

INVESTIGATION OF POSSIBLE INTERMOLECULAR BONDING IN SOME MIXTURES OF PHOSPHATE EXTRACTANTS BY USE OF DIELECTRIC MEASUREMENTS¹

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INTRODUCTION

In the treatment of reactor fuel reprocessing solutions it is desirable to selectively remove some of the more hazardous isotopes, such as strontium 90, as quickly as possible to reduce the dangers involved in subsequent operations. A process for the selective extraction of strontium by di(2 ethylhexyl)phosphoric acid (HDEHP or HA) was developed at ORNL (1) and has been used extensively. The fundamental chemistry of this process has been investigated and has been recently reported (2).

In the usual process the HDEHP is used as a solution in a carrier diluent such as a simple aromatic or aliphatic hydrocarbon. There is some difficulty in keeping the metal salts of the acid soluble in the organic diluent. Under certain conditions the metal salts (particularly the sodium salt, NaDEHP or NaA) may distribute to the aqueous phase or separate into a third phase soluble in neither phase. Certain compounds such as long chain alcohols or ethers added to the organic phase aid in preventing this behavior.

Workers at Hanford Laboratories found that tri-*n*-butyl phosphate (TBP) was not only effective in solubilizing the organic phase HDEHP salts but also increased the distribution of strontium to the organic phase (3). TBP itself does not extract strontium from these solutions. Such a combination of reagents which is more effective than the simple sum of their effects is called a synergistic combination. Subsequent work here at ORNL has confirmed the presence of this synergistic effect when an aliphatic hydrocarbon diluent was used (*n*-octane or *n*-nonane) and has further shown an almost complete lack of such effect when the organic diluent is benzene (4). Fundamental studies now in progress are attempting to determine the nature of the interaction or interactions responsible for this effect in the case of strontium extraction.

In the interpretation of equilibrium measurements on the synergistic strontium extraction system, it is necessary to know whether there is intermolecular bonding between TBP and HDEHP (or NaDEHP). Such interactions would be expected to oppose the synergistic effect. Baker and Baes found molecular-compound formation in mixed solutions of HDEHP and tri-*n*-octylphosphine oxide (TOPO) using infrared methods (5). By analogy TBP might, be expected to form a similar, though probably somewhat weaker, compound. Baker and Baes were not able to determine this interaction because the expected peak from the intermolecular com-

pound ($\sim 1250 \text{ cm}^{-1}$) concurred with the sum of the peaks (1230 and 1270 cm^{-1}) of the two separate phosphate species. In the work described here, these and several other phosphate extractant species mixtures are examined by dielectric methods. Qualitative conclusions regarding the intermolecular bonding in these solutions were drawn by reasoning generally parallel to that used in any of the common continuous-variation-type measurements. In addition the dipole moments of several phosphate species are determined in *n*-octane.

EXPERIMENTAL

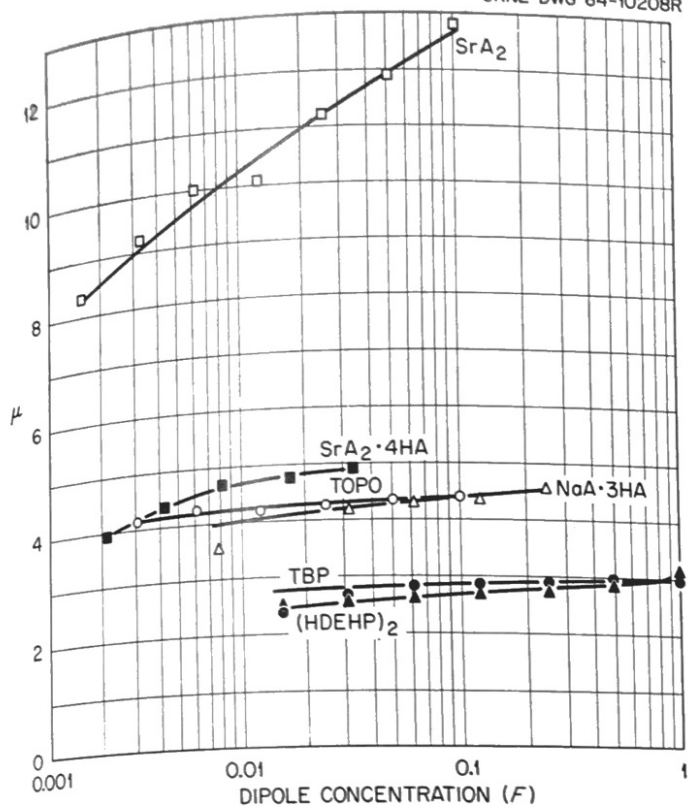
The capacitance bridge and cell have been described in detail in an earlier work (6). The capacitance measurements were accurate to $\pm 0.02 \mu\text{f}$ and were taken at 1 Mc, at $25 \pm 0.1^\circ\text{C}$. The resulting dielectric constants, therefore, have a relative accuracy of $\pm 0.01\%$. Their absolute accuracy depends on the accuracy of the value used for the standard of reference, cyclohexane, which in this case is probably also correct to within $\pm 0.01\%$ (7). Refractive indices, η , were measured with an Abbe refractometer at $25 \pm 0.1^\circ\text{C}$, with an accuracy of ± 0.00005 . Calculated dipole moments, μ , which depend primarily on the quantity $(\epsilon - \eta^2)$, are less accurate at low solute concentrations, where ϵ and η^2 are near the same value. At the lowest concentrations used here, about $0.005 M$, the total uncertainty in μ (including uncertainty in solute concentration) is of the order of $\pm 5\%$. The range of best accuracy of μ is 0.05 to $0.10 M$ in these measurements being better than $\pm 1.0\%$. Above $\sim 0.1 M$ interaction of the dipole electric fields is generally considered to become important so that the calculated dipole moment is less meaningful.

The reagents and solvent *n*-octane were greater than 99 mole % pure.

RESULTS AND DISCUSSION

Dipole Moments: The dielectric constants of TBP, TOPO, HDEHP, $\text{NaA}\cdot 3\text{HA}$ (where $\text{A} = \text{DEHP}$), $\text{SrA}_2\cdot 4\text{HA}$, and SrA_2 solutions in *n*-octane were determined over a range of concentration. There were no discontinuities nor inflections in plots of the dielectric constant ϵ vs concentration; they were linear except for very small deviations at the highest concentrations (0.5 to $1.0 M$ phosphorus) such as are generally attributed to increased solute dipole interaction. Dipole moments, μ , in Debye units calculated by the method of Guggenheim are shown over the concentration range examined for the various species in Fig. 1.

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Dipole Moments of some Phosphate Extractant Species in *n*-Octane.
Fig. 1

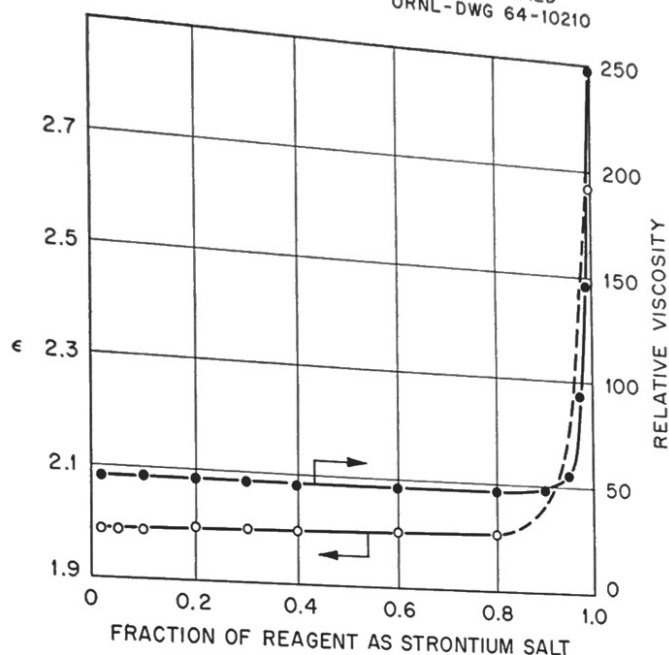
Values compared at 0.03 mole of the stated dipole per liter or at 0.03 mole of contained phosphorus per liter, are:

Dipole	D per formula wt. at 0.03 F cpd	D per mole P at 0.03 M P
TBP	2.6	2.6
TOPO	4.3	4.3
(HA) ₂	2.5	1.9
NaA·3HA	4.1	1.7
SrA ₂ *	11.5	7.6
SrA ₂ ·4HA	4.9	1.9

*Probably a hydrate; analyses indicate 4 moles of water per mole of strontium from 0.005 M Sr to 0.1 M Sr.

When the value of μ based on the phosphorus concentration is compared, the order is about as one would expect except for the somewhat high value for SrA₂, that is, with TOPO most polar and the probably symmetrical complex NaA·3HA least polar per phosphorus.

The value of 7.6D per phosphate in SrA₂ suggest either that the compound is not symmetrical or that the salt is polymerized, thus producing very large dipoles. Dielectric-constant and relative-viscosity measurements as a function of the fraction of the reagent in the strontium salt both show a very rapid increase as the fraction approaches 1 (see Fig. 2). In addition, measurements show that dielectric loss due to combined conductivity and frictional loss in dipole rotation increases rapidly in this region. These measurements all indicate that SrA₂ is polymerized, in agree-

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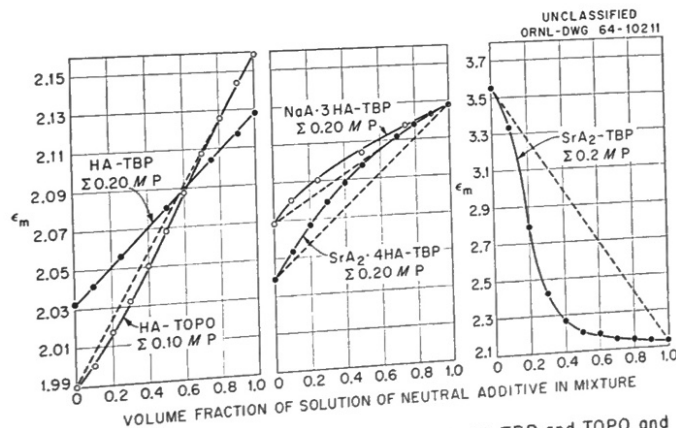
Dielectric Constant and Relative Viscosity of Sr-HDEHP as a Function of the Fraction in Salt Form.

Fig. 2

ment with earlier (unpublished) vapor pressure measurements. The relatively rapid increase of μ with concentration (Fig. 1) is probably due to increasing polymerization with increasing solute concentration.

Dielectric Constants of Mixtures: Mixtures of organophosphorus species in *n*-octane examined were TBP-HA, TOPO-HA, NaA·3HA-TBP, SrA₂·4HA-TBP, and SrA₂-TBP. Plots of ϵ vs composition at constant total phosphorous concentration are shown in Fig. 3.

Although it is easy to show (as is done below) that in dilute solutions the dielectric properties of mixtures should be an additive function of the dielectric properties of the individual components, such measurements have been little used to investigate compound formation. Trinh (8), Chretien and Laurent (9), and Laurent (10) have used dielectric constant to investigate compound formation in dilute organic solutions of



Dielectric Constants of Mixtures of HDEHP with TBP and TOPO and Some HDEHP-Metal Species with TBP. Total Organophosphorus Concentration Constant at the Level Indicated for Each Curve.

Fig. 3

Lewis acids and bases. In addition, we have attempted to provide a basis for comparison for the type of compounds of interest here by examining mixtures in which compound formation is known to occur. According to infrared measurements (5), HDEHP-TOPO is known to interact; and from extraction equilibria, $\text{NaA}\cdot 3\text{HA}\cdot \text{TBP}$, $\text{SrA}_2\cdot 4\text{HA}\cdot \text{TBP}$, and $\text{SrA}_2\cdot \text{TBP}$ are also known to interact. Supporting data for the latter interactions will be published later.

It can be demonstrated as follows that the dielectric constant of a mixture of two such solutions should be a linear combination of the dielectric constants of the two separate solutions, if no molecular interaction occurs. For dilute solutions of polar solutes in nonpolar solvents,

$$\epsilon_{1s} = \epsilon_s + \alpha_1 n_1,$$

$$\epsilon_{2s} = \epsilon_s + \alpha_2 n_2,$$

where α is the polarizability and n the volume concentration of the solute. When two dilute solutions are mixed, the dielectric constant of the mixture is:

$$\epsilon_m = \epsilon_s + \alpha_1 n_{1m} + \alpha_2 n_{2m}.$$

If there is no molecular interaction and hence the polarizability of the two species remain unchanged on mixing, that is, if $\alpha_{1m} = \alpha_1$, and $\alpha_{2m} = \alpha_2$, we may obtain by substitution:

$$\epsilon_m = \epsilon_s + n_{1m} \frac{\epsilon_{1s} - \epsilon_s}{n_1} + n_{2m} \frac{\epsilon_{2s} - \epsilon_s}{n_2}.$$

But n_{1m}/n_1 and n_{2m}/n_2 are the dilution ratios, that is, the volume fraction of each solution in the mixture. If we let $n_{2m}/n_2 = y$, and $n_{1m}/n_1 = 1-y$,

$$\epsilon_m = \epsilon_s + (1-y)(\epsilon_{1s} - \epsilon_s) + y(\epsilon_{2s} - \epsilon_s),$$

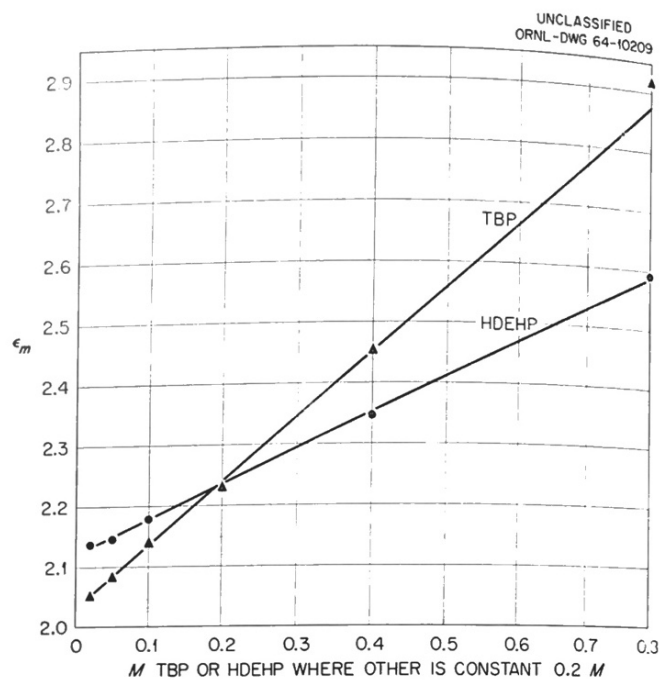
$$\epsilon_m = \epsilon_{1s} - y\epsilon_{1s} + y\epsilon_{2s},$$

$$\epsilon_m = y(\epsilon_{2s} - \epsilon_{1s}) + \epsilon_{1s}.$$

Figure 3 shows linear results in the TBP-HA system but not in the other systems. Thus, these results give evidence of moderately strong molecular interactions between HDEHP and TOPO (in agreement with the infrared work)⁵ and between TBP and the sodium and strontium species of HDEHP, but no evidence of interaction between TBP and HDEHP. Measurements of ϵ at constant TBP—varying HDEHP and constant HA—varying TBP further support the latter conclusion (Fig. 4) and serve to illustrate the linearity of ϵ with

concentration for these two mixtures well beyond the region for which conclusions were drawn.

These observations are consistent with the extraction equilibria in the TBP-DEHP system, which suggest a moderately strong interaction between TBP and the strontium complex or strontium salt (viz., the interaction producing the synergistic effect), a less strong interaction between TBP and the sodium complex, and little or no interaction between TBP and (HDEHP)₂.



Dielectric Constants of Solutions of TBP and HDEHP in a Constant 0.2 M Solution of the Other in *n*-Octane.

Fig. 4

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