-
	303.15	916.3	1009.6 ^[21]	1324	1321.6 ^[13]
	308.15	959.2	1008.2 ^[21]	1304	1302.2 ^[13]
	313.15	955.8	1003.1 ^[21]	1284	1283.4 ^[13]
	298.15	873.6	873.68 ^[8]	1302	1299.3 ^[20]
Benzene	303.15	868.2	868.26 ^[20]	1276	1276.0 ^[20]
	308.15	862.8	862.89 ^[20]	1254	1252.8 ^[20]
	313.15	854.4	857.49 ^[20]	1230	1229.8 ^[20]
	298.15	859.8	859.87 ^[9]	1321.5	1321.0 ^[21]
m-Xylene	303.15	855.4	-	1303.7	-
	308.15	851.5	851.24 ^[9]	1283.5	1279 ^[9]
	313.15	847.2	-	1234.3	-

Table 2. Experimentally determined values of density (ρ), ultrasonic velocity (U) and calculated values of isentropic compressibility (K_s), intermolecular free length (L_f), acoustic impedance (Z), surface tension (σ), molar volume (V_m) and Wada's constant (W) at different temperatures

x_1	x_2	x_3	ρ Kg m^{-3}	U m s^{-1}	K_s $10^{10} \text{N}^{-1} \text{m}^2$	L_f 10^{-11}m	Z $10^{-6} \text{Kg m}^{-2} \text{s}^{-1}$	σ 10^{-4}Nm^{-1}	V_m $10^{-5} \text{m}^3 \text{mol}^{-1}$	W $[10^{-8} \text{m}^3 \text{mol}^{-1} / (\text{Nm}^{-2})]$
298.15 K										
0.034	0.559	0.408	874.2	1236	7.4847	5.6282	1.0805	84.137	11.2038	0.2254
0.072	0.542	0.386	881.2	1243	7.3465	5.5748	1.0950	85.754	12.0922	0.2439
0.124	0.506	0.370	894.1	1249	7.1695	5.5073	1.1167	87.872	13.2857	0.2689
0.186	0.471	0.343	900.1	1253	7.0763	5.4714	1.1278	89.029	14.7959	0.3001
0.250	0.434	0.316	911.2	1256	6.9568	5.4249	1.1444	90.559	16.2486	0.3304
0.334	0.386	0.280	922.5	1263	6.7956	5.3617	1.1651	92.77	18.1647	0.3706
0.421	0.334	0.245	933.2	1269	6.6543	5.3057	1.1842	94.675	20.1291	0.4119
0.555	0.267	0.178	944.3	1274	6.5246	5.2537	1.2031	96.558	23.1603	0.4752
0.729	0.163	0.108	955.4	1299	6.2029	5.1226	1.2411	100.156	27.1352	0.5608
303.15 K										
0.034	0.559	0.408	870.8	1217	7.7535	5.7794	1.0597	81.2531	11.2475	0.2252
0.072	0.542	0.386	880.2	1224	7.5833	5.7156	1.0773	83.077	12.1032	0.2431
0.124	0.506	0.370	891.1	1230	7.4176	5.6528	1.0961	84.933	13.3305	0.2685
0.186	0.471	0.343	897.2	1235	7.3076	5.6107	1.1081	86.211	14.8437	0.2997
0.250	0.434	0.316	908.0	1237	7.1974	5.5683	1.1232	87.531	16.3058	0.3299
0.334	0.386	0.280	921.0	1245	7.0049	5.4933	1.1466	89.937	18.1943	0.3696
0.421	0.334	0.245	930.9	1251	6.8641	5.4378	1.1645	91.782	20.1787	0.4111
0.555	0.267	0.178	941.4	1257	6.7229	5.3816	1.1833	93.709	23.2316	0.4747
0.729	0.163	0.108	954.9	1282	6.3719	5.2392	1.2241	98.872	27.1494	0.5591
308.15 K										
0.034	0.559	0.408	866.2	1202	7.9905	5.9201	1.0411	78.843	11.3073	0.2254
0.072	0.542	0.386	876.2	1209	7.8081	5.8521	1.0593	80.685	12.1584	0.2431
0.124	0.506	0.370	888.9	1215	7.6207	5.7814	1.0800	82.669	13.3635	0.2682
0.186	0.471	0.343	895.1	1219	7.5183	5.7425	1.0911	83.795	14.8786	0.2992
0.250	0.434	0.316	905.0	1222	7.3996	5.6970	1.1059	85.139	16.3599	0.3297
0.334	0.386	0.280	919.6	1229	7.1994	5.6194	1.1301	87.507	18.2220	0.3687
0.421	0.334	0.245	927.4	1237	7.0468	5.5595	1.1471	89.401	20.2548	0.4111
0.555	0.267	0.178	937.2	1245	6.8838	5.4948	1.1668	91.519	23.3357	0.4752
0.729	0.163	0.108	953.3	1268	6.5243	5.3973	1.2087	96.562	27.1950	0.5581
313.15 K										
0.034	0.559	0.408	859.1	1187	8.2614	6.0735	1.0197	76.2580	11.4007	0.2262
0.072	0.542	0.386	869.6	1194	8.0663	6.0013	1.0383	78.1031	12.2507	0.2438
0.124	0.506	0.370	885.2	1197	7.8844	5.9333	1.0595	79.9043	13.4193	0.2680
0.186	0.471	0.343	889.5	1202	7.7812	5.8943	1.0691	80.9646	14.9722	0.2996
0.250	0.434	0.316	901.5	1205	7.6394	5.8404	1.0863	82.4671	16.4239	0.3295
0.334	0.386	0.280	916.3	1213	7.4172	5.7548	1.1112	84.9375	18.2876	0.3684
0.421	0.334	0.245	923.4	1221	7.2640	5.6951	1.1274	86.7284	20.3426	0.4112
0.555	0.267	0.178	933.2	1229	7.0945	5.6282	1.1469	88.8012	23.4357	0.4752
0.729	0.163	0.108	947.9	1235	6.7195	5.4774	1.1877	93.7573	27.3499	0.5589

The measurement of ultrasonic velocity in ternary mixture provides some reliable information in the study of molecular interaction. The isentropic compressibility (K_s), intermolecular free length (L_f), acoustic impedance (Z), surface tension (σ), molar volume (V_m) and Wada's constant (W) for ternary mixture, DEHPA (x_1) + benzene (x_2) + m-xylene (x_3) at different temperatures are listed in Table 2. The deviation values, viz. ΔK_s , ΔL_f , ΔZ and ΔU of the ternary mixture have been calculated and displayed in Figures 2-5.

From Table 2, it is observed that the values of ultrasonic velocity (U) and density (ρ) increase nonlinearly with increase in DEHPA mole fraction (x_1). Table 2 shows that the density and ultrasonic velocity are in increasing trend with increase in mole fraction of DEHPA. According to Arul *et al.*¹⁴, the increase in ultrasonic velocity in any mixture indicates the association among molecules of a mixture. It is observed from Table 2 that the values of K_s and L_f decrease with mole fraction of DEHPA and increases with increase in temperature. The rapid decrease in K_s with increase in concentration of DEHPA indicates the formation of large number of tightly bound systems. According to Pandey *et al.*¹⁵, as velocity and density increase with concentration, isentropic compressibility (K_s) must decrease with increase in concentration, as they vary inversely with each other. The free length is the distance between the surfaces of the neighboring molecules. It indicates significant interactions between the solute and solvent molecules, due to which the structural arrangement in the neighborhood of constituent solute particles is considerably affected. Values of acoustic impedance (Z), surface tension (σ), molar volume (V_m) and Wada's constant (W) show a nonlinear increasing trend with increasing mole fraction of DEHPA. According to the model proposed by Eyring and Kincaid¹⁶, the trend of variation of ultrasonic velocity and isentropic compressibility (intermolecular free length) is opposite which corroborates our findings. Furthermore, the nonlinear increase in the value of Z , σ , V_m and W with composition of DEHPA lends support to the interaction between the component molecules.

A continuous decrease in K_s and L_f and increase of acoustic impedance with concentration at the experimental temperatures are clear evidence for the existence of strong interactions like dipole-dipole, dipole-induced dipole, formation of charge transfer complex *etc.*

It is observed that the increasing trend of Wada's constant (W) and surface tension (σ) with mole fraction of DEHPA indicates strong solute - solvent interactions¹³. The dimeric structure of DEHPA molecule (Figure 1) is characterized by intermolecular hydrogen bonding between OH group of one molecule with P=O of the other molecule.

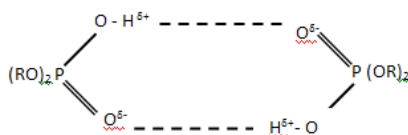


Figure. 1. Dimeric form of DEHPA

where R is ethylhexyl.

The simultaneous participation of both groups affects the extraction ability. As benzene and m-xylene are ring type structure and they are non polar, the attractive interactions are less, because DEHPA is polar and other two (benzene & m-xylene) are non-polar and each component maintains its identity. Thus molar volume V_m between the components is in an increasing trend with increase in the mole fraction of DEHPA. This reduces the net attractive forces.

The deviation in the physical property from its ideal behaviour is a measure of the degree of interaction between component molecules of the ternary liquid mixture. The deviation parameters play a major role in understanding the nature of molecular interactions

in liquid mixtures. The various types of solute-solvent interactions¹⁷ that are operating between the unlike molecules are dispersive forces, which make a positive contribution to deviation parameters and hence H-bonding, dipole-dipole interactions, and dipole-induced dipole interactions are expected to make a negative contribution. The interstitial accommodation which regulates the voids in the liquid structure might be a regulating factor in the magnitudes of deviation parameters.

The deviations in intermolecular free length, isentropic compressibility, ΔK_s (Figure 2) and ΔL_f (Figure 3) are positive throughout the whole range of composition of DEHPA in the ternary mixture. On the other hand, the deviations in acoustic impedance, ΔZ (Figure 4) and ultrasonic velocity ΔU (Figure 5) show the inverse trend to that of ΔK_s and ΔL_f . According to Fort and Moore¹⁸, positive values of deviation functions correspond to the existence of dispersive force. Positive value of ΔK_s is associated with a structure breaking tendency due to hetero-molecular interaction between the component molecules of the mixtures. The shape and size of the molecules in the mixture are loosely packed which is due to the positive excess isentropic compressibility. In this ternary system, the positive deviation in ΔK_s and ΔL_f with concentration and temperatures have been attributed to dispersive forces that show weak interaction between the unlike molecules. This may be due to possible $\pi \cdots \pi$ interaction between π · electrons of benzene and m-xylene with functional groups of DEHPA.

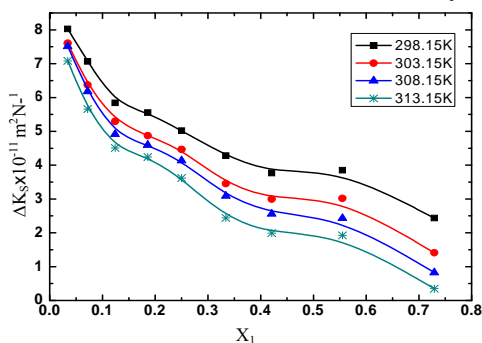


Figure 2. Deviation in isentropic compressibility (ΔK_s) vs. molefraction (X_1) of DEHPA

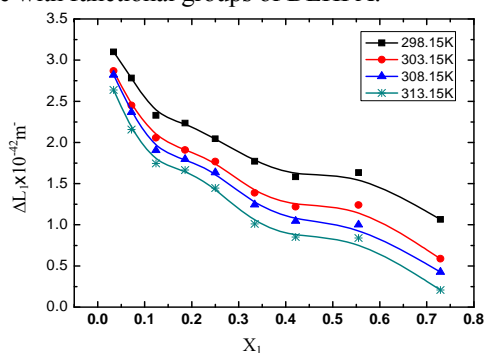


Figure 3. Deviation in intermolecular free length (ΔL_f) vs. molefraction (X_1) of DEHPA

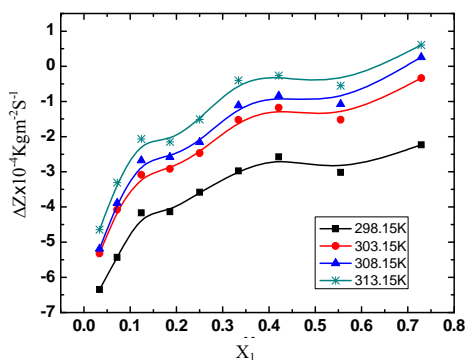


Figure 4. Deviation in acoustic impedance (ΔZ) vs. molefraction (X_1) of DEHPA

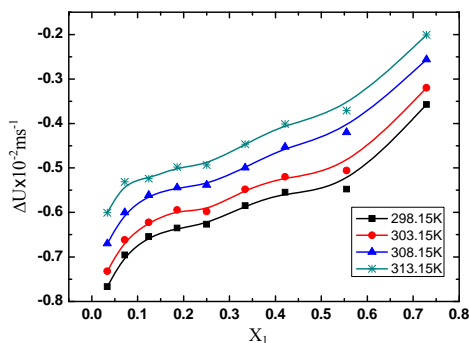


Figure 5. Deviation in ultrasonic velocity (ΔU) vs. mole fraction (X_1) of DEHPA

The values of ΔU and ΔZ are negative over entire composition range at four different temperatures. Negative deviation values suggest the presence of weak interaction between the component molecules^{11,13}. The deviation in ultrasonic velocity may be explained in terms of relative molecular interactions between like and unlike molecules. In the present case, the mutual loss of dipolar association among DEHPA molecules would contribute to negative ΔU indicating dispersive interaction among the components. The variation of ΔZ follows similar trend as deviation in ultrasonic velocity for the system at different temperatures which agrees well with the results of ΔK_s and ΔL_f . Positive values of ΔK_s , ΔL_f and negative values of ΔZ , ΔU in the ternary mixture indicate the presence of weak molecular interactions among the components of molecules in the mixture.

The observed deviations of the theoretical ultrasonic velocity from the experimental values are attributed to the presence of intermolecular interactions¹⁹ between the component molecules of the mixture. The observed deviations (Table 3) following all theories illustrate molecular interaction between unlike molecules in the liquid mixtures. The suitability of these theories based on percentage deviation value is $U_{IDR} > U_N > U_R$.

Table 3. The Comparison between experimental and theoretical values of ultrasonic velocity with mole fraction (x_1) of DEHPA made at four different temperatures, but is given at a single temperature (303.15K)

Mole fraction, x_1	Ultrasonic Velocity, U				Percentage deviation, ($\Delta U/U$) %		
	$U_{Exp.}$ m/s	U_{IDR} m/s	U_N m/s	U_R m/s	U_{IDR} m/s	U_N m/s	U_R m/s
0.034	1217	1273.9	1293.2	1311.5	-4.7	-6.3	-7.8
0.072	1224	1272.7	1296.4	1338.6	-4.0	-5.9	-9.4
0.124	1230	1271.3	1300.3	1368.5	-3.4	-5.7	-11.1
0.186	1235	1269.5	1304.1	1371.5	-2.8	-5.6	-11.3
0.250	1237	1267.7	1307.3	1394.9	-2.5	-5.7	-12.8
0.334	1245	1265.4	1310.7	1419.6	-1.6	-5.3	-14.0
0.421	1251	1263.0	1313.6	1428.2	-1.0	-5.0	-14.2
0.555	1257	1259.3	1317.0	1417.1	-0.2	-4.8	-12.7
0.729	1282	1254.9	1320.3	1401.8	2.1	-3.0	-9.3

Conclusion

The values of density and ultrasonic velocity of the ternary mixture containing DEHPA, benzene and m-xylene are reported at atmospheric pressure and temperatures from 298.15 K to 303.15 K. From these data, several acoustical parameters were calculated. The values of ΔK_s and ΔL_f are found to be positive whereas ΔZ and ΔU are negative for the ternary mixture. All these parameters indicate the presence of specific interactions between the component molecules. Again, the computed ultrasonic velocities from different theories have been correlated with the experimentally measured values. The results indicate that IDR relation predicts the experimental data well, showing smallest deviations in comparison to other two theories.

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References

1. Swain N, Singh S K, Panda D and Chakravortty V, *J Mole Liq.*, 2001, **94**, 233.
2. Swain N, Panda D, Singh S K and Chakravortty V J, *J Chem Engg Data*, 1999, **44**, 32.
3. Das J K, Dash S K, Swain N and Swain B B, *J Mol Liq.*, 1999, **81**, 163.
4. Lee M S, Ahn J G and Lee E C, *Hydrometallurgy*, 2002, **63**, 269.
5. Kumar D S and Rao D K, *Ind J Pure Appl Phys.*, 2007, **45**, 210-220.
6. Nomoto O, *J Phys Soc Jpn.*, 1958, **13**, 1528-1532.
7. Rao M R, *J Chem Phy.*, 1941, **9**, 682-686.
8. Mariano A, Mussari L, Camacho A, Canzonieri and Postigo M, *Phys Chem Liq.*, 2013, **51**, 731-741.
9. Bhatia S C, Rani R and Bhatia R, *J Mol Liq.*, 2011, **159**, 132-141.
10. Lide D R and Haynes W M, *CRC Handbook of Chemistry and Physics*, 91st Edn., CRC Press, Boca Raton 2010-2011.
11. Dalai B, Dash S K and Singh S K, *Ind J Pure Appl Phys.*, 2014, **52**, 24-29.
12. Dash S K, Pradhan S K, Dalai B, Moharana L and Swain B B, *Phys Chem Liq.*, 2012, **50**, 735-749.
13. Mishra S and Paikaray R, *Res J Physical Sci.*, 2013, **1**, 15-21.
14. Arul G and Palaniappan, *Indian J Pure Appl Phys.*, 2001, **39**, 561-564.
15. Pandey J D, Shukla S A K and Singh A K, *Pramana*, 1994, **43**, 353-360.
16. Kincaid J F and Eyring H, *J Chem Phys.*, 1938, **6**, 620-629.
17. Sastry S S, Babu S, Vishwam T and Tiong H S, *J Chem Thermodyn*, 2014, **68**, 183-192.
18. Fort R J and Moore W R, *Trans Faraday Soc.*, 1966, **62**, 1112.
19. Ali A, Nain A K, Sharma V K and Ahmad S, *Phys Chem Liq.*, 2004, **42**, 375-383.
20. Malek N I, Ijardar S P, Master Z R and Oswal S B, *Thermochemica Acta*, 2012, **539**, 71-83.
21. Swain N, Chakravorthi V, Singh S K and Panda D, *Indian J Chem.*, 1999, **38A**, 1116-1122.