

A COMPARATIVE STUDY OF DONOR PROPERTIES OF SULPHOXIDES AND PHOSPHINE OXIDES IN SOLVENT EXTRACTION

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Abstract—A comparative study of the donor properties of sulphoxides and phosphine oxides in solvent extraction is reported. It was believed earlier that the stretching frequency of the phosphoryl group could serve as a measure of its basicity. In sulphoxides, however, the S→O frequency in different sulphoxides is nearly constant and cannot be a guide to their donor properties. A new method of assessing the relative donor strengths of both phosphine oxides and sulphoxides is described, based on the shift of the symmetric stretching frequency of OH of water on coordination with the donor. It is found that both phosphine oxides and sulphoxides form a single group, whose solvent extraction properties are determined by their relative donor strengths, as determined by this procedure.

The extractions of water, perchloric acid, hydrochloric acid and pertechnic acid by dibutyl sulphoxide (DBSO) are reported. The extracted species are $\text{H}_2\text{O} \cdot 2\text{DBSO}$ and $\text{H}_2\text{O} \cdot \text{HClO}_4$.

1. INTRODUCTION

ORGANO phosphorus compounds, where the function group $\text{P} \rightarrow \text{O}$ has basic properties, such as tri-*n*-butylphosphate, have found wide application as solvent extractants. However, only a few studies have been directed towards the general use of sulphoxides in solvent extraction although dimethyl sulphoxide is a good solvating agent. Korpak [1–3] has studied the extraction of some mineral acids and uranium salts by aliphatic sulphoxides, while extraction of thorium from hydrochloric acid solutions was investigated by Gaur *et al.* [4]. Recently during their studies on solvent extraction of some trivalent cations with mixed ligands, Sekine and Dryssen [5] have employed dibutyl sulphoxide as one of the ligands whose donor properties appear to be similar to those of tributyl phosphate as adduct formation constants are almost identical for dibutyl sulphoxide and tributyl phosphate. Moffitt [6] has concluded that in sulphoxides, the sulphur-oxygen linkage is essentially a double bond. A similar conclusion was reached by Pauling [7] on the basis of his charge neutralization postulate. Sulphur has vacant 3*d* orbitals which could be used in bond formation. Craig *et al.* [8] have indicated that when sulphur is attached to oxygen, which has compact *pπ* orbitals, their overlap with sulphur *d* orbitals is small. However, the fractional positive charge on the sulphur

1. W. Korpak, *Nukleonika* **7**, 715 (1962).
2. W. Korpak, *Nukleonika* **8**, 747 (1963).
3. W. Korpak, *Nukleonika* **9**, 1 (1964).
4. P. K. Gaur, S. R. Mohanty and A. S. Reddy, *Proc. Symp. Nucl. Rad. Chem.*, p. 56. Waltair (1966).
5. T. Sekine and D. Dyrssen, *J. inorg. nucl. Chem.* **29**, 1481 (1967).
6. W. Moffitt, *Proc. R. Soc. A* **200**, 409 (1950).
7. L. Pauling, *J. phys. Chem.* **56**, 361 (1952).
8. D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. chem. Soc.* 332 (1954).

(due to the polar character of the σ bond) contracts its d orbitals so they become commensurate with the p orbitals of oxygen, thus improving the overlap. In later studies Craig and Magnusson[9] showed that the overlap between the d orbitals of sulphur and the p orbitals of oxygen is substantial. Thus $\text{S}=\text{O}$ bonds also have a substantial amount of double bond character, as in $\text{P}=\text{O}$, arising from $d\pi-p\pi$ interactions.

This paper presents a systematic investigation of the donor properties of some sulfoxides and the corresponding organo phosphorus compounds.

2. EXPERIMENTAL

Dibutyl sulfoxide (DBSO), diphenyl sulfoxide (DPSO), tributyl phosphate (TBP), tri-*n*-butyl phosphine oxide (TBPO) tri-*n*-octylphosphine oxide (TOPO) and triphenylphosphine oxide (TPPO) were obtained from Eastman Organic Chemicals. Perchloric acid employed was Baker "Analysed quality" while hydrochloric acid was of E. Merck, G. R. grade. Ammonium pertechnetate used in these studies were obtained from the Oak Ridge National Laboratory, U.S.A.

Benzene solutions of sulfoxides and phosphine oxides were used as organic phase in the solvent extraction experiments. For infrared work Eastman Organic Chemicals "Spectro" grade carbon tetrachloride served as the diluent instead of benzene. Equal volumes of organic and aqueous phases were equilibrated for 10 min and the phases separated by centrifuging. The course of extraction was followed by i.r. analysis in the case of water, titrations in the case of acids and spectrophotometry for NH_4TcO_4 .

3. RESULTS AND DISCUSSIONS

3.1. *Donor properties of sulfoxides.* The donor properties of coordinating agents like phosphine oxides, sulfoxides sulphones, etc., were examined by Drago *et al.*[10] and Joesten and Drago[11]. They measured the shift in the i.r. frequency of the OH stretching in phenol on adduct formation with a donor. A linear relationship between $\Delta\nu_{\text{OH}}$ and the enthalpy of adduct formation was observed. Dimethyl sulfoxide (DMSO) obeys this relationship and is a poor donor as compared to triphenyl, trimethyl and triethylphosphine oxides, while it is slightly better than triethylphosphate. It appears that substitution of longer alkyl chains increases the donor properties of the phosphoryl group while the reverse is the case if phenyl groups are present. These considerations show that DBSO (one of the compounds of the present studies) is expected to be a better donor than DMSO. In solvent extraction work, it would be useful to study the extraction of water itself. Analogous to the shift in OH frequency of phenol on adduct formation, Whitney and Diamond[12] and Conocchioli *et al.*[13] observed a shift of the 3640 cm^{-1} symmetric frequency of water on coordination and extraction by TBP and TOPO. This frequency shifts to 3450 cm^{-1} on coordination with TBP, while it shifts to 3370 cm^{-1} for TOPO. In the present studies equal molarities of DBSO, DPSO,

9. D. P. Craig and E. A. Magnusson, *J. chem. Soc.* 4895 (1956).
10. R. S. Drago, B. Wayland and R. N. Carlson, *J. Am. chem. Soc.* **85**, 3125 (1963).
11. M. D. Joesten and R. S. Drago, *J. Am. chem. Soc.* **84**, 3817 (1962).
12. D. C. Whitney and R. M. Diamond, *J. phys. Chem.* **67**, 209 (1963).
13. T. J. Conocchioli, M. I. Tocher and R. M. Diamond, *J. phys. Chem.* **69**, 1106 (1965).

TBPO and TPPO in carbon tetrachloride were equilibrated with triple distilled water. The i.r. spectra of the organic phase in the 3000–4000 cm^{-1} region were recorded on Perkin Elmer recording spectrophotometer, model 21 using a LiCl prism and CaF_2 cell (path length 0.1 mm). Carbon tetrachloride preequilibrated with triple distilled water was used as the blank. The i.r. shifts are tabulated along with the known shifts for TBP and TOPO in Table 1.

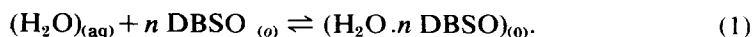
Table 1. Shift of the OH frequency of coordinated water bonded to different extrac-
tants. OH frequency of uncoordinated water 3640 cm^{-1}

Compounds	$\nu_s \rightarrow 0$ or $\nu_p \rightarrow 0$	Position of ν_{OH} on extraction	$\Delta\nu_{\text{OH}}$
Diphenylsulphoxide, DPSO	1050	3480	160
Triphenylphosphine oxide, TPPO	1200	3450	190
Tributylphosphate, TBP	1275	3450	190
Dibutylsulphoxide, DBSO	1040	3420	220
Tributylphosphine oxide, TBPO	1160	3400	240
Tri- <i>n</i> -octylphosphine oxide, TOPO	1150	3370	270

It was earlier believed[14–16] that the infrared frequency of the phosphoryl group could serve as a measure of its basicity. In sulfoxides, however, the $\text{S} \rightarrow \text{O}$ frequency in different compounds is nearly constant and thus could not be a guide to their donor properties. On the other hand the increase in values of $\Delta\nu_{\text{OH}}$ in Table 1 clearly indicates the increase in donor strenghts of the solvating agents. The shift in OH frequency is a result of hydrogen bonding of water with these compounds with a corresponding weakening of the OH bond. Thus this appears to be a better measure of their relative donor strengths than the i.r. frequencies of their functional groups alone. It is seen that both the phosphine oxides and sulfoxides from a single group whose solvent extraction properties can be assessed by this procedure.

3.2. *Extraction of water.* Different molarities of DBSO (0.75, 1.0 and 2.0 M) in CCl_4 were equilibrated with equal volumes of triple distilled water for 10 min. The phases were separated by centrifuging. The i.r. spectra of the organic phase was recorded as mentioned earlier. DBSO itself has no absorption in the region of interest. The peaks for the coordinated water are seen at 3690 cm^{-1} and 3420 cm^{-1} . Since the optical density was greater for the peak at 3420 cm^{-1} , in interpolating the amount of coordinated water, the OD values at this wavelength have been used. It is assumed that the concentration of water bound to DBSO is proportional to the optical density.

For the equilibrium under study one can write



14. L. L. Burger, *USAEC Rep.*, HW 4488 (1957).

15. L. L. Burger, *J. phys. Chem.* **62**, 590 (1958).

16. L. C. Thomas and R. A. Chittenden, *Spectrochim. Acta* **20**, 467, and 489 (1964).

The equilibrium constant is given by

$$K = \frac{(\text{H}_2\text{O} \cdot n\text{DBSO})_{(0)}}{(\text{H}_2\text{O}) \cdot (\text{DBSO})_{(0)}^n} = \frac{[\text{H}_2\text{O} \cdot n\text{DBSO}]_{(0)} \gamma_{\text{H}_2\text{O} \cdot n\text{DBSO}}}{[\text{DBSO}]_{(0)}^n \gamma_{\text{DBSO}}^n (\text{H}_2\text{O})_{(\text{aq})}} \quad (2)$$

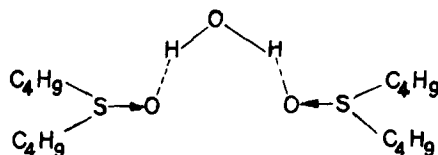
The square brackets refer to concentration and γ to the activity coefficients. Following the treatment of Conocchioli *et al.* [13] the ratio of the activity coefficients was assumed to be constant. Hence Equation (2) may be rewritten as

$$K' = \frac{[\text{H}_2\text{O} \cdot n\text{DBSO}]_{(0)}}{[\text{DBSO}]_{(0)}^n (\text{H}_2\text{O})_{(\text{aq})}} \quad (3)$$

Taking logarithms and rearranging of the terms one gets

$$\log [\text{H}_2\text{O} \cdot n\text{DBSO}] = n \log [\text{DBSO}] + \log K' + \log (\text{H}_2\text{O}). \quad (4)$$

Since water activity can be taken as constant, a plot of $\log [\text{H}_2\text{O} \cdot n\text{DBSO}]$ against $\log [\text{DBSO}]$ will give the number of DBSO molecules coordinated with one molecule of water. A plot of $\log OD$ obtained in this study against $\log [\text{DBSO}]$ is shown in Fig. 1. A slope of nearly 2 is obtained, indicating that two molecules of DBSO are coordinated to one molecule of water:



This is in contrast to TBP-H₂O and TOPO-H₂O systems where the ratio is 1:1. In view of this difference one can imagine a situation wherein for a given concentration of DBSO, the number of free DBSO molecules available for coordination with solutes other than water will be smaller as compared to TBP or TOPO of the same concentration. This might result in a lowering of the extraction efficiency in DBSO systems.

3.3. Extraction of acids with DBSO. In solvent extraction studies of inorganic species, extraction of strong acids by basic extractants has attracted considerable attention [12, 13]. The active group of the extractants either had a basic nitrogen or oxygen donor. Investigations have been reported with tertiary alkylamines, tertiary alkyl and alkoxyphosphine oxides, ethers and ketones. The sulfoxides have not been studied extensively.

Perchloric acid solutions were prepared by dilution with distilled water. The solutions were standardized by titrating with NaOH to the phenolphthalein end point. Benzene was used as diluent for DBSO.

In one set of experiments the concentration of DBSO was kept constant at 0.1 M and the perchloric acid concentration in the aqueous phase was varied. In the other set different molarities of DBSO in benzene were used for the acid extraction at fixed perchloric acid concentration (3 M).

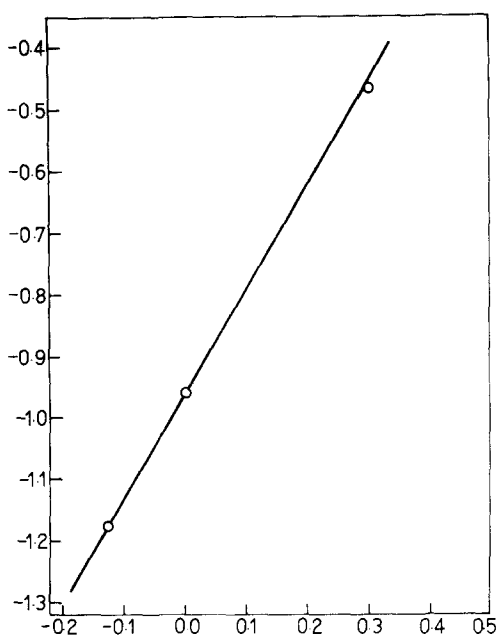
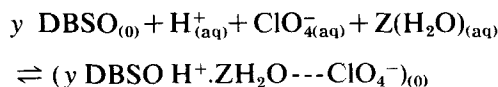


Fig. 1. Extraction of water with DBSO. y axis: Log optical density of O-H at 2.92μ , $1 \text{ cm} = 0.05$; x axis: Log DBSO molarity, $1 \text{ cm} = 0.05$.

The general equilibrium for the extraction of perchloric acid by DBSO may be represented as



or



Equation (5) represents the perchloric acid as an ion pair in the organic phase while Equation (6) represents it as dissociated ions. In order to find out whether perchloric acid is extracted as an ion pair or as dissociated ions, one can study the dependence of the extraction on perchloric acid concentration and analyse the data. The equilibrium constants for Equations (5) and (6) can be written as:

$$K_{\text{HClO}_4} = \frac{[y \text{ DBSO} \cdot \text{H}^+ \cdot z\text{H}_2\text{O} \cdots \text{ClO}_4^-]_{(0)} \cdot \gamma}{(\text{HClO}_4)_{(\text{aq})} (\text{H}_2\text{O})_{(\text{aq})}^z [\text{DBSO}]_{(0)}^y \cdot \gamma_{\text{DBSO}}^y} \\ = \frac{[y \text{ DBSO} \cdot \text{H}^+ \cdot z\text{H}_2\text{O}]_{(0)} \cdot \gamma + (\text{H}) [\text{ClO}_4^-]_{(0)} \cdot \gamma (\text{ClO}_4^-)}{(\text{HClO}_4)_{(\text{aq})} (\text{H}_2\text{O})_{(\text{aq})}^z [\text{DBSO}]_{(0)}^y \cdot \gamma_{\text{DBSO}}^y} \quad (8)$$

Equations (7) and (8) can be made easier to solve if it is realized that $[y \cdot \text{DBSO} \cdot \text{H}^+ \cdot z\text{H}_2\text{O} \cdots \text{ClO}_4^-] \cdot \gamma = [\text{H}^+]_{(0)} \cdot \gamma$ and $[y \text{ DBSO} \cdot \text{H}^+ \cdot z\text{H}_2\text{O}] \cdot \gamma + [\text{ClO}_4^-] \cdot \gamma =$

$[H^+]_{(0)}^2 \cdot \gamma_{\pm}^2$, where $[H^+]_{(0)}$ is the hydrogen ion concentration in the organic phase. Generally the numerator is equal to $[H^+]_{(0)}^x \gamma_{H^+}^x$, where $x=1$ for the ion pair and $x=2$ for the dissociated ions. Once again the ratio of the activity coefficients ($\gamma_{H^+}^x/\gamma_{BBSO}^x$) in the organic phase may be assumed to be constant. Thus

$$K'_{HClO_4} = \frac{[H^+]_{(0)}^x}{(HClO_4)_{(aq)}(H_2O)_{(aq)}^y [DBSO]^y} \quad (9)$$

At constant activity of DBSO and water

$$x \log [H^+]_{(0)} = \log a_{HClO_4(aq)} + \log K''_{HClO_4} \quad (10)$$

A plot of Equation 10 should give a straight line with a slope $1/x$. Such an analysis is shown in Fig. 2 which shows that the slope $1/x$ is equal to 1 or $x=1$. In other words perchloric acid is extracted as an ion pair rather than as dissociated ions. This is also in keeping with the fact that there is very little dissociation of ion pairs in benzene.

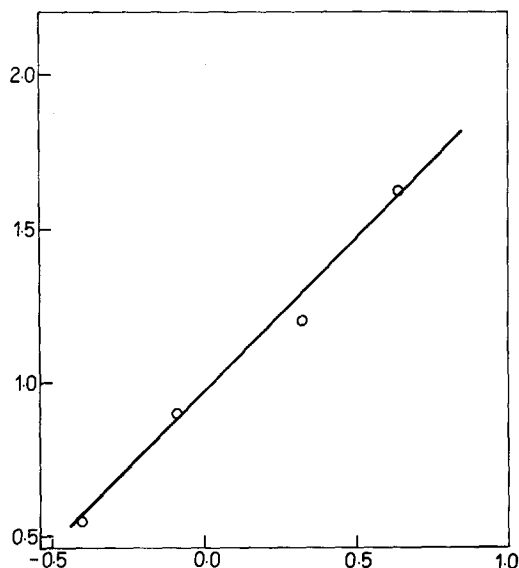


Fig. 2. Extraction of perchloric acid with DBSO.
y axis: Log mmole $H^+_{(0)}$, 1 cm = 0.1; x axis
Log $a_{\pm HClO_4}$, 1 cm = 0.1.

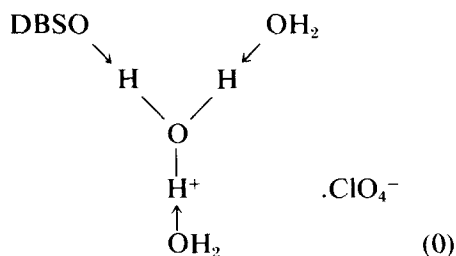
Equation (9) may also be used for the determination of the number of DBSO molecules associated with one ion pair. Since x is found to be unity, at constant activities of perchloric acid and water one can derive from Equation (9)

$$\log D = y \log [DBSO] + \log K''_{HClO_4} \quad (11)$$

where D is the ratio of total $H^+_{(0)}/H^+_{(aq)}$. Figure 3 gives a plot of $\log D$ against \log

[DBSO], which shows that the dependence on DBSO is ~ 1 indicating that only one DBSO molecule is associated with the extracted species.

The extraction of strong acids like perchloric acid by basic extractants involves competition between the basic extractant, the anion and water for the proton. In aqueous solutions the proton exists as the hydronium ion H_3O^+ . Using a mass spectrometer with a field emission source, Becay[17] has shown the existence of singly charged species with masses corresponding to H_3O^+ , H_5O_2^+ , H_7O_3^+ and H_9O_4^+ . He suggested that H_9O_4^+ could be the main species in the absence of a field. On the basis of the above evidence Whitney and Diamond [12] have concluded that in dilute acid solutions the proton is present as the tri-hydrated hydronium ion. The basic organic compounds such as TBP and TOPO compete with water for the solvation of the hydronium ion. The primary hydration cell of the hydronium ion is replaced by a solvent cage. However, with its marked affinity for water, DBSO probably cannot replace the entire primary hydration shell of the hydronium ion. The DBSO proton ratio was determined above to be unity. Thus one can formulate a possible structure for the extracted species of perchloric acid as



The extraction of hydrochloric acid with DBSO dissolved in benzene was studied similarly. The data is shown in Fig. 4. Compared with the extraction of HCl with TOPO[18] that by DBSO does not show any saturation effect at higher molarity. The extraction of HCl is enough to compete with the extraction of other inorganic species at tracer level from hydrochloric acid solutions.

3.4. *Non extraction of technetium (VII) with DBSO.* In view of the extraction of perchloric acid by DBSO it was thought worthwhile to extend the observation to the extraction of pertechnic acid (HTcO_4). The high extinction coefficient of TcO_4^- at $\sim 290 \text{ m}\mu$ could be used to carry out the investigation at a low concentration of HTcO_4 . $5 \times 10^{-4} \text{ M}$ solutions of NH_4TcO_4 containing an equivalent amount of HCl was extracted with 0.1 M DBSO in benzene and the optical density of the aqueous phase was measured directly before and after the extraction on a Beckman DU spectrophotometer at $290 \text{ m}\mu$. No extraction was observed.

The extraction experiments were repeated in 1 M HCl medium to find out whether HTcO_4 is co-extracted with HCl. No extraction was observed in this

17. H. D. Z. Becay, *Z. Naturf.* **14A**, 712 (1959).

18. J. C. White and W. J. Ross, *Separation by solvent extraction with tri-n-octylphosphine oxide*, NAS-NS-3102 (1961).

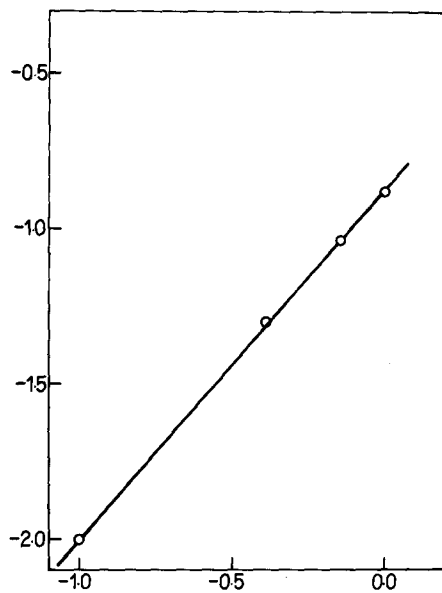


Fig. 3. Extraction of perchloric acid with DBSO: solvent dependency. y axis: Log D, 1 cm=0.1; x axis: Log DBSO molarity, 1 cm=0.1.

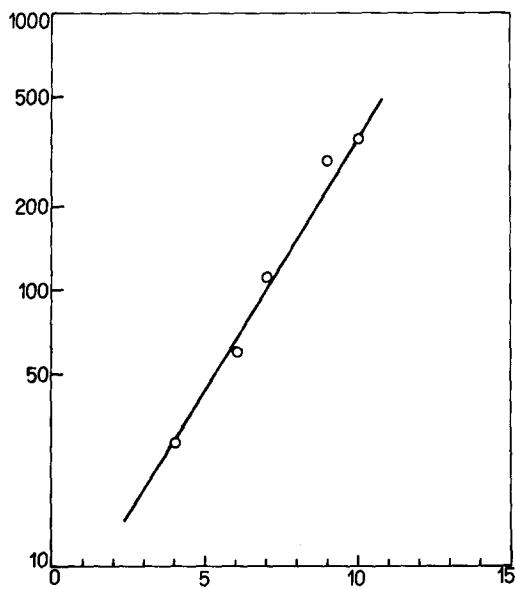


Fig. 4. Extraction of HCl with DBSO. y axis: Acid extracted (mmole); x axis: HCl molarity, 1 cm=1.

case either. This behaviour is very different from the ready extraction of Tc(VII) by organophosphorus compounds[19].

3.5. *Extraction of technetium (VII) with phosphine oxides.* In their work on the solvent extraction of heptavalent technetium, Boyd and Larson[19] noted that the presence of donor atoms in the molecule of the extractants was not a sufficient condition for extraction. Their data do not support any correlation between the solvent basicity as given by the i.r. frequency and the percentage extraction of Tc(VII). They considered the polar nature of the TBP molecule important for the extraction of Tc(VII) and found tri-*n*-alkylphosphine oxides as usual to be better than TBP. The length of the alkyl chains attached to $P \rightarrow O$ appeared to be unimportant, as shown by the approximately equal distribution coefficients for tri-*n*-hexylphosphine oxide, TOPO and tri-*n*-decylphosphine oxide. Branching in the straight chain, however, reduced the distribution coefficient.

We have studied the extraction of pertechnetate from hydrochloric and sulphuric acid solutions with TOPO and TPPO and have found a remarkable contrast in their behaviour. The course of extraction was followed spectrophotometrically, as mentioned earlier. The data given in Table 2 clearly show TPPO,

Table 2. Percentage extraction of TcO_4^-
(5×10^{-4} M)

Acid	0.1 M TOPO in benzene	0.1 M TPPO in benzene
HCl 0.05 N	41.8	Nil
0.1 N	58.1	Nil
0.5 N	85.9	Nil
1.0 N	93.2	Nil
H ₂ SO ₄ 0.01 N	15.8	Nil
0.05 N	32.3	Nil
0.1 N	39.3	Nil
0.8 N	83.3	Nil

though more basic than TBP as shown by i.r. frequency of its $P \rightarrow O$ group, is a relatively very poor extractant for $HTcO_4$. On the other hand the relative donor strength of TPPO by our method is less than that of TBP and much less than of TOPO. Thus the extraction of $HTcO_4$ could be very low.

CONCLUSION

It has been clearly brought out by the data presented here, as well as those of other workers like Boyd and Larson[19], that a mere knowledge of the i.r. frequency of $P \rightarrow O$ and $S \rightarrow O$ groups will not directly give a measure of the donor properties of the solvents containing these groups. This is especially so with sulfoxides where the i.r. frequency of $S \rightarrow O$ in DMSO, DMSO and TMSO is approximately the same ($\sim 1045 \text{ cm}^{-1}$). It is suggested that the shift in the symmetric frequency of coordinated water from the value of 3640 cm^{-1} is a reliable guide to the solvent donor strength.

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