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Molecular Interaction in Ternary Systems of Tri-*n*-octylamine/Tri-*n*-butyl Phosphate/ Octanoic Acid with *n*-Hexane and 1-Hexanol at Different Temperatures

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Density, dielectric constant and refractive index were measured for three ternary systems *viz.* tri-*n*-octylamine/tri-*n*-butyl phosphate/ octanoic acid (TOA/TBP/OA), with *n*-hexane and 1-hexanol at T = 303.15, 308.15 and 313.15 K. Derived properties like molar volume, molar polarization, molar refraction and excess parameters were calculated from the measured density, dielectric constant and refractive index values, respectively. The excess values were also calculated with the Redlich-Kister polynomial and the fitting coefficients and standard deviations are reported. The density of the ternary mixtures increased with the increase in the mole fraction of the solute and decreased with the rise of temperature. The negative dielectric constant values for all the systems indicate a reduction in effective dipoles due to the dipolar self-association of the polar molecules. The FT-IR spectra of all the systems indicate a feeble interaction among the extractants, diluent and modifier.

Keywords: Density, Molar volume, Dielectric constant, Refractive index, Ternary mixture.

INTRODUCTION

Thermophysical properties play a dominant role in judging the different kinds of molecular associations that prevail among binary and ternary mixture components [1-3]. From the practical and theoretical point of view, knowledge of density and volumetric data is vital as they help to illustrate the structure and properties of the liquid mixtures. Dielectric studies provide insight into the inter and intramolecular associations due to the dipole-dipole interactions and hydrogen bonding [4,5]. Many researchers [6-8] have performed dielectric studies on the mixtures of polar and non-polar components which are useful in characterizing the solute–solvent interactions. Sengwa & Sankhla [9] studied the dielectric properties of binary and ternary mixtures of alcohols. In case of ethyl alcohol and ethylene glycol binary mixtures, there is a reduction in the parallel aligned number of effective dipoles due to heterogenous H-bonded structures. While in case of ternary mixtures, the presence of glycerol results in a parallel dipolar arrangement to form a H-bonded ternary complex. Martínez-Jiménez *et al.* [10] investigated the dielectric behaviour and molar polarization process in some polar and non-polar mixtures of alkanes and alcohols. At the low concentrations, the polar association reduces and allows the orientation process at small relaxation times. Yin *et al.* [11] reported the volumetric and viscometric properties of binary and ternary mixtures of 1-butyl-3-methyl-imidazolium tetrafluoroborate monoethanolamine and water. The positive volumetric analysis reveals the molecular associations and structural rearrangement in the molecules. In contrast, the negative excess volumetric results indicate that monoethanolamine fills the interstices of the ionic liquid.

Solvent extraction is an effective hydrometallurgical technique that helps to extract and separate metal ions through the mass transfer phenomenon [12]. In the extraction process, the extraction efficiency can be improved by selecting the appropriate extractant, diluent and modifier for the process [13]. Diluents are mainly hydrocarbons, which are aromatic and non-aromatic in nature. They reduce the viscosity of the extractants and make the mass transfer phenomenon easier. Some of the commonly used diluents in the extraction process are kerosene, toluene, xylene and benzene. Another significant concern in the liquid-liquid separation process is the occurrence of a third phase, namely the emergence of two organic phases. This phenomenon arises due to the challenge presented by the aqueous solubility of the extractant. It has been found that the difficulty associated with the third phase is overcome by the addition of a third component known as modifier. Modifiers in the extraction system are known for eliminating the third phase and increasing the compatibility of the extracted species. Few reports are available on the studies of physico-chemical properties of ternary mixtures consisting of various types of extracting agents and diluents [14-21].

By adding a third component to the organic phase of the biphasic extraction system the constitution becomes more complex and it would be quite exciting and challenging to dwell into the physico-chemical characteristics of the organic phase comprising of extractant, diluent and modifier in order to obtain information about the optimum extraction conditions. In this regard, density, dielectric constant and refractive properties provide indications of the molecular arrangement between the dissimilar components.

The multi-component mixtures are usually applied for different industrial procedures [22]. Tri-*n*-octylamine (TOA), tri-*n*-butyl phosphate (TBP) and octanoic acid (OA) in diluted forms have been extensively used by the researchers to extract and separate the metal ions [23-26]. It has also been reported that *n*-hexane serves as an efficient diluent for TOA, OA and TBP [27,28]. As a continuing study of measurements for the physico-chemical properties of extractant–diluent systems, herein we present a report on density, dielectric and refractive studies of a ternary mixture of TOA/TBP/OA + *n*-hexane + 1-hexanol at T = 303.15, 308.15 and 313.15 K to study the effect of 1-hexanol as a modifier in the extraction systems.

EXPERIMENTAL

Tri-*n*-octylamine (TOA), tri-*n*-butyl phosphate (TBP) and octanoic acid (OA), *n*-hexane and 1-hexanol were purchased from Merck and have 99% purity. A comparison of the experimental density values of TOA, OA and TBP with the literature at different temperatures is presented in Table-1 along with the chemicals details.

General procedure: Ternary mixtures of TOA/TBP/OA, *n*-hexane and 1-hexanol were prepared using the density and volume data. The ternary systems exist in one phase throughout the composition range. An equal volume of 1-hexanol was added to the TOA/TBP/OA and *n*-hexane mixture to study the ternary system. The solutions were kept under care to avoid volume loss. The density of the ternary mixtures and the pure components were measured from the relative mass differences using a 25 mL specific gravity bottle. The weight of the samples was taken using Citizen digital balance (CY 320C) with an accuracy of ± 0.0001 g in the temperature range of 303.15-313.15 K with 5 K interval. The dielectric measurements were carried out using a dipole meter supplied by Mittal Enterprises, India. The instrument was calibrated with air and the reference liquid. The uncertainty value in the dielectric measurement was ± 0.005. The refractive index of the liquid mixtures was recorded using Abbe's refractometer (MA-02) at 589 nm. The calibration of the instrument was done with millipore water. The uncertainty in the refractive index was ± 0.0002. In all experiments, the temperature was controlled using a water bath with an accuracy of ± 0.01 K. FTIR spectra of liquid mixtures have been recorded on a Perkin-Elmer Spectrum Two with UTAR spectrometer.

Data analysis: The molar volumes (V_{123}) of the ternary mixture of TOA/TBP/OA + *n*-hexane + 1-hexanol were calculated using the density (ρ_{123}) values at T = 303.15, 308.15 and 313.15 K using eqn. 1:

$$V_{123} = \frac{(X_1M_1 + X_2M_2 + X_3M_3)}{\rho_{123}} \tag{1}$$

where X_1, X_2, X_3, M_1, M_2 and M_3 represent the mole fractions and molecular masses of *n*-hexane, TOA/TBP/OA, 1-hexanol respectively and ρ_{123} is the density of the ternary mixtures of TOA/TBP/OA + *n*-hexane + 1-hexanol.

The excess properties A^E_{123} is calculated using eqn. 2:

$$A^E_{123} = A_{123} - (A_1X_1 + A_2X_2 + A_3X_3) \tag{2}$$

where A_1, A_2, A_3 represent the molar volume, dielectric constant and refractive index of ternary mixtures of TOA/TBP/OA + *n*-hexane + 1-hexanol.

The values of the excess properties are estimated by fitting experimental data into the Redlich-Kister polynomial using eqn. 3 [32]:

$$A^E_{123} = [X_1X_2X_3(a + bX_1(X_2 - X_3) + cX_1^2(X_2 - X_3)^2] \tag{3}$$

TABLE-1
DETAILS OF THE CHEMICALS USED AND DENSITY VALUES WITH EXPERIMENTAL AND LITERATURE AT 303.15, 308.15 AND 313.15 K

Chemicals	Extractant/diluent	CAS No.	m.f.	Temp. (K)	Density (ρ) (g/cm³)	
					Lit.	Expt.
Tri-*n*-octyl amine (TOA)	Basic extractant	1116-76-3	$C_{24}H_{51}N$	303.15	0.8070	0.8030 [29]
				308.15	0.8068	–
				313.15	0.8054	–
Tri-*n*-butyl phosphate (TBP)	Neutral extractant	126-73-8	$C_{12}H_{27}O_4P$	303.15	0.9756	0.9766 [30]
				308.15	0.9720	0.9763 [30]
				313.15	0.9686	0.9761 [30]
Octanoic acid (OA)	Acidic extractant	124-07-2	$C_8H_{16}O_2$	303.15	0.9129	0.8980 [31]
				308.15	0.9096	–
				313.15	0.9063	0.8900 [31]
n-Hexane	Diluent	–	C_6H_{14}	–	–	–
1-Hexanol	Modifier	111-27-3	$C_6H_{14}O$	–	–	–

where a, b and c are the fitting coefficients in the polynomial equation.

The standard deviations, $\sigma(A^{E}_{123})$, have been reported using the following expression:

$$\sigma\left(A^{E}_{123}\right)=\left[\frac{\sum\left(A^{E}_{123\ \text{exp}}-A^{E}_{123\ \text{cal}}\right)^{2}}{(n-m)}\right]^{1/2} \qquad (4)$$

where n symbolizes the experimental data points and m is the number of coefficients respectively.

The molar refraction R_{123} is evaluated using the following expression.

$$R_{123}=\left(\frac{n^{2}_{D123}-1}{n^{2}_{D123}+2}\right)\left(\frac{(M_1X_1+M_2X_2+M_3X_3)}{\rho_{123}}\right) \qquad (5)$$

The molar polarization for the mixture P_{123} is expressed as the following equation:

$$P_{123}=\left(\frac{\varepsilon_{123}-1}{\varepsilon_{123}+2}\right)\left(\frac{(M_1X_1+M_2X_2+M_3X_3)}{\rho_{123}}\right) \qquad (6)$$

where n_{D123} is the refractive index and ε_{123} is the dielectric constant of the ternary mixture of TOA/TBP/OA with *n*-hexane and 1-hexanol.

RESULTS AND DISCUSSION

The density, dielectric constant and refractive index of the ternary mixtures of TOA/TBP/OA in *n*-hexane +1-hexanol at 303.15, 308.15 and 313.15 K were measured.

Table-2 represents the experimental density (ρ_{123}) of the TOA/TBP/OA in *n*-hexane + 1-hexanol at 303.15, 308.15 and 313.15 K and atmospheric pressure. It was observed that the density of the systems increases with the increase in mole fraction of TOA/TBP/OA for all the systems. But with the rise of temperature, the density decreases [27].

The dielectric constants of the ternary mixtures at different temperatures are presented in Table-3. It is observed that the dielectric constant of the ternary mixture varies with the mole fraction at the measured temperatures. In all the systems, there is a slight elevation of dielectric constants, indicating the structure making property between the extractants and diluent/modifier at higher mole fractions of the extractants. Particularly in the TBP mixture, there is a mutual association among the components in the mixture, which leads to the formation of clusters due to association between the oxygen atom of TBP carrying partial negative charge and hydrogen atom with partial positive charge present in the alcohol. There is a possibility for parallel and antiparallel orientation among the constituents in the ternary mixture. However, there is a greater possibility for antiparallel orientation [33].

P = O··········H-O-R

This specifies that a cage-like structure is formed for all the extractants and serves as a sound system for entrapping the metal ions in solvent extraction.

The refractive index of the systems TOA/TBP/OA + *n*-hexane/1-hexanol has been recorded at T = 303.15, 308.15 and 313.15 K. Table-4 presents the refractive index of all the systems. A close inspection reveals that the refractive index of

TABLE-2
DENSITY VALUES OF TOA/TBP/OA + *n*-HEXANE + 1-HEXANOL AT 303.15, 308.15 AND 313.15 K

Temp. (K)	TOA + *n*-hexane + 1-hexanol				OA + *n*-hexane + 1-hexanol				TBP + *n*-hexane + 1-hexanol			
	X_2 (0.0689)	X_2 (0.165)	X_2 (0.3073)	X_2 (0.5395)	X_2 (0.1678)	X_2 (0.3531)	X_2 (0.5504)	X_2 (0.7639)	X_2 (0.1065)	X_2 (0.2412)	X_2 (0.4161)	X_2 (0.6533)
303.15	0.7143	0.7425	0.7715	0.7988	0.7330	0.7816	0.8369	0.8771	0.7442	0.8054	0.8686	0.9249
308.15	0.7109	0.7399	0.7682	0.7960	0.7305	0.7797	0.8299	0.8739	0.7420	0.8031	0.8658	0.9237
313.15	0.7101	0.7391	0.7680	0.7946	0.7315	0.7818	0.8280	0.8729	0.7415	0.8071	0.8689	0.9247

Standard uncertainties (0.68 level of confidence) for T = 0.001 K, U(c) ρ = 0.0001 g cm^{-3}

TABLE-3
DIELECTRIC VALUES OF TOA/TBP/OA + *n*-HEXANE + 1-HEXANOL AT 303.15, 308.15 AND 313.15 K

Temp. (K)	TOA + *n*-hexane + 1-hexanol				OA + *n*-hexane + 1-hexanol				TBP + *n*-hexane + 1-hexanol			
	X_2 (0.0689)	X_2 (0.165)	X_2 (0.3073)	X_2 (0.5395)	X_2 (0.1678)	X_2 (0.3531)	X_2 (0.5504)	X_2 (0.7639)	X_2 (0.1065)	X_2 (0.2412)	X_2 (0.4161)	X_2 (0.6533)
303.15	2.074	2.084	2.175	2.282	2.020	2.148	2.319	2.459	2.920	4.007	5.247	6.455
308.15	1.978	2.042	2.138	2.255	2.010	2.218	2.320	2.502	2.969	4.041	5.207	6.542
313.15	2.919	2.108	2.274	2.305	2.053	2.208	2.363	2.634	2.807	3.846	5.042	6.212

TABLE-4
REFRACTIVE INDEX VALUES OF TOA/TBP/OA + *n*-HEXANE + 1-HEXANOL AT 303.15, 308.15 AND 313.15 K

Temp. (K)	TOA + *n*-hexane + 1-hexanol				OA + *n*-hexane + 1-hexanol				TBP + *n*-hexane + 1-hexanol			
	X_2 (0.0689)	X_2 (0.165)	X_2 (0.3073)	X_2 (0.5395)	X_2 (0.1678)	X_2 (0.3531)	X_2 (0.5504)	X_2 (0.7639)	X_2 (0.1065)	X_2 (0.2412)	X_2 (0.4161)	X_2 (0.6533)
303.15	1.402	1.418	1.429	1.440	1.408	1.407	1.415	1.412	1.398	1.403	1.411	1.415
308.15	1.401	1.416	1.427	1.439	1.412	1.405	1.413	1.414	1.395	1.402	1.410	1.414
313.15	1.400	1.415	1.426	1.438	1.399	1.404	1.411	1.414	1.394	1.401	1.409	1.413

the system decreases with an increase in temperature. This may be attributed to the fact that the variation in density of the liquid mixture compensates for the variation in refractive index with temperature. As the density decreases, the speed of light in the medium becomes faster, so the refractive index decreases.

The derived properties like molar volume, molar polarization and molar refraction have been calculated using the density, dielectric constant and refractive index values, respectively and presented in Table-5. It was observed that with an increase in the mole fraction of solute (TOA/TBP/OA) molecules, there is an increase in values.

Excess properties

Excess molar volume (V^E_{123}): The V^E_{123} trend generally arises from three types of interactions between the components of the liquid mixtures. First is the physical interaction arising from the dispersion forces making a positive contribution, resulting in an expansion in volume. Second is the negative contribution arising from the chemical or specific interaction, including charge transfer, hydrogen bond formation and other complex-forming interactions. Finally, there is a chance of fitting component molecules into each other's structure, resulting in compression in volume. The V^E_{123} values are negative for the TOA system at the studied temperatures and this holds true for the whole composition range (Fig. 1). With increasing temperature, the V^E_{123} values become more negative. The trend of V^E_{123} depends on the chemical, physical and structural characteristics of the components of the liquid mixture [27]. The negative V^E_{123} suggests the association of components forming hydrogen bonds between molecules (TOA and 1-hexanol) and significant differences in molar volumes allow interstitial accommodation between TOA and *n*-hexane. Since, the hexyl groups are like the octyl groups of TOA, the linear alkanes can be easily trapped within the free space of TOA and 1-hexanol molecules. But in case of OA and TBP, positive V^E_{123} values are observed for 303.15 and 308.15 K, indicating weak interaction between the unlike components, but at 313.15 K, there is negative V^E_{123}, indicating there is structural rearrangement and the results in interstitial accommodation where the hexane molecules are trapped between OA/TBP and 1-hexanol molecules. TBP is known to be a self-associated liquid and tends to remain either in a wood pile or head-tail arrangement in the liquid mixture. The presence of 1-hexanol in the mixture tempts the formation of a hydrogen bond between the phosphoryl group of TBP and the OH group of hexanol. The positive V^E_{123} in the case of TBP and OA ternary mixture suggests that the H-bond formation in OA and TBP systems at 303.15 and 308.15 K is weaker than the self-interactions between OA, TBP and 1-hexanol molecules. For all the

TABLE-5
MOLAR VOLUME, MOLAR POLARIZATION AND MOLAR REFRACTION FOR
TOA/TBP/OA + *n*-HEXANE + 1-HEXANOL AT 303.15, 308.15 AND 313.15 K

TOA (X_2) + hexane (X_1) + 1-hexanol (X_3)				OA (X_2) + hexane (X_1) + hexanol (X_3)				TBP (X_2) + hexane (X_1) + hexanol (X_3)			
X_2	V_{123}	P_{123}	R_{123}	X_2	V_{123}	P_{123}	R_{123}	X_2	V_{123}	P_{123}	R_{123}
T = 303.15 K				T = 303.15 K				T = 303.15 K			
0.0689	149.120	39.324	36.309	0.1678	132.914	41.929	32.789	0.1065	144.051	56.221	34.767
0.1650	178.593	46.058	45.006	0.3531	138.743	48.400	34.227	0.2412	163.532	81.866	39.906
0.3073	221.934	62.469	57.214	0.5504	144.549	53.763	36.197	0.4161	188.269	110.339	46.746
0.5395	293.238	87.828	77.282	0.7639	150.981	59.522	38.207	0.6533	223.456	144.178	55.957
T = 308.15 K				T = 308.15 K				T = 308.15 K			
0.0689	149.833	36.863	36.403	0.1678	133.369	33.611	33.185	0.1065	144.478	57.264	34.637
0.1650	179.220	47.576	44.974	0.3531	139.081	40.177	34.088	0.2412	164.001	82.565	39.933
0.3073	222.887	61.318	57.226	0.5504	144.880	44.266	36.126	0.4161	188.878	110.265	46.796
0.5395	294.269	86.822	77.401	0.7639	151.534	50.560	37.866	0.6533	223.747	145.166	55.911
T = 313.15 K				T = 313.15 K				T = 313.15 K			
0.0689	149.998	42.620	36.323	0.1678	133.187	34.612	32.216	0.1065	144.576	54.359	34.583
0.1650	179.419	48.370	44.879	0.3531	138.885	39.872	33.966	0.2412	163.188	79.450	39.648
0.3073	222.940	66.469	57.109	0.5504	144.444	45.136	35.864	0.4161	188.204	108.030	46.529
0.5395	294.765	89.248	77.2481	0.7639	151.707	53.499	37.909	0.6533	223.505	141.860	55.732

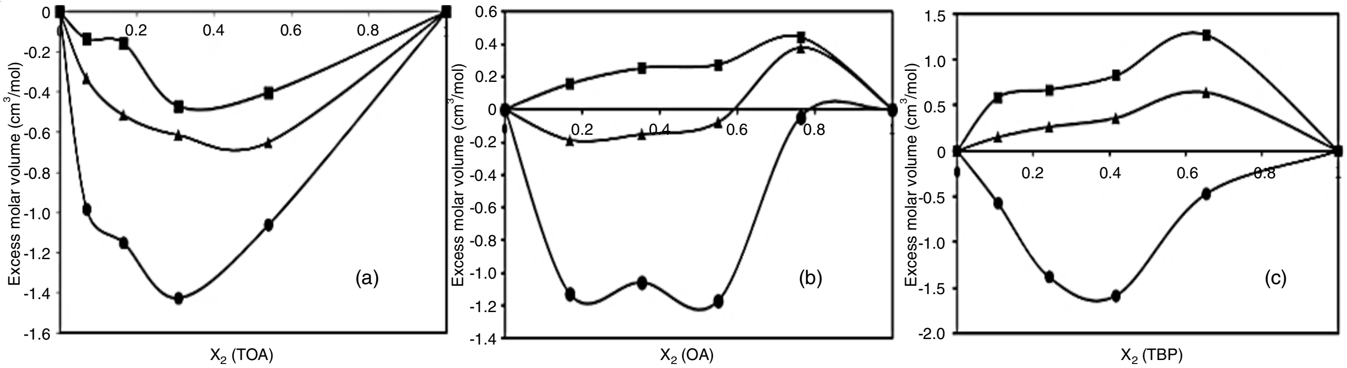

Fig. 1. Plot of V^E_{123} *versus* the mole fraction of (a) TOA, (b) OA and (c) TBP at T = 303. 15 (■), 308.15 (▲) and 313.15 (●) K

ternary systems the V^E_{123} reaches a minimum at 0.4 mole fraction of the solute molecules.

The fitting coefficients of the Redlich-Kister polynomial and standard deviation is presented in Table-6.

Excess dielectric constant (ε^E_{123}): The evaluation of ε^E_{123} of a mixture furnishes information about the extent of heterogenous molecular association. The interaction arises with the alteration in the total number of effective dipoles that contributes to the dielectric constant of the mixture. It indicates the molar ratio that signifies the strongest complex formed between the mixture's constituents. The ε^E_{123} were measured for ternary mixtures of TOA/TBP/OA + *n*-hexane + 1-hexanol at T = 303.15, 308.15 and 313.15 K over the entire mole fraction range of solute molecules. The variation in ε^E_{123} as a function of the mole fraction of solute molecules is represented in Fig. 2. For all the systems, negative ε^E_{123} values are obtained. The negative ε^E_{123} trend arises from the dipolar self-association of the more polar component to form species of lower dipole moment [9]. As reported earlier, for TOA and *n*-hexane binary mixture, the ε^E_{123} values exhibited a positive trend [27]. But in case of ternary mixtures of TOA + *n*-hexane + 1-hexanol, the observed negative ε^E_{123} indicates the heterogeneous inter-actions through hydrogen bonds with many effective dipoles. In case of the TBP system, the dipoles are aligned with the P=O bond of the phosphate head group and undergo a significant conformational change.

The fitting coefficients of ε^E_{123} and standard deviations for the ternary mixtures at different temperatures are presented in Table-7.

Deviation in refractive index (Δn_{D123}): The positive Δn_{D123} for the ternary mixtures of TOA/TBP/OA + *n*-hexane + 1-hexanol at T = 303. 15, 308.15 and 313.15 K indicate the presence of specific interactions between the like molecules (Fig. 3). When *n*-hexane and 1-hexanol were added to the solute molecules, it can stimulate the mutual association of hydrogen-bonded partners between the pure components, creating a new weak hydrogen bond between them. The declustering of the self-associated species at higher temperatures leads to an increase in the refractive indices of the ternary mixtures.

TABLE-6
POLYNOMIAL FITTING COEFFICIENTS AND STANDARD DEVIATION FOR V^E_{123} AT 303.15, 308.15 AND 313.15 K

System	Temp. (K)	a	b	c	σ
TOA + *n*-hexane + 1-hexanol	303.15	0.012	-1.990	4.386	0.224
	308.15	-0.043	-3.700	2.443	0.730
	313.15	-0.224	-9.423	7.992	1.060
OA + *n*-hexane + 1-hexanol	303.15	-0.043	-3.700	5.688	0.219
	308.15	0.028	-2.860	11.185	0.001
	313.15	-0.002	-9.333	29.169	1.890
TBP + *n*-hexane + 1-hexanol	303.15	0.123	2.075	-0.215	1.840
	308.15	0.035	0.256	2.898	0.324
	313.15	0.136	-11.039	35.144	0.005

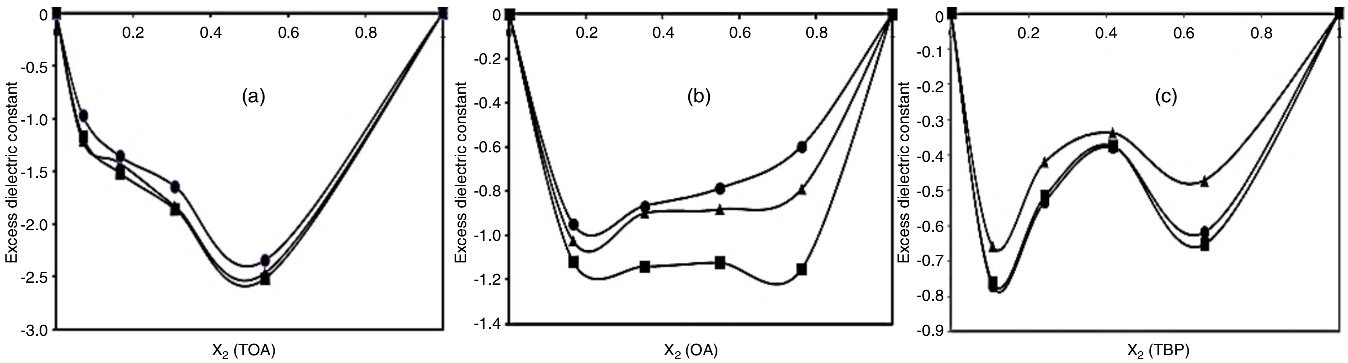

Fig. 2. Plot of ε^E_{123} *versus* the mole fraction of (a) TOA, (b) OA and (c) TBP at T = 303. 15 (■), 308.15 (▲) and 313.15 (●) K

TABLE-7
POLYNOMIAL FITTING COEFFICIENTS AND STANDARD DEVIATION FOR ε^E_{123} AT 303.15, 308.15 AND 313.15 K

System	Temp. (K)	a	b	c	σ
TOA + *n*-hexane + 1-hexanol	303.15	-0.237	-8.931	17.963	0.158
	308.15	-0.257	-8.457	16.645	0.162
	313.15	-0.198	-7.562	13.681	0.175
OA + *n*-hexane + 1-hexanol	303.15	-0.105	-5.495	12.057	0.250
	308.15	-0.096	-5.284	13.056	0.323
	313.15	-0.073	-5.560	15.360	0.212
TBP + *n*-hexane + 1-hexanol	303.15	-0.187	-2.430	6.244	0.491
	308.15	-0.152	-2.370	6.781	0.600
	313.15	-0.168	-1.784	7.496	0.856

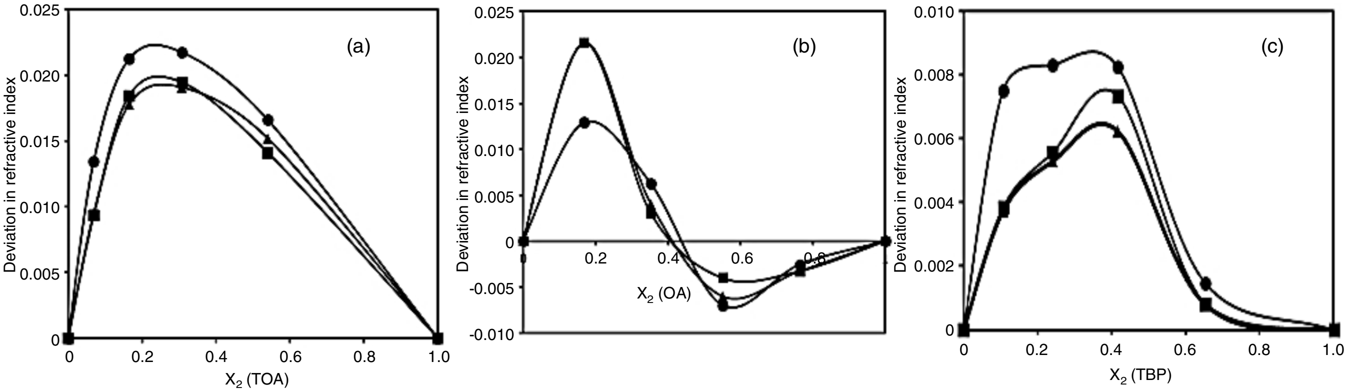

Fig. 3. Plot of Δn_{D123} *versus* the mole fraction of (a) TOA, (b) OA and (c) TBP at T = 303. 15 (■), 308.15 (▲) and 313.15 (●) K

The fitting coefficients of Δn_{D123} and standard deviations for the ternary mixtures at different temperatures are presented in Table-8.

FTIR analysis: The FTIR spectra of the TOA/TBP/OA + *n*-hexane + 1-hexanol systems have been recorded at 0.4 mole fraction of solute. The effect of diluent (*n*-hexane) and modifier (1-hexanol) on the extractants (TOA/TBP/OA) was studied and shown in Fig. 4. In case of Fig. 4a, the FT-IR spectrum of pure TOA, the major peak at 1096 cm^{-1} is attributed to C-N out-of-phase stretching. It is observed there is no change in this peak in case of TOA + hexane binary mixture [27] but a slight reduction and splitting is observed at this wavenumber in case of TOA + *n*-hexane + 1-hexanol mixture indicating the formation of hydrogen bond between the N of amine of TOA and the hydrogen of 1-hexanol. The CH_2 bending at 1470 cm^{-1}, CH_2 in phase stretching at 2850 cm^{-1}, CH_2 out of phase stretching at 2930 cm^{-1} tend to remain intact in neat TOA, TOA + *n*-hexane and TOA + *n*-hexane + 1-hexanol. In Fig. 4b, the bands at 3030.03, 2955.81, 2925 and 2671 cm^{-1} correspond to the vibration bands of broad peak due to the O-H stretching. The vibrations bonds of C=O stretching is observed at 1706 cm^{-1} [28]. The C-O stretching is observed at 1460 and 1412 cm^{-1} and the band at 932 cm^{-1} indicates the C-H bend in octanoic acid [34]. For octanoic acid, no significant shifts are observed upon addition of *n*-hexane and 1-hexanol. Likewise in case TBP mixtures, Fig. 4c no prominent shifts are observed in the absorption bands in pure TBP; P=O stretching at 1272 cm^{-1} and C-H stretching at 2965 and 2875 cm^{-1} [4,28].

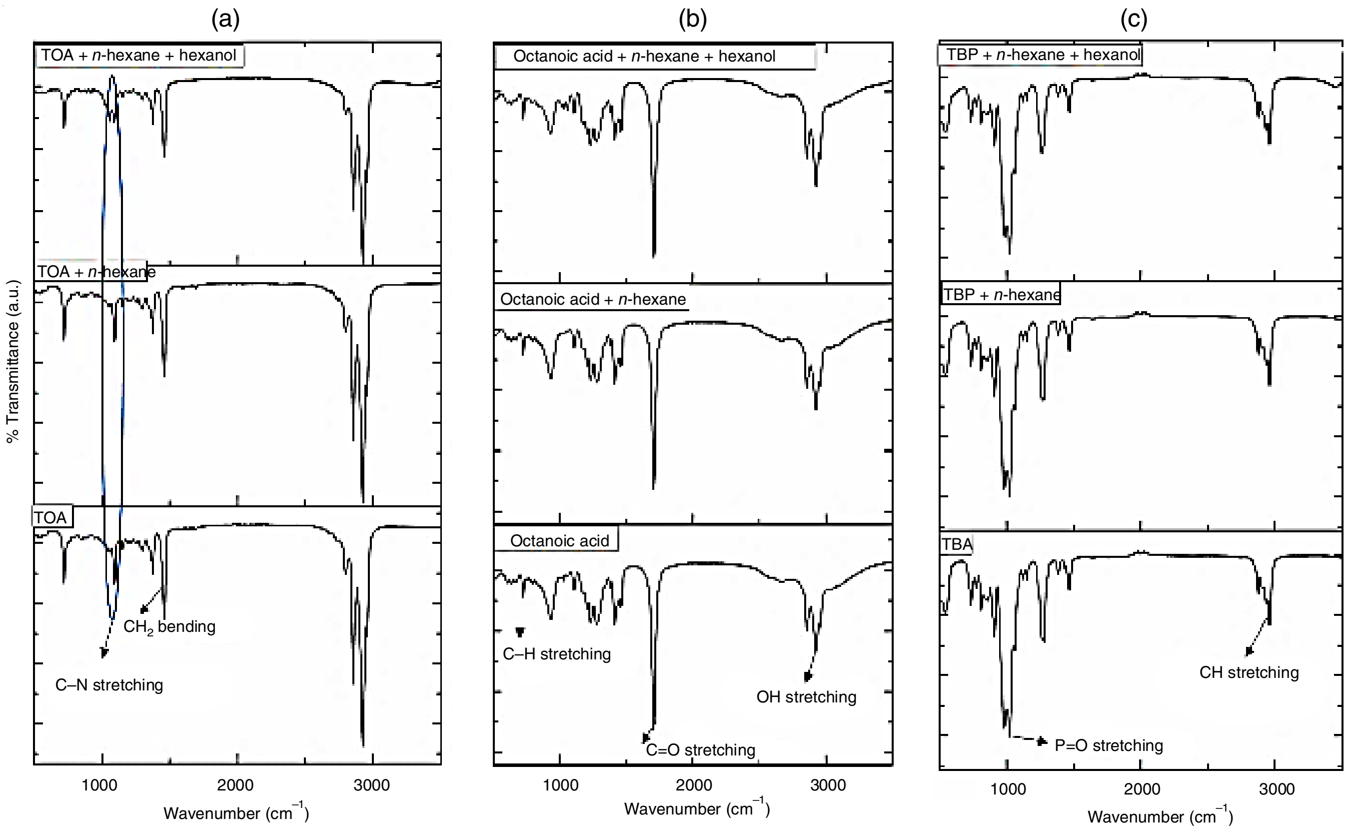

Fig. 4. FTIR spectra of (a) TOA + *n*-hexane + 1-hexanol (b) OA + *n*-hexane + 1-hexanol (c) TBP + *n*-hexane + 1-hexanol at T = 303.15, 308.15 and 313.15 K

TABLE-8
POLYNOMIAL FITTING COEFFICIENTS AND STANDARD DEVIATION FOR Δn_{D123} AT T = 303.15, 308.15 AND 313.15 K

System	Temp. (K)	a	b	c	σ
TOA + *n*-hexane + 1-hexanol	303.15	0.0004	0.151	-0.485	0.00016
	308.15	0.0006	0.142	-0.442	0.00017
	313.15	0.0015	0.169	-0.545	0.00030
OA + *n*-hexane + 1-hexanol	303.15	0.0033	0.1018	-0.417	0.00041
	308.15	0.0034	0.1058	-0.436	0.00046
	313.15	0.0017	0.0824	-0.337	0.00011
TBP + *n*-hexane + 1-hexanol	303.15	-0.0004	0.055	0.071	0.00015
	308.15	-0.0002	0.050	-0.166	0.00010
	313.15	-0.0004	0.074	-0.255	0.00060

Conclusion

In this work, the experimental values of density, dielectric constant and refractive index were studied for the ternary liquid mixtures of tri-*n*-octylamine/tri-*n*-butyl phosphate/octanoic acid (TOA/TBP/OA) + *n*-hexane + 1-hexanol at T = 303.15, 308.15 and 313.15 K over the entire composition range of solute molecules. The deviations and excess properties calculated from the experimental values exhibited good fittings to Redlich-Kister polynomial. The negative excess molar volume indicated the formation of hydrogen bonds and interstitial accommodation for all temperatures in case of TOA ternary mixtures and for OA and TBP mixtures at 313.15 K. The positive humps at lower temperatures (303.15 and 308.15 K) indicated the self-interactions between OA and TBP molecules. The negative trend of excess dielectric constant signifies the dipolar self-association of the more polar component to form species carrying low dipole moment. Deviation in refractive index enhanced with temperature indicated the dissociation of self-associated components. The FT-IR findings also indicate negligible interaction among the components in the ternary system. Thus, the present investigation furnishes vital information regarding the extractant-diluent-modifier system that can be effectively employed in the metal extraction process.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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