

ANODIC PROCESSES IN DIMETHYL SULFOXIDE WATER SOLUTION

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Introduction. Methanesulfonic acid (MSA) is a strong organic acid which can be applied as a catalyst in nitration, alkylation and etherification of olefins [1] and can also be applied for preparation of electrolytes in chemical, electronic and radio technical branches of industry [2], in pharmaceuticals [3]. MSA can be produced by chemical and electrochemical method. Chemical method has been studied and realized quite well. Electrochemical one has not been realized in industry nevertheless it can allow to obtain a wide range of organic substances. Dimethyl sulfoxide (DMSO) and methylsulfonylmethane (MSM), which are the by-products in the oil-desulphurization processes, may be used as a source for electrochemical synthesis of MSA [4,5].

Experimental part. Electrode processes were performed by voltammetry method applying the potentiostat P-45X. Kinetics of anodic process was studied on a smooth platinum anode with an surface about $1,2 \text{ cm}^2$. Sulphuric acid with a concentration $0,2 \text{ mol}\cdot\text{dm}^{-3}$ was applied as an indifferent electrolyte. The objects of study are influence of DMSO ($0,5 \dots 4,0 \text{ mol}\cdot\text{dm}^{-3}$) and MSM ($0,5 \dots 1,5 \text{ mol}\cdot\text{dm}^{-3}$) concentration on a kinetics of anodic process. The temperature is $288 \dots 363 \text{ K}$. The current load is 15 A . Working anodic current density - $150 \dots 850 \text{ A}\cdot\text{m}^{-2}$. Material of anode is platinum, material of cathode is steel X10CrNiTi18-10. MSA was extracted through the sedimentation by cooling of solutions to the temperature 291 K and lower. The resulting products were analyzed by IR spectrometer Agilent Cary 630 FTIR [4, 6].

Results and discussion. Electrochemical method allows to manage the process by varying the anodic potential, catalytic activity of material, temperature of electrolyte, promoting admixtures. Analyzing the current-voltage curves we can justify the parameters of electrochemical synthesis. DMSO water solution has a low effective conductivity. Sulphuric acid with a concentration $0,2 \text{ mol}\cdot\text{dm}^{-3}$ was applied as an indifferent electrolyte. Diluted sulphuric acid is stable and doesn't interact with the DMSO and products of its oxidation. Mechanism of oxygen releasing on a platinum electrode in sulphuric acid solution has been well-studied [7, 8].

Oxidation of DMSO into DMS on a platinum surface is performed with a combined reaction which is oxygen release and the potential of peroxide formation is not reached yet. Anodic release of oxygen has an intermediate step – the formation of radical oxygen particles.

Significant difference between straight and backward parts of current-voltage curves in potential range from $1,6$ to $1,8 \text{ V}$ indicates an adsorption of DMSO on a platinum electrode surface and verifies the hypothesis about the participation of DMSO in anodic process.

The release of oxygen from the $0,2 \text{ mol}\cdot\text{dm}^{-3}$ of H_2SO_4 is performed with a large overvoltage at the potentials of formation of peroxide compounds on a platinum surface [7,8]. Presence of organic sulphur compounds in the anode layer and their involving into the anodic process was proved by the shift of anodic potentials into posi-

tive area after addition of DMSO to the $0,2 \text{ mol}\cdot\text{dm}^{-3}$ solution of H_2SO_4 . The most significant shift was noticed after addition of $1 \text{ mol}\cdot\text{dm}^{-3}$ of DMSO. Rise of DMSO concentration down to $3 \text{ mol}\cdot\text{dm}^{-3}$ leads to reduction of anodic potential due to the reduction of energy costs for the electrochemical desorption of MSA from the platinum surface comparing to the combined reaction of the formation peroxide by recombination of OH radical particles.

MSA was obtained by the cooling of electrolyte to $278\dots300 \text{ K}$. MSA was separated by filtration as the colorless crystals with the further washing with distillate water at a temperature under 278 K . The stock solution after the adjustment was applied in the next electrolysis cycle.

Conclusion. The mechanism for electrochemical synthesis of DMS and MSA from the DMSO water solution was described. Oxidation of DMSO to DMS is performed in the potential range $1,5\dots1,7 \text{ V}$ on the platinum electrode surface. In the potential range higher than $1,87\dots1,89 \text{ V}$ the oxidation of DMS to MSA is performed. There has been proposed a stage-mechanism for electrolysis of DMSO solution. Production of MSA is combined with electrochemical synthesis of hydrogen peroxide. Radical oxygen parts, generated on the platinum anodic surface, are involved in the MSA formation .

References

- [1] P. Kulkarni, *Orient. J. Chem.* 31 (2015) 447-451.
- [2] F. C. Walsh, C. Ponce de León, *Surface and Coatings Technology* 259 (2014) 676 – 697.
- [3] M.D. Gernon, M. Wu, T. Buszta, P. Janney, *Green Chem.* 1 (1999) 127-140.
- [4] M.A. Akhmedov, Sh.Sh. Khidirov, M.Yu. Koparova, Kh.S. Khibiev, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, 2016, pp. 100 –106.
- [5] O.L. Matrunchyk, G.G. Tulsy, S.A. Leshchenko, A.G. Tulskaia, K.S. Rutkovskaya (2017) *Razrabotka tekhnologicheskikh pokazatelej ehlektrohimicheskogo sinteza metansul'fonovoj kisloty* [Development of technological indices of electrochemical synthesis of methanesulphonic acid]. *Proceedings of the Modern Electrochemical Technologies and Equipment – 2017* (Republic of Belarus, Minsk, November 28-30, 2017) Minsk: BGTU, pp. 321 – 325.