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**THE PURIFICATION OF  
DIMETHYLSULPHOXIDE FOR  
ELECTROCHEMICAL  
EXPERIMENTATION**

*Prepared for publication by*

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ANALYTICAL CHEMISTRY DIVISION  
COMMISSION ON ELECTROANALYTICAL CHEMISTRY†

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**INTRODUCTION**

Dimethylsulphoxide (DMSO) is a highly associated, moderately viscous solvent with a dielectric constant higher than that of most organic liquids. The molecule is pyramidal<sup>1</sup> and highly polar<sup>2</sup>. DMSO has been shown to have basic properties comparable to those of water, but to have very much weaker acidic properties<sup>3</sup>. The DMSO which is commercially available in the U.S.A. (Crown Zellerbach Corporation, Chemical Products Division, Camas, Washington) is synthesized from dimethylsulphide, a byproduct of the manufacture of paper. The spectroscopic-grade solvent (Matheson, Coleman and Bell, Division of the Matheson Company, East Rutherford, N.J.) is presumably the purified Crown Zellerbach product. The European product (Union Rheinische Braunkohlen Kraftstoff A. G., Wesseling, Germany) is reported to contain 0.4 per cent water, a small amount of dimethylsulphide, and a trace of dimethylsulphone<sup>1,5</sup>.

**PHYSICAL PROPERTIES OF DMSO**

The vapour pressure/temperature relationship has been determined by Douglas<sup>14</sup>.

$$\log P = 26.49558 - 3539.32/T - 6.00000 \log T$$

$P$  is given in mm of mercury and  $T$  in degrees absolute assuming  $0^\circ\text{C} = 273.16^\circ\text{K}$ . *Table 1* is a critical compilation of the physical properties of DMSO.

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Table 1. Physical properties of dimethylsulphoxide

		Ref.
Formula weight	78.134 ± 0.003	21
Melting point	18.55 ± 0.02°C	15
Boiling point	189.0 ± 0.2°C	15
Viscosity (20°C)	2.473 c.p.s.	15
Dielectric constant (25°C)	46.7	16
Density (25°C)	1.09575 g/cm <sup>3</sup>	18
Heat of vaporization	12.64 ± 0.1 kcal/mole	14
Vapor pressure (25°C)	0.600 mm Hg	14, 20
Dipole moment (25°C)	3.9 debyes	2
Refractive index ( $n_D$ , 25°C)	1.4773	18
Heat of formation (25°C)	-35.5 kcal/mole	17
Free energy of formation (25°C)	-18.9 kcal/mole	17
Entropy of vaporization (Trouton's constant)	29.5 e.u.	5

## METHODS OF PURIFICATION OF DMSO

Water is the principal impurity present in DMSO and the purified solvent will readily absorb water vapour if exposed to the atmosphere. Evidence for the presence of an organic impurity has been found from the n.m.r. spectrum of the unpurified solvent<sup>4</sup>.

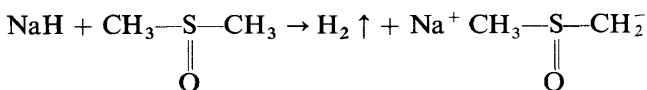
Sears, Lester and Dawson<sup>5</sup> proposed the following method. DMSO was refluxed over calcium oxide for several hours and then fractionated through a column at a pressure of about 5 mm of mercury. The middle fraction was collected and fractionated again one or more times until the specific conductance was  $3 \times 10^{-8}$  ohm<sup>-1</sup> cm<sup>-1</sup> or less. The density, viscosity and dielectric constant were all measured and compared with known values but the water content of the solvent was not determined. This procedure cannot be recommended because refluxing at atmospheric pressure leads to extensive decomposition of the solvent and necessitates removal of the decomposition products. Only about 30 per cent of the water is removed in each distillation cycle when calcium oxide is used<sup>6</sup> and a more efficient dehydrating agent is needed.

Gutman and Schober<sup>7</sup> subsequently proposed the following method. Technical grade DMSO was triply distilled by using a 50 cm packed fractionating column at a pressure of 12 mm of mercury. Distillation over phosphorus pentoxide or sodium metal led to decomposition of the solvent starting at 60°C and was not recommended. The fraction boiling at 81°C was collected and the residue discarded. The melting point of the purified solvent was 18°C and its specific conductivity  $4.5 \times 10^{-7}$  ohm<sup>-1</sup> cm<sup>-1</sup> at 21°C. Gutman and Schober felt that this method is adequate for polarographic use since no change in the waves of a number of metal ions was observed when the solution was exposed to the atmosphere for an hour. Unfortunately, the conductivity indicates that this method does not produce truly anhydrous solvent and that an efficient dehydrating agent which does not decompose the solvent is needed. Schlafer and Schaffernicht<sup>15</sup> have described an elaborate fractionation system to produce pure DMSO. A 20 per cent fore fraction is distilled into one part of the system to remove water and

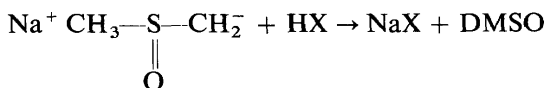
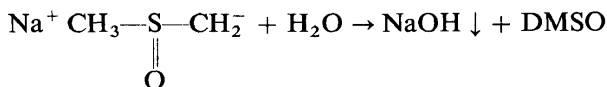
dimethylsulphide. This part of the system is then shut off and the product, about 70 per cent of the starting material, collected in another part of the apparatus. Using a one-metre column of 5 cm internal diameter packed with glass Raschig rings, solvent containing only 4 p.p.m. of water was obtained. The conductivity of this solvent,  $3 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$  at  $20^\circ\text{C}$ , is no better than that obtained by other methods, however. Schlafer and Schaffernicht advocated using Teflon sleeves lubricated with DMSO to seal ground glass joints because of the solubility of silicone greases in DMSO.

Kolthoff and Reddy<sup>3, 6, 8</sup> recommended the following purification process. DMSO was shaken overnight with acidic activated alumina (Woelm chromatographic grade—activity I) which had been fired to  $600^\circ\text{C}$  and cooled. The solvent was then siphoned into a distillation flask and vacuum fractionated under a nitrogen atmosphere at a pressure of a few millimetres of mercury through a heated 20 in. column packed with porcelain saddles. Some alumina was transferred in the siphoning operation. The first fraction, amounting to ten per cent of the total, was rejected and the second fraction of about 80 per cent of the starting material collected. The procedure was repeated two more times or until the specific conductivity was  $2 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$  or less and the water content was 0.01 per cent or less as determined by the Karl Fischer method. This method removes about 65 per cent of the water present for each cycle of purification and has the advantage that a significant amount of water is removed through the use of a good dehydrating agent without decomposition of the solvent. Basic impurities should also be removed by the acidic alumina. The use of a more efficient dehydrating agent would reduce the number of cycles necessary to obtain anhydrous solvent.

Price and Whiting<sup>9</sup> employed the following procedure. DMSO was purified by adding a little triphenylmethane indicator to the commercial material and then enough dimethylsodium solution until a strong red colour was developed. Dimethylsodium solution is the term employed by these authors to describe the solution in DMSO of the sodium salt of the lyate ion of DMSO (methylsulphinylcarbanion) prepared by the method of Corey and Chaykovsky<sup>10, 11</sup>. DMSO (500–600 ml) was reacted with one mole of sodium hydride at  $65^\circ\text{--}70^\circ\text{C}$  under a nitrogen atmosphere for 45 minutes.



Following treatment with dimethylsodium solution, Price and Whiting distilled at 0.5 mm of mercury and  $40^\circ\text{C}$  and collected the product. Dimethylsodium is a very strong base and reacts with water and any other substances which are stronger acids than DMSO.



The products are either insoluble or ionic and will not distill. The triphenylmethane acts as an indicator since excess dimethylsodium reacts to produce the triphenylmethyl anion with a resulting red colour. This method is extremely clever, but the purity of the product would probably be improved by the use of a fractionating column. The method suffers from the disadvantages that considerable effort is involved in the preparation of the dimethylsodium solution and basic impurities will not be removed by this method. The authors used the solvent purified in this manner for titrimetric purposes with considerable success.

Maricle and Hodgson<sup>12</sup> employed the following purification procedure. DMSO was heated over sodium hydroxide at 90°C for two hours and then flash-distilled under vacuum. This method apparently is very efficient since one treatment reduces the water content to 0.01 per cent (Karl Fischer method).

Bovey, Longworth and Hood<sup>4</sup> have reported that the n.m.r. spectrum of unpurified DMSO contains lines due to two impurities, one of which is water. Treatment with calcium hydride in a nitrogen atmosphere eliminates both lines. Roberts and Sawyer<sup>13</sup> employed the Purified (Matheson) Solvent and vacuum-distilled over calcium hydride (4-40 mesh, 10 g/litre). This procedure produced solvent of sufficient purity for polarographic purposes.

Mann<sup>22</sup> has recommended purification by a procedure involving fractional crystallization. About 80 per cent of a solvent batch was slowly frozen. The liquid was then discarded and the solid melted. 50 ml of benzene per litre of solvent was then added and the mixture distilled to remove water. The remaining DMSO was very rapidly distilled under vacuum. The product contains some water but only a small amount of other low boiling impurities. Mann states that a drier product could be obtained by using type 5A molecular sieves before distillation. Butler and Cogley<sup>23, 24</sup> have used Linde molecular sieve type 5A to remove water efficiently. The sieve is first dried in argon for 16 h at 500°C. Matheson, Coleman and Bell chromatographic or spectrograde material was then treated with the cooled sieve for a period of one week following which the solvent was filtered through a 10-20 micron glass frit to remove suspended matter and then used directly. The product was found to contain less than 10 p.p.m. of water and less than 5 p.p.m. of low boiling organic impurities. Butler and Cogley<sup>24</sup> have also shown that treatment of non-aqueous electrolyte solutions with molecular sieves can reduce significantly the water content resulting from the water associated with the salt. This technique can be particularly useful for electrolyte solutions of salts which are difficult to dry such as tetra-alkyl ammonium compounds. Butler and Cogley have also found that some ion exchange occurs between the electrolyte and the sieve introducing small amounts of sodium ion into the solution.

### RECOMMENDED PROCEDURE

Treatment with pre-dried type 5A molecular sieve eliminates water and low boiling impurities<sup>23, 24</sup>. Although this procedure reduces the impurity level remarkably, it may also introduce some ionic impurities into the solvent.

Careful vacuum distillation after filtration will serve to remove ionic impurities and any residual suspended matter from the sieve.

## TESTS FOR PURITY OF DMSO

### (A) Karl Fischer determination of water

The Karl Fischer method may be used for the determination of water in DMSO<sup>6</sup>. Ten millilitres of reagent grade methanol are introduced into a 25 ml volumetric flask and titrated with Karl Fischer reagent to a definite brown colour due to excess iodine. Then, 1 ml of DMSO is added with a calibrated pipette, and the solution is again titrated to the same colour. The Karl Fischer reagent is standardized in the same manner, except that water is introduced from an ultra-microburette instead of the sample of DMSO. For samples containing less than 100 p.p.m. of water, coulometric generations of Karl Fischer reagent with electrometric end point detection<sup>25</sup> can be employed.

### (B) Gas chromatographic determination of water and organic impurities

Cogley and Butler<sup>23, 24</sup> have employed gas chromatography to determine both water and low boiling organic impurities. They recommend the use of a hydrophilic polystyrene resin such as Poropak Q according to the procedures developed by Jasinski and Kirkland<sup>26</sup> for the analysis of impurities in propylene carbonate. Severe 'tailing' of the water peak was observed with other adsorbents and Cogley and Butler emphasize the need for careful control of inlet temperature and other variables in order to obtain reliable gas chromatographic data. The sensitivity of the method is stated to be 1 p.p.m. of water in the solvent.

### (C) The n.m.r. spectrum

Water is detectable in DMSO by an n.m.r. line at 6.75 $\tau$  versus tetramethylsilane<sup>4</sup>. The unknown organic impurity gives a line at 8.0  $\tau$ . This line may be due to dimethylsulphide which is known to give an n.m.r. line at 7.942  $\tau$  in carbon tetrachloride<sup>19</sup>. The DMSO methylproton line appears<sup>19</sup> at 7.489  $\tau$ . Both lines due to impurities are removed by treatment with calcium hydride.

### (D) Conductivity

The lowest specific conductivity reported<sup>3</sup> for DMSO is  $2 \times 10^{-8}$  ohm<sup>-1</sup> cm<sup>-1</sup>. Since water dissociates more readily than DMSO, the specific conductivity will be a measure of the concentration of both water and other ionizable substances.

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