ELECTROREDUCTION OF A BENZENEDIAZONIUM SALT IN THE PRESENCE OF A RADICAL ACCEPTOR

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Potentiostatic reduction of *p*-methoxybenzenediazoniumtetrafluoroborate was studied in acidic aqueous solutions and in dimethylformamide. The mean number of electrons transferred to a molecule of the depolarizer is influenced by the presence of a radical acceptor, acrylamide, and depends on its concentration. The course of electrolysis in the presence of acrylamide was investigated by measuring the relative viscosity of the electrolysed solution. A polymer was isolated from both aqueous and nonaqueous solutions, and its mean relative molecular mass was determined by viscosimetry in an aqueous solution.

The first step of the electrochemical reduction of benzenediazonium salts (DAS) corresponds, according to several authors[1-4], to the transfer of one electron in both aqueous and nonaqueous solutions, as determined by several methods including coulometry. The electroreduction is complicated by adsorption of the product and follow-up chemical reactions involving the primary radical. When dimethylformamide (DMF) was used as a solvent, coulometry indicated anomalous, non-integer numbers of electrons consumed by one DAS molecule[5], e.g. we obtained 0·5 ± 0·05 electron per DAS molecule at the potential of the limiting diffusion current of the first reduction step. This implies that DAS is consumed more rapidly than would correspond to the charge transferred, hence that DAS participates in follow-up reactions. (Spontaneous decomposition of DAS was excluded by a blank experiment.) We proposed the following mechanism[5]:

$$\text{X—DAS}^{+} + \text{X—DAS}^{\bullet} \rightarrow (\text{X—DAS})_2^{+\bullet}$$

or

$$\text{X—DAS}^{+} + (\text{X—C}_6\text{H}_4)^{\bullet} \rightarrow (\text{X—DAS—C}_6\text{H}_4\text{—X})^{+\bullet}$$

involving a specific role of DMF. When other aprotic solvents were used, a one-electron transfer was found by coulometry (acetone, acetonitrile, dimethylsulfoxide). Only the existence of a secondary radical, $\text{X—C}_6\text{H}_4^{\bullet}$, was proved in DMF by the ESR method[5].

In accord with the proved one-electron transfer with the formation of a radical, it has been assumed that the electrode process or the mechanism of follow-up reactions of the primary radical could be influenced by adding a radical acceptor. A similar system was studied by Kovalchuk et al.[6] using chemiluminiscence during galvanostatic reduction of benzenediazoniumtetrafluoroborate in acetone and acetone–water mixtures[7] in the presence of radical acceptors.

We used acrylamide (AAD) as radical acceptor with respect to its high solubility in both the solvents used. This compound is polarographically active only at high negative potentials ($E_{1/2} < -1{\cdot}8$ V)[8]. Acrylamide was polymerized electrochemically during both cathodic and anodic polarization in aqueous or mixed media[9–15].

The purpose of the present work is to propose an explanation of the anomalous consumption of electrons during electroreduction of DAS in DMF.

EXPERIMENTAL

TAST polarography, slow cyclic voltammetry on a hanging mercury drop, and coulometry with a mercury pool electrode were already described[5]. The base electrolyte was 0·1M $NaClO_4$ in DMF or an aqueous Britton–Robinson buffer of pH 2·21. A saturated aqueous AgCl electrode served as reference in a three-electrode mode, however the potential values given below were recalculated against a saturated aqueous calomel electrode. The temperature of measurement was 20°C; the thermal decomposition of DAS during the measurement was negligible compared to the errors of measurement (the error in the determination of the number of electrons transferred per one DAS molecule was below ±10%).

The relative viscosity was measured with a flow-through viscosimeter according to Ubelohde at 25 ± 0·2°C (the constant of the viscosimeter $k = 0{\cdot}005008$); the constants of the Mark–Houwink equation[16], $K = 6{\cdot}8 \text{ m } 10^{-4} \text{ g mol}^{-1}$ and $a = 0{\cdot}66$ for acrylamide were taken from the literature[8].

Dimethylformamide (DMF) (pure, BASF) was free from electrochemically active impurities in the potential range used; it was dehydrated by azeotropic distillation with benzene, drying over P_2O_5, neutralizing with KOH, and vacuum distillation (cf. ref.[17]). The content of water was $1-5 \,.10^{-3}$ mol l^{-1} according to the Fischer reagent.

Solutions were prepared from doubly distilled water. Sodium perchlorate was recrystallized from water, dried at least 48 h at 90°C and stored in an exsiccator over P_2O_5. Nitrogen was freed from oxygen and dried by passing over a BTS catalyst and a molecular sieve. Acrylamide pure (Reanal, Hungary) was resublimated in vacuo. The preparation and characteristic of DAS were described earlier[5]. Other chemicals were used as such.

RESULTS AND DISCUSSION

Aqueous Medium

The voltammetric curve of p-CH_3O—DAS in acidic aqueous medium (pH 2·21 to hinder the thermal decomposition) has, similarly to that in the medium of DMF, ref.[5], an adsorption prepeak p_{k1} and the same character of the first reduction step.

However, further course of the reduction is different (Fig. 1). The value of pH in the range from 1·75 to 5·03 has no influence on the peak potential and on the current. At a potential of −0·15 V, we determined coulometrically the consumption of 1·0 ± 0·05 electron per DAS molecule in the whole concentration range under study, whereas 4 ± 0·5 electrons were found at a potential of −0·9 V.

Addition of acrylamide (up to 1·3 mol l^{-1}) causes a shift of both cathodic peak potentials to more negative values and an increase of the adsorption prepeak, whose height depends on the concentration of acrylamide in the form of an adsorption isotherm. The other cathodic peak does not change.

The effect of acrylamide is more pronounced during coulometric electrolysis. With respect to the assumed radical formation in the first reduction step, the process was investigated only at the potential of −0·15 V. It turned out that the mean number of electrons transferred per DAS molecule increases with the concentration of acrylamide and decreases with rising concentration of DAS at constant concentration of acrylamide, but it is always higher than 1 (Fig. 2). Fractional numbers of transferred electrons per DAS molecule are evidence for the competition of several reactions with and without charge transfer. The polymer formation during electrolysis was investigated by repeated measurement of the relative viscosity after passing 1, 2, and 3 coulombs (Fig. 3), corresponding to the reduction of 26, 52, and 79%

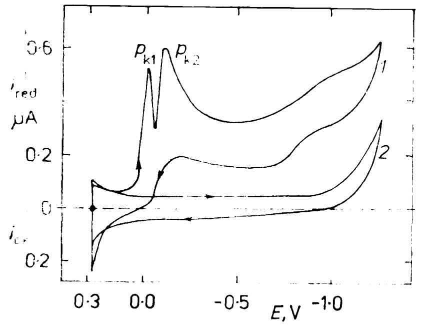

FIG. 1

Voltammetric curves for DAS on hanging mercury drop. *1* 3·7 . 10^{-4} mol l^{-1} CH_3O—DAS in Britton–Robinson buffer, pH 2·21, v = 100mV s^{-1} (p_{k1} is an adsorption prepeak); *2* as *1* but without CH_3O—DAS

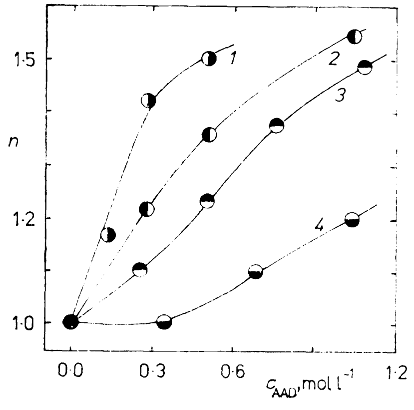

FIG. 2

Dependence of the number of electrons, *n*, transferred during electrolysis to one DAS molecule on the concentrations of DAS and acrylamide (c_{AAD}). Concentration of DAS (mol l^{-1}): *1* 9·8 . 10^{-5}; *2* 2·61 . 10^{-4}; *3* 4·55 . 10^{-4}; *4* 1 . 10^{-3}

of the DAS content (3·86 C would correspond to reduction of the total DAS assuming one-electron reduction, 1 . 10^{-3} mol l^{-1} starting concentration and 40 ml solution volume). An increase of the relative viscosity indicates formation of macromolecular compounds and their increasing concentration or mean relative molecular mass.

Electrolysis in DMF

Addition of acrylamide to a solution of CH_3O—DAS in DMF causes two effects on the voltammetric curves. First, the maximum in the medium potential region is suppressed. The same effect is, naturally, provoked by adding a surfactant, e.g. octanol (neutral surfactant) and especially Septonex (N-(α-carbethoxypentadecyl)-trimethylammonium bromide, cation active surfactant). Second, the mean number of electrons transferred per one DAS molecule is increased (Fig. 4).

During electrolysis, a white precipitate, identified as a polymer, was formed at the potential of both the first and the assumed second reduction step. Its mean relative molecular mass was determined viscosimetrically as 16 000. This is close to

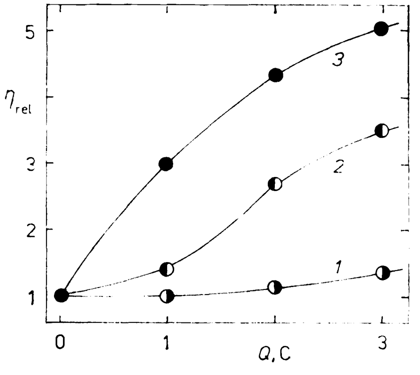

Fig. 3

Dependence of relative viscosity η_{rel} on the charge Q passed at DAS concentration 1 . 10^{-3} mol l^{-1} and acrylamide concentration (mol l^{-1}): *1* 0·28; *2* 0·56; *3* 0·84

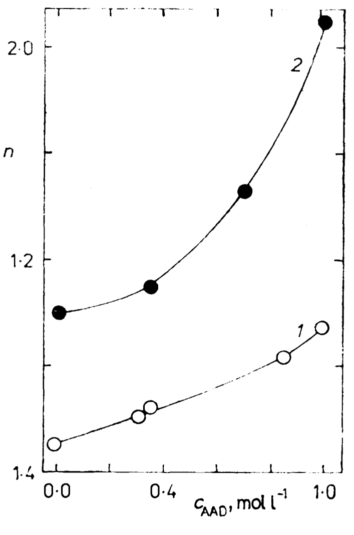

Fig. 4

Dependence of the mean number of electrons, *n*, transferred to a DAS molecule on the concentration of acrylamide in DMF. Concentration of DAS 9 . 10^{-4} mol l^{-1}; potential (V): *1* −0·15 *2* −1·65 the figure found for a polymer formed in aqueous solution at −0·15 V, 32 000.

The influence of acrylamide on the consumption of electrons during reduction of DAS can be, in our opinion, elucidated as follows. Addition of a radical acceptor gradually eliminates the reaction of the $DAS^{\bullet}$ radical with the starting DAS^{+} ion. With increasing acrylamide concentration, the consumption of electrons per one DAS molecule approaches the theoretical value. However, the dependences shown in Fig. 4 suggest that the theoretical consumption of electrons would be exceeded at still higher acrylamide concentrations, similarly to an aqueous solution.

A higher electron consumption than the theoretical may be elucidated by the following mechanism. In solutions containing acrylamide, the transfer of an electron to a DAS molecule is followed by growth of the polymer chain initiated by the $DAS^{\bullet}$ radical or by the secondary $X—C_6H_4^{\bullet}$ radical. Let us admit that, besides the common ways of termination including that by recombination of macroradicals with the primary or secondary DAS radical, there is a possibility of the reaction

$$P^{\bullet} + e^{-} + H^{+} \rightarrow PH\,,$$

where $P^{\bullet}$ is a macroradical and PH is a terminated polymer molecule; then the resulting consumption of electrons per one DAS molecule will lie between 1 and 2. At a low DAS concentration, most of the radicals formed by electroreduction are consumed in the initiation or in another way. Thus, the above-mentioned reaction is dominant and this results in higher apparent electron consumptions per one DAS molecule. At higher DAS concentrations, there is also a higher number of macroradicals, and therefore other termination mechanisms come into play, requiring no further electron transfer.

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