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Volumetric and acoustic properties of binary mixtures of tri-*n*-butyl phosphate with *n*-hexane, cyclohexane, and *n*-heptane from $T = (298.15 \text{ to } 323.15)$ K

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Densities (ρ) and speed of sound (u) of the binary mixtures of tributyl phosphate (TBP) and alkanes (*n*-hexane, cyclohexane, and *n*-heptane) were measured at temperatures from (298.15 to 323.15) K over the entire composition range and at atmosphere pressure. Using these experimentally determined quantities, the excess molar volume (V^E), deviation in isentropic compressibility (Δk_s), internal pressure (p_i), solubility parameter (δ) and excess cohesive energy of mixing (U^E) have been calculated. The excess molar volume and deviation in isentropic compressibility data have been fitted to a Redlich–Kister type polynomial equation. The positive or negative deviations shown by these quantities have been interpreted in terms of intermolecular interactions and structure of components.

1. Introduction

Organophosphorus esters represent a major class of solvent extraction reagents [1–4] amongst which tributyl phosphate (TBP) is the most commonly used solvating type of extractant. It has been widely used for extraction of various types of organic compounds, metal ions including ones used as nuclear fuel and inorganic acids from aqueous solutions [5–9]. A proper choice of a diluent is equally important whether it is for the dissolution of the extractant or for decreasing the extent of metal loading to avoid criticality, for example in case of extraction of Pu by PUREX process. The diluent structure also influences the interactions of the diluents with the extractant or the extracted complex which primarily involves cohesive forces that arise either due to cavity formation in the solvent to create space for the extractant and the extracted complex or due to bonding between the solvent and the extracted complex. Knowledge of the intermolecular interactions among the diluent and extractant is of primary importance since it is one of the factors which help to design the solvent extraction process with greater efficacy. Although some reports on compressibility and/or density studies in various TBP-diluent systems are present in the literature [10–17], to the best of the knowledge of the authors, both density and compressibility data on TBP + hexane, TBP + cyclohexane, and TBP + heptane are not available. Our aim is provide new experimental data on density and speed of sound and other derived properties of these binary mixtures in the temperature range of $T = (298.15 \text{ to } 323.15)$ K over the entire composition range and to explore, from density and sound velocity measurements, how the strength and nature of interactions between polar TBP and non-polar alkane molecules change when an additional methylene moiety gets incorporated in the chain or when the conformation changes from open chain to a closed one. We have chosen hexane, cyclohexane, and heptane as the diluents and derived various parameters like excess molar volume and its temperature derivative, partial molar volumes at infinite dilution, isentropic compressibility and its deviation due to mixing. Thermodynamic parameters like the internal pressure, solubility parameter and the excess cohesive energy of mixing for the binary mixtures have also been calculated.

2. Experimental

The TBP was purchased from E. Merck, Germany (purity $\geqslant$ 0.99 mass fraction), hexane and cylcohexane were purchased from SD Fine Chemicals Limited (purity $\geqslant$0.99 and 0.997 mass fractions respectively) and used as received. Heptane was purchased from Spectrochem Pvt. Limited (purity $\geqslant$ 0.995 mass fraction) and used as received. These data are summarized in table 1. Three sets of experiments were carried out taking (TBP + hexane), (TBP + heptane), and (TBP + cyclohexane) binary mixtures with the mole fraction of TBP varying from 0.1 to 0.9 in each case. The liquid mixtures were prepared by weight using a Mettler balance with an accuracy of ±0.0001 g. The density and sound velocity of the

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TABLE 1
Sample provenance and purity.

Chemical name	Source	Mass fraction purity
Tributyl phosphate	E. Merck, Germany	⩾0.99
n-Hexane	SD Fine Chemical Ltd.	⩾0.99
Cyclohexane	SD Fine Chemical Ltd.	⩾0.997
n-Heptane	Spectrochem Pvt. Ltd.	⩾0.995

solutions were measured in a temperature range of (298.15 to 323.15) K (with temperature measuring accuracy of ±0.01 °C) in an automated density and sound velocity meter DSA 5000 M having a density measurement accuracy of ±0.000005 $g \cdot cm^{-3}$ and sound velocity measurement accuracy of ±0.5 $m \cdot s^{-1}$. The accuracies of the density and speed of sound measurements were ascertained by comparing the experimental values for pure liquids with literature [18–20] at several temperatures (table 2). The precision obtained in measurement with our samples considering the data recorded during heating and cooling and making independent measurements at each temperature was ±0.000005 $g \cdot cm^{-3}$ for density and ±0.5 $m \cdot s^{-1}$ for sound velocity. Considering the accuracy of the instrument and the precision obtained in our measurements the uncertainty obtained in our data were ±0.000007 $g \cdot cm^{-3}$ for density and ±0.7 $m \cdot s^{-1}$ for sound velocity. The density and sound velocity values of doubly distilled water were compared with those provided in the instruction manual of the instrument. The uncertainty in excess molar volume (V^E) and deviation in isentropic compressibility (Δk_s) obtained from density and sound velocity measurements were within $7 \cdot 10^{-4}\ m^3 \cdot mol^{-1}$ and $0.1 \cdot 10^{-11}\ m^2 \cdot N^{-1}$, respectively.

3. Results and discussion

3.1. Excess properties and intermolecular interactions

The experimental values of densities, ρ and speed of sound, u of pure TBP, hexane, heptane, and cyclohexane and those of their binary mixtures over the entire composition range, expressed by mole fraction x_1 of TBP and at temperatures (298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K, listed in table 3. From the experimental ρ and u results, the excess molar volume V^E, isentropic compressibility k_s, deviations in isentropic compressibility Δk_s and excess thermal expansion coefficient, α^E have been calculated by using the following relations:

TABLE 2
Comparison of experimentally measured densities, ρ and speed of sound, u of pure components with literature values.

Component	T/K	$\rho/(kg \cdot m^{-3})$		$u/(m \cdot s^{-1})$	
		Exp.	Lit.	Exp.	Lit.
Doubly distilled water	298.15	997.04	997.043	1498	1497.00
Tributyl phosphate (TBP)	298.15	973.85	972.70[a] 972.49[b]	1272	
n-Hexane	293.15	659.85	659.44[c]	1100	1083.00[a]
	298.15	655.21	660.60[a] 654.93[c]	1077	
Cyclohexane	292.15	779.51		1284	1280.00[a]
	298.15	773.86	773.90[a]	1254	
n-Heptane	293.15	684.16		1152	1162.00[a]
	298.15	679.91	679.50[a]	1131	

[a] Reference [18].
[b] Reference[19].
[c] Reference[20].

TABLE 3
Densities (ρ) and speed of sound (u) of pure tri butyl phosphate (TBP), hexane, cyclohexane, and heptanes and {TBP(1) + hexane/cyclohexane/heptane(2)} binary mixtures at different temperatures.

x_1	$\rho/(kg \cdot m^{-3})$					
	T/K = 298.15	303.15	308.15	313.15	318.15	323.15
1.0000			*TBP*			
	973.85	969.44	965.04	960.62	956.19	951.75
1.0000			*n-Hexane*			
	655.21	650.64	646.03	641.37	636.67	631.92
1.0000			*Cyclohexane*			
	773.86	769.12	764.35	759.56	754.74	749.88
1.0000			*n-Heptane*			
	679.91	675.63	671.33	667.01	662.65	658.26
			{TBP(1) + n-hexane(2)}			
0.0995	715.09	710.52	705.92	701.29	696.61	691.95
0.2006	765.08	760.52	755.94	751.33	746.72	742.04
0.3037	808.12	803.59	799.05	794.49	789.9	785.3
0.3959	840.45	835.96	831.45	826.92	822.35	817.78
0.4988	871.21	866.74	862.27	857.77	853.27	848.75
0.6091	899.46	895.04	890.61	886.18	881.73	877.28
0.7086	921.7	917.3	912.9	908.49	904.07	899.63
0.8011	940.17	935.77	931.36	926.95	922.53	918.1
0.8999	957.99	953.61	949.23	944.83	940.44	936.03
			{TBP(1) + cyclohexane(2)}			
0.0990	814.12	809.42	804.71	799.98	795.24	790.47
0.1993	846.89	842.23	837.55	832.86	828.15	823.42
0.3025	874.05	869.46	864.84	860.21	855.57	850.91
0.4042	896.02	891.48	886.94	882.38	877.81	873.23
0.5063	914.55	910.06	905.53	901.04	896.51	891.96
0.6083	930.06	925.63	921.2	916.76	912.31	907.86
0.7024	942.9	938.5	934.1	929.69	925.28	920.86
0.8027	954.19	949.8	945.4	941.01	936.6	932.19
0.9020	964.39	960.02	955.65	951.27	946.89	942.5
			{TBP(1) + n-heptane(2)}			
0.0999	729.57	725.23	720.87	716.49	712.09	707.66
0.1972	771.17	766.8	762.39	758.01	753.61	749.14
0.2996	809.21	804.83	800.43	796.02	791.59	787.14
0.3947	840.14	835.74	831.33	826.9	822.45	817.99
0.4977	869.71	865.44	861.03	856.61	852.17	847.71
0.5999	895.55	891.18	886.81	882.44	878.05	873.65
0.697	917.57	913.22	908.86	904.49	900.11	895.73
0.7999	938.62	934.25	929.88	925.5	921.11	916.71
0.9005	957.3	952.9	948.48	944.06	939.62	935.17
			$u/(m \cdot s^{-1})$			
			TBP			
1.0000	1272	1255	1238	1221	1204	1188
			n-Hexane			
1.0000	1077	1054	1032	1010	988	965
			Cyclohexane			
1.0000	1254	1229	1205	1181	1157	1134
			n-Heptane			
1.0000	1131	1109	1088	1066	1045	1024
			{TBP(1) + n-hexane(2)}			
0.0995	1097	1076	1055	1034	1013	992
0.2006	1118	1097	1077	1057	1038	1018
0.3037	1141	1122	1102	1083	1064	1045
0.3959	1161	1143	1124	1105	1087	1068
0.4988	1183	1165	1146	1128	1110	1092
0.6091	1205	1187	1169	1151	1133	1116
0.7086	1222	1205	1187	1170	1152	1136
0.8011	1239	1222	1204	1187	1170	1153
0.8999	1255	1238	1221	1204	1187	1170
			{TBP(1) + cyclohexane(2)}			
0.0990	1237	1214	1192	1170	1148	1127
0.1993	1232	1211	1190	1169	1148	1128
0.3025	1233	1213	1193	1173	1154	1134
0.4042	1237	1218	1199	1180	1161	1142
0.5063	1242	1223	1205	1187	1168	1150
0.6083	1247	1229	1211	1193	1175	1157
0.7024	1252	1234	1216	1199	1181	1164
0.8027	1258	1240	1223	1206	1188	1171