

# Dipole-Dipole and Dipole-Induced-Dipole Interactions in the Binary Mixtures of Phosphinic Acid with Some Diluents at 303.15K

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**Abstract:** Speed of sound and densities of binary mixtures involving phosphinic acids (Cyanex 301) with different diluents such as benzene, toluene, xylene and n-butanol have been studied over the entire range of mole fraction at 303.15 K and at atmospheric pressure. This study involves evaluation of different thermo-acoustic parameters along with the excess properties, which are interpreted in the light of inter-molecular interaction between polar extractants with non-polar and polar diluents. Besides, the experimental velocities have been compared with theoretically estimated velocities using different empirical theories and relations, and the relative merits of these theories and relations have been discussed in terms of percentage variations.

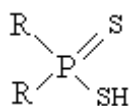
**Keywords:** *Speed of sound; inter-molecular interaction; thermo-acoustic parameters and excess properties*

## 1. Introduction

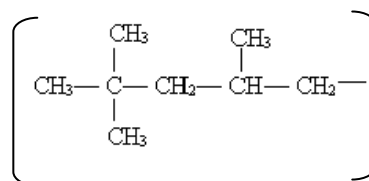
Knowledge of acoustic properties reveals the presence of hetero-molecular interactions between the component molecules in the multi-component liquid systems. Acoustic measurements of commercially available various solvent extractants with diluents are having increasing interest due to their applications in hydrometallurgy. In the field of separation sciences, different phosphinic acids in the trade name Cyanex have been utilized in combination with various diluents

and modifiers for the extraction of various metal ions <sup>[1-5]</sup>. Besides, review of literature shows that Cyanex 301 has been employed most frequently by many workers for such extraction <sup>[4,5]</sup>. However, in the field of molecular interaction involving thermo-acoustic studies, such binary systems are very scarce in literature.

Cyanex 301 is basically acidic type of extractants, and structurally represented as:



Cyanex 301



R

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In continuation of our earlier work on different solvent extractants<sup>[6-8]</sup>, it is a further attempt to study systematically the physico-chemical behaviour of Cyanex 301 with benzene, toluene, xylene and n-butanol by evaluating different thermo-acoustic parameters like, isentropic compressibility,  $\beta_s$ , intermolecular free length,  $L_f$ , acoustic impedance,  $Z$ , degree of inter-molecular attraction,  $\alpha$ , molar sound velocity,  $R$ , molar compressibility,  $W$ , and the relevant excess data. In addition, the ultrasonic velocity has been calculated theoretically using Nomoto's<sup>[9]</sup> as well as Van Dael-Vangeel's ideal mixing relation<sup>[10]</sup>. Review of literatures<sup>[11,12]</sup> shows that many successful attempts have been made to compute ultrasonic velocity for quite a number of binary liquid systems employing the afore-said relations.

## 2. Materials and methods

Cyanex 301 was supplied by Cytec Canada Inc. and was used as received. Benzene, toluene, xylene and n-butanol A. R. grade, mass fraction >0.99, were supplied from the Qualigens Chemicals and were purified by standard procedure<sup>[13]</sup>. Binary solutions were prepared on percentage basis (v/v) by dissolving known volumes of Cyanex 301 in appropriate volumes of benzene, toluene, xylene and n-butanol, and measuring their masses on a Metler-Toledo AB 54 electronic balance.

The ultrasonic velocities were measured at temperature 303.15 K and atmospheric pressure by using a single crystal variable path ultrasonic interferometer operating at a frequency of 2 MHz. The temperature of the solution was maintained constant within  $\pm 0.01^\circ\text{C}$  by circulation of water from thermostatically regulated water bath through the water-jacketed cell. The velocity measurements were precise to  $\pm 0.5\text{ m s}^{-1}$ . The densities were measured by a bicapillary pycnometer calibrated with deionised double distilled water with  $0.9960 \times 10^3\text{ kg m}^{-3}$  as its

density at temperature 303.15 K. The precision of density measurement was within  $\pm 0.0003\text{ kg m}^{-3}$ .

Different thermo-acoustical parameters such as isentropic compressibility,  $\beta_s$ , intermolecular free length,  $L_f$ , acoustic impedance,  $Z$ , molar sound velocity,  $R$ , molar compressibility,  $W$ , and degree of inter molecular attraction,  $\alpha$ , have been evaluated from the experimentally measured values of density,  $\rho$ , and ultrasonic velocity,  $U$ <sup>[6-12]</sup>

$$\beta_s = 1/\rho U^2, \quad (1)$$

$$L_f = K \beta_s^{1/2}, \quad (2)$$

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

$$R = (M/\rho)U^{1/3}, \quad (4)$$

$$W = (M/\rho) \beta_s^{-1/7}, \quad (5)$$

$$\alpha = (U^2/U_{im}^2) - 1 \quad (6)$$

where,  $K$  is Jacobson's temperature-dependent constant and is equal to  $(93.875 + 0.375T) \times 10^{-8}$ ,  $M$  is the relative molar mass;  $M_1$  and  $M_2$  are the molar masses of component 1 and 2, respectively.

The excess properties  $A^E$  ( $\beta_s^E$ ,  $L_f^E$  and  $Z^E$ ) that shed light on the deviation from ideality, and thus is responsible for assessing the structural variation and the type of molecular interactions have been computed with the help of the following equation:

$$A^E = A - [x_1 A_1 + (1-x_1) A_2] \quad (7)$$

where  $A$ ,  $A_1$ ,  $A_2$  are the corresponding parameters ( $\beta_s$ ,  $L_f$ ,  $Z$ ) for binary mixtures, component 1 and component 2, respectively, and  $x_i$  is the mole fractions of Cyanex(s). Besides, the theoretical values of ultrasonic velocity in the present binary mixtures were calculated using Nomoto's relation, and Van Dael and Vangeel ideal mixing relation.

Nomoto established the empirical relation for the velocity of sound for binary liquid mixtures [ $U_{NOM}$ ] basing on the assumption of the linearity of the molar sound velocity

$$U_{NOM} = \left[ \frac{x_1 R_1 + x_2 R_2}{x_1 V_1 + x_2 V_2} \right]^3 \quad (8)$$

where  $R_1$ ,  $R_2$  and  $V_1$ ,  $V_2$  are the molar sound velocities and molar volumes of component 1 and 2 respectively.

According to Van Dael assumption, basing on ideal mixing relation, velocity of sound,  $U_{IMR}$  is evaluated as

$$U_{IMR} = U_1 U_2 \times \left\{ M_1 M_2 / \left[ \frac{x_1 M_2 U_2^2 + x_2 M_1 U_1^2}{(x_1 M_1 + x_2 M_2)} \right] \right\} \quad (9)$$

where  $M_1$ ,  $M_2$  are the molar masses and  $U_1$ ,  $U_2$  are the ultrasonic velocities of components 1 and 2, respectively.

### 3. Results and Discussion

The measured values of ultrasonic velocity,  $U$  and density,  $\rho$  and computed values of isentropic compressibility,  $\beta_s$ , intermolecular free length,  $L_f$  and acoustic impedance,  $Z$  have been summarized in Table 1 & 2, and the excess values along with other relevant parameters are graphically presented in Figures 1-6. In addition, theoretically calculated ultrasonic velocity with the respective experimental values and the percentage variations at different mole fractions of Cyanex 301 are listed in Table 3 & 4. Comparison of experimentally observed ultrasonic velocities with those obtained theoretically in the above binary system has been displayed graphically in Figures 7-10.

The non-linear variation of excess properties with mole fraction of Cyanex 301 is responsible for non-ideality in the binary liquid mixture<sup>[14]</sup>. The factors responsible for

such departure from ideality may either be due to the presence of intermolecular forces between the constituents in the mixture, or to compound formation between solute and solvent, or as a result of association of either to form complex molecules<sup>[15]</sup>. These excess parameters throw light upon the strength of interaction, and their variation with mole fraction finds application in characterizing the physico-chemical behaviour of liquid mixtures<sup>[16]</sup>. The curves highlighted in Figures 1 and 2 show that the behaviour of  $\beta_s^E$  with composition of all the mixtures is reflected in that of  $L_f^E$  and both  $\beta_s^E$  and  $L_f^E$  curves are negative for all the systems under investigation. The nature of  $\beta_s^E$  and  $L_f^E$  play vital role in assessing the compactness due to molecular rearrangement. The extent of molecular interactions in liquid mixtures may be due to charge transfer, dipole-induced-dipole, dipole-dipole interactions<sup>[17]</sup> and interstitial accommodation<sup>[18]</sup>, leading to more compact structure making  $\beta_s^E$  and  $L_f^E$  negative. The curve of  $Z^E$  in Figure 3 shows the opposite trends as observed in Figures 1 and 2 for  $\beta_s^E$  and  $L_f^E$ , which in fact supports the above view. The positive deviation of  $Z^E$  is attributed to specific interaction between the hetero-molecules.

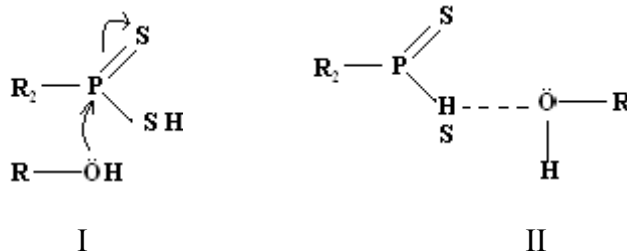
The molar sound velocity,  $R$  in Figure 4 and molar compressibility,  $W$  in Figure 5 was increasing linearly with mole fraction of Cyanex 301 in all the systems, indicating solute-solvent interactions<sup>[19]</sup>. The degree of inter-molecular attraction parameter,  $\alpha$  has also been evaluated to study the structural variation and the nature of interaction occurring in the system. It is observed that the maximum value of  $\alpha$  occurs at about the same mole fraction for all the systems as shown in Figure 6. According to Kannappan<sup>[20]</sup> et al, this suggests the presence of inter-molecular interaction in the systems. As these systems are polar-non-polar or

polar-polar types so the possible hetero-molecular association may be due to dipole-induced-dipole or dipole-dipole type. Another factor, whose contribution to structural variations may arise from the spatial aggregation of unlike molecules [21] due to differences in the molar volume and free volume between component molecules [22].

However, the negative values of  $\beta_s^E$  and  $L_f^E$  for Cyanex 301+benzene, + toluene, + xylene indicates the existence of molecular interactions between delocalised  $\pi$ -electron cloud over the phosphorous and sulphur atoms of phosphinic group present in Cyanex 301 and  $\pi$ -electron cloud of the aromatic

hydrocarbons. Further, more negative values of  $\beta_s^E$  and  $L_f^E$  for Cyanex 301+benzene, + toluene than Cyanex 301 + xylene mixture suggest that benzene and toluene give relatively more compact structure than xylene with Cyanex 301 [23].

The interaction between the molecules of Cyanex 301 and butanol is quite specific type due to more negative  $\beta_s^E$  and  $L_f^E$  values than that of Cyanex 301 with all the aromatic hydrocarbons. The intermolecular interaction may be due to dipole-dipole type and H-bonding between the OH group of n-butanol and phosphinic group of Cyanex.



Possible interaction of n-butanol and Cyanex 301

The inter-molecular interaction between molecules of Cyanex 301 and that of benzene, toluene and xylene are of dipole-induced-dipole and dipole-dipole types, where the association may be due to the delocalised  $\pi$ -electron cloud over the phosphorous and sulphur atoms of phosphinic group present in Cyanex and  $\pi$ -electron cloud of the aromatic hydrocarbon [23].

A close perusal of Table 3 and 4 for the velocities of Cyanex reagents with different diluents indicate that Nomoto's relation, with minimum percentage variations fits the experimental data well, followed by ideal mixing relation, which is found to show the maximum variations from the experimental values.

From Figures [Figure 7 to Figure 10], it reveals that the experimental velocities,  $U_{EXP}$

are in a regular increase with the concentrations for all the systems under investigation.  $U_{NOM}$  values show approximately similar trends with  $U_{EXP}$  data, whereas those for  $U_{IMR}$  decrease first with concentration and then increase giving minima at around 0.3-0.5 mole fraction for all the binary systems, which indicates that Nomoto's relation is quite satisfactory and seems to be equally good in predicting the experimental data, rather there is not any remarkable deviation between the experimental velocity values and those calculated from this theory. But, however, the ideal mixing relation is on the other hand shown to deviate more from the experimental findings than that of Nomoto's for all the systems. The limitations and approximation incorporated in the ideal mixing theory is supposed to be responsible for such variations.

According to the assumption for the formation of ideal mixing relation, the ratio of specific heats of the components is equal to the ratio of specific heats of ideal mixtures, indicating the equality in volumes <sup>[12]</sup>. This implies that no interaction should be entitled here. But, on mixing of components, specially polar-polar and non-polar-polar types of components there is the probability of various types of forces like hydrogen bonding, dipole-dipole, dipole-induced-dipole, dispersion forces, charge transfer etc. operating in them, which may result in violating the assumption. The deviations in the ideal mixing relation is therefore, supposed to indicate as the presence of

inter-molecular interaction in these binary mixtures. On the other hand the ultrasonic velocities obtained from Nomoto's relation are better fitted to the experimental values having minimum percentage of variations. Thus, the linearity of molar sound velocity as suggested by Nomoto <sup>[9]</sup> in deriving the empirical relation, is rather more appropriate for the binary liquid mixtures studied. It is, however, concluded that there is inter-molecular interaction present in all the binary mixtures under investigations and the interaction is supposed to be more in case of Cyanex 301 with n-butanol relative to with benzene, toluene and xylene (%Variations of  $U_{IMR}$  from Tables III and IV).

Table 1. Experimentally determined ultrasonic velocity,  $U$ , and density,  $\rho$ , and calculated values of isentropic compressibility,  $\beta_s$ , intermolecular free length,  $L_f$ , and acoustic impedance,  $Z$ , of binary mixtures of (Cyanex 301 + Benzene + Toluene)

Mole fraction Cyanex 301	$U$ $m\ s^{-1}$	$\rho$ $kg\ m^{-3}$	$\beta_s * 10^{10}$ $m^2\ N^{-1}$	$L_f * 10^{11}$ $m$	$Z * 10^{-6}$ $kg\ m^{-2}\ s^{-1}$
<b>Cyanex 301 + Benzene</b>					
0.0000	1257.0	872.0	7.258	5.388	1.096
0.0282	1265.0	876.7	7.128	5.340	1.109
0.0614	1270.0	884.1	7.013	5.296	1.123
0.1485	1276.7	898.2	6.830	5.227	1.147
0.2073	1290.0	906.2	6.631	5.150	1.169
0.3790	1303.0	922.3	6.386	5.054	1.202
0.5113	1318.9	927.7	6.197	4.979	1.223
0.7019	1325.6	936.8	6.075	4.929	1.242
0.8325	1330.9	938.9	6.013	4.904	1.249
1.0000	1340.4	940.4	5.919	4.866	1.260
<b>Cyanex 301 + Toluene</b>					
0.0000	1271.9	866.7	7.132	5.341	1.102
0.0720	1289.1	877.6	6.857	5.237	1.131
0.1174	1292.5	884.7	6.766	5.202	1.143
0.1715	1296.3	893.1	6.663	5.163	1.158
0.2369	1300.2	902.7	6.553	5.119	1.174
0.3177	1311.2	911.1	6.384	5.053	1.195
0.4201	1323.6	917.6	6.221	4.988	1.214

0.5539	1330.2	927.6	6.093	4.937	1.234
0.7364	1338.7	934.7	5.970	4.886	1.251
1.0000	1340.4	940.4	5.919	4.865	1.260

Table 2. Experimentally determined ultrasonic velocity,  $U$ , and density,  $\rho$ , and calculated values of isentropic compressibility,  $\beta_s$ , intermolecular free length,  $L_f$ , and acoustic impedance,  $Z$ , of binary mixtures of (Cyanex 301 + Xylene, + n-butanol)

<b>Mole fraction Cyanex 301</b>	$U$ $\text{m s}^{-1}$	$\rho$ $\text{kg m}^{-3}$	$\beta_s * 10^{10}$ $\text{m}^2 \text{N}^{-1}$	$L_f * 10^{11}$ $\text{m}$	$Z * 10^{-6}$ $\text{kg m}^{-2} \text{s}^{-1}$
<b>Cyanex 301 + Xylene</b>					
0.0000	1296.5	865.4	6.874	5.244	1.122
0.0822	1297.7	879.2	6.754	5.198	1.141
0.1331	1304.7	888.9	6.609	5.141	1.160
0.1928	1313.6	898.5	6.450	5.079	1.180
0.2638	1316.2	904.0	6.385	5.054	1.190
0.3495	1321.5	912.4	6.276	5.010	1.206
0.4553	1329.5	920.8	6.144	4.957	1.224
0.589	1335.1	929.5	6.036	4.913	1.241
0.7633	1340.5	936.4	6.943	4.876	1.255
1.0000	1340.4	940.4	6.919	4.866	1.260
<b>Cyanex 301 + n-butanol</b>					
0.0000	1221.6	803.6	8.339	5.775	0.982
0.0631	1233.4	832.6	7.895	5.619	1.027
0.1035	1242.4	845.4	7.663	5.536	1.050
0.1522	1253.6	857.1	7.424	5.449	1.074
0.2122	1265.9	866.0	7.206	5.369	1.096
0.2877	1277.8	885.5	6.916	5.260	1.131
0.3859	1293.1	897.7	6.662	5.162	1.161
0.5186	1302.7	914.6	6.443	5.076	1.191
0.7080	1320.1	929.1	6.176	4.970	1.226
1.0000	1340.4	940.4	5.918	4.865	1.260

Table 3. Theoretical values of ultrasonic velocities calculated from Nomoto's ( $U_{NOM}$ ) and Van Deal and Vangeel's ideal mixing relation ( $U_{IMR}$ ) along with experimental values of ultrasonic velocities ( $U_{EXP}$ ) and percentage variations for the binary liquid systems of Cyanex 301+benzene, toluene.

$x_i$	$U \text{ ms}^{-1}$	% Variations				
		<i>EXP</i>	<i>NOM</i>	<i>IMR</i>	<i>NOM</i>	<i>IMR</i>
<b>Cyanex 301</b>						
		<b>Cyanex 301 + Benzene</b>				
0.0000	1257.0	1257.0	1257.0	0.0000	0.0000	
0.0282	1257.0	1265.1	1218.6	0.6489	3.0502	
0.0614	1270.0	1273.4	1180.3	0.2669	7.0615	
0.1485	1276.7	1289.9	1105.6	1.0359	13.4036	
0.2073	1290.0	1298.2	1070.5	0.6389	17.0111	
0.2790	1303.0	1315.0	1015.4	0.9210	22.0703	
0.5113	1318.9	1323.4	1008.9	0.3437	23.4999	
0.7019	1325.6	1331.9	1051.4	0.4754	20.6844	
0.8325	1330.9	1336.1	1127.8	0.3944	15.2568	
1.0000	1340.4	1340.4	1340.4	0.0000	0.0000	
		<b>Cyanex 301+ Toluene</b>				
0.0000	1271.9	1271.9	1271.9	0.0000	0.0000	
0.0720	1289.1	1285.4	1203.7	-0.2859	6.6264	
0.1174	1292.5	1292.2	1170.8	-0.0230	9.4174	
0.1715	1296.3	1299.0	1139.4	0.2100	12.1020	
0.2369	1300.2	1305.8	1110.7	0.4350	14.5702	
0.3177	1311.2	1312.7	1086.7	0.1156	17.1187	
0.4201	1323.6	1319.6	1071.4	-0.3018	19.0547	
0.5539	1330.2	1326.5	1074.0	-0.2772	19.2589	
0.7364	1338.7	1333.4	1121.5	-0.3924	16.2229	
1.0000	1340.4	1340.4	1340.4	0.0000	0.0000	

Table 4. Theoretical values of ultrasonic velocities calculated from Nomoto's ( $U_{NOM}$ ) and Van Deal and Vangeel's ideal mixing relation ( $U_{IMR}$ ) along with experimental values of ultrasonic velocities ( $U_{EXP}$ ) and percentage variations for the binary liquid systems of Cyanex 301+Xylene, + n-butanol.

$x_i$	$U \text{ ms}^{-1}$			% Variations	
	<i>EXP</i>	<i>NOM</i>	<i>IMR</i>	<i>NOM</i>	<i>IMR</i>
<b>Cyanex 301</b>		<b>Cyanex 301 + xylene</b>			
0.0000	1296.5	1296.5	1295.5	0.0000	0.0000
0.0822	1297.7	1305.2	1235.7	0.5783	4.7748
0.1331	1304.7	1309.6	1207.1	0.3733	7.4814
0.1928	1313.6	1313.9	1180.4	0.0264	10.1389
0.2638	1316.2	1318.3	1156.8	0.1621	12.1073
0.3495	1321.5	1322.7	1138.4	0.0926	13.8568
0.4553	1329.5	1327.1	1128.7	-0.1782	15.0991
0.589	1335.1	1331.5	1136.1	-0.2661	14.9071
0.7633	1340.5	1335.9	1181.2	-0.3378	11.8856
1.0000	1340.4	1340.4	1340.4	0.0000	0.0000
		<b>Cyanex 301+ n-butanol</b>			
0.0000	1221.6	1221.6	1221.6	0.0000	0.0000
0.0631	1233.4	1244.8	1139.5	0.9221	7.6103
0.1035	1242.4	1256.5	1099.9	1.1324	11.4666
0.1522	1253.6	1268.2	1061.9	1.1670	15.2870
0.2122	1265.9	1280.1	1026.5	1.1201	18.9109
0.2877	1277.8	1292.0	995.6	1.1103	22.0861
0.3859	1293.1	1304.0	973.2	0.8416	24.7392
0.5186	1302.7	1316.0	969.6	1.0248	25.5720
0.7080	1320.1	1328.2	1018.3	0.6131	22.8648
1.0000	1340.4	1340.4	1340.4	0.0000	0.0000



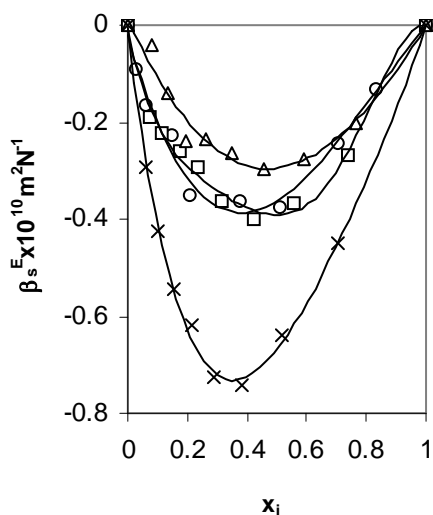


Figure 1. Plot of  $\beta_s^E$  vs  $x_i$  of Cyanex 301 in binary mixtures of Cyanex 301 + benzene (o), + toluene (□), + xylene (Δ), + n-butanol(x).

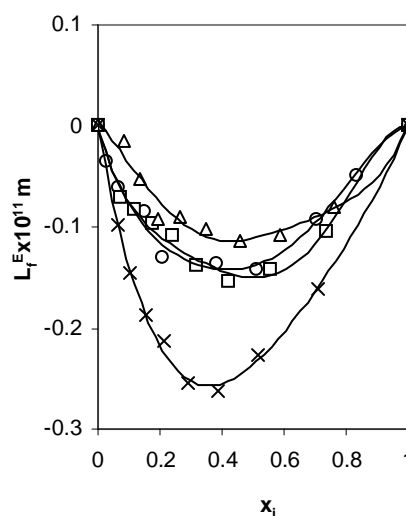


Figure 2. Plot of  $L_f^E$  vs  $x_i$  of Cyanex 301 in binary mixtures of Cyanex 301 + benzene (o), + toluene (□), + xylene (Δ), + n-butanol(x).

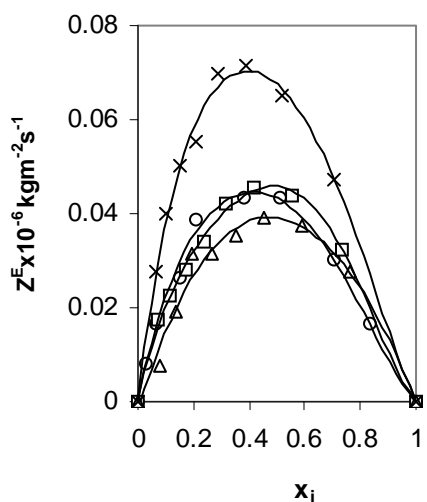


Figure 3. Plot of  $Z^E$  vs  $x_i$  of Cyanex 301 in binary mixtures of Cyanex 301 + benzene (o), + toluene (□), + xylene (Δ), + n-butanol(x).

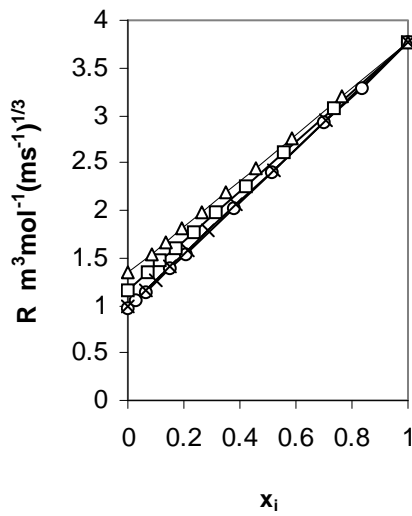


Figure 4. Plot of R vs  $x_i$  of Cyanex 301 in binary mixtures of Cyanex 301 + benzene ( $\circ$ ), + toluene ( $\square$ ), + xylene ( $\Delta$ ), + n-butanol( $\times$ ).

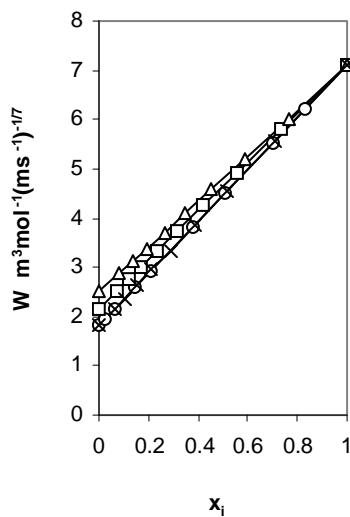


Figure 5. Plot of W vs  $x_i$  of Cyanex 301 in binary mixtures of Cyanex 301 + benzene ( $\circ$ ), + toluene ( $\square$ ), + xylene ( $\Delta$ ), + n-butanol( $\times$ ).

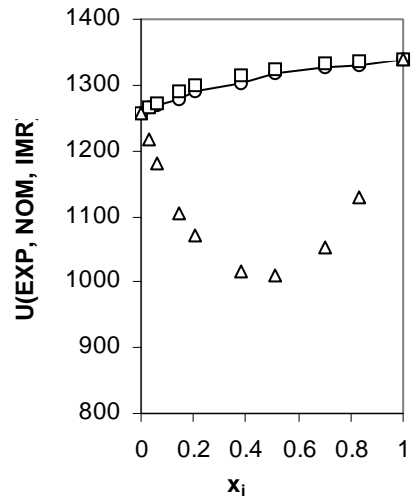


Figure 7. Plot of variation of ultrasonic velocities as a function of mole fraction of Cyanex 301 in the mixture of Cyanex 301 + benzene [ $\circ$ -EXP,  $\square$  NOM,  $\Delta$  IMR].

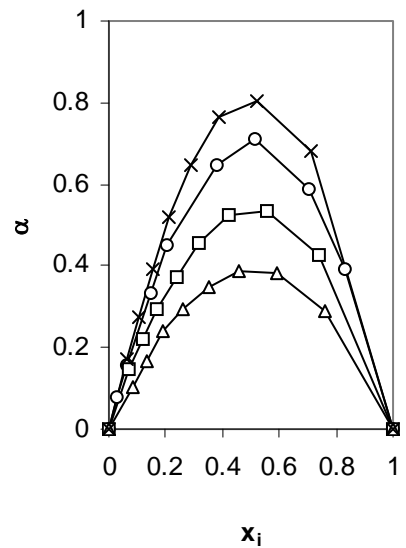


Figure 6. Plot of  $\alpha$  vs  $x_i$  of Cyanex 301 in binary mixtures of Cyanex 301 + benzene ( $\circ$ ), + toluene ( $\square$ ), + xylene ( $\Delta$ ), + n-butanol( $\times$ ).

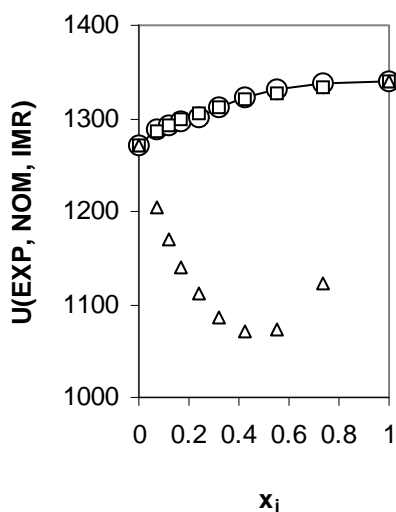


Figure 8. Plot of variation of ultrasonic velocities as a function of mole fraction of Cyanex 301 in the mixture of Cyanex 301 + toluene [-○-EXP, □ □ NOM, △ △ IMR].

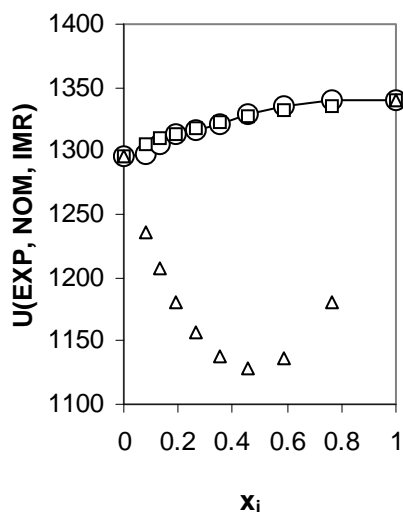


Figure 9. Plot of variation of ultrasonic velocities

The inter-molecular interaction between molecules of Cyanex 301 and that of benzene, toluene and xylene are of dipole-induced-dipole and dipole-dipole types,

as a function of mole fraction of Cyanex 301 in the mixture of Cyanex 301 + xylene [-○-EXP, □ □ NOM, △ △ IMR].

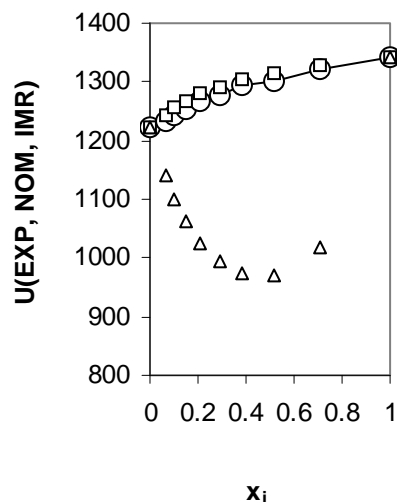


Figure 10. Plot of variation of ultrasonic velocities as a function of mole fraction of Cyanex 301 in the mixture of Cyanex 301 + n-butanol [-○-EXP, □ □ NOM, △ △ IMR].

where the association may be due to the delocalised  $\pi$  – electron cloud over the phosphorous and sulphur atoms of phosphinic

group present in Cyanex and  $\pi$ -electron cloud of the aromatic hydrocarbon<sup>[23]</sup>.

A close perusal of Table 3 and 4 for the velocities of Cyanex reagents with different diluents indicate that Nomoto's relation, with minimum percentage variations fits the experimental data well, followed by ideal mixing relation, which is found to show the maximum variations from the experimental values.

From Figures [Figure 7 to Figure 10], it reveals that the experimental velocities,  $U_{EXP}$  are in a regular increase with the concentrations for all the systems under investigation.  $U_{NOM}$  values show approximately similar trends with  $U_{EXP}$  data, whereas those for  $U_{IMR}$  decrease first with concentration and then increase giving minima at around 0.3-0.5 mole fraction for all the binary systems, which indicates that Nomoto's relation is quite satisfactory and seems to be equally good in predicting the experimental data, rather there is not any remarkable deviation between the experimental velocity values and those calculated from this theory. But, however, the ideal mixing relation is on the other hand shown to deviate more from the experimental findings than that of Nomoto's for all the systems. The limitations and approximation incorporated in the ideal mixing theory is supposed to be responsible for such variations. According to the assumption for the formation of ideal mixing relation, the ratio of specific heats of the components is equal to the ratio of specific heats of ideal mixtures, indicating the equality in volumes<sup>[12]</sup>. This implies that no interaction should be entitled here. But, on mixing of components, specially polar-polar and non-polar-polar types of components there is the probability of various types of forces like hydrogen bonding, dipole-dipole, dipole-induced-dipole, dispersion forces, charge transfer etc. operating in them, which may result in violating the assumption. The deviations in the ideal mixing relation is therefore,

supposed to indicate as the presence of inter-molecular interaction in these binary mixtures. On the other hand the ultrasonic velocities obtained from Nomoto's relation are better fitted to the experimental values having minimum percentage of variations. Thus, the linearity of molar sound velocity as suggested by Nomoto<sup>[9]</sup> in deriving the empirical relation, is rather more appropriate for the binary liquid mixtures studied. It is, however, concluded that there is inter-molecular interaction present in all the binary mixtures under investigations and the interaction is supposed to be more in case of Cyanex 301 with n-butanol relative to with benzene, toluene and xylene (%Variations of  $U_{IMR}$  from Tables III and IV).

#### 4. Conclusion

From our investigation, it shows that Cyanex 301 interacts more strongly with n-butanol than with benzene, toluene and xylene, and the point of inflexion is relatively sharp in the mole fraction range of 0.3-0.4 of Cyanex 301 suggesting strong interaction. Further scope of this investigation is to correlate this finding with liquid-liquid extraction behaviour to characterize the effect of extraction conditions in the afore-mentioned binary liquid mixtures.

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