RESEARCH ON ELECTROCHEMICAL CORROSION IN NONAQUEOUS ORGANIC SOLVENTS

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Nonaqueous solutions are being more and more extensively employed for various syntheses and electrochemical processes. In the study of electrochemical corrosion processes in these media their specific methodological difficulties are not always taken into account. Thus, since traces of moisture in the organic solvents can significantly alter the rate of chemical reactions [1], effective means are required for drying the solvents and techniques for monitoring the moisture content, both in the work of preparation and also when carrying out the experiment. A serious problem also is the choice of a suitable reference electrode with a stable, reproducible potential precluding the ambiguity involved with different kinds of salt bridges. An underestimate of these factors leads frequently to the appearance of contradictory data.

To prevent contact of the reaction medium with the surrounding atmosphere the preparative work and experimental determinations in nonaqueous organic agents are normally conducted in special boxes filled

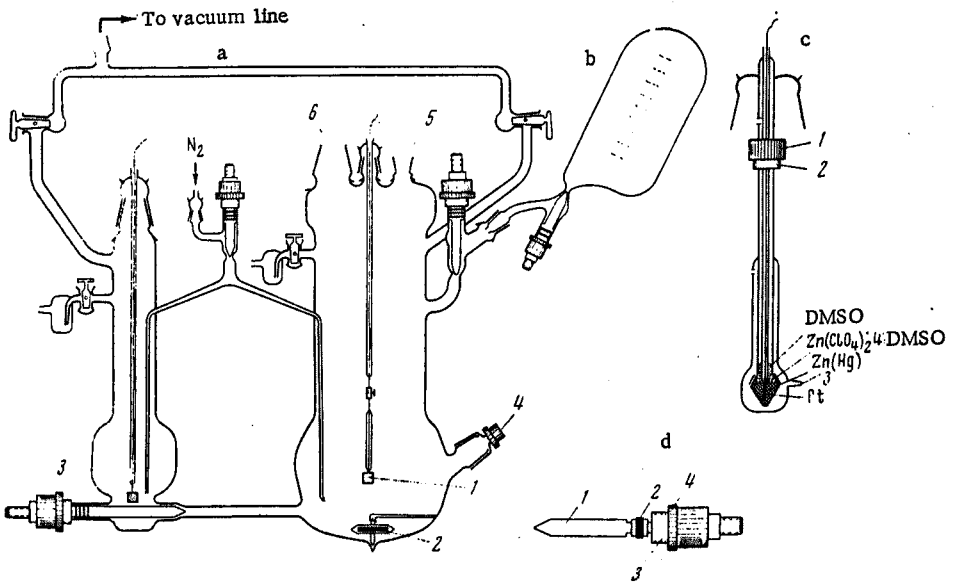

Fig. 1. a) Electrochemical cell for determinations in nonaqueous organic agents: 1) working electrode; 2) stirrer; 3) auxiliary electrode; 4) ground-glass joint with clamped vacuum rubber, by piercing which the additives can be introduced and samples taken; 5) ground-glass joint for thermometer; 6) ground-glass joint for reference electrode; b) vacuum flask with working solution; c) reference electrode: 1) coupling; 2) fluoroplastic insert; 3) Luggin capillary; d) fluoroplastic vacuum cock: 1) stem; 2) vacuum rubber; 3) fluoroplastic insert; 4) coupling.

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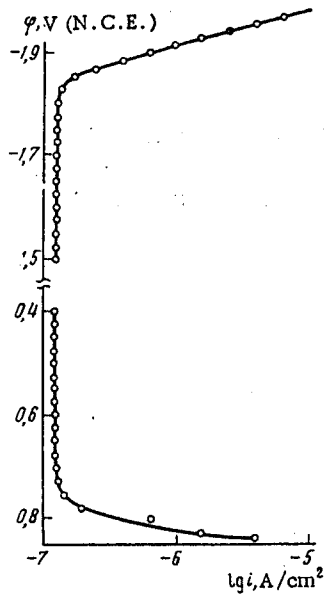

Fig. 2. Polarization curve on platinum in stationary 0.5 M dimethylsulfoxide solution of $NaClO_4$. Rate of potential shift 10 mV/min.

with pure, dry, inert gas. However, the preparation of gases of the required quality is an independent problem, and access to the reaction vessel in such boxes is extremely restricted. We have devised a more convenient and reliable method of carrying out these operations. A diagram of such an electrochemical vacuum box which removes the working solution from contact with the atmosphere is shown in Fig. 1.

When using the normal apparatus reliable results can only be obtained in a solvent which has adequate polarity ($\varepsilon \geq 20$), in which inorganic salts are readily soluble, and which is easily freed from organic contamination and traces of water.

The model solvent of such a type is dimethylsulfoxide (DMSO). It is a polar ($\varepsilon = 46.7$), aprotic liquid with setting and boiling points respectively 18.5 and 189°C in which the majority of univalent salts are fully dissociated [2, 3]. A large number of methods for purifying and drying DMSO has been described. The method we have selected accords with the recommendations of the committee on electroanalytical chemistry [4] and consists in the following. Commercial DMSO is shaken for ten hours with type 4 Å molecular sieves which are previously activated by heating at 200°. Solvent dried in this way at the rate of 150 ml/h is passed through a column filled with "Wolfen-Zeosorb, 5 Å" zeolite activated for 50 h at 450° and $1 \cdot 10^{-4}$ mm Hg pressure. After that the solvent is fractionally distilled at 55° and $(1\text{-}3) \cdot 10^{-4}$ mm Hg pressure. The middle fraction of distillate is collected in special vacuum flasks containing the admixed salt (Fig. 1b) and used for preparing the nonaqueous solution. Twice-recrystallized sodium perchlorate, introduced in excess into the solvent ($C_{NaClO_4} \geq 0.5$ M) as supporting electrolyte, is preheated in these flasks for 50 h at 100° at a pressure of $3 \cdot 10^{-4}$ mm Hg.

The resulting solution of $NaClO_4$ in DMSO is analyzed for water content by Fisher electrometric titration by means of an LTV-375 automatic titrator, devised jointly with the Tbilisi Automatic Plant Special Design Bureau. The bulk moisture content of the dried solution does not exceed 10^{-3}%.

Frequently, the necessity arises to vary the composition of the test solution, in the first instance its acidity. The direct incorporation in the organic solvent of appropriate aqueous acids leads to an undesirable increase in the water content and certain solvents and acids explode when in contact; an example is DMSO and concentrated aqueous $HClO_4$ solution [5]. To prepare perchloric acid solutions in DMSO we used an ion-exchange method. KU-2 cationite, containing 80% of divinylbenzene with a grain diameter of 0.5 mm, was repeatedly washed with a 1 M solution of HCl, and with water until the chlorine ions were completely removed. The resin, converted to the H form, was dried for 24 h at 60-70° and then directly in the ion-exchange column at 100° in a vacuum, also for 24 h. Before the exchange the resin was washed with the pure solvent. Then the DMSO, in which the $NaClO_4$ was dissolved, was passed at a rate of 85 ml/h. The amount of $NaClO_4$ was calculated for total replacement of sodium ions by hydrogen ions. All the exchange operations were carried out in vacuum. The acid content of the DMSO was determined by titration with standard NaOH solution. An almost total exchange was observed in the $1 \cdot 10^{-3}$-$5 \cdot 10^{-1}$ M range of $NaClO_4$ concentrations.

There is quite a full survey of reference electrodes in aprotic organic solvents in [6]. In DMSO, like a number of other organic solvents, an aqueous saturated calomel reference electrode is used which is connected with a Luggin capillary by several salt bridges. Here, however, a diffusion potential of up to 0.12 V can possibly arise [2]. An electrode of the type $Ag/AgCl_2/KCl$, DMSO is often used [7]. In both cases the access of chlorine ions to the reaction mixture is not excluded.

We employed a reference electrode of the $Zn(Hg)/Zn(ClO_4)_2 \cdot 4$ DMSO type (Fig. 1c). The salt, $Zn(ClO_4)_2$, twice recrystallized from aqueous solutions and dried at 90°, was dissolved in DMSO until saturation. The potential of this electrode did not vary over three months, even after polarization of the circuit with current of a few milliamperes, and, in good agreement with [8], amounted to −1.06 V with respect to an aqueous saturated calomel half-cell.

The procedure developed was verified from the results of steady polarization measurements on a platinum electrode in a neutral perchlorate solution of dimethylsulfoxide. Over the potential range + 0.75 to −1.9 V the background currents on the electrode do not exceed $3 \cdot 10^{-7}$ A/cm^2 (Fig. 2). With $\varphi < -1.9$ V a cathodic wave appears on the polarization curve, accompanied by gas evolution on the electrode; with $\varphi > +0.75$ V an anodic wave appears. This is similar to the results obtained by cyclic voltammetry in [9] where, based on an analysis of the cathodic gas, the hypothesis has been formulated that the cathodic wave is due to the electrochemical formation of sodium, which then reacts with DMSO to form a mixture of hydorgen and methane. The nature of the anodic wave is still obscure.

Thus, the system Pt/0.5 M $NaClO_4$, DMSO is electrochemically inert in a potential range roughly 2.6 V in extent and the low concentration of organic impurities and water enables the electrochemical reactions which take place in this medium with a rate exceeding 10^{-7} A/cm^2 to be investigated.

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