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DIELECTRIC CONSTANTS AND REFRACTIVE INDICES OF SOLUTIONS OF SOME ORGANOPHOSPHORUS COMPOUNDS IN n-OCTANE

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ABSTRACT

Dielectric constant and refractive index data are presented for n-octane solutions of several high molecular weight organophosphorus compounds used in solvent extraction systems. Dielectric constant data are included for di(2-ethylhexyl)phosphoric acid (HDEHP), its sodium and strontium salts (and complexes of these salts with additional acid), for tri-n-butylphosphate (TBP), tri-n-octylphosphine oxide (TOPO) and mixtures of these neutral organophosphorus compounds with HDEHP, its salts and complexes. Refractive indices of HDEHP, TBP, $\text{Sr}(\text{DEHP})_2$, $\text{NaDEHP} \cdot 3 \text{ HDEHP}$ and TOPO solutions are included.

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DIELECTRIC CONSTANTS AND REFRACTIVE INDICES OF SOLUTIONS OF SOME ORGANOPHOSPHORUS COMPOUNDS IN n-OCTANE

The accompanying tabulation of dielectric constants and refractive indices of organophosphorus compounds in n-octane has been made so that the original data used in calculations and plots in "Investigation of Possible Intermolecular Bonding in Some Mixtures of Phosphate Extractants by Use of Dielectric Measurements," W. J. McDowell and C. F. Coleman, J. Tenn. Academy of Sci., Vol. XLI (No. 2) 78 (1966) might be more readily available.

A description of the method used in making these measurements may be found in J. Phys. Chem. 63, 747 (1959). In brief, the measurements were made in a thermostated cell at $25 \pm 0.1^\circ\text{C}$. The capacitance measurements were taken at 1 Mc and were accurate to $\pm 0.02 \mu\text{f}$. The resulting dielectric constants have a relative accuracy of $\pm 0.01\%$. Their absolute accuracy referred to specially purified cyclohexane is also probably correct to $\pm 0.01\%$. Refractive indices, n , were also measured at $25 \pm 0.1^\circ\text{C}$ and were accurate to ± 0.00005 .

The solvent n-octane was Phillips 99+ % purity material, which was further purified by washing with concentrated sulfuric acid until no further darkening of the acid was observed. The di(2-ethylhexyl)phosphoric acid was purified by the method Schmitt and Blake (ORNL-3548). The neutral equivalent of the purified material was 324 (Theo. 322). Monoalkyl acid content was less than 0.2 eq. % as determined by two endpoint titrations of an ethylene glycol extract. The tri-n-butyl phosphate was obtained from Chemicals and Plastics Division, Food Machinery and Chemicals Corporation. Tests for the extraction of $^{95}\text{Zr-Nb}$ tracer, usually a sensitive indication of the presence of alkylphosphate hydrolysis product, was negative, and the TBP was used as received.

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Dielectric Constants of Solutions in *n*-Octane

X TBP-HDEHP Mixtures			X HDE-P		X Sr(DEHP) ₂		X Sr(DEHP) ₂ -HDEHP Mixtures		X NaA·3HA*		X NaA·3HA in 0.2 M TBP		X TBP-HDEHP Mixtures total P = 0.20 M	
Molarity of TBP	Molarity of HDEHP	ε	Molarity	ε	Normality	ε	Equiv. frac. as Sr(DEHP) ₂	ε	Molarity	ε	Molarity of Complex	ε	Fract. of Total Phosphate as TBP	ε
0.20	0.80	2.5915	0.000975	1.9423	0.003125	1.9581	0.02	1.9873	0.00195	1.9468	0.005	2.1456	0.10	2.0808
0.20	0.40	2.3456	0.00195	1.9424	0.00625	1.9752	0.05	1.9873	0.00390	1.9502	0.0125	2.1658	0.25	2.0853
0.20	0.20	2.2321	0.0039	1.9432	0.0125	2.0133	0.10	1.9878	0.00781	1.9589	0.025	2.2049	0.50	2.1042
0.20	0.10	2.1803	0.0078	1.9448	0.025	2.0964	0.20	1.9878	0.0156	1.9826	0.050	2.2783	0.75	2.1182
0.20	0.05	2.1455	0.0156	1.9485	0.050	2.2806	0.30	1.9892	0.03125	2.0096	0.100	2.4209	0.90	2.1231
0.20	0.02	2.1358	0.3125	1.9558	0.100	2.7015	0.40	1.9944	0.0625	2.0797	0.200	2.6808		
0.30	0.20	2.9190	0.0625	1.9690	0.200	3.7028	0.60	2.0196	0.125	2.2244				
0.40	0.20	2.4497	0.125	1.9963			0.80	2.0724	0.250	2.5447				
0.10	0.20	2.1403	0.250	2.0533			1.00	2.6711						
0.05	0.20	2.0820	0.500	2.1719										
0.02	0.20	2.0514	1.00	2.4341										
0.02	0.18	2.0414	2.00	3.0884										
0.05	0.15	2.0564												
0.10	0.10	2.0803												
0.15	0.05	2.1046												
0.18	0.02	2.1175												

The average value of ε of pure *n*-octane found was 1.9440.

*The complex of sodium with di(2-ethylhexyl)phosphoric acid (HA).

Dielectric Constants of Solutions in n-Octane (continued)

X TOPO-HDEHP Mixtures Total P = 0.20 M		X SrA ₂ -TBP Mixtures Total P = 0.20 M		X SrA ₂ ·4HA** TBP Mixtures Total P = 0.20 M		X HDEHP		X TBP		X TOPO	
Fract. of Total Phos. as TOPO	ε	Fract. of Total Phos. as TBP	ε	Fract. of Total Phos. as TBP	ε	Molarity	ε	Molarity	ε	Molarity	ε
0.10	2.0039	0	3.5541	0	2.0398	0.000975	1.9423	0.000975	1.9426	0.00313	1.9518
0.20	2.0174	0.10	3.3386	0.10	2.0531	0.00195	1.9424	0.00195	1.9430	0.00625	1.9582
0.30	2.0327	0.20	2.7916	0.20	2.0670	0.00390	1.9432	0.00390	1.9444	0.0125	1.9702
0.40	2.0503	0.30	2.4245	0.30	2.0792	0.00780	1.9448	0.00780	1.9480	0.0250	1.9961
0.50	2.0682	0.40	2.2683	0.40	2.0888	0.0156	1.9485	0.0156	1.9548	0.050	2.0480
0.60	2.0878	0.50	2.2010	0.50	2.0974	0.03125	1.9558	0.03125	1.9690	0.100	2.1592
0.70	2.1074	0.60	2.1971	0.60	2.1053	0.0625	1.9690	0.0625	1.9976		
0.80	2.1260	0.70	2.1560	0.70	2.1124	0.125	1.9963	0.125	2.0551		
0.90	2.1442	0.80	2.1449	0.80	2.1181	0.250	2.0533	0.250	2.1728		
0	1.9897	0.90	2.1385	0.90	2.1239	0.500	2.1719	0.500	2.4223		
		1.0	2.1277	1.00	2.1282	1.00	2.4341	1.00	2.9025		
						2.00	3.0884	2.00	3.8896		

**The complex of strontium with di(2-ethylhexyl)phosphoric acid (H-A).

Refractive Indices of Solutions in n-Octane

X HDEHP		X TBP		X $\text{Sr}(\text{DEHP})_2$		X NaA-3HA		X TOPO	
Molarity	η	Molarity	η	Normality	η	Molarity	η	Molarity	η
0.000975	1.3948	0.000975	1.3947	0.003125	1.3952	0.00195	1.3953	0.00313	1.3950
0.00195	1.3950	0.00195	1.3947	0.00625	1.3952	0.00390	1.3958	0.00625	1.3951
0.0039	1.3950	0.0039	1.3947	0.0125	1.3952	0.00781	1.3958	0.0125	1.3953
0.0078	1.3950	0.0078	1.3947	0.025	1.3952	0.0156	1.3960	0.0250	1.3958
0.0156	1.3950	0.0156	1.3947	0.050	1.3960	0.03125	1.3972	0.050	1.3965
0.0313	1.3950	0.0313	1.3946	0.100	1.3972	0.0625	1.3990	0.10	1.3980
0.0625	1.3960	0.0625	1.3950	0.200	1.3992	0.125	1.4033		
0.125	1.3970	0.125	1.3953			0.250	1.4110		
0.250	1.3990	0.250	1.3962						
0.500	1.4030	0.500	1.3980						
1.00	1.4108	1.00	1.4015						
2.00	1.4262	2.00	1.4090						

Average η for n-octane was 1.3950.

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