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CHEMISTRY - SEPARATIONS
PROCESSES FOR PLUTONIUM
AND URANIUM

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DENSITY AND VISCOSITY OF SOLUTIONS IN THE TRIBUTYL PHOSPHATE PROCESS FOR URANIUM RECOVERY

BY

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TECHNICAL DIVISIONS

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1 Chemistry - Separation Processes
for Plutonium and Uranium

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DENSITY AND VISCOSITY OF SOLUTIONS IN

THE TRIBUTYL PHOSPHATE PROCESS FOR URANIUM RECOVERY

I. INTRODUCTION

The use of TBP (tributyl phosphate) for the recovery of uranium from waste solution by solvent extraction has been studied at ORNL. (1) In that work hexane and "Varsol" have been employed as diluents for the TBP. Deo Base has been considered as a diluent due to its low cost, availability and relatively high flash point (170°F.). It is a predominantly paraffinic hydrocarbon mixture boiling within the kerosene range and has a higher viscosity than hexane and "Varsol". The question then arises as to whether higher viscosities of the Deo Base - TBP systems, and a change in density differences between the two phases will lead to unsatisfactory column operation. The present discussion has as its primary purpose the presentation of preliminary density and viscosity data which may be of value in answering that question. 7

II. SUMMARY AND CONCLUSION

1. Density and viscosity data for solutions of $\text{UO}_2(\text{NO}_3)_2$ and HNO_3 in TBP mixtures are presented.
2. The density of a 15% by volume TBP solution in Deo Base changes on saturation with $\text{UO}_2(\text{NO}_3)_2$ from 0.808 to 0.891 gms/cc at 25°C. The viscosity changes from 18.3 millipoises to 25 millipoises. The effect of HNO_3 on these properties, especially viscosity, is much smaller.

A typical aqueous phase may vary in density from about 1.24 to 1.14 gms/cc while the viscosity changes from 14.4 to 13.1 millipoises. The differences in densities between the two phases is nearly the same as for Redox IA operation.

3. While the viscosity of the organic phase is fairly high, compared to the hexane solutions of the Redox Process, the changes in viscosity accompanying uranium extraction are relatively small.
4. Density and viscosity data for 15% TBP in Deo Base suggest that this solution does not deviate greatly from ideality but a small positive deviation from Raoult's law might be expected. The properties of solutions of HNO_3 , $\text{UO}_2(\text{NO}_3)_2$ and water in TBP are those expected as a result of strong interaction between the oxygen from the phosphate and molecules containing vacant orbitals or molecules capable of being polarized easily.
5. From the point of view of the variables, viscosity and density, it would appear that the solutions encountered in the TBP process neither introduce sufficiently detrimental factors nor possess properties far enough removed from successful operating experience such that they cannot be compensated for in column design.

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III. RESULTS

TBP is a colorless oily liquid having a boiling point of 289°C. at 760 mm. The density at 25°C. is 0.9730 and the viscosity 33.2 millipoises. It is nearly insoluble in water, about 0.2 gm per liter. The solubility of water in TBP is, on the other hand, about 64 gms per liter or 50 mole per cent. The vapor pressure and some chemical properties are discussed in HW-15172.

Deo Base is a petroleum fraction of the kerosene range having a boiling point of about 220 to 270°C. The density at 25°C. is 0.7804 and the viscosity 17.3 millipoises.

A solution of 15 volume per cent in Deo Base is not far from an ideal solution. The calculated density is 0.809 compared to an observed value of 0.808 at 25°C. The viscosity, a better indication of ideality, is calculated⁽²⁾ to be 18.8 millipoises compared to an observed value of 18.3. The difference of two per cent would indicate a slight positive deviation from Raoult's law.

In Table I the density, viscosity and composition of a number of solutions are listed. Figure 1 shows the density as a function of $\text{UO}_2(\text{NO}_3)_2$ concentration while Figure 2 is a similar plot of the viscosity. The density data can be related to composition by the equation

$$\rho_{25^\circ\text{C.}} = 0.808 + 0.328 \frac{M_{\text{UO}_2(\text{NO}_3)_2}}{M_{\text{HNO}_3}} + 0.028 \frac{M_{\text{HNO}_3}}{M_{\text{HNO}_3}}$$

The curve in Figure 1 is actually drawn through three points which have a nitric acid concentration of 0.03 M.

Table I

DENSITY AND VISCOSITY OF 15% TBP - DEO BASE SOLUTIONS
OF $\text{UO}_2(\text{NO}_3)_2$ AT 25°C.

$\text{UO}_2(\text{NO}_3)_2$ (M)	HNO_3 (M)	Density ρ gms/cc	Viscosity η millipoises
0	0	0.8081	18.3
0.0988	0.030	0.8407	20.8
0.198	0.034	0.8736	23.4
0.248	0.00	0.8885	24.9
0.253	0.030	0.8914	25.0
0	0.496	0.8218	18.7

The change in density and viscosity going from zero uranium content to saturation, 0.25 M., is relatively small by comparison to the hexone solutions encountered in the Redox Process. This results from the small range in concentration together with the comparatively high viscosity of the inert solvent Deo Base.

The effect of nitric acid on the density and especially on the viscosity is much smaller than of uranyl nitrate. Saturating the TBP - Deo Base with nitric acid,

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giving a solution 0.5 M in HNO_3 or a mole ratio of HNO_3 to TBP of 1:1, only raised the viscosity from 18.3 to 18.7 millipoises. It may be mentioned that water added to dry TBP or dry TBP - Deo Base mixtures has an affect on the viscosity slightly greater in magnitude than has HNO_3 . This is undoubtedly the result of strong hydrogen bonds which may lead to a chain structure in TBP - water mixtures.

A point of interest here is that the water content of TBP solutions decreases rapidly as uranyl nitrate is dissolved. Not only are hydrogen bonds holding water to TBP broken but the water molecules from the coordination sphere of $\text{UO}_2(\text{NO}_3)_2$ are eliminated when the uranyl group is surrounded by two TBP molecules. The steric hindrance imposed by the large $-\text{O}-\text{C}_4\text{H}_9$ groups may be a factor in water elimination. The high complexing ability of TBP for $\text{UO}_2(\text{NO}_3)_2$ compared to that of the aliphatic ketones and ethers suggests that the oxygen atom involved is very basic in character.

Data for representative aqueous solutions for a typical countercurrent extraction are listed in Table II. Solution IAS is the scrub solution, IAF, the metal feed, WR 4 represents a composition in the vicinity of the feed plate and WR-8 and WR-10 correspond to compositions towards the bottom of the extraction section.

Table II

DENSITY AND VISCOSITY AT 25°C. OF
AQUEOUS SOLUTIONS FOR URANIUM RECOVERY

<u>Solution</u>	<u>$\text{UO}_2(\text{NO}_3)_2$ (M)</u>	<u>Na_2SO_4 (M)</u>	<u>Na_3PO_4 (M)</u>	<u>NaNO_3 (M)</u>	<u>HNO_3 (M)</u>	<u>Density (gms/cc)</u>	<u>Viscosity (millipoises)</u>
IAS	0	0	0	0	4.0	1.1591	
IAF	0.188	0.18	0.16	1.81	3.0	1.2826	16.4
WR-4	0.152	0.12	0.10	1.21	3.2	1.2407	14.3
WR-8	0.136	0.12	0.10	1.21	3.2	1.2370	
WR-10	0.015	0.12	0.10	1.21	3.1	1.1976	13.2

Two factors of importance in column operation are the density difference between phases and the viscosity of the continuous phase. Comparison of data from Tables I and II show that the density difference changes from 0.27 in the scrub section through 0.35 at the feed plate to about 0.39 at the bottom of the column. This compares to 0.36 for the density difference in a IA Redox extraction. The lower aqueous viscosity as compared to a Redox IA system indicates a considerably higher sedimentation velocity for the organic phase droplets in the TBP system as compared to Redox. Also the organic phase is more viscous than in Redox, i.e., a range of 18.3 to 25.0 millipoises for 15% TBP - Deo Base compared to 6 to 13 millipoises for hexone in the Redox system. This would suggest a somewhat lower diffusion rate in the organic phase. On the other hand diffusion in the aqueous phase by the same argument would be more rapid. It is, of course, possible to modify both the density difference and the viscosity of the organic phase by substituting a small amount of another inert liquid for Deo Base, or changing the ratio of TBP to Deo Base.

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The above data were obtained from a few exploratory experiments and do not, of course, give the complete picture. From the information at hand, though, it is probable that these solutions neither introduce sufficiently detrimental factors nor possess properties far enough removed from successful operating experience such that they cannot be compensated for in column design.

IV. REFERENCES

1. ORNL-258, 260.
2. Glasstone, Laidler and Eyring. Theory of Rate Processes.

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