NONEQUILIBRIUM ELECTROCAPILLARY CURVES OF β-IODO- AND β-BROMOPROPIONITRILES

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The electrocapillary curves (ECC) of β-iodopropionitrile (IPN) and β-bromopropionitrile (BPN) were obtained with the aid of a Gouy capillary electrometer in a 1 N aqueous solution of Na_2SO_4. A comparison of the ECC of BPN and its i vs. φ curves leads to the conclusion that at BNP concentrations above 10^{-2} M there is a transition from the process of two-electron reduction observed in polarography to a process of one-electron reduction according to the type of IPN. The ECC of IPN with two maxima is explained as the result of mutual superposition of the ECC of IPN, I^-, dicyanoethylmercury, and possibly cyanoethylmercury iodide, at concentration and surface activity of I^- and other components of the system varying with the potential. A generalized treatment of the electrocapillary phenomena observed in the case of IPN is given, on the basis of the concept of a complete and free charge of the electrode in the redox system.

In our previous communication [1] we mentioned some peculiarities of the electrocapillary curves (ECC) of β-iodopropionitrile (IPN). On the ECC of this compound, obtained with a Gouy capillary electrometer with renewal of the mercury surface before each reading, there are two maxima, and its negative branch in the potential region studied exhibits no tendency for fusion with the ECC of the supporting electrolyte, 1 N Na_2SO_4 (Fig. 1). At the same time, the ECC of β-chloropropionitrile at all concentrations and the ECC of β-bromopropionitrile (BPN) at concentrations not exceeding $1.3 \cdot 10^{-2}$ M take the usual form. However, at BPN concentrations greater than $1.3 \cdot 10^{-2}$ M, the negative branches of its ECC, just as in the case of IPN, do not merge with the ECC of the supporting electrolyte (Fig. 2).

Earlier [1] we reported on the high surface activity of dicyanoethylmercury (DCEM) – the product of one-electron reduction of IPN on mercury [2, 3]. The reduction of IPN begins rather early ($\varphi_{1/2} \approx -1$ V) [4]; moreover, the initial compound undergoes reduction, and not cyanoethylmercury iodide (CEMI) ($\varphi_{1/2} \approx -0.4$ V) – the product of chemical conversion of IPN on the surface of mercury [3, 5]. The first wave of IPN corresponds to the formation of DCEM, so that it is natural to relate the fact that the negative branches of the ECC of IPN do not merge with the ECC of the supporting electrolyte to the formation of DCEM.

The reduction of BPN under the usual polarographic conditions occurs at potentials almost 1 V more negative than the potentials of the reduction of IPN [4]. However, at BPN concentrations above 10^{-2} M, appreciable currents of the reduction of BPN on a dropping mercury electrode already occur at potentials of about −1.0 V, that is, in the region where a change in the slope, indicating an increase in the surface activity of BPN, is observed on the ECC. Evidently, in this case also the absence of fusion of the ECC of BPN with the ECC of the supporting electrolyte is associated with the formation of DCEM. It should be mentioned that the measurement of the ECC permits the detection of the transition from the region of two-electron reduction of BPN, observed in the usual polarographic conditions, to the process of one-electron reduction according to the type of IPN, suggested in [4], as a result of the substantial difference in the adsorption properties of the starting material and the product of its reduction and the accumulation of the latter on the electrode surface. The accumulation of DCEM leads to a gradual decrease in σ in this region of potentials in the presence of BPN.

Considering the possible causes of the appearance of two maxima on the ECC of IPN, we should consider that during its reduction iodide ions, which are extremely surface active on the positive branch of the ECC, are formed. The source of I^- may be either IPN or CEMI, which is reduced earlier than IPN (the dif-

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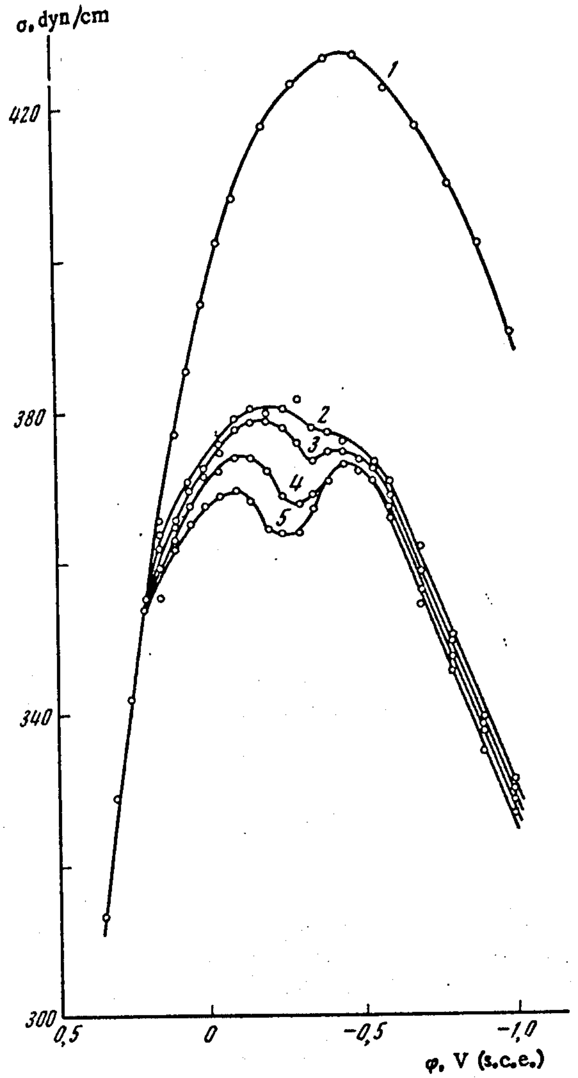

Fig. 1. Electrocapillary curves of iodopropionitrile at the concentration 2.84 · 10^{-2} M with supporting electrolyte 1 N Na_2SO_4 as a function of the time interval from the moment of renewal of the mercury surface to the moment of the reading ($\Delta\tau$): 2) 1; 3) 2; 4) 5; 5) 10 min (supporting electrolyte – curve 1).

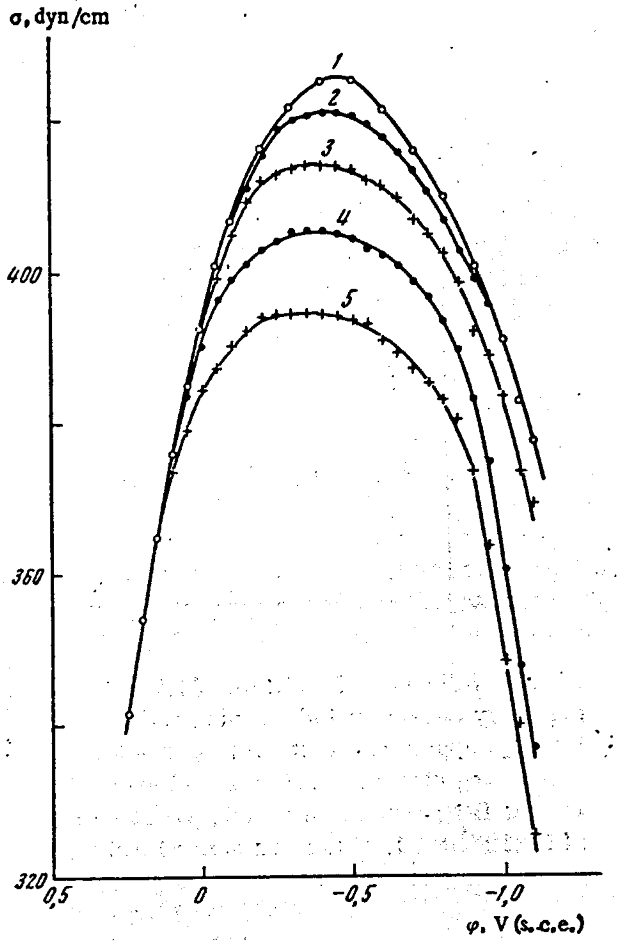

Fig. 2. Electrocapillary curves of bromopropionitrile at concentrations: 1) 0; 2) 1.29 · 10^{-2}; 3) 2.59 · 10^{-2}; 4) 5.17 · 10^{-2}; 5) 1.03 · 10^{-1} M; supporting electrolyte 1 N Na_2SO_4, $\Delta\tau$ = 2 min.

ference of the half-wave potentials reaches 0.6 V [3]). In contrast to the conditions of polarography, in the recording of the ECC with a Gouy electrometer, we should reckon with the possibility of the occurrence of a surface reaction of formation of CEMI, since the time of contact of IPN with mercury increases tens and hundreds of times. It is therefore not surprising that iodide ions already appear in the capillary at potentials of about −0.2 V. The more negative the potential, the higher the rate of reduction, and, consequently, the higher the concentration of I^-. Correspondingly, the value of the boundary tension becomes smaller, which leads to the appearance of a left-hand maximum on the ECC of IPN. Since diffusion in the capillary is hindered, the amount of iodide on the mercury surface increases with time, and the decrease in the boundary tension is greater, the longer the time interval from the moment of renewal of the surface until the moment of the measurement (Fig. 1). As a potential of −0.5 V is approached, the surface activity of I^- decreases, and despite the increase in its concentration, the boundary tension begins to increase, which leads to a drop in the second ascending branch and, consequently, the right-hand maximum on the ECC of IPN.

An additional argument in support of such an explanation can be found in the following facts. When KI is added to a solution of IPN, the right-hand maximum on the ECC of IPN remains, while the left-hand maximum disappears, since there is a constant concentration of I^- in solution (Fig. 3). On the ECC of IPN,

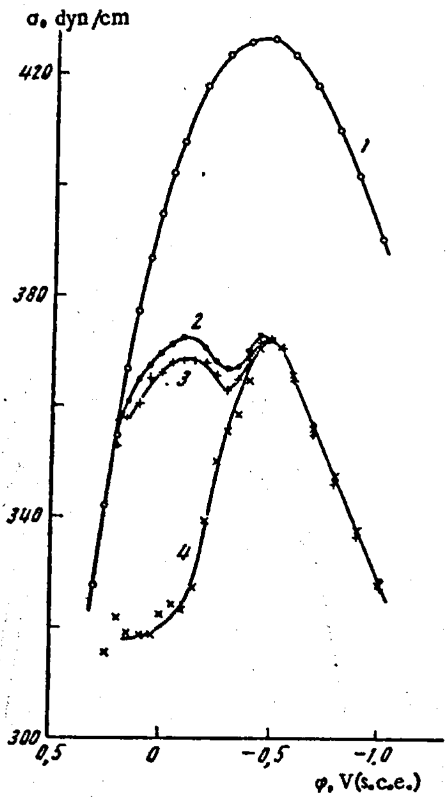

Fig. 3. Influence of addition of KI on the electrocapillary curves of iodopropionitrile with a 1 N Na_2SO_4 supporting electrolyte ($\Delta\tau$ = 5 min): 1) supporting electrolyte; 2) with addition of $2.84 \cdot 10^{-2}$ M IPN; 3) the same as 2, with an addition of $1 \cdot 10^{-4}$ N KI; 4) the same as 2, with an addition of $1.5 \cdot 10^{-3}$ N KI.

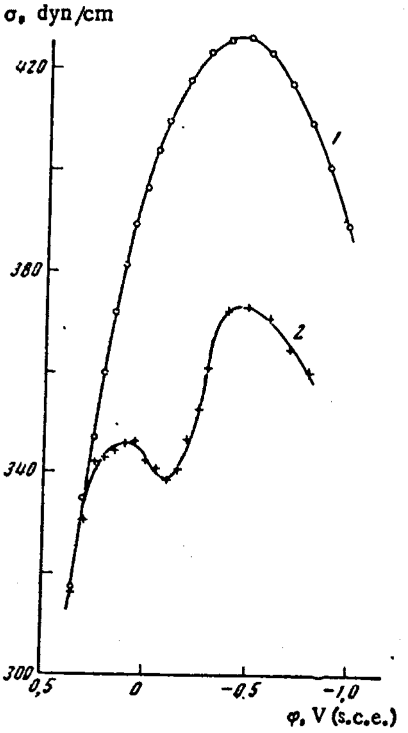

Fig. 4. Electrocapillary curve (2) of $1.25 \cdot 10^{-2}$ M iodopropionitrile with a 1 N Na_2SO_4 supporting electrolyte on a nonrenewed mercury surface during the application of potential from negative to positive values (curve 1 – supporting electrolyte).

taken on a nonrenewed mercury surface when the potential is varied from −0.8 V in the positive direction, the right-hand maximum is substantially higher than the left on account of the fact that I^- formed at negative potentials partially remains in the capillary in the transition to more positive potentials, although its concentration decreases on account of diffusion out of the capillary (Fig. 4).

Thus, the ECC of IPN with two maxima that we obtained can be explained by mutual superposition of the ECC of IPN, DCEM, I^-, and possibly CEMI in the case of a concentration and surface activity of I^- and other components of the system varying with the potential.

We might give the following generalized treatment of the electrocapillary phenomena observed in the case of iodopropionitrile, on the basis of the concepts developed in [6-8]. Let us denote the components of the redox system so that $O \equiv ICH_2CH_2CN + \frac{1}{2}Hg$, $R \equiv I^- + \frac{1}{2}(CNCH_2CH_2)_2Hg$, and consider that the condition $[O] + \gamma[R] = \text{const}$ is fulfilled, where in this case $\gamma \approx D_R/D_0$; for simplicity, let us assume $\gamma = 1$. Then let us denote as $\alpha = [O]/([O]+[R])$ the mole fraction of the ox component in the layer near the electrode (but not in the adsorbed layer). For the conditions that we have adopted, Eq. (46a) from [7, 8] is approximately applicable.*

$$\frac{\partial\sigma}{\partial(-\varphi)}=(1-\alpha)Q''+\alpha Q', \qquad (1)$$

where Q' is the total change in the case of constancy of the chemical potential of the ox component; Q" is

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*This is a rough approximation, since the assumption of reversibility of the redox system,used in the derivation of Eq. (1), is not fulfilled in the case under consideration. Moreover, from Fig. 1 it is quite evident that flow nonequilibrium processes occur in the system.

the total charge in the case of constancy of the chemical potential of the red component of the redox system.* Since Q' and Q" are related to the free charge of the electron ε and the surface excesses of the red and ox components, A_R and A_O, respectively, by the functions $Q' = \varepsilon - A_R$ and $Q'' = \varepsilon + A_0$, from (1) it follows that

$$\frac{\partial\sigma}{\partial(-\varphi)} = \varepsilon + (1-\alpha)A_0 - \alpha A_R. \quad (2)$$

At the most positive potentials, when $\alpha = 1$ (initially only the ox-component is present in solution), the derivative $\partial\sigma/\partial(-\varphi) = \varepsilon > 0$, which means a normal increase with decreasing positive value of φ. As φ is further decreased, the red component appears in solution ($\alpha < 1$); its adsorption capacity is determined chiefly by iodide ions up to a potential of −0.5 V, while at more negative potentials it is determined by DCEM, adsorbed more weakly in comparison with I^-. The shift of the potential in the negative direction leads at first to a decrease in ε, an increase in $(1-\alpha)A_0$, and a sharp increase in αA_R, as a result of which the derivative $\partial\sigma/\partial(-\varphi)$ decreases and, passing through zero, becomes negative; the potential at which $\partial\sigma/\partial(-\varphi) = 0$ corresponds to the left-hand maximum of the ECC. When the potential is further shifted in the negative direction, on account of the decrease in αA_R caused by the beginning of desorption of I^- ions at positive values of ε, the value of $\varepsilon + (1-\alpha)A_O - \alpha A_R$ becomes zero a second time (which corresponds to the minimum on the ECC), after which it begins to increase (second ascending portion of the ECC). The positive value of the derivative $\partial\sigma/\partial(-\varphi)$ on the second ascending portion is determined by the positive (although decreasing) value of ε in the case of a value of the factor αA_R decreasing on account of the decrease in α and A_R (desorption of I^-). The decrease (and change of sign) of ε, however, leads to the fact that at even more negative φ the value of $\partial\sigma/\partial(-\varphi)$ again passes through zero (right-hand maximum) and becomes negative (second descending branch of the ECC). A more detailed analysis of the possible variations of the quantities $\partial\sigma/\partial(-\varphi)$ and ε in the reversible redox system with variation of φ is given in [9, 10].

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*In Eq. (46a) in the footnote to [7,8], as a result of a typographical error, the superscripts of Q" and Q' were interchanged, as can easily be ascertained by a comparison of Eqs. (46a) and (46). The letters O and R in the next-to-last line of the footnote should also be reversed.