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POLAROGRAPHIC BEHAVIOUR OF UNSATURATED ACIDS IN DIOXANE — WATER MIXTURES

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Maleic, fumaric, citraconic and mesaconic acids give each one well-formed cathodic wave in the mixture of dioxane and water of different ratios (1 : 3, 1 : 1, 3 : 1) and acidity (pH 2—4) containing 0.1 mol dm^{-3} tetrapropyl ammonium iodide, 0.05 mol dm^{-3} citric acid and 0.01% gelatin. The separation of waves of *cis* and *trans* isomers is the best in 75% dioxane at pH 1.8. Under these conditions simultaneously the pairs of *cis* and *trans* acids can be determined by measuring the height of waves and finding out the corresponding concentration value in the calibration curve. An explanation is proposed of the the influence of relative permittivity, viscosity, solvation, etc. on the intensity of the diffusion current and half-wave potential value. The processes on the electrode frcm the data on acid dissociation constants and dependence of half-wave potential on pH were explained.

While there are approximately twenty studies[1] about the polarographic behaviour of maleic and fumaric acids and their methyl-derivatives in water solution, there is only one study[2] dedicated to the polarographic behavious in organic solvents dealing with the investigation in ethanol. Dioxane has been recommended as a preferable solvent for certain organic[3,4] and inorganic[5,6] compounds. Therefore we have tried to apply this solvent for the purpose of investigating the influence of the solvent nature on the polarographic behaviour of maleic, fumaric, citraconic and mesaconic acids.

The conditions of this investigation has been similar as during investigatons in the water solvent[1]. Because of the presence of peroxide in dioxane, it had to be distilled just prior to application. Tetrapropyl ammonium iodide (conc. 0.1 mol dm^{-3}) and citric acid (0.05 mol dm^{-3}) has been used as a supporting electrolyte. The acidity of the solution has been changed from pH 2 to 4 by adding HCl or KOH of 0.7 mol dm^{-3} concentration. Above pH 4 the investigations could not be perfomred due to precipitation, which prevented work also in pure dioxane. As a maximum suppressor 0.01% gelatin soluton has been used. The maxima which despite addition of gelatin have appeared at acid concentrations above 1.5 mmol dm^{-3}, could not be eliminated neither by increasing of gelatin concentration (to 0.05%) nor by adding of other depressors: 0.1% Triton X-100, 0.01% methyl hydroxyethyl cellulose, 0.001% methylene blue etc.

RESULTS

a) *Maleic and fumaric acids*

Both in water and mixtures of dioxane and water of different ratios (1 : 3, 1 : 1 and 3 : 1) and acidities (pH 2 to 4) containing 0.1 mol dm^{-3} of tetrapropyl ammonium iodide, 0.05 mol dm^{-3} citric acid and 0.01% gelatin, maleic and fumaric acids give each a well defined cathodic wave.

The wave heights of maleic and fumaric acids (1 mmol dm^{-3}) in water and in 25%, 50% and 75% dioxane at various pH values in the mentioned supporting electrolyte are shown in Fig. 1a. It is evident from the figure that in water solution the wave height of fumaric acid is about 8% lower than the maleic acid wave and this difference decreases by the increase of the dioxane fraction in the solvent, so that the wave heights of both the acids in 75% dioxane are almost the same. The wave heights of both the acids considerably decrease in case the solvent contains larger quantity of dioxane. The reduction of wave heights with respect to water is with maleic acid 20, 35.7 or 38% in 25, 50 and 75% dioxane respectively, while fumaric acid it is 18, 34 or 35% in the same solvents. These data relate to pH 1.8—2.0 in acid concentration 1 mmol dm^{-3}. Wave heights of both the isomeric forms of acids slightly differ at pH change from 2 to 4.

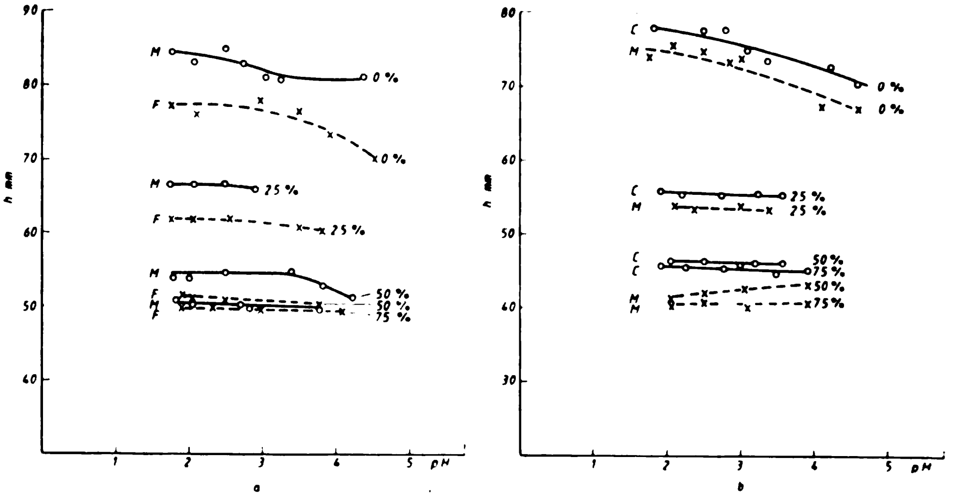

Fig. 1. Dependence of wave heights of a) maleic (M) and fumaric (F) and b) citraconic (C) and mesaconic (M) acids on pH values, in water, 25, 50 and 75% dioxane supporting electrolyte: 0.1 mol dm^{-3} $(CH_3CH_2CH_2)_4NI$ and 0.05 mol dm^{-3} citric acid)

As regards half-wave potentials, it is evident from Fig. 2 that fumaric acid appears at more negative potentials than maleic acid, where differences are greater in case the solvent contains more dioxane (about 0.2 V in 75% dioxane at pH 2.2). While the maleic acid wave both in water and dioxane moves towards more negative values with pH increase, the half-wave potential of fumaric acid remains almost the same in solutions of dioxane, by the change of pH value (Fig. 2).

The change of tetrapropyl ammonium iodide concentration from 0.1 to 0.2 mol dm^{-3} and citric acid from 0.03 to 0.09 mol dm^{-3} does not essentially influence the position change and wave height change. Good separation of maleic and fumaric acid waves can be achieved in 75% dioxane in the presence of 0.2 mol dm^{-3} tetrapropyl ammonium iodide at pH 2.6 without application of a buffer (citric acid). However, the wave heights considerably change in case pH is not maintained within limits of ± 0.02 pH. This makes difficult the determination and provokes a great relative error.

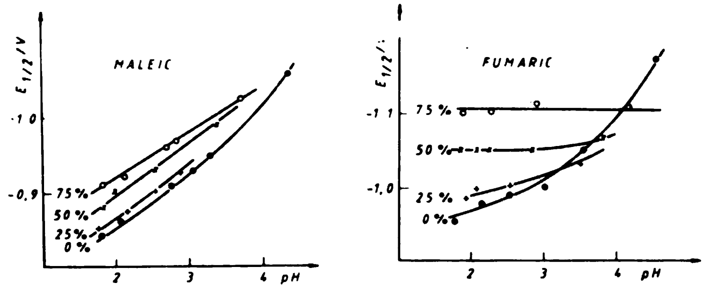

Fig. 2. Dependence of half-wave potential of maleic and fumaric acids on pH values, in water and 25, 50 and 75% dioxane (supporting electrolyte 0.1 mol dm^{-3} $(CH_3CH_2CH_2)_4NI$ and 0.05 mol dm^{-3} citric acid)

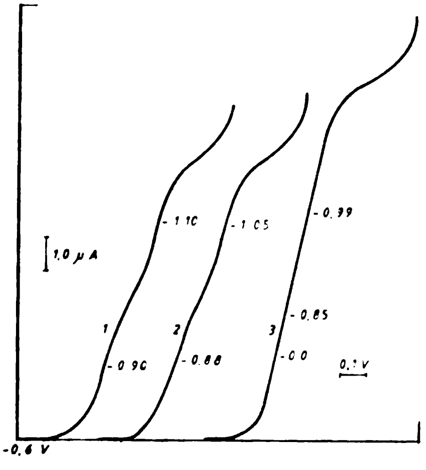

Fig. 3. Polarograms of a mixture of maleic (1 mmol dm^{-3}) and fumaric (1 mmol dm^{-3}) acids in 75% (*1*), 50% (*2*) and 25% (*3*) dioxane (supporting electrolyte 0.1 mol dm^{-3} $(CH_3CH_2CH_2)_4NJ$, 0.05 mol dm^{-3} citric acid, pH = 1.9)

The maleic and fumaric acid waves in 75% dioxane result from the diffusion current and the reduction process on the electrode is irreversible. There exists a linear dependence of the wave height on the acid concentration. The possibility of separating maleic and fumaric acids in solutions containing different quantities of dioxane are shown in Fig. 3, and at various pH values in 75% dioxane in Fig. 4. These polarograms as well as results of polarographic behaviour of both the isomeric acids in dioxane solution show that the separation of maleic and fumaric acids are best in 75% dioxane in the presence of 0.1 mol dm^{-3} tetrapropyl ammonium iodide as supporting electrolyte, 0.05 mol dm^{-3} citric acid and 0.01% gelatin, at pH below 2.2. These are the optimal conditions for quantitative determination of maleic and fumaric acids one in the presence of the other in dioxane solution. Since under the mentioned conditions the separation of both the acid waves is good, the values of the concentrations for each acid separately can be read from the measured wave heights by means of corresponding calibration curves. The relative error at determination of maleic acid at concentrations from 0.0232 to 0.1741 mg cm^{-3} is below 4.5%, while for determination of fumaric acids at concentrations of 0.0464 to 0.150 mg cm^{-3}, is below 5%. In the course of these investigations the ratio of acid concentrations has been between 1 : 3 and 3 : 1.

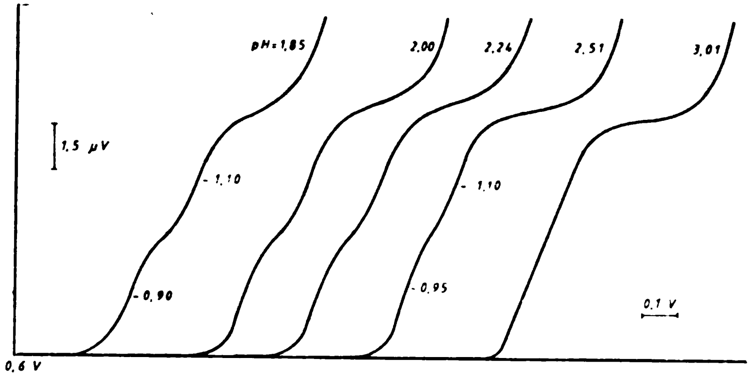

Fig. 4. Polarograms of a mixture of maleic (1 mmol dm^{-3}) and fumaric (1 mmol dm^{-3}) acids in 75% dioxane at different pH values (supporting electrolyte 0.1 mmol dm^{-3} $(CH_3CH_2CH_2)_4NI$, 0.05 mol dm^{-3} citric acid)

b) *Citraconic and mesaconic acids*

Citraconic and mesaconic acids give each one well-formed cathodic wave in water as in mixture of dioxane and water of different ratios (1 : 3, 1 : 1 and 3 : 1) and acidity (pH 2 to 4), containing 0.1 mol dm^{-3} of tetrapropyl ammonium iodide, 0.05 mol dm^{-3} citric acid and 0.01% gelatin.

Wave heights of both the isomeric acids are highest in water and then they decrease in case solution contains increasing quantities of dioxane. Figure 1b clearly shows that in water solution the wave height of mesaconic acid is approximately 5% lower than that of citraconic acid and that reduction of the wave height with respect to water as solvent, amounts with citraconic acid to 28, 39.8 or 40.9% in 25, 50 and 75% dioxane respectively, while with mesaconic acid 27, 44 and 44.2% in the same solvents. These data are valid for pH 1.8—2.0 and acid concentration 1 mmol dm^{-3}. Wave heights of both the isomeric acids remain almost constant in the pH range 1.8—4.0 for a solution having defined contents of dioxane.

The half-wave potential changes by changing pH values only with citraconic acid, while with mesaconic acid the slope of the curve $E_{1/2} = f(pH)$ is zero in dioxane solutions (Fig. 5). As we could expect[1], citraconic acid is being reduced at a more positive potential than mesaconic acid. The differences in half-wave potential values are larger at higher dioxane percentages and lower pH values.

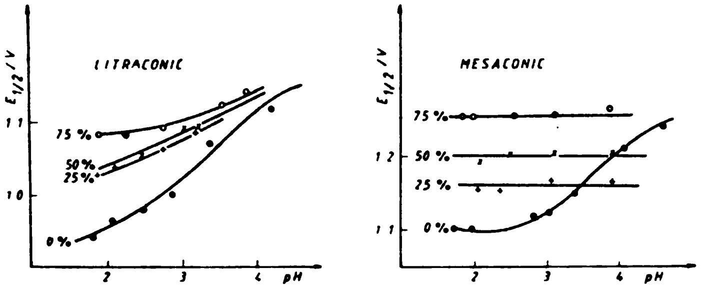

Fig. 5. Dependence of half-wave potential of citraconic and mesaconic acids on pH in water and 25, 50 and 75% dioxane (supporting electrolyte 0.1 mol dm^{-3}(CH$_3$CH$_2$CH$_2$)$_4$-NI and 0.05 mol dm^{-3} citric acid)

In order to find the most favourable conditions for the separation of citraconic and mesaconic acid waves, we have recorded polarograms of acid mixtures at pH 1.8 and various contents of dioxane (Fig. 6) and at constant contents of dioxane (75%) and different pH values. From the results obtained it can be concluded that the most favourable conditions for the separation of isomeric acid waves in mixture are in 75% dioxane at pH 1.8. Under these conditions, the wave heights of both the acids are proportional to the square root of the height of the mercury column, which means that the current is controlled by diffusion. The transfer coefficient calculated from the slope of the straight line log $[(i_q - i)/i] =$ $= \mathrm{f}(E)$ shows that the reduction on electrode is irreversible. There exists a linear dependence of the wave height on the concentration.

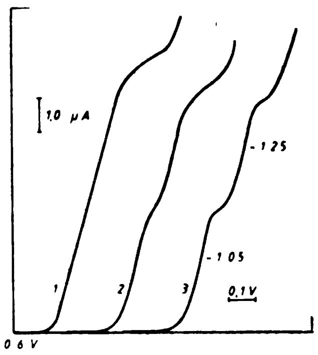

Fig. 6. Polarograms of a mixture of citraconic (1 mmol dm^{-3}) and mesaconic (1 mmol dm^{-3}) acids in 25% (*1*), 50% (*2*) and 75% (*3*) dioxane (supporting electrolyte 0.1 mol dm^{-3}(CH$_3$CH$_2$-CH$_2$)NI and 0.05 mol dm^{-3} citric acid, pH = = 1.8)

On the basis of all the previous investigations, we have reached the conclusion that the optimal conditions for simultaneous quantitative determination of citraconic and mesaconic acids in dioxane solution are as follows: Solvent: 75% dioxane; Supporting electrolyte: 0.1 mol dm^{-3} tetrapropyl amminoum iodide and 0.05 mol dm^{-3} citric acid, pH = 1.8; Maximum-suppressor: 0.01% gelatin.

Since under the mentioned conditions the separation of both the acid waves is good, the concentration values for each acid separately can be read from the measured wave heights by means of corresponding calibration curves. Due to occurrence of a maximum on the polarographic curve, despite the addition of a maximum-suppressor, the highest acid concentration measurable under the conditions is 1.5 mmol dm^{-3}. According to our investigations, citraconic acid can be determined within the concentration range from 0.078 to 0.156 mg cm^{-3} with a relative error below 3.3%, while mesaconic in the interval from 0.052 to 0.156 mg cm^{-3} with an error below 4%. The acid concentration ratio was between 1 : 3 and 3 : 1.

The separation of citraconic and mesaconic acid waves is good when the determination is performed in 75% dioxane in the supporting electrolyte of 0.2 mol dm^{-3} tetrapropyl ammonium iodide at pH 3.2 but without adding of citric acid. At the constant pH value which must not vary more than ± 0.02 pH a linear dependence of the wave height on the acid concentration exists. Nevertheless, the relative error is considerably larger and reaches 8%.

DISCUSSION

The polarographic waves recorded in non-aqueous solutions differ frequently in height, in half-wave potential values or in shapes compared to the waves recorded in aqueous solutions. These changes are the result of the influence of various factors: diffusion coefficient of the depolarizer, solvation, ion pair formation, complexing etc. Between dioxane and water great differences exist in relative permittivities (water 78.54, dioxane 2.21 at 298 K), dipole moments (water 6.24×10^{-28}C cm, dioxane 1.50×10^{-28}C cm), electric conductivities (water 8×10^{-8}S cm^{-1}, dioxane 5×10^{-15}S cm^{-1} at 298 K) and viscosities (data in Table I). The low relative permittivity of dioxane is favourable for the formation of ion pairs between the depolarizer and ions of the supporting electrolyte[7], which results in the change of half-wave potential of the ion which is being reduced. A more important influence, primarily on the change of the diffusion current intensity has the viscosity and the radius of solvated particles. According to Ilkovič's equation and under supposition that it is a reduction of same species on the electrode in question, namely the transfer of the same number of electrons, the difference in wave heights is conditioned by the change of coefficient of diffusion value D of the species which is being reduced. This change depends, according to the Stokes-Einstein equation ($D = kT/6\pi r\eta$) on the viscosity of the medium η and the radius of solvated particles r.

In order to find the dependence of viscosity and the size of solvated particles on the intensity of the diffusion current, a product $i_d \eta^{1/2}$ has been calculated for investigated acids in water and dioxane solution (Table I). The deviation of the product $i_q\eta^{1/2}$ in water and dioxane solutions is the smallest with fumaric and highest with mesaconic acid. Hence we have supposed that the solvatioe effect of solvents has an influence on the intensity of the diffusion current with mesaconic acid in addition to viscosity. This effect has influence on both thn maleic and citraconic acids in 75% dioxane. This is in accordance with Grunwald's standpoint[6] that acid molecules are solvated with a greater number of molecules of dioxane than with water.

TABLE I. Viscosity of mixtures of different ratios of dioxane and water, and the values of the product $i_4\mu_{1/2}$ for some unsaturated acids

Mass fraction of dioxane in %	$\eta \times 10^{-3}$ Pa s	$\eta^{1/2}$	$i_d\eta^{1/2}$ maleic	fumaric	citraconic	mesaconic
0	0.88	0.94	6.22	5.71	5.62	5.47
25	1.35	1.96	6.19	5.75	5.44	4.97
50	1.85	1.36	5.83	5.50	5.02	4.59
75	1.95	1.40	5.64	4.60	5.10	4.59

The change of the half-wave potential of maleic and fumaric acids in the pH function in the dioxane-water mixture was investigated with different contents of dioxane. The curves which represent the dependence $E_{1/2} = f(\mathrm{pH})$ (Fig. 2) in 25% dioxane have in the pH range from 2 to 3 very close values of the curve slopes as the ones in water. Since the dissociation constant of fumaric and especially maleic acids in 25% dioxane is very close to the dissociation constant of the acid in water[8], then n, namely the average number of hydrogen ion species to be found in the solution is approximately the same in both cases. Since the slopes $E_{1/2}/\mathrm{pH}$ are close, from the equation[9]: it follows that q is the same, namely

$$\mathrm{d}E_{1/2}/\mathrm{dpH} = 2.3\,(n - q)\,RT/2\alpha F,$$

the number of hydrogen atoms of the species, which is being reduced on the electrode. This means that on the electrode in 25% dioxane the acid molecules are being reduced.

By increasing the contents of dioxane, the pK value of the acid[8] increases while simultaneously the slope of curves decreases which represent a dependence $E_{1/2} = f(\mathrm{pH})$. The difference in values of the dissociation constants is more expressed with fumaric acid. In 50% dioxane the slope $\Delta E_{1/2}/\Delta\,\mathrm{pH}$ with this acid is zero (Fig. 2), namely the acid molecules are reduced on the electrode in the form in which they are to be found in the solution. The electrode process is performed without participation of the hydrogen ion.

Analogously to maleic and fumaric acids behave also citraconic and mesaconic acids. The pK values of these acids are very close in water to the values of maleic and fumaric acids, so we have supposed that their pK values in dioxane are also close. With mesaconic acid $\Delta E_{1/2}/\Delta\,\mathrm{pH}$ is already zero in 25% dioxane (Fig. 5), which shows that acid molecules are reduced on the electrode in the form in which they are to be found in the solution.

ИЗВОД

ПОЛАРОГРАФСКО ПОНАШАЊЕ НЕЗАСИЋЕНИХ КИСЕЛИНА У СМЕШИ ДИОКСАН-ВОДА

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Малеинска, фумарна, цитраконска и мезаконска киселина дају по један добро формиран катодни талас у смеши диоксана и воде различитих односа (1 : 3, 1 : 1 и 3 : 1) и киселости (pH 2 до 4), који садрже 0,1 mol dm^{-3} тетрапропиламонијум-јодид, 0,05 mol dm^{-3} лимунску киселину и 0,01% желатина. Раздвајање таласа *цис* и *транс*-изомера је најбоље у 75% диоксану и при pH 1,8. Под овим условима могу се истовремено одредити парови *цис* и *транс* киселина мерењем висине таласа и налажењем одговарајуће вредности за концентрацију са калибрационе криве. У раду је покушано да се објасни утицај релативне пермитивности, вискозитета, солватације итд. на јачину дифузионе струје и вредност полуталасног потенцијала. Из података о константи дисоцијације киселина и зависности полуталасног потенцијала од pH вредности, протумачени су процеси на електроди.

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