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Potentiometric analysis of Dimethyl Sulfoxide, Di-n-octyl Sulfoxide, Diphenyl Sulfoxide, p-di-tolyl Sulfoxide and Indium Complex of Diphenyl Sulfoxide in Non Aqueous Solvents

Swaroopa Rani N. Gupta
Department of Chemistry, Brijlal Biyani Science College, Amravati, Maharashtra, India
swargupta@yahoo.com

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Abstract

In medicine Dimethyl Sulfoxide is predominantly used as a topical analgesic, a vehicle for topical application of pharmaceuticals, as an anti-inflammatory, and an antioxidant. This paper deals with Potentiometric Analysis of Dimethyl Sulfoxide, Di-n-octyl Sulfoxide, Diphenyl Sulfoxide, p-di-tolyl Sulfoxide and Indium Complex of Diphenyl Sulfoxide in Non Aqueous Solvents such as sulphuric acid, phosphoric acid, glacial acetic acid and acetic anhydride. In present analysis two types of potentiometric titrations Oxidation-Reduction and Acid-Base titrations in nonaqueous solvents have been performed, and interest is focused upon changes in the e.m.f. of an electrolytic cell as a titrant of precisely known concentration is added to a solution of the analyte. OSAW direct reading potentiometer was used to carry out redox titrations using platinum and saturated calomel electrodes. The pH-titrations were made with an ELICO LI-10 pH-meter in conjunction with Glass (EM-42) and calomel (ER-70) electrodes. An end point is located more precisely by plotting successive values of the rate of change of cell e.m.f. vs each increment of titrant in the vicinity of the inflection point. The position of the maximum on the first derivative curve corresponds to the inflection point on the normal titration curve. Fairly accurate results with high degree of precision are observed.

Keywords: Dimethyl Sulfoxide, Di-n-octyl Sulfoxide, Diphenyl Sulfoxide, p-di-tolyl Sulfoxide, Indium Complex of Diphenyl Sulfoxide.

Introduction

DMSO is frequently used as a solvent for chemical reactions involving salts, most notably Finkelstein reactions and other nucleophilic substitutions. It is also extensively used as an extractant in biochemistry and cell biology[1]. Because of its ability to dissolve many kinds of compounds, DMSO plays a role in sample management and high-throughput screening operations in drug design[2]. In medicine, DMSO is predominantly used as a topical analgesic, a vehicle for topical application of pharmaceuticals, as an anti-inflammatory, and an antioxidant[3]. Because DMSO increases the rate of absorption of some compounds through organic tissues, including skin, it is used in some transdermal drug delivery systems. Its effect may be enhanced with the addition of EDTA. It is frequently compounded with antifungal medications, enabling them to penetrate not just skin but also toe and fingernails. In medical research, DMSO is often used as a drug vehicle in *in vivo* and *in vitro* experiments. DMSO is commonly used in veterinary medicine as a liniment for horses, alone or in combination with other ingredients.

An investigation was conducted to develop a method for the direct analysis of DMSO in blood and cerebrospinal fluid by gas liquid chromatography[4]. The equilibrium constants for the association between sulfoxides and phenol in toluene at 27 ± 1°C obey the Hammett relationship[5]. Extraction behavior of plutonium (IV), uranium (VI), and some fission products from aqueous nitric acid media with di-n-octylsulfoxide (DOSO) has been studied over a wide range of conditions[6]. Determination of Dimethyl sulfoxide was also done in air[7]. A novel and highly specific method has been developed for the determination of dimethyl sulfoxide (DMSO) at nanomolar levels in aqueous solution by gas chromatography[8]. ^{31}P NMR and IR studies of the interaction of tributyl phosphate (TBP) and di-n-octyl sulfoxide (DOSO) with polymer molecules of uranyl di-2-ethylhexyl phosphate $(UO_2X_2)_p$ (I) in C_6H_6 solutions have been reported[9]. A chemoreduction-purge-and-trap gas chromatographic method has been developed for the determination of trace dimethylsulfoxide (DMSO) in seawater[10].

Sulfoxides are frequently used in organic synthesis as chiral auxiliaries and reagents to mediate a wide variety of chemical transformations. Diphenyl sulfoxide and triflic anhydride can be used to activate a wide range of glycosyl donors including hemiacetals, glycals and thioglycosides. Mechanistic Studies on a Sulfoxide Transfer Reaction Mediated by Diphenyl Sulfoxide/Triflic Anhydride was done[11].

This paper deals with Potentiometric Analysis of Dimethyl Sulfoxide, Di-n-octyl Sulfoxide, Diphenyl Sulfoxide, p-di-tolyl Sulfoxide and Indium Complex of Diphenyl Sulfoxide in Non Aqueous Solvents such as sulphuric acid, phosphoric acid, glacial acetic acid and acetic anhydride. In present analysis two types of potentiometric titrations Oxidation-Reduction and Acid-Base titrations in nonaqueous solvents have been performed, and interest is focused upon changes in the e.m.f. of an electrolytic cell as a titrant of precisely known concentration is added to a solution of the analyte namely dimethyl sulfoxide, di-n-octyl sulfoxide, diphenyl sulfoxide, p-di-tolyl sulfoxide and indium complex of diphenyl sulfoxide.

Methodology

All chemicals were of A. R. grade. Solvents were purified before use. Sulfoxide samples were synthesized from A.R. grade chemicals. 0.1 N perchloric acid was prepared by adding 8.5 ml of 72% perchloric acid slowly with continuous stirring to 900 ml of purified dioxane followed by 30 ml of acetic anhydride. The mixture was allowed to stand for 24 hr before use and then standardized it by titrating potentiometrically with standard solution of potassium hydrogenphthlate. OSAW direct reading potentiometer was used to carry out redox titrations using platinum and saturated calomel electrodes. The pH-titrations were made with an ELICO LI-10 pH-meter in conjunction with Glass (EM-42) and calomel (ER-70) electrodes.

Redox titrations of sulfoxides: 25 ml of sample solution containing about 0.2 g accurately weighed dimethyl sulfoxide in 2M sulphuric acid was taken in a reaction vessel and the titration was performed with addition of standard potassium permanganate solution in 2 M sulphuric acid using platinum-calomel electrode system.

In the similar way 37.5 ml of dimethyl sulfoxide solution (≃ 0.2 g dimethyl sulfoxide) in 2 M H_2SO_4 – 2.67 M H_3PO_4 mixture was titrated with standard solution of $KMnO_4$ in 2 M H_2SO_4.

In case of di-n-octyl sulfoxide, diphenyl sulfoxide, p-di-tolyl sulfoxide and indium complex of diphenyl sulfoxide, 0.1 g accurately weighed sample was dissolved in 10ml of glacial acetic acid and titrated with standard solution of $KMnO_4$ in 2 M H_2SO_4. The e.m.f. was plotted against volume of titrant and $\Delta E/\Delta V$ against V. Hence the equivalence point was deduced.

Titration of sulfoxides in acetic anhydride: An accurately weighed 0.01-0.1 g sample of dimethyl sulfoxide, di-n-octyl sulfoxide, diphenyl sulfoxide, p-di-tolyl sulfoxide and indium complex of dipenyl sulfoxide was dissolved in 15 ml of acetic anhydride and titrated potentiometrically with freshly standardized 0.09 N perchloric acid in dioxane. The end points of the titration curves were detected with a glass-calomel electrode couple.

Observation: Redox titration curves and corresponding first derivative plots for dimethyl sulfoxide, di-n-octyl sulfoxide, diphenyl sulfoxide, p-di-tolyl sulfoxide and indium complex of dipenyl sulfoxide are shown in Figure 1 to 6. Titration curves of dimethyl sulfoxide, di-n-octyl sulfoxide, diphenyl sulfoxide, p-di-tolyl sulfoxide and indium complex of dipenyl sulfoxide in acetic anhydride are shown in Figure 7 to 11. Over most of titration range the cell e.m.f. varies gradually, but near the end point the cell e.m.f. changes vary abruptly as the logarithm of the concentration undergoes a rapid variation.

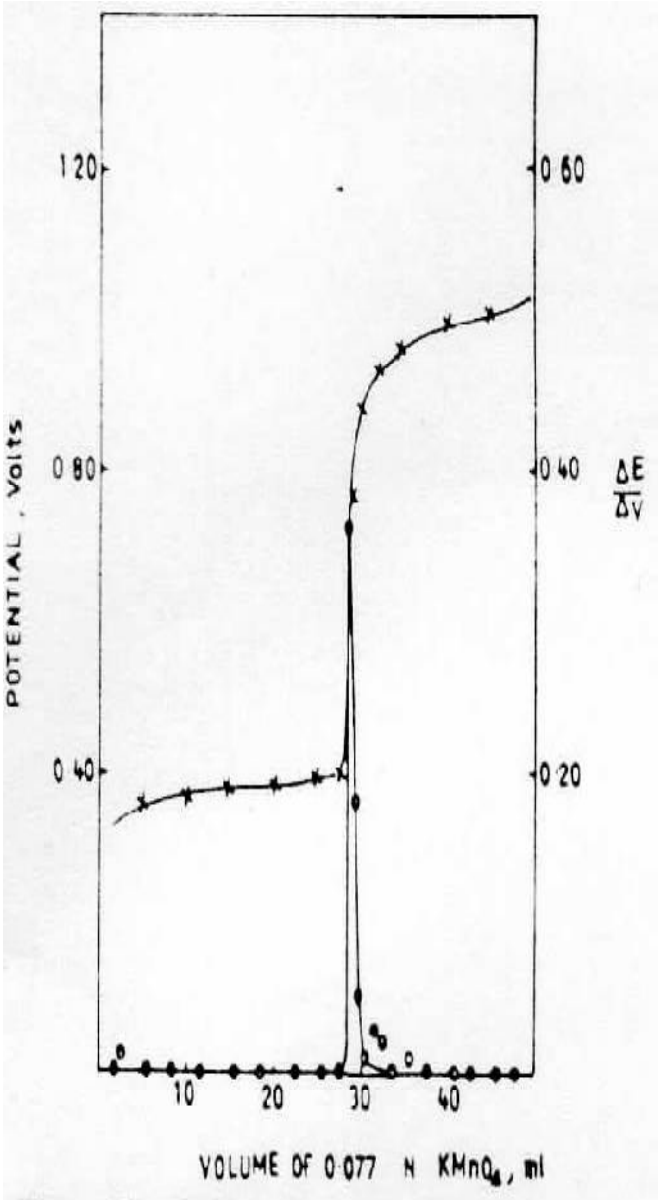


Figure-1
Redox Titration of dimethyl sulfoxide in 2 M H_2SO_4 with 0.077 N $KMnO_4$ in 2M H_2SO_4

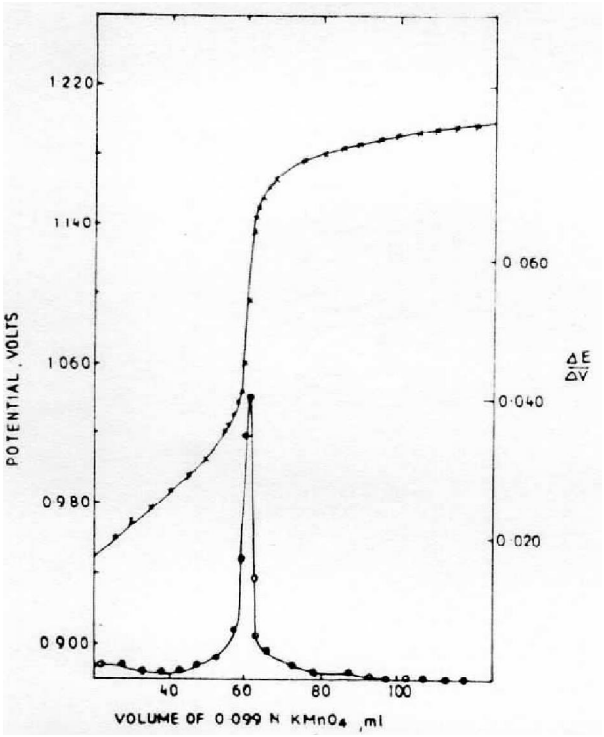


Figure-2
Redox Titration of dimethyl sulfoxide in 2 M H_2SO_4 - 2.67 M H_3PO_4 with 0.099 N $KMnO_4$ in 2M H_2SO_4

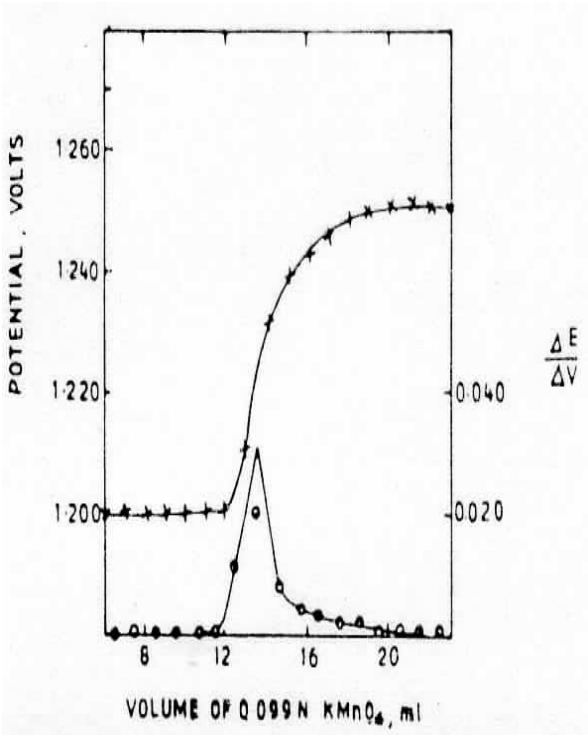


Figure-4
Redox Titration of Diphenyl sulfoxide in glacial acetic acid with 0.099 N $KMnO_4$ in 2M H_2SO_4

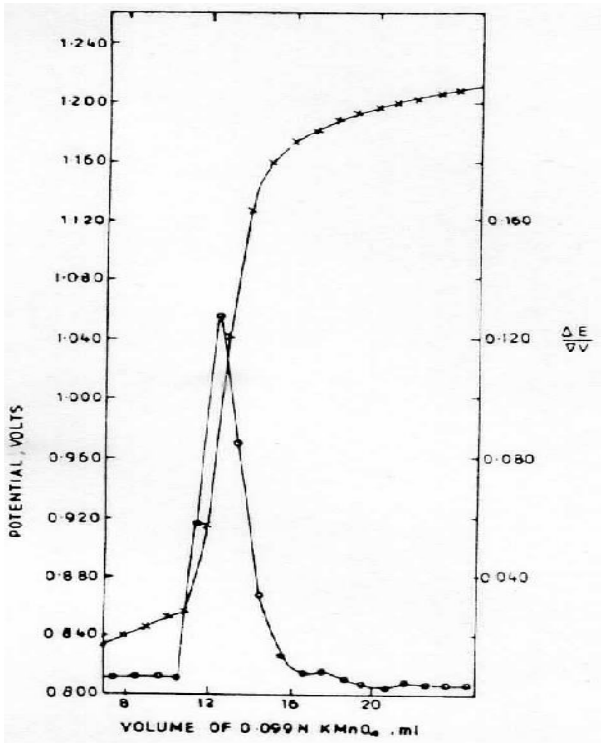


Figure-3
Redox Titration of di-n-octyl sulfoxide in glacial acetic acid with 0.099 N $KMnO_4$ in 2M H_2SO_4

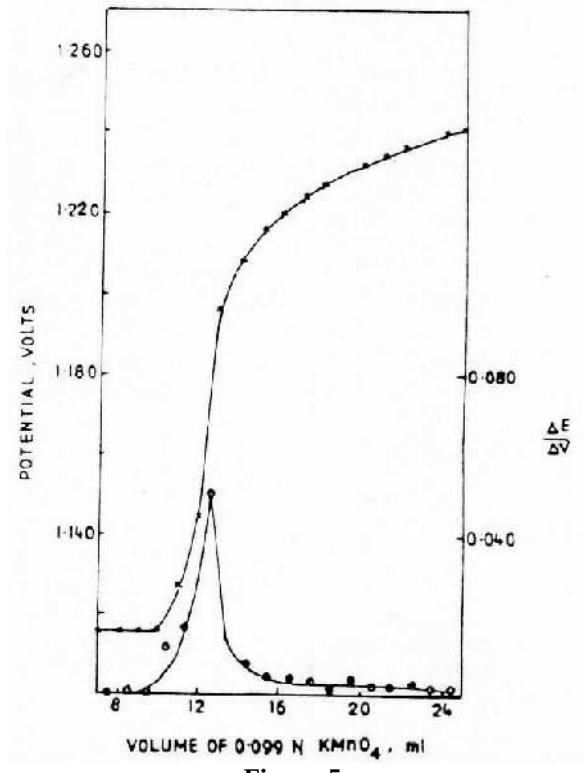


Figure-5
Redox Titration of p-di-tolyl sulfoxide in glacial acetic acid with 0.099 N $KMnO_4$ in 2M H_2SO_4

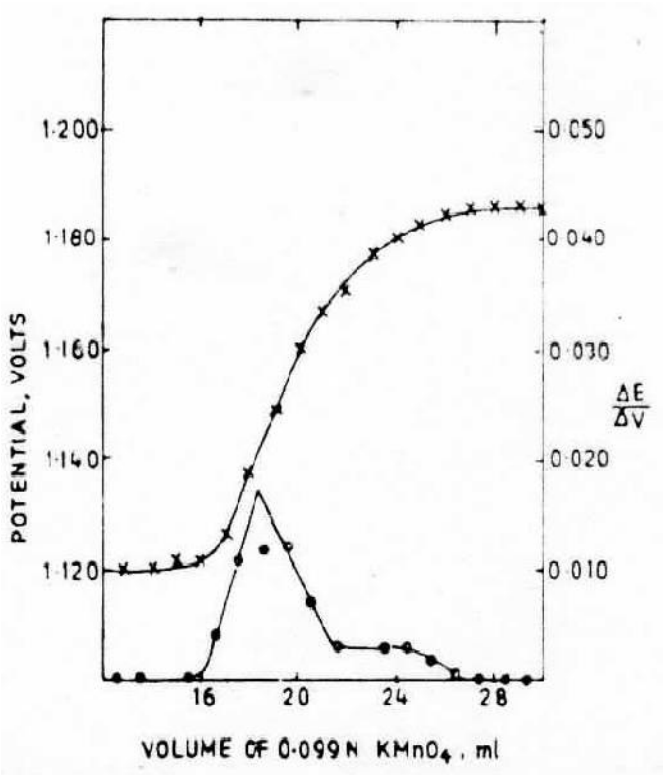


Figure-6
Redox Titration of Indium complex of Diphenyl sulfoxide in glacial acetic acid with 0.099 N $KMnO_4$ in 2M H_2SO_4

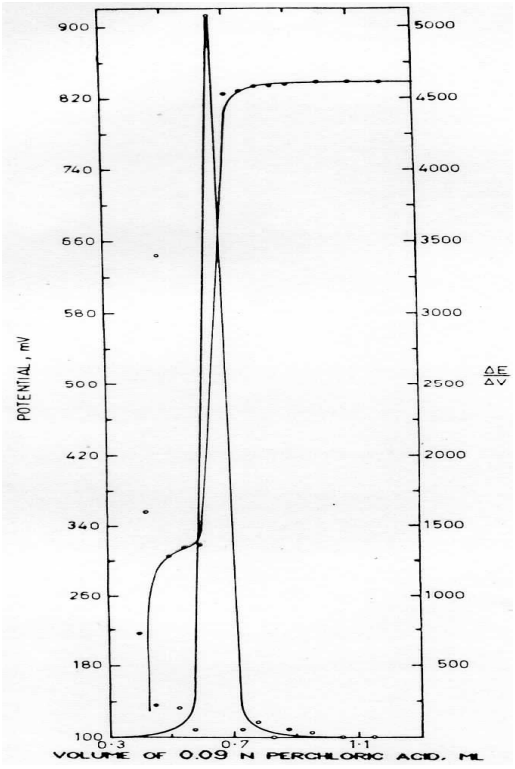


Figure-8
Titration of di-n-octyl sulfoxide in acetic anhydride with 0.09 N $HClO_4$ in dioxane

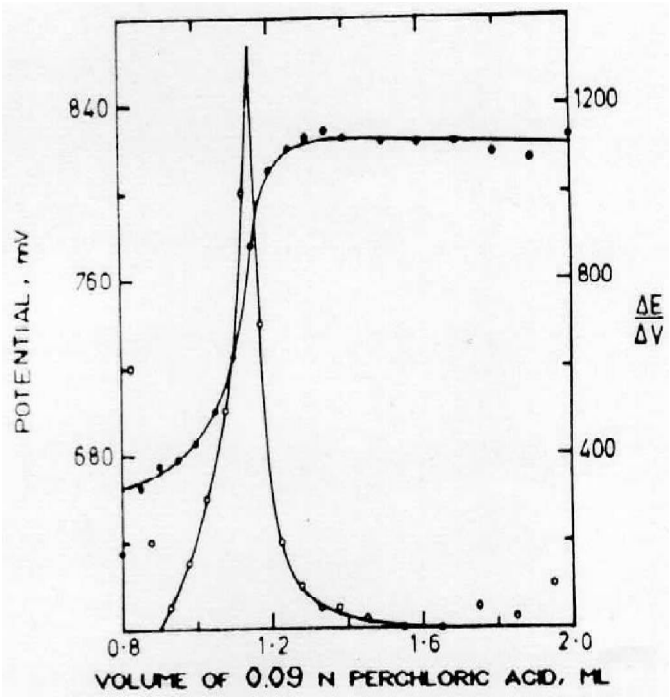


Figure-7
Titration of Dimethyl sulfoxide in acetic anhydride with 0.099 N $KMnO_4$ in 2M H_2SO_4

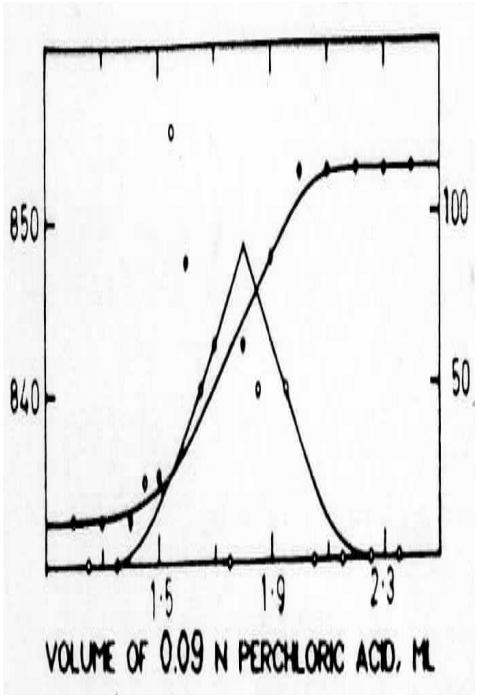


Figure-9
Titration of diphenyl sulfoxide in acetic anhydride with 0.09 N $HClO_4$ in dioxane

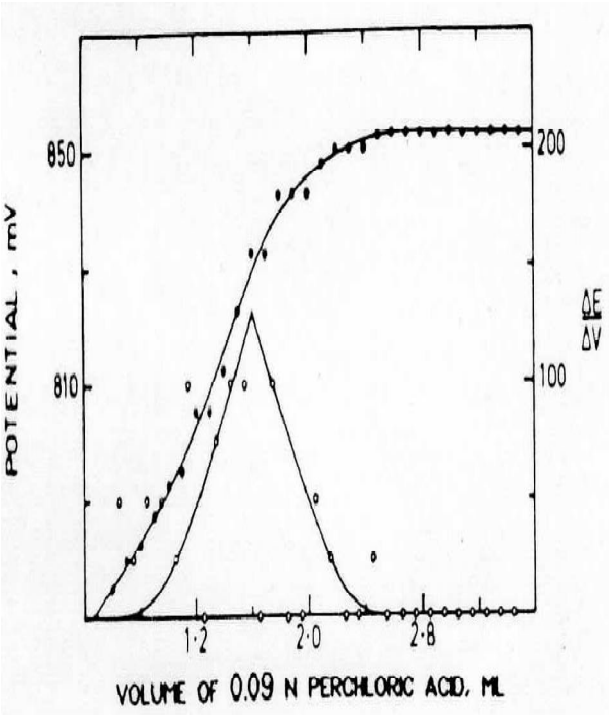


Figure-10
Titration of p-di-tolyl sulfoxide in acetic anhydride with 0.09 N $HClO_4$ in dioxane

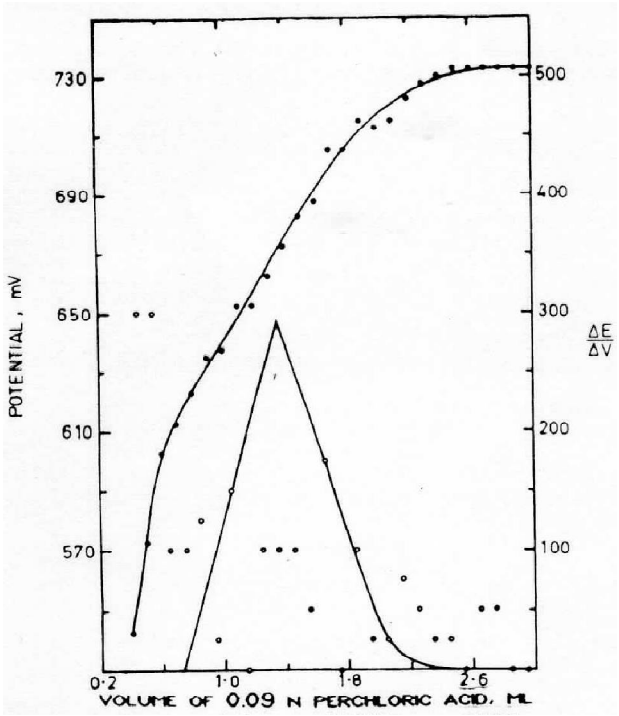


Figure-11
Titration of Indium complex of diphenyl sulfoxide in acetic anhydride with 0.09 N $HClO_4$ in dioxane

Table-1
Analysis of Sulfoxides by Potentiometric methods

Compound	Solvent	Ttrant	Inflection Point	Amount of Sulfoxide, g	
				Taken	Found
Dimethyl sulfoxide	2 M H_2SO_4	0.077 N $KMnO_4$ in 2M H_2SO_4	28.5	0.1953	0.1718
Dimethyl sulfoxide	2 M H_2SO_4- 2.67 M H_3PO_4	0.099 N $KMnO_4$ in 2M H_2SO_4	61.5	0.1953	0.4757
di-n-octyl sulfoxide	Glacial acetic acid	0.099 N $KMnO_4$ in 2M H_2SO_4	12.5	0.1	0.2826
Diphenyl sulfoxide	Glacial acetic acid	0.099 N $KMnO_4$ in 2M H_2SO_4	13.5	0.1	0.2283
p-di-tolyl sulfoxide	Glacial acetic acid	0.099 N $KMnO_4$ in 2M H_2SO_4	12.5	0.1	0.2371
Indium complex of Diphenyl sulfoxide	Glacial acetic acid	0.099 N $KMnO_4$ in 2M H_2SO_4	18.4	0.1	2.1438
Dimethyl sulfoxide	Acetic anhydride	0.09 N $KMnO_4$ in dioxane	1.15	0.0078	0.0081
di-n-octyl sulfoxide	Acetic anhydride	0.09 N $KMnO_4$ in dioxane	0.65	0.0113	0.0161
Diphenyl sulfoxide	Acetic anhydride	0.09 N $KMnO_4$ in dioxane	1.8	0.0263	0.0328
p-di-tolyl sulfoxide	Acetic anhydride	0.09 N $KMnO_4$ in dioxane	1.6	0.0306	0.0332
Indium complex of Diphenyl sulfoxide	Acetic anhydride	0.09 N $KMnO_4$ in dioxane	1.35	0.1431	0.1614

Results and Discussion

The results of estimation of various sulfoxides namely dimethyl sulfoxide, di-n-octyl sulfoxide, diphenyl sulfoxide, p-di-tolyl sulfoxide and indium complex of diphenyl sulfoxide by potentiometric method are represented in Table-1.

Fairly accurate results with high degree of precision are observed in case of redox titrimetric analysis of dimethyl sulfoxide in 2 M sulphuric acid with $KMnO_4$ in 2 M H_2SO_4 as well as in titrimetric analysis of dimethyl sulfoxide, di-n-octyl sulfoxide, diphenyl sulfoxide, p-di-tolyl sulfoxide and indium complexof diphenyl sulfoxide all in acetic anhydride with perchloric acid in dioxane.

In case of redox titrations in dimethyl sulfoxide in 2 M H_2SO_4 - 2.67 M H_3PO_4 mixture and di-n-octyl sulfoxide, diphenyl sulfoxide, p-di-tolyl sulfoxide and indium complex of dipenyl sulfoxide in glacial acetic acid with $KMnO_4$ in 2 M sulphuric acid the inflection point occurs after the equivalence point, this clearly shows slow oxidation of these sulfoxides with $KMnO_4$ and hence higher titer value.

Potentiometric methods embrace two major types of analyses the direct measurement of an electrode potential from which the concentration of an active ion may be derived and the changes in the electromotive force of an electrolytic cell brought about through the addition of a titrant. In present analysis two types of potentiometric titrations Oxidation-Reduction and Acid-Base titrations in nonaqueous solvents have been performed, and interest is focused upon changes in the e.m.f. of an electrolytic cell as a titrant of precisely known concentration is added to a solution of the analyte namely dimethyl sulfoxide, di-n-octyl sulfoxide, diphenyl sulfoxide, p-di-tolyl sulfoxide and indium complex of diphenyl sulfoxide. An end point is located more precisely by plotting successive values of the rate of change of cell e.m.f. vs each increment of titrant in the vicinity of the inflection point. The position of the maximum on the first derivative curve as shown in Figure-1 to 11 corresponds to the inflection point on the normal titration curve.

Redox reactions of sulfoxides: Oxidation-reduction (Redox) reactions can be followed by an inert indicator electrode such as platinum. The only role of this type of electrode is to provide or accept electrons (and therefore potential-indicators). The electrode assumes a potential proportional to the logarithm of the concentration ratio of the two oxidation states of the reactant or the titrant, whichever is capable of properly poising the electrode. For e.g., the dimethyl sulfoxide/dimethyl sulfone sytem in the titration with potassium permanganate. At the start of the titration the minute amount of dimethyl sulfoxide leaves the system without a definite electrode potential. However, as soon as a drop of potassium permanganate has been added, the concentration ratio of dimethyl sulfoxide/dimethyl sulfone assumes a definite value and, likewise, the electrode potential of the indicator electrode. During the major portion of the titration the electrode potential changes gradually. Near equivalence point concentration ratio changes rapidly. After equivalence point, the indicator electrode ceases to be affected by the dimethyl sulfoxide / dimethyl sulfone sytem and assumes a potential dictated by the permanganate / manganous system.

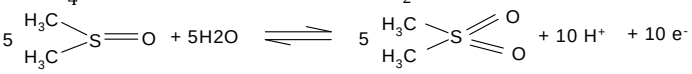
At the equivalence point in an oxidation-reduction reactions, $a_{ox1} + b_{red2} = a_{red1} + b_{ox2}$; the electrode potential is the weighted mean of the standard electrode potentials of reactant and titrant:

$$E_{euiv.pt.} = \frac{bE_1^0 + aE_2^0}{a + b}$$

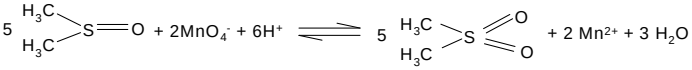
When a = b , the titration curve is symmetrical around the equivalence point, but when a≠ b, the titration curve will be markedly asymmetrical and the point of inflection will not coincide with the equivalence point. The difference will depend upon the ratio a/b. If a > b, the inflection point will occur when excess oxidant$_1$ is present in solution, that is, before the equivalence point. The inverse is true when b > a.

Chemical reactions (acid-base changes, complexation) can displace the electrode potentials in a way that often lends itself to a quantitative treatment. For example, dimethyl sulfoxide can be titrated potentiometrically with standard potassium permanganate solution in the presence of a high concentration of sulphuric acid as shown in Figure 1. Under these conditions, the dimethyl sulfoxide can be oxidized quantitatively to the dimethyl sulfone by the permanganate as shown below-

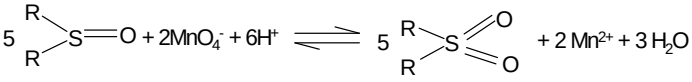
$$2MnO_4^- + 16H^+ + 10e \leftrightarrows 2Mn^{2+} + 8\,H_2O$$

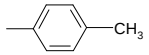


Hence the overall redox reaction is



While in case of equimolar proportion (mixture) of H_2SO_4 : H_3PO_4 solution the end point has shifted to higher titer value as shown in Figure 2. Same thing happens in case of di-n-octyl sulfoxide, diphenyl sulfoxide, p-di-tolyl sulfoxide and indium complex of diphenyl sulfoxide i.e. $[In(NO)_3)_3\ (DPSO)_3]^{3+}$ all in glacial acetic acid while performing redox titration with $KMnO_4$ in 2 H_2SO_4 as shown in Figure 3-6. Thus the reaction:



Where –R = $–CH_3$, $–C_8H_{17}$,  , 

, do not proceed quantitatively to completion because of slow oxidation.

Titration of sulfoxides in acetic anhydride: During present investigation of the titration of various sulfoxides using glass-calomel electrode system, dimethyl sulfoxide and di-n-octyl

sulfoxide as shown in Figure-7 and 8 are found to exhibit sharp end point inflections in acetic anhydride. The procedure is applied to other sulfoxides with the purpose of developing a general analytical method, and reproducible results are obtained with aliphatic and aromatic sulfoxides. Phenyl substitution results in electron withdrawal and nearly complete reduction in basic properties; no sharp breaks are observed, still quantitative results can be obtained as shown in Figure-9, 10 and 11.

Conclusion

Based on potentiometric studies of sulfoxides following conclusions may be drawn.

Redox reactions of sulfoxides can be followed by platinum electrode. Dimethyl sulfoxide can be titrated potentiometrically with standard potassium permanganate solution in the presence of 2 M sulphuric acid. Under these conditions the DMSO can be oxidized quantitatively to the dimethyl sulfone by the permanganate.

In case of DMSO in equimolar proportion of H_2SO_4 : H_3PO_4 solution and di-n-octyl sulfoxide, diphenyl sulfoxide, p-di-tolyl sulfoxide and indium complex of diphenyl sulfoxide all in glacial acetic acid the oxidation reaction do not proceed quantitatively to completion because of slow oxidation.

Dimethyl sulfoxide and di-n-octyl sulfoxide are found to exhibit sharp end point inflexions in acetic anhydride using glass-calomel electrode system. The procedure can be applied to other sulfoxides, namely, di-n-octyl sulfoxide, diphenyl sulfoxide, p-di-tolyl sulfoxide and indium complex of diphenyl sulfoxide, and reproducible results are obtained. Phenyl substitution results in electron withdrawal and nearly complete reduction in basic properties; no sharp breaks are observed, still quantitative results can be obtained.

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