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THE ATTEMPTS TENDING TOWARDS THE DISCOVERY ON THE ANALYTICAL THERMOVOLTAMPEROMETRIC METHOD ON THE BASIS OF THE SUITABLE INVESTIGATIONS OF CROTONALDEHYDE

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ABSTRACT

It was carried out the attempts tending towards the discovery on the analytical thermovoltamperometric method on the basis of the suitable investigations of crotonaldehyde in the presence of butyraldehyde, butanol and their mixture.

INTRODUCTION

The thermal analysis is used to a solid or rigid phase. There are no data available in the literature concerning the systematic thermal investigations of the liquid systems. Among the fragmentary studies of this type one can meet the works of polarography discussing the mechanism and parameters of kinetics of thermal decomposition of selected compounds[1,2].

The aim of the described voltamperometric studies is to define the conditions under which the effects of temperature on the course of the selected electrode processes would allow to obtain the best analytical results. The choice of the investigated system results from the fact that crotonaldehyde is one of the contaminations occuring in many products obtained from acetylene, e.g. in the butyraldehyde and butanol.

MEASURING METHODS

Polarographic investigations were performed using an polarograph type OH-102. The polarographic measurements were made in 0.1 M solution HCl in DMF.
Because till now exists non a apparatus-system for measuring of the heights of polarographic current dependent from temperature $I_{lim} = f/T/$, therefore in here these investigations were carried through recording series of curves $I_{lim} = f/E/$ at different temperatures. From these curves the very charac-

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teristic points at the same potentials were selected and plotted in the coordinate system $I_{lim} = f/T/$. Thus the thermovoltamperometric curves were obtained.

RESULTS AND DISCUSSION

It was found from the obtained results /Fig.1a/ that in the presence of butyraldehyde the maximum appears on the crotonaldehyde wave /at the concentration above 0.03% /. Its height increases along with the growth of the concentration of the studied component.

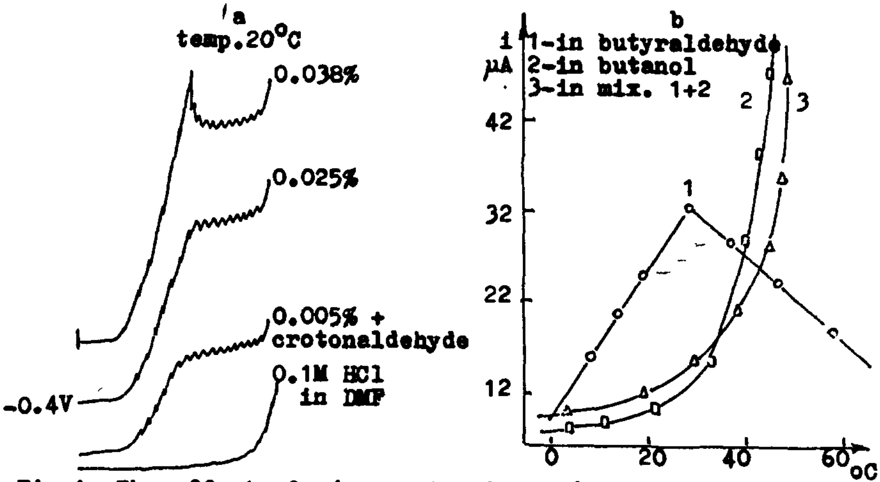

Fig.1. The effect of a/concentration; b/temperature on the polarographic behaviour of crotonaldehyde in 0.1 M HCl in DMF

The investigations for different temperatures showed, that under these conditions and at the temperature 36.5°C the rapid increase of the wave height of crotonaldehyde occurs /Fig.1b, curve 1/. It was found that at the temperature above 50°C this maximum disappears. It is very adventageous, because the chances of the use of I_{lim} measurement for analytical determinations are evaluated both from the wave height and from its shape.

The analysis of Majranovski's [3] dependence $d \ln \bar{I}_{lim} = f/d \frac{1}{T}/$ allows to conclude about the changes of composition occuring in the studied system. It follows from the obtained results, at the relatively lower temperatures in the studied system establishes the equilibrium between the solvates or associated molecules and free molecules of crotonaldehyde. As the temperature increases, the equilibrium shifts towards the formation of the free molecules. Under these conditions the increase of $\bar{I}_{lim}$ can be also due to the formation of 2-ethyl-2-heksene-1-al[4,5].

The comparative determination of the crotonaldehyde in the presence of butyraldehyde followed that the detection limit at 20°C equals 1×10^{-4} M/l, but at 50°C increases 5 times and is equal to 0.2×10^{-4} M/l.

On the curve $\bar{I}_{lim} = f/T/$ for this system containing crotonaldehyde and butanol /Fig.1b, curve 2/, well-defined maximum appears. In the temperature range 0-30°C the crotonaldehyde wave increased, while in the temperature range 30-60°C - rapidly decreased. Under these conditions probably forms /from butanol and hydrochloric acid/ the compound of ionic character: $C_4H_9OH_2^+Cl^-$ which improves the electric conductances of solution[6,7]. Nevertheless[8], the value of $d \ln i_{lim}/dT$, depends on $d \ln \lambda^o/dT$ /where λ^o - limiting conductance of studied solution/, the distinctness of the wave increases then the precision of the $\bar{I}_{lim}$ measurement also increases, even for lower concentrations of crotonaldehyde /2×10^{-6} M/l/, particularly at a lower temperatures. However, the negative temperature coefficient in the range 30-60°C may suggest the decomposition of ion $C_4H_9OH_2^+Cl^-$ or the occuring adsorption process in the solution containing a large amounts of alcohol.

On the basis of the dependence $d \ln i_{lim} = f/d \frac{1}{T}/$ one can find that the measurement of crotonaldehyde concentration in the presence of butanol better should be carried out in the temperature range 0-10°C, considering the shape of observed wave. Then the detection limit is equal to 2.0×10^{-6} M/l.

It was also studied the temperature dependence on the behaviour of system containing crotonaldehyde, butyraldehyde and butanol. In the Fig.1b, curve 3 has the similar course as the first described system. In the temperature range 35-45°C the value of I_{lim} alaways increases. It was observed that for lower concentrations of butanol its growth follows more rapidly then others. We were found that the determination of crotonaldehyde in the presence of butyraldehyde and butanol should carry out in the range 35-45°C.

The aim of realized investigations was to define the dependence of other parameters, besides the temperature, on the above system.

CONCLUSIONS

From performed research work results that the temperature dependence of I_{lim} can give the informations about the changes of composition of studied system. Then, this analysis should be taken into account in the determination of measurement conditions. It is necessary to choose the suitable temperature range, in which one can carry out the analysis of composition.

The aim of further investigations should be the construction of a apparatus for recording the $i = f/T/$ dependence, concerning the voltamperometric systems. This instrument,thermovoltammeter could contribute to the simplification of the investigations of liquid systems.

REFERENCES

1 H.A.El Shayeb, F.M.Abd El-Wahab, Egypt.J.Chem.,21/3/.179 /1970/, pub. 1980
2 I.I.Artym, K.R.Gorbaczewskaja, M.A.Kowbuz, W.W.Konowalenko, S.S.Iwanczew, Z.O.Ch., 51 /4/, 940 /1981/
3 S.G.Majranowskij, Ja.P.Stradyn, W.D.Biezugłyj, Polarografija w organiczeskoj chimii. "Chimija" 1975, p.65
4 R.E.Kirk, D.F.Othmer, Encyclopedia of Chemical Technology, t.2, p.684. The Interscience Encyclopedia, Inc.New York 1948
5 J.Paściak, M.Paściak, Chem.Anal., 9, 577 /1964/
6 W.Gerrard, H.R.Hudson, Proc.Chem.Soc., 467 /1961/
7 J.Paściak, Chem.Anal., 9, 929 /1964/
8 J.P.Segretario, P.Zuman, L.Meites. J.Electroanal.Chem.,151, 11 /1982/