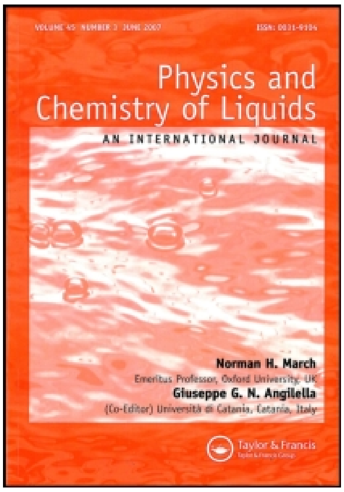

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Hetero-molecular association in binary mixtures of solvent extractants and diluents at temperature 303.15 K

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Hetero-molecular association in binary mixtures of solvent extractants and diluents at temperature 303.15 K

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Ultrasonic velocity and viscosity measurements have been made for binary liquid mixtures of solvent extractants, LIX reagents such as LIX 84 and LIX 984 in benzene, amyl alcohol and tri-*n*-butyl phosphate (TBP) at temperature 303.15 K and at atmospheric pressure. The measured values of ultrasonic velocity, density and viscosity have been utilised to compute various thermo-acoustic parameters and their excess functions, which provide information about the nature and strength of intermolecular interactions present in the systems.

Keywords: Ultrasonic velocity; Solvent extractant; Excess function

1. Introduction

Thermo-acoustic parameters are of recent interest in studying the physico-chemical behaviour and molecular arrangement in various liquid mixtures. Different liquid ion exchangers in the trade name LIX reagents have been reported earlier for use as extractants for extracting different metal ions [1–3]. These are mainly the substituted aceto-phenone and benzo-phenone oximes. Detailed structures and compositions of LIX reagents have been given earlier [5]. Tri-*n*-butyl phosphate (TBP) is known to be used in PUREX (Plutonium Uranium Extraction) process for the processing of nuclear fuel. Benzene and amyl alcohol are generally used as diluent and modifier, respectively, in solvent extraction. The binary mixtures, studied in the present investigation may be employed as the organic phases in the process of solvent extraction, where the metal ions present in the aqueous phase is to be extracted by organic phase forming

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different complexes. It is therefore, important to study the physico-chemical properties of such phase, which may shed light into the molecular environment.

In continuation of our earlier work [4–6] on molecular interactions of various liquid mixtures involving solvent extractants, here we report the results for binary liquid mixtures of LIX 84 and LIX 984 with benzene, amyl alcohol and TBP over the entire range of mole-fraction of LIX reagents at 303.15 K and atmospheric pressure. The physico-chemical behaviours of such mixtures have been studied in order to explore the strength and nature of interactions between different polar and non-polar components by computing thermo-acoustical parameters such as isentropic compressibility, β_s, intermolecular free length, L_f, acoustic impedance, Z, excess free energies of activation of viscous flow, ΔG^{*E}, molar sound velocity, R and molar compressibility, W, from the density, ultrasonic velocity and viscosity data. The dependence of these parameters on composition of the liquid mixtures reveals the extent of interaction between the component molecules, which may enable us to have a better insight of the extraction behaviour of different liquid mixtures for extracting the metal ions.

2. Materials and methods

The LIX reagents were supplied by Henkel Corporation, Ireland and were used in the form as received. Tri-*n*-butyl phosphate TBP (SRL), benzene and amyl alcohol (Merk), AR grade, were used. All the binary mixtures were prepared on percentage basis (v/v) by dissolving known volumes of LIX reagents in appropriate volumes of TBP, benzene and amyl alcohol, and measuring their mass on a Metler-Toledo AB 54 electronic balance.

The densities of all the mixtures were measured by a bicapillary pyknometer calibrated with deionised double distilled water with $0.9960 \times 10^3\,\mathrm{kg\,m^{-3}}$ as its density at 303.15 K. The precision of density measurement was within $\pm 0.0003\,\mathrm{kg\,m^{-3}}$. The ultrasonic velocities of the liquids were measured at 303.15 K temperature and at atmospheric pressure by a single crystal variable path ultrasonic interferometer operating at 5 MHz frequency. The temperature of the solution was maintained constant within ±0.01 K by circulation of water from thermostatically regulated water bath through a water-jacketed cell. The velocity measurement was precise up to $\pm 0.5\,\mathrm{m\,s^{-1}}$. Viscosities of the solutions were measured by Ostwald viscometer immersed in a constant temperature water bath maintained within ±0.01 K. The values of the viscosities so obtained were precise up to $\pm 0.0004\,\mathrm{N\,s\,m^{-2}}$.

3. Results and discussion

The experimental values of density, ρ, viscosity, η and ultrasonic velocity, U were used to calculate the values of β_s, L_f, Z, ΔG^{*E}, R and W using the standard formulae [4–6]. The values of ρ, η, U, β_s, L_f, Z, R and W as functions of mole fraction, x_i of LIX reagents at 303.15 K are listed in tables 1 and 2.

The excess properties A^E (β_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

Table 1. Experimentally determined ultrasonic velocity, U, density, ρ, viscosity, η, and calculated values of isentropic compressibility, β_s, intermolecular free length, L_f, acoustic impedance, Z, molar sound velocity, R and molar compressibility, W, of binary mixtures of LIX 84 in amyl alcohol, TBP and benzene.

Mole fraction of LIX 84(x_i)	U ($\mathrm{m\,s^{-1}}$)	ρ ($\mathrm{kg\,m^{-3}}$)	$\eta \times 10^3$ ($\mathrm{N\,s\,m^{-2}}$)	$\beta_s \times 10^{10}$ ($\mathrm{m^2\,N^{-1}}$)	$L_f \times 10^{11}$ (m)	$Z \times 10^{-6}$ ($\mathrm{kg\,m^{-2}\,s^{-1}}$)	$R \times 10^{-3}$ ($\mathrm{m^3\,mol^{-1}\,(m\,s^{-1})^{1/3}}$)	$W \times 10^{-3}$ ($\mathrm{m^3\,mol^{-1}\,(m^2\,N^{-1})^{-1/7}}$)
LIX 84 + amyl alcohol								
0.0000	1210.3	811.5	2.921	8.412	5.801	0.982	1.1556	2.1460
0.0398	1239.2	856.3	3.499	7.605	5.515	1.061	1.3523	2.5277
0.0663	1253.2	867.5	3.906	7.340	5.418	1.087	1.5103	2.8267
0.0995	1278.2	881.8	4.436	6.941	5.269	1.127	1.7019	3.1898
0.1422	1289.5	891.4	5.116	6.746	5.195	1.149	1.9551	3.6686
0.1992	1306.8	903.8	6.047	6.479	5.091	1.181	2.2871	4.2973
0.3987	1338.6	925.5	9.857	6.030	4.911	1.238	3.4550	6.5063
0.5989	1355.8	932.0	14.743	5.837	4.832	1.264	4.6519	8.7635
0.7591	1356.0	941.0	20.122	5.779	4.808	1.276	5.5694	10.5065
1.0000	1361.0	947.6	32.229	5.697	4.774	1.290	6.9689	13.1573
LIX 84 + TBP								
0.0000	1252.8	975.5	3.700	6.531	5.111	1.222	2.9393	5.5945
0.0440	1254.1	982.0	3.800	6.475	5.089	1.231	3.0803	5.8681
0.1515	1264.8	983.5	5.470	6.356	5.042	1.244	3.4743	6.6175
0.2172	1281.0	978.5	7.050	6.228	4.991	1.253	3.7475	7.1283
0.2941	1290.5	973.9	8.320	6.165	4.966	1.257	4.0581	7.7112
0.3874	1301.0	969.8	10.080	6.092	4.936	1.262	4.4227	8.3958
0.4929	1314.0	964.5	12.850	6.005	4.901	1.267	4.8672	9.2279
0.6250	1326.0	960.5	15.670	5.921	4.867	1.273	5.4008	10.2291
0.7895	1348.5	947.3	20.010	5.805	4.819	1.277	6.1398	11.5965
1.0000	1361.0	947.6	32.229	5.697	4.774	1.290	6.9689	13.1573
LIX 84 + benzene								
0.0000	1257.2	895.0	0.657	7.069	5.317	1.125	0.9419	1.7706
0.0071	1266.8	901.3	0.699	6.914	5.259	1.142	0.9818	1.8468
0.0327	1272.6	906.5	0.835	6.811	5.220	1.153	1.1362	2.1383
0.1689	1295.8	925.0	2.338	6.438	5.075	1.198	1.9513	3.6800
0.2472	1304.3	930.7	3.476	6.316	5.026	1.214	2.4419	4.5657
0.5496	1355.5	939.5	12.851	5.793	4.814	1.273	4.2724	8.0579
0.6431	1359.4	941.2	16.604	5.745	4.795	1.279	4.8385	9.1268
0.7263	1361.5	942.3	19.949	5.725	4.785	1.283	5.3421	10.0776
0.8642	1363.8	943.5	25.330	5.698	4.774	1.287	6.1775	11.6548
1.0000	1361.0	947.6	32.229	5.697	4.774	1.290	6.9689	13.1573

type of molecular interactions have been computed with the help of the following equation:

$$A^{\mathrm{E}} = A - [x_i A_1 + (1 - x_i) A_2] \tag{1}$$

where A, A_1, A_2 are the corresponding parameters (β_s, L_f, Z) for binary mixtures, components 1 and 2, respectively. The excess values from experimental results were fitted by the method of least squares with all points weighed equally to the Redlich–Kister polynomial equation [8].

$$Y^{\mathrm{E}} = x_i(1 - x_i) \sum_{j=0}^{4} A_j (2x_i - 1)^j \tag{2}$$

where Y^{E} represent the excess values of the parameters (β_s^{E}, L_f^{E}, Z^{E}), A_j the polynomial coefficients, j the polynomial degree, respectively, and n represent the number of experimental data.

Table 2. Experimentally determined ultrasonic velocity, U, density, ρ, viscosity, η, and calculated values of isentropic compressibility, β_s, intermolecular free length, L_f, acoustic impedance, Z, molar sound velocity, R, and molar compressibility, W, of binary mixtures of LIX 984 in amyl alcohol, TBP and benzene.

Mole fraction of LIX 984(x_i)	U ($\mathrm{m\,s^{-1}}$)	ρ ($\mathrm{kg\,m^{-3}}$)	$\eta \times 10^3$ ($\mathrm{N\,s\,m^{-2}}$)	$\beta_s \times 10^{10}$ ($\mathrm{m^2\,N^{-1}}$)	$L_f \times 10^{11}$ (m)	$Z \times 10^{-6}$ ($\mathrm{kg\,m^{-2}\,s^{-1}}$)	$R \times 10^{-3}$ ($\mathrm{m^3\,mol^{-1}\,(m\,s^{-1})^{1/3}}$)	$W \times 10^{-3}$ ($\mathrm{m^3\,mol^{-1}\,(m^2\,N^{-1})^{-1/7}}$)
LIX 984 + amyl alcohol								
0.0000	1210.3	811.5	2.921	8.412	5.801	0.982	1.1556	2.1460
0.0160	1222.0	837.0	3.526	8.001	5.657	1.023	1.2187	2.2722
0.0710	1264.4	870.0	4.454	7.438	5.363	1.100	1.5028	2.8127
0.1060	1290.8	884.6	5.295	6.785	5.209	1.142	1.6878	3.1635
0.1520	1297.7	892.9	6.359	6.650	5.158	1.158	1.9356	3.6317
0.2940	1333.0	911.2	10.159	6.176	4.970	1.214	2.7087	5.0905
0.4710	1341.8	928.4	14.174	5.982	4.892	1.246	3.3416	6.2949
0.6170	1364.6	931.6	16.252	5.764	4.802	1.271	4.4526	8.3851
0.7730	1366.5	946.1	18.689	5.660	4.758	1.293	5.2345	9.8786
1.0000	1367.3	948.5	22.125	5.639	4.749	1.297	6.4535	12.1832
LIX 984 + TBP								
0.0000	1252.8	975.5	3.700	6.531	5.111	1.222	2.9393	5.5945
0.0477	1255.4	976.7	3.710	6.496	5.097	1.226	3.0882	5.8783
0.1618	1282.6	988.0	6.000	6.152	4.961	1.267	3.4330	6.5387
0.2309	1290.5	985.0	7.423	6.096	4.938	1.271	3.6686	6.9823
0.3102	1312.0	979.0	9.890	5.934	4.872	1.284	3.9646	7.5333
0.4032	1326.0	975.0	13.140	5.833	4.830	1.293	4.2942	8.1506
0.5124	1336.2	967.0	17.560	5.792	4.813	1.292	4.6595	8.8994
0.6431	1349.5	963.0	25.040	5.702	4.776	1.299	5.1593	9.7671
0.8021	1363.5	952.9	35.360	5.645	4.752	1.299	5.7602	10.8830
1.0000	1367.3	948.5	22.125	5.639	4.749	1.297	6.4535	12.1832
LIX 984 +benzene								
0.0000	1257.2	895.0	0.657	7.069	5.317	1.125	0.9419	1.7706
0.0076	1260.0	898.6	0.702	7.009	5.295	1.132	0.9821	1.8469
0.0160	1267.6	903.3	0.747	6.890	5.250	1.145	1.0266	1.9315
0.0590	1275.0	911.4	1.047	6.749	5.196	1.162	1.2616	2.3761
0.1277	1288.9	922.4	1.839	6.526	5.109	1.189	1.6348	3.0826
0.2547	1316.0	932.9	3.913	6.189	4.976	1.228	2.3338	4.4035
0.5687	1343.0	944.8	10.761	5.868	4.845	1.269	4.0559	7.6592
0.6600	1349.2	944.9	13.297	5.814	4.822	1.275	4.5671	8.6228
0.8770	1361.8	947.5	18.856	5.691	4.771	1.290	5.7705	10.8942
1.0000	1367.3	948.5	22.125	5.639	4.749	1.297	6.4535	12.1832

The excess values corresponding to each of the said parameters, along with ΔG^{*E}, are shown graphically in figures and the coefficients (A_0, $A_1, \ldots$) obtained from polynomial regression as well as the deviations, d, between the calculated and the experimental values are shown in table 3.

A perusal of tables 1 and 2 shows that the values of isentropic compressibility, β_s, and intermolecular free length, L_f, vary exactly in the reverse trend with those of the velocities for all the systems studied. According to Evans *et al.* [8], ultrasonic velocity should increase if the intermolecular free length decreases, and vice versa, as a result of mixing components. The mixing of various liquids tends to cause breaking of self-associated molecules present in their original state, forming hetero-molecular association with a consequent increase in ultrasonic velocity, U. It is because the sound waves cover longer distances due to decrease in intermolecular free lengths, L_f, and as a result, the isentropic compressibility, β_s, also decreases. Decrease in the values of β_s as well as L_f with concentration of LIX reagents indicates significant interactions

Table 3. Coefficients of the various parameters using Redlich–Kister type equation and their deviations, *d*.

Systems	A_0	A_1	A_2	A_3	A_4	*d*
Coefficients for excess isentropic compressibility β_s^E						
LIX 84 + amyl alcohol	−47.1050	36.1400	15.5600	18.6400	−134.3000	0.3380
LIX 84 + TBP	−0.4444	0.3408	−0.3959	−0.5584	0.5981	0.0930
LIX 84 + benzene	−22.5630	5.7870	22.1190	5.3500	42.4750	0.5530
LIX 984 + amyl alcohol	−47.8690	34.6400	7.5600	11.4300	−268.9400	1.5160
LIX 984 + TBP	−1.2847	0.6237	1.5295	−0.6690	−4.5750	0.0759
LIX 984 + benzene	−19.4650	18.0780	16.5250	−11.8390	−53.4620	0.2972
Coefficients for excess intermolecular free length L_f^E						
LIX 84 + amyl alcohol	−5.5110	4.0080	1.4520	2.3490	−13.9300	0.0370
LIX 84 + TBP	−0.1694	0.1327	−0.1522	−0.2298	0.2253	0.2243
LIX 84 + benzene	−2.8180	0.9490	2.4890	0.2300	−4.8560	0.0623
LIX 984 + amyl alcohol	−5.5720	3.8750	0.1650	2.8910	−14.3460	0.0550
LIX 984 + TBP	−1.2847	0.6237	1.5295	−0.6690	−4.5752	0.0759
LIX 984 + benzene	−2.3090	2.0710	1.5450	−1.2370	−5.5230	0.0351
Coefficients for excess acoustic impedance Z^E						
LIX 84 + amyl alcohol	48.6120	−38.7000	−19.8260	−5.3200	136.7060	0.3870
LIX 84 + TBP	0.0487	−0.0339	0.0369	−0.0932	−0.0729	0.0747
LIX 84 + benzene	24.3820	−3.5560	24.7600	15.4430	51.4430	0.4420
LIX 984 + amyl alcohol	48.8990	−37.3650	−8.9280	−2.2820	144.5040	0.4480
LIX 984 + TBP	0.1437	−0.0778	−0.0291	−0.0171	0.2229	0.0617
LIX 984 + benzene	22.712	−20.255	−20.255	15.770	63.048	0.2966

between the component molecules [10], due to which the structural arrangements are considerably affected in all the binary systems. Decreasing values in L_f between the component molecules in different systems are suggesting that the systems are more resistant to the sound propagation, which is supported by the increasing values of acoustic impedance, *Z* (tables 1 and 2) with mole fraction of LIX reagents. The molar sound velocity, *R* and molar compressibility, *W*, increase linearly with mole fraction of solute (LIX reagents) indicating the presence of solute–solvent interactions [10].

The excess parameters play a major role in understanding the nature of molecular interaction in liquid mixtures. The non-linear variation in such parameters indicates deviation from ideality [11]. The sign and magnitude of deviations in parameters from linear dependence on composition indicate the nature and strength of interaction between unlike molecules, respectively. In the present investigation, β_s^E and L_f^E values show negative variations, whereas those for Z^E are positive (figure 1a–d) over the entire range of composition, suggesting either chemical or specific interaction including dipole–dipole, dipole-induced–dipole, charge–transfer forces, H-bonds or complex formation [9–12] may occur between the component molecules present in the systems.

The positive values of excess free energy of activation of viscous flow, ΔG^{*E} figure 2(c) and (d), for the whole range of composition indicate the difference in molecular sizes and the specific interactions between the unlike molecules [13,14], which further strengthened the above findings.

The inter-molecular interaction between LIX molecules and benzene are of polar–non-polar types, where the association may be due to the delocalised π-electron cloud over the nitrogen and oxygen atoms of oxime groups present in LIXs and π-electron cloud of the aromatic hydrocarbon (benzene) [4,15] and it is also assumed that the hetero-molecular association may otherwise happen between the π-electron cloud of benzene ring and hydroxyl group of substituted oximes [16].

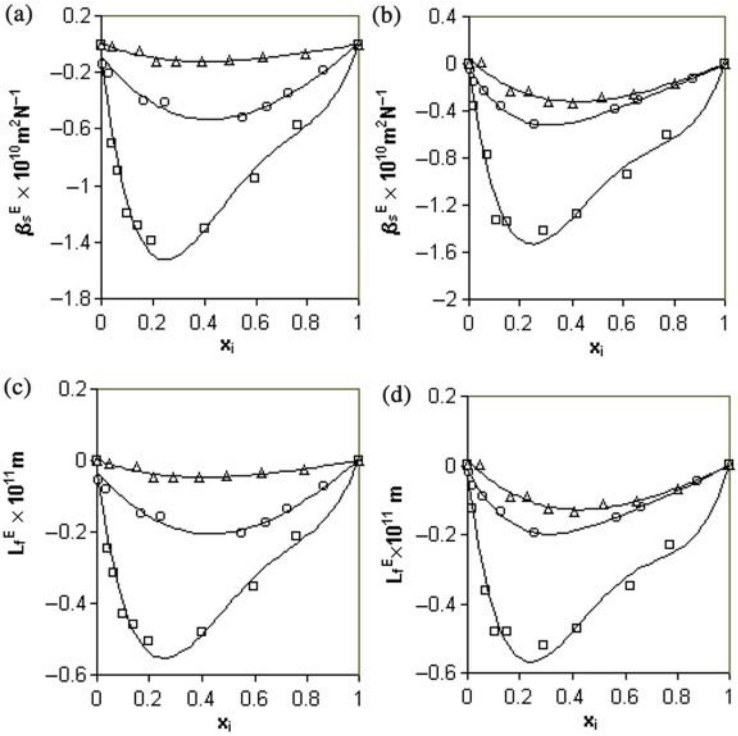

Figure 1. (a) Plot of β_s^E *vs.* x_i of LIX 84 in the mixture of LIX 84 + amyl alcohol (□), +TBP (△), +benzene (○), (b) plot of β_s^E *vs.* x_i of LIX 984 in the mixture of LIX 984 + amyl alcohol (□), +TBP (△), + benzene (○), (c) plot of L_f^E *vs.* x_i of LIX 84 in mixture of LIX 84 + amyl alcohol (□), +TBP (△), +benzene (○), (d) plot of L_f^E *vs.* x_i of LIX 984 in the mixture of LIX 984 + amyl alcohol (□), +TBP (△), +benzene (○).

The interaction lies between LIXs and TBP molecules are of polar–polar types and the interaction may be the result of H-bonding between the polar –OH group of substituted oximes of LIX molecules and the lone pair of electrons of oxygen in TBP.

In case of LIX reagents and amyl alcohol, both the components are polar, and therefore, the interaction present is supposed to be of dipole–dipole type in the form of H-bonding between the OH groups present in both the molecules. The unlike components may, therefore, be associated with a denser packing through H-bonding.

In the present investigation, hydrogen bonding seems to be the predominant interaction mechanism and from the observations of the curves figures 1(a–d) and 2(a–b), it is presumed that the interactions between LIXs + amyl alcohol is maximum due to H-bonding in comparison to that in LIXs + benzene and LIXs + TBP. Although H-bonding may also be expected to be the predominance force in case of LIXs + TBP, the hetero-molecular association is, however, least in comparison to all other binary systems. It is because at higher concentration of TBP, the TBP molecules may interact among themselves more strongly, rather than with LIX molecules.

Tri-*n*-butyl phosphate in general is known to be a mildly associated liquid having two possible arrangements namely, wood-pile, or head-tail structures (figure 3a and b) [5,17],

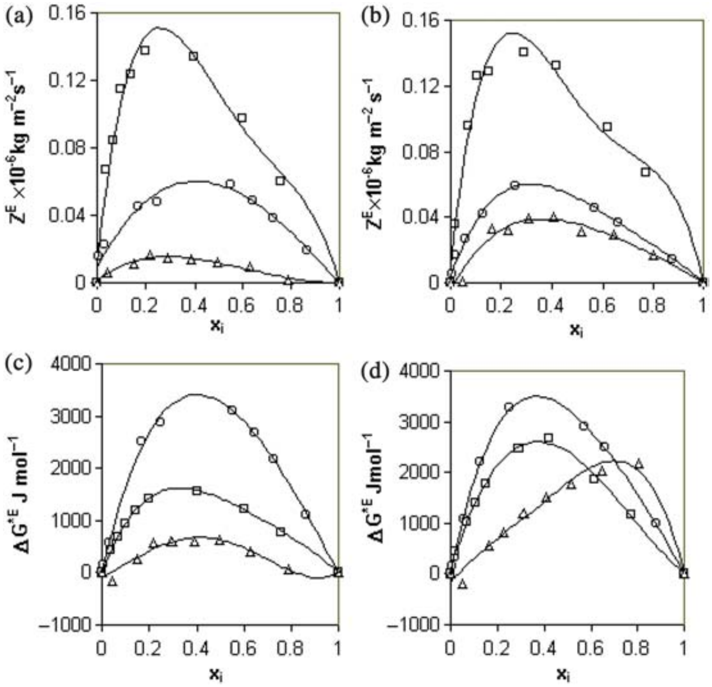

Figure 2. (a) Plot of Z^E *vs.* x_i of LIX 84 in the mixture of LIX 84 + amyl alcohol (□), +TBP (△), + benzene (○), (b) plot of Z^E *vs.* x_i of LIX 984 in the mixture of LIX 984 + amyl alcohol (□), +TBP (△), +benzene (○), (c) plot of ΔG^{*E} *vs.* x_i of LIX 84 in the mixture of LIX 84 + amyl alcohol (□), +TBP (△), +benzene (○), (d) plot of ΔG^{*E} *vs.* x_i of LIX 984 in the mixture of LIX 984 + amyl alcohol (□), +TBP (△), +benzene (○).

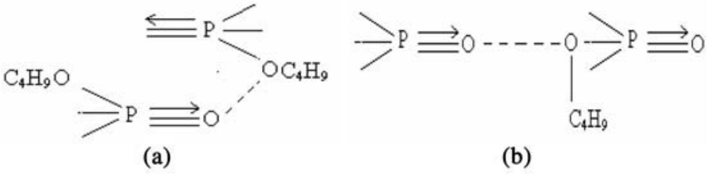

Figure 3. (a) Wood-pile arrangement of TBP, (b) Head-tail arrangement of TBP.

and the later arrangement with parallel orientation happens to be the predominant one. However, with lowering of TBP concentration, the isolated TBP molecules may fail to establish any correlation among themselves on their own, and ultimately these scarce molecules may be surrounded by the cage of LIX molecules resulting in a hetero-molecular association.

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