

INTERNATIONAL UNION OF  
PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION  
COMMISSION ON ELECTROANALYTICAL CHEMISTRY

SULPHOLANE: PURIFICATION, TESTS  
FOR PURITY, AND PROPERTIES

Prepared for publication by  
J. F. COETZEE

PERGAMON PRESS  
OXFORD · NEW YORK · PARIS · FRANKFURT

## Analytical Chemistry Division

## Commission on Electroanalytical Chemistry

SULPHOLANE: PURIFICATION, TESTS FOR PURITY, AND PROPERTIES<sup>†</sup>

## INTRODUCTION

Sulpholane (tetrahydrothiophene-1,1-dioxide; tetramethylenesulphone) is one of the more recently introduced members of the class of dipolar aprotic solvents. Some of its physical properties are listed in Table 1. It offers major advantages as a medium for proton trans-

TABLE 1. Physical properties of sulpholane

Property <sup>a</sup>	Value	Ref.
Freezing temperature, °C	28.45	1
Boiling temperature, °C (1 atm., decomp.)	285	2
Density, g cm <sup>-3</sup>	1.2625	3
	1.2623	4
Dynamic viscosity, poise	0.1029	4
Refractive index, n <sub>D</sub> <sup>30</sup>	1.4820	5
Dipole moment, μ (in benzene)	4.7	1
Relative permittivity, ε	43.3	3,4

<sup>a</sup>For temperature-dependent properties, temp. = 30°C

fer and other reactions. It is one of the more inert of the dipolar aprotic solvents with respect to its acid-base properties as well as other types of chemical attack, yet its relative permittivity (dielectric constant) is relatively high. These are generally desirable properties which are to some extent mutually exclusive and which appear to be in optimum compromise in the case of sulpholane.

The proton basicity of sulpholane is much lower than that of water or even acetonitrile, as shown by its pK<sub>a</sub>(SH<sup>+</sup>) value of -12.9 (Ref. 6), as compared to ca. -9.5 for acetonitrile (Ref. 7). However, the Lewis base properties of sulpholane are somewhat more pronounced. For example, the donor numbers (with respect to antimony pentachloride) of sulpholane and acetonitrile are similar: 14.8 and 14.1, respectively (Ref. 8), and sulpholane does form an adduct with boron trifluoride (Ref. 9). Sulpholane is a very weak Brønsted acid, as shown by its pK<sub>a</sub>(S) value of > 31 (Ref. 10), and it is highly resistant to electrochemical oxidation or reduction (Ref. 3) and to chemical attack, even by the reactive nitronium ion (Ref. 11). Its main limitation for many (but not all) applications is its high viscosity, approximately ten times that of water and thirty times that of acetonitrile.

Typical fundamental studies recently carried out in sulpholane are the following: hydrogen bonding and proton transfer reactions (Ref. 12-15), transport properties of electrolytes (Ref. 4 and 16), and voltammetry of inorganic compounds (Ref. 17). For analytical purposes, the response of hydrogen ion indicator electrodes is of particular interest. In buffer solutions of not too high acidity, the response of both the hydrogen and the glass electrodes is clearly Nernstian; however, there is some doubt whether the same is true for the most acidic solutions (HClO<sub>4</sub>, HSBCl<sub>6</sub>) (Ref. 14 and 15).

<sup>†</sup>Titular Members: R. G. Bates, Chairman (USA); J. F. Coetzee, Secretary, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa. 15260, USA; Members: E. Bishop (UK), T. Fujinaga (Japan), Z. Galus (Poland), J. Jordan (USA), H. W. Nürnberg (FRG), P. Zuman (USA); Associate Members: M. Branica (Yugoslavia), A. K. Covington (UK), L. Gierst (Belgium), K. Izutsu (Japan), L. Meites (USA), E. Pungor (Hungary), O. A. Songina (USSR), B. Trémillon (France); National Representatives: D. D. Perrin (Australia), G. Kraft (FRG), R. C. Kapoor (India), N. Tanaka (Japan), W. Kemula (Poland), P. O. Kane (UK).

## COMMERCIAL PREPARATION AND KNOWN IMPURITIES

Sulpholane is prepared commercially by Diels-Alder reaction of 1,3-butadiene with sulfur dioxide, giving 2,5-dihydrothiophene-1,1-dioxide (3-sulpholene), which is then hydrogenated in the presence of Raney nickel to give sulpholane (Ref. 18). Principal impurities are reported to be water and 3-sulpholene, while 2-sulpholene and isopropyl sulpholanil ether may also be present (Ref. 19). The 3-sulpholene present as an impurity dissociates into sulphur dioxide and 1,3-butadiene at temperatures above 70°C, but 2-sulpholene has much greater thermal stability and a boiling temperature of 143°C at a pressure of 5 torr, as compared with 118°C for sulpholane itself. The other impurity, isopropyl sulpholanil ether, has a boiling temperature of 133-136°C at 5 torr. Finally, in view of the existence of other patents for the preparation of sulpholane (Ref. 20), the possibility exists that pyridine, thiophene and sulphoxides may be present in certain commercial products.

## PURIFICATION PROCEDURES

In view of the relative inertness of sulpholane, several of the impurities listed may modify its properties significantly. As for other relatively inert solvents, it is unlikely that an all-purpose purification procedure can be devised which will give optimum results in all possible applications. Consequently, purification should be tailored to the intended use of the solvent.

Several substantially different procedures, differing widely in complexity, have been described. However, in the majority of cases, only limited information has been provided on tests for impurities, so that it is difficult to assess the relative effectiveness of different procedures.

Among the simplest procedures described are those of Morman and Harlow (Ref. 12) and Fernández-Prini and Prue (Ref. 4). The former authors obtained sulpholane suitable for a variety of acid-base titrations by simple treatment of the commercial solvent with activated alumina. The latter workers obtained sulpholane with the low conductivity of  $2-5 \times 10^{-9} \Omega^{-1} \text{ cm}^{-1}$ , a water content of less than  $5 \times 10^{-3} \text{ M}$ , and the other properties listed in Table 1, by carrying out two vacuum distillations of a product supplied by Whiffen and Sons, Ltd., the second from solid sodium hydroxide. It appears that this straightforward purification should be suitable for many applications, provided that the starting material is not too contaminated, as has sometimes been our experience.

Benoit *et al.* (Ref. 21) pretreated the solvent with sulphuric acid and hydrogen peroxide (to oxidise possible sulphoxide impurities), extracted it with methylene chloride and, after further pretreatment, distilled it in vacuo. This procedure eliminated an optical absorption band at 220 nm and an anodic wave at -1.2 V at the DME vs. an  $\text{Ag}/(10^{-2} \text{ M Ag}^+ \text{ in sulpholane})$  reference electrode observed with the starting material. The product contained  $8 \times 10^{-2} \text{ M}$  water, but solutions of salts could be dried further with molecular sieves or calcium sulphate.

A detailed procedure was developed by Coetzee *et al.* (ref. 3 and 19) specifically to reduce to a minimum the content of sulphur dioxide and other acidic or basic impurities. A similar procedure was used by Benoit *et al.* in subsequent work (Ref. 13). It has the disadvantages that it is time-consuming and that it leaves some of the (unknown) impurity responsible for the absorption at 220 nm. Commercial sulpholane is heated with  $10 \text{ g l}^{-1}$  of solid sodium hydroxide at 170-180°C for 24 hours while a slow stream of nitrogen is bubbled through it by means of a gas dispersion tube. This treatment should result in essentially complete thermal decomposition of 3-sulpholene and elimination of sulphur dioxide and other volatile impurities. Sulpholane itself is thermally stable up to 200°C (Ref. 18). The product at this stage has a dark reddish-brown colour and a conductivity of *ca.*  $5 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ . It is decolorised by stirring with  $10 \text{ g l}^{-1}$  of decolorising carbon (e.g., Fisher Norit-A Decolorizing Carbon-Neutral) at 80-90°C for 6 hours, followed by suction filtration (while hot) through a medium porosity glass filter. The light yellow product is then passed through a 4-foot column packed with a mixed bed of acid "macroreticular" ion exchange resins (Rohm and Haas Amberlyst-15 and Amberlyst-A-21). Conventional ion exchange resins have been shown to function inadequately in many nonaqueous solvents on account of physical breakdown of the resin and unfavorable exchange kinetics; macroreticular resins appear to be superior in these respects (Ref. 22). The column should be heated to 70-80°C to increase the exchange rate and also the flow rate, because the viscosity of sulpholane is high. The effluent should be clear and have a low conductivity of *ca.*  $2 \times 10^{-9} \Omega^{-1} \text{ cm}^{-1}$ . Finally, it is vacuum distilled from  $5 \text{ g l}^{-1}$  of calcium hydride, preferably in a rotary still (e.g., a Büchi rotary vacuum evaporator) at a pressure of 0.01-0.02 torr and an oil bath temperature of 90-100°C. The 80% centre cut is collected and transferred under nitrogen to a darkened storage vessel from which it can be dispensed by nitrogen pressure.

## TESTS FOR IMPURITIES

Sulpholane purified by the procedure of Coetzee *et al.* had a conductivity of  $2 \times 10^{-9} \Omega^{-1} \text{cm}^{-1}$ , a water content of  $1 \times 10^{-3} \text{ M}$  as determined by Karl Fischer titration, and the other properties listed in Table 1. Acidic and basic impurities were determined by potentiometric titration of sulpholane diluted with an equal volume of methanol, using methanolic solutions of sodium methoxide and perchloric acid as titrants and a glass electrode as indicator (limit of detection: *ca.*  $1 \times 10^{-6} \text{ M}$ , calculated for transfer of one proton). Commercial sulpholane was found to contain  $4 \times 10^{-3}$  and  $2 \times 10^{-4} \text{ M}$  acidic and basic impurities, respectively, while corresponding concentrations in the purified solvent were  $5 \times 10^{-6}$  and less than  $1 \times 10^{-6} \text{ M}$ , respectively (Ref. 3 and 19). Voltammetric discharge potentials in 0.1 M  $\text{Et}_4\text{NClO}_4$  vs. an  $\text{Ag}/(0.1 \text{ M AgClO}_4$  in sulpholane) reference electrode (AgRE) were the following: +0.04 and -3.50 V at the dropping mercury electrode, and +2.3 and -2.9 V for a current of 2  $\mu\text{A}$  at a platinum electrode of 9-mm<sup>2</sup> area rotated at 60 rad sec<sup>-1</sup>. (Corresponding potentials vs. an aqueous SCE are 0.70 V more positive). Residual currents at the dropping mercury electrode could be considered low, even when making due allowance for the high viscosity of the solvent. For example, at -2.7 V vs. AgRE, the residual current (with  $m^{2/3}t^{1/6} = 1.0$ ) was only 0.2  $\mu\text{A}$ , which is of the order expected for the capacitor current alone; the shape of the current-potential trace also indicated that the faradaic component of the residual current was negligible. Sulphur dioxide, which gives cathodic waves at -1.4 and -2.8 V vs. AgRE, could not be detected. At the rotated platinum electrode and also at the glassy carbon electrode (Ref. 20) anodic residual currents increased smoothly with increasingly positive potential and revealed no definite waves up to about +2 V which could be attributed to oxidisable impurities. However, the absorption spectrum showed that some of the impurity responsible for the absorption at 200 nm was still present. Furthermore, the solvent had some capacity to decolorise bromine and also alkaline permanganate. Photometric titration with the latter indicated an oxidisable impurity level of *ca.*  $3 \times 10^{-4} \text{ M}$ , calculated as sulpholene (Ref. 20). If it is important to reduce the concentration of oxidisable impurities to a minimum, it is advantageous to include in the purification procedure a step involving treatment with permanganate. A significant reduction was obtained in absorption at 220 nm and also in the anodic residual current at the rotated glassy carbon electrode (at the expense of a threefold increase in conductivity) by omitting the ion-exchange step in the procedure of Coetzee *et al.* (Ref. 3 and 19) and substituting digestion with potassium permanganate (2 g l<sup>-1</sup>) for 3 hours at 90°C, followed by filtration (Ref. 20). Alternatively, the procedure of Benoit *et al.* (Ref. 21) may be used.

## REFERENCES

1. L. Jannelli, M. Della Monica, and A. Della Monica, *Gazz. Chim. Ital.* **94**, 552 (1964).
2. R. W. Alder and M. C. Whiting, *J. Chem. Soc.* 4707 (1964).
3. J. F. Coetzee, R. M. Simon, and R. J. Bertozzi, *Anal. Chem.* **41**, 766 (1969).
4. R. Fernández-Prini and J. E. Prue, *Trans. Faraday Soc.* **62**, 1257 (1966).
5. J. W. Vaughn and C. J. Hawkins, *J. Chem. Eng. Data* **9**, 140 (1964).
6. S. K. Hall and E. A. Robinson, *Can. J. Chem.* **42**, 1113 (1964).
7. N. C. Deno and M. J. Wisotsky, *J. Amer. Chem. Soc.* **85**, 1735 (1963).
8. V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions", Springer-Verlag, Wien, New York, 1968, p. 19.
9. J. G. Jones, *Inorg. Chem.* **5**, 1229 (1966).
10. F. G. Bordwell, R. H. Imes, and F. C. Steiner, *J. Amer. Chem. Soc.* **89**, 3905 (1967).
11. J. Jones and J. Jones, *Tetrahedron Letters* **31**, 2117 (1964).
12. D. H. Morman and G. A. Harlow, *Anal. Chem.* **39**, 1869 (1967).
13. R. L. Benoit, A. L. Beauchamp, and R. Domain, *Inorg. Nucl. Chem. Lett.* **7**, 557 (1971).
14. J. F. Coetzee and R. J. Bertozzi, *Anal. Chem.* **45**, 1064 (1973).
15. R. L. Benoit and P. Pichet, *J. Electroanal. Chem.* **43**, 59 (1973).
16. M. Della Monica and L. Senatore, *J. Phys. Chem.* **74**, 205 (1970).
17. J. F. Coetzee and J. M. Simon, *Anal. Chem.* **44**, 1129 (1972).
18. Shell Chemical Co., *Technical Bulletins* IC: 63-13R (Sulfolane) and PD-146 (3-Sulfolene).
19. J. M. Simon, Ph.D. thesis, University of Pittsburgh, 1969.
20. J. C. Spurgeon, Ph.D. thesis, University of Pittsburgh, 1972.
21. J. Desbarres, P. Pichet, and R. L. Benoit, *Electrochim. Acta* **13**, 1899 (1968).
22. Rohm and Haas Co., "Technical Notes on Amberlyst 15 and Amberlyst A 21", Philadelphia, Pa., 1968.