THE SO-CALLED TENSAMMETRIC WAVES

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The adsorption of surface-active organic compounds at the mercury/electrolyte interface was first studied by GOUY[1] by the method of measuring the interfacial tension σ. A characteristic electrocapillary curve of a solution containing a surface-active substance (heptyl alcohol) is shown in Fig. 1. As seen from the figure, the organic sub-

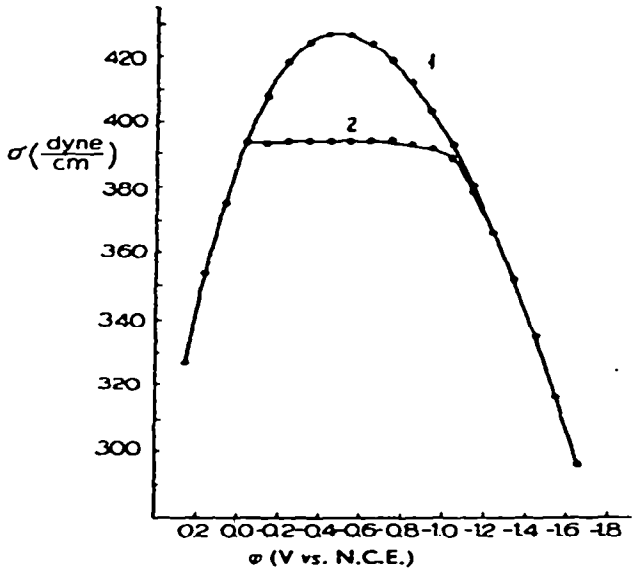

Fig. 1. Electrocapillary curves: (1) 1 N Na_2SO_4; (2) 1 N Na_2SO_4 saturated with n-$C_7H_{15}OH$ (GOUY[1]).

stance is desorbed from the mercury surface at a sufficiently large positive or negative charge density of the electrode. At the desorption potentials there are sharp changes in the slopes of the electrocapillary curves; these, according to the determination of the differential capacity C and LIPPMAN's equation:

$$C = \frac{d\varepsilon}{d\varphi} = -\frac{d^2\sigma}{d\varphi^2} \qquad (1)$$

correspond to similar changes in the charge density ε over a narrow range of electrode potentials φ and to maxima on the $C-\varphi$ curves. The interfacial tension itself, how-

ever, does not undergo any sharp changes at the desorption potentials, as the decrease in σ due to the adsorption of the organic substance is replaced by a decrease in the interfacial tension due to the ionic adsorption on the charged surface of the electrode.

In the case of strongly adsorbed substances with a carbon chain of sufficient length, the desorption process proceeds like a two-dimensional phase transition[2,3]. In this case, we can speak of a quite definite value of the desorption potential at which the equilibrium between a relatively dense adsorption layer and that corresponding to a very small coverage of the surface is established. Such two-dimensional phase equilibria agree well with the theory of monolayers at the water/air interface[4]. The only difference lies in the fact that at the water/air interface the role of an independent variable, the change of which determines the transition of the surface from one state to another, is played by the surface pressure or the temperature, whereas in the case under consideration such a variable is the potential difference between the electrode and the solution. It is evident that in the course of a two-dimensional phase transition the interfacial tension does not suffer any changes, since the equality of surface pressures of the two surface phases is the condition for equilibrium in the surface layer. In the case of substances with smaller chain lengths the desorption process does not proceed stepwise, but, instead, gradually, so that, to be precise, one should speak of a range of potentials over which the desorption occurs rather than of a desorption potential. In many cases, however, this range is very narrow. The value σ changes somewhat over it, but in a lesser degree than it would over the same range of potentials in the absence of a surface-active substance.

A quantitative theory of the effect of the electric field upon the adsorption of neutral molecules, with the complete equation of the state of the surface layer taken into consideration, has been developed by FRUMKIN[5]. This theory explains why the desorption of adsorbed molecules must proceed over a narrow range of potentials. It follows also from this theory, that when the values of the double-layer capacity are constant in the absence of an adsorbed substance ($C_{\theta=0}$ = const.), as well as at a coverage θ approaching unity ($C_{\theta=1}$ = const.), the desorption potentials φ_d are connected with the concentration of the adsorbed substance c by the equation:

$$\left| \varphi_d \left(\varphi_d \frac{C_{\theta=0} - C_{\theta=1}}{2} + C_{\theta=1} \varphi_N \right) \right| = k_1 + k_2 \ln c \qquad (2)$$

where k_1 and k_2 are constants and φ_N is the shift in the zero charge point upon coverage of the surface by the adsorbed organic substance. Eqn. 2 is in good agreement with the experimental data[3], but is applicable only at such concentrations of the surface-active substance that the adsorption limit is practically attained. The problem of the relationship between the desorption potential and the concentration over a wider range of concentrations and, in particular, that of the limits of applicability of the linear relationship between the desorption potential and the log of the concentration of the substance being adsorbed, which was pointed out in the literature[6,7], will be considered in another paper. FRUMKIN's theory was further developed by HANSEN, MINTURN AND HICKSON[8], who took into consideration the dependence of the double-layer capacity on the electrode potential.

The peaks on the curves of the differential capacity of the double-layer at the desorption potentials of organic substances were first observed by PROSKURNIN AND FRUMKIN[9]. The $C-\varphi$ curve of a solution containing n-octyl alcohol measured by these authors is shown in Fig. 2. In this work the values of the double-layer capacity were

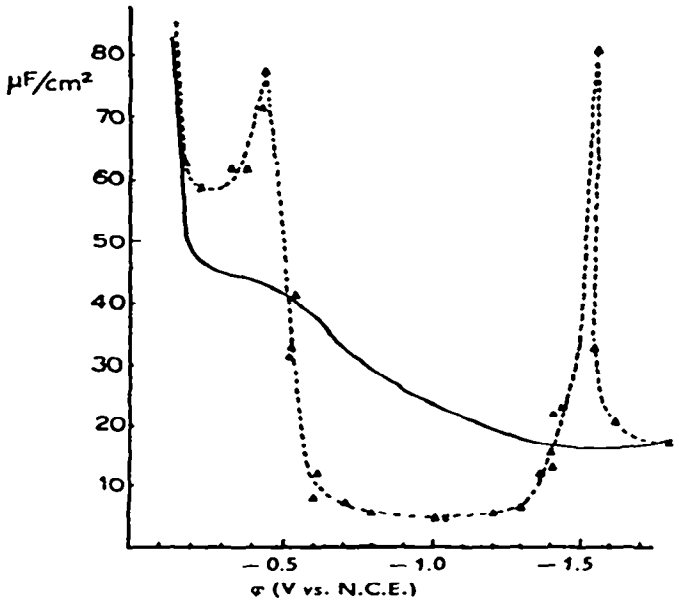

Fig. 2. Differential capacity–voltage curves measured by the method of comparison with a a standard capacity; frequency 50 cycles. Solid curve, N Na_2SO_4; broken curve, N Na_2SO_4 saturated with $C_8H_{17}OH$ (PROSKURNIN AND FRUMKIN[9]).

determined by the method of comparison with a standard capacity C_1. This method consists in measuring at a constant a.c. strength, $\widetilde{\Delta i}$, the voltage drops over the cell, $\Delta\varphi_x$, and over a standard capacity, $\Delta\varphi_1$; the double-layer capacity required can be equated with the quantity:

$$C_{obs.} = C_1\frac{\Delta\varphi_1}{\Delta\varphi_x} = C_1\frac{\widetilde{\Delta i}\frac{1}{C_1\omega}}{\widetilde{\Delta i}\sqrt{R_x^2+\frac{1}{C_x^2\omega^2}}} = \frac{C_x}{\sqrt{R_x^2C_x^2\omega^2+1}} \tag{3}$$

where R_x and C_x are the ohmic and capacity components of the total impedance of the cell, provided they are connected in series. If no electrochemical reaction occurs on the electrode, R_x corresponds to the resistance of the solution and C_x to the differential capacity of the double layer. From eqn. 3 it is evident that in the case of an ideally polarized electrode the measured value, $C_{obs.}$, can be equated with the double-layer capacity C_x only at a low a.c. frequency and with small resistance of the solution R_x, when the following inequality is fulfilled:

$$R_x^2C_x^2\omega^2 \ll 1 \tag{4}$$

The drawback of this method of comparison which consists in the necessity of satisfying condition (4) was later eliminated by DOLIN AND ERSHLER[10] by using a bridge arrangement providing for separate compensation of the capacity and ohmic components. The bridge method as applied to the case of a dropping electrode was first developed by GRAHAME[11].

In 1952 BREYER AND HACOBIAN[7] proposed a method for the study of the adsorption of surface-active organic compounds at the electrode/solution interface called by these authors "tensammetry" (from the words "surface tension" and "ammetry")[12]. Later this term was widely used in polarographic literature (see reviews)[12,13]. The method consists of measuring the a.c. flowing through a cell $\widetilde{\Delta i}$ depending on the electrode potential which is varied in accordance with the technique generally used in polarography. Since in the general case the impedance of the electrochemical cell can be represented as a resistance R_x and a capacity C_x connected in series,

$$\widetilde{\Delta i} = \frac{\Delta\varphi}{\sqrt{R_x^2 + \frac{1}{C_x^2\omega^2}}} = \Delta\varphi\omega\frac{C_x}{\sqrt{R_x^2C_x^2\omega^2 + 1}} \qquad (5)$$

If no electrode process with a reversible step occurs on the electrode surface, the value of C_x is equal to the double-layer capacity and the resulting $\widetilde{\Delta i}-\varphi$ curve is similar in its shape to the $C-\varphi$ curve. By comparing eqns. 3 and 4 we see that the "tensammetric" method yields, in principle, the same results as the comparison method, *i.e.* it yields a value proportional to the differential capacity of the double layer if conditon (4) is fulfilled.

In the paper by BREYER AND HACOBIAN[7] the maxima on the $\widetilde{\Delta i}-\varphi$ curves (the so-called "tensammetric waves") are explained, by analogy with a.c. polarography[14], to be due to periodic shifts of the charges in the a.c. field. However, the charges located on the ends of dipoles of adsorbed molecules are considered, rather than the free charges forming part of the double layer. The "tensammetric waves" are supposed to be a result of the periodical reversal of dipoles of the adsorbed substances which are on a high energy level.

It should be pointed out that the term "tensammetric waves" as applied to the desorption peaks on the curves appears unsuitable, since, as has already been noted at the beginning of this paper, there is no characteristic change in the interfacial tension corresponding to the desorption potentials. Moreover, in a number of cases the desorption of a surface-active substance from the electrode surface proceeds stepwise, and at the desorption potential there is a vertical line on the $C-\varphi$ curve (Fig. 3) to which the term "wave" is obviously inapplicable. In our opinion, it would be more correct, in distinction to a.c. polarograms, to call the $\widetilde{\Delta i}-\varphi$ curves obtained in the case of the adsorption of organic substances, curves of nonfaradaic admittance, whereas the maxima on these curves at the desorption potentials should be called adsorption–desorption peaks or maxima.

As has been shown above, the peaks on the differential capacity curves, as well as on the $\Delta i-\varphi$ curves, observed at the desorption potentials of organic substances in the case of low a.c. frequencies result from the shape of the electrocapillary curves in accordance with thermodynamical relationships, and, consequently, their height and

shape are fully determined by the dependence of the adsorption of the organic substance on the potential and by its effect on the double-layer capacity*.

The height of the capacity peak, however, varies considerably with the a.c. frequency (see Fig. 4), so that the behaviour of the electrode in the a.c. field should be examined in more detail.

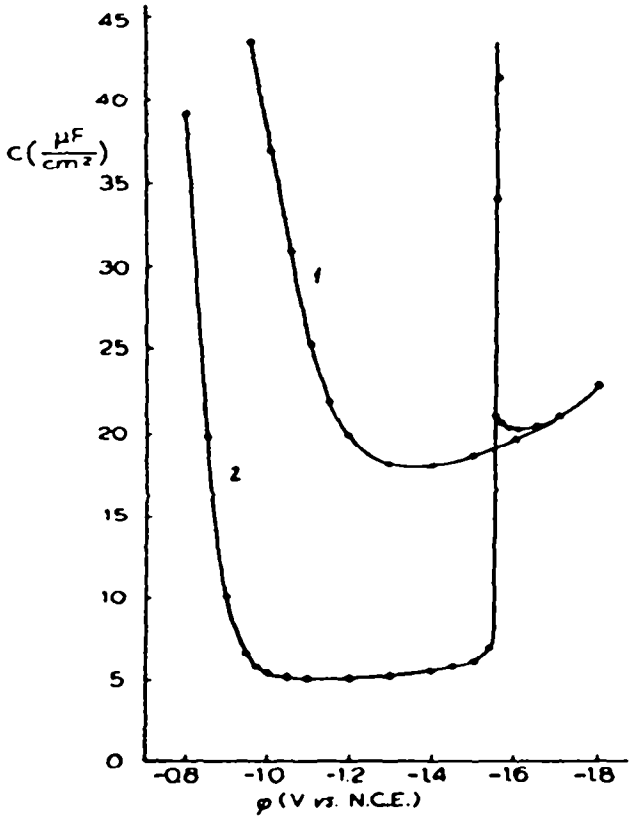

Fig. 3. Differential capacity–voltage curves: 400 cycles; 25°; (1) 1 N KI; (2) 1 N KI + 10^{-3} N $[(C_4H_9)_4N_3]I$.

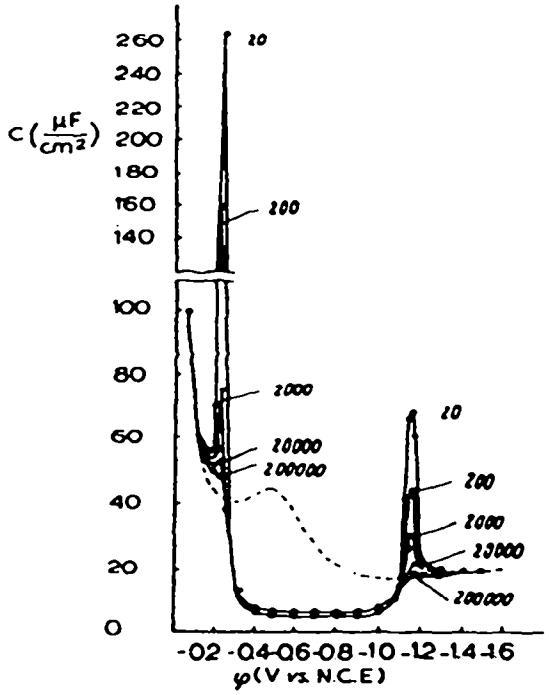

Fig. 4. Differential capacity–voltage curves in 1 N KCl + $5 \cdot 10^{-3}$ N $C_8H_{13}OH$ at different frequencies: 25°; broken curve, 1 N KCl (MELIK-GAIKASJAN[20]).

When the a.c. voltage is applied to the electrode, the charging current resulting from a change in the electrode surface charge density ε with time is equal to

$$i = \frac{d\varepsilon}{dt} \tag{6}$$

* The hypothesis has been advanced that the "electro-capillaryphoretic effect", *i.e.* the tangential motion of mercury due to adsorption/desorption processes, exerts a considerable influence upon the peaks on the $\widehat{\Delta i}$–φ (or C–φ) curves[15,19]. As has been shown in our laboratory, however, the values of the differential capacity measured by the bridge method in thoroughly cleaned and deoxygenated KCl solutions do not depend on stirring. Consequently, the tangential motion of mercury cannot result in an appreciable increase in the capacity measured. On the other hand, at the desorption potentials of organic substances the capacity peaks are known to be sharply defined in the case of solid electrodes[16–18] as well, where there is no surface motion.

If there is a surface-active organic substance in the solution, the charge density of the electrode surface is a function of the electrode potential φ and of the amount of the surface-active substance adsorbed Γ, *i.e.* $\varepsilon = f(\varphi,\Gamma)$. Therefore

$$i = \frac{d\varepsilon}{dt} = \left(\frac{\delta\varepsilon}{\delta\varphi}\right)_\Gamma \frac{d\varphi}{dt} + \left(\frac{\delta\varepsilon}{\delta\Gamma}\right)_\varphi \frac{d\Gamma}{dt} = C_e \frac{d\varphi}{dt} + i' \tag{7}$$

where C_e is the so-called "true capacity" of the double layer at a constant quantity of the substance being adsorbed (Γ = const) and

$$i' = \left(\frac{\delta\varepsilon}{\delta\Gamma}\right)_\varphi \frac{d\Gamma}{dt}$$

is the additional charging current density due to the change in adsorption with time.

When the oscillations are of a sinusoidal shape and the equivalent electric scheme shown in Fig. 5 is chosen, the value i' can be written as:

$$i' = \Delta\varphi'\left(\frac{1}{R_i}\cos\omega t - C_i\omega\sin\omega t\right) \tag{8}$$

where C_i and R_i are the additional capacity and additional resistance due to the adsorption/desorption process. As has been shown by FRUMKIN AND MELIK-GAIKASJAN[19],

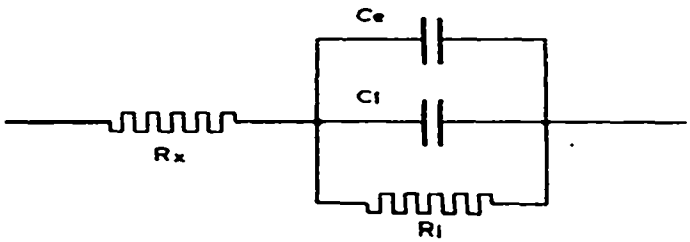

Fig. 5. The equivalent electric scheme of a cell in the case of an adsorption/desorption process occurring on the electrode.

when the rate of the adsorption process is determined by the diffusion step

$$C_i = C_0 \frac{\alpha\omega^{1/2} + 2}{(\alpha\omega^{1/2} + 1)^2 + 1} \tag{9}$$

and

$$R_i = \frac{1}{C_0} \frac{(\alpha\omega^{1/2} + 1)^2 + 1}{\alpha\omega^{3/2}} \tag{10}$$

where C_0 is the value of C_i at ω = 0 and

$$\alpha = \sqrt{\frac{2}{D}}\left(\frac{\partial\Gamma}{\partial c}\right)$$

D being the diffusion coefficient.

The values of C_i and R_i can be readily determined by means of bridge measurements (but not from $\widetilde{\Delta i}-\varphi$ curves), and from their dependence on the a.c. frequency, conclusions concerning the kinetics of adsorption of surface-active organic substances can be drawn[19-22]. Thus, it has been shown[19-20] that the dependence of C_i on the frequency can be well expressed by eqn. 9 and, consequently, the slowest step in the process of adsorption of a number of organic substances is that of diffusion of the molecules being adsorbed towards the electrode surface. The considerable decrease in the height of capacity peaks with an increase in the frequency (Fig. 4) in this case is due mainly to diffusion difficulties, although according to LORENZ AND MÖCKEL[22], the step due to the real adsorption, proceeding at a large but still finite rate, can also exert an influence upon the dependence of the height of capacity peaks on the a.c. frequency.

It should be noted that in a number of cases peaks are observed on the differential capacity curves, which are not connected with adsorption/desorption processes, but which are caused by changes in the structure of the double layer, in particular, by changes in the orientation of adsorbed particles. As an example the $C-\varphi$ curve measured in 0.01 N Na_2SO_4 + 10^{-3} N $C_{12}H_{25}OSO_3Na$ solution is shown in Fig. 6[23]. The right-hand side capacity peak is due to the process of desorption of the $C_{12}H_{25}OSO_3^-$ anion from the mercury surface and the dependence of C_i on ω for this peak corre-

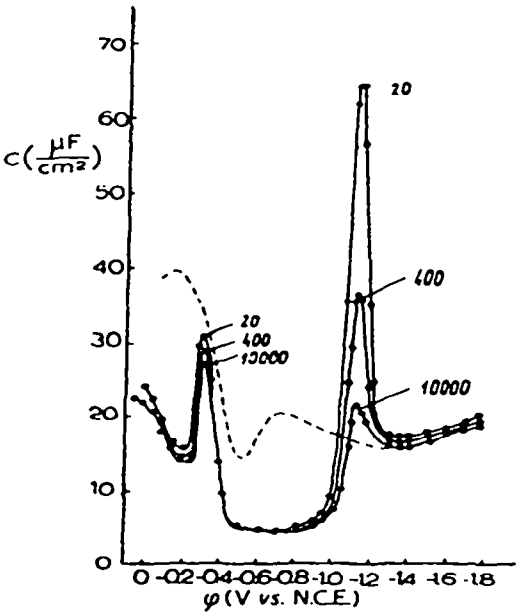

Fig. 6. Differential capacity–voltage curves in 0.01 N Na_2SO_4 + 10^{-3} N $C_{12}H_{25}OSO_3Na$ at different frequencies: 25°; broken curve, 0.01 N Na_2SO_4 (DAMASKIN, NIKOLAEVA-FEDOROVICH AND IVANOVA[23]).

sponds to eqn. 9. In contrast, the left-hand side capacity peak on the $C-\varphi$ curve shown in Fig. 6 is not a desorption peak and the dependence of the height of this peak on the a.c. frequency cannot be expressed by eqn. 9. This dependence is much less sharply expressed, which points to a larger rate for the process. As has been shown[23], the most likely cause of the appearance of this capacity peak is the reorientation of

adsorbed particles on the electrode surface with the formation of a micellar film. Similar maxima on the $C-\varphi$ curves not connected with the process of adsorption/desorption have been observed in a number of other investigations[24-26].

Although in the case in question, in contrast to that examined previously, the appearance of the capacity maxima can be due to a change in the orientation of adsorbed particles, BREYER AND HACOBIAN'S theory[7] is still not applicable. Irrespective of the nature of the phenomenon occurring in the surface layer at a given potential, the charging current and the differential capacity measured are always determined by the change in the electronic charge density of the mercury surface which is a function of the electrode potential and of the amount of the surface-active substance adsorbed $\varepsilon = f(\varphi,\Gamma)$. In BREYER AND HACOBIAN'S theory[7], however, the adsorbed dipoles of the organic substance are considered as "active" charges and the double-layer capacity measured is supposed to be determined by a change in these charges with a change in the electrode potential. In reality, although the electric field acts upon the dipole with a definite force, the total charge of the dipoles of a neutral substance, being always equal to zero, cannot bear a direct relation to the charging current.

It is of interest to compare eqn. 9 of the present paper with eqn. 54 of ref.[7], which gives an expression for the value of the additional ("tensammetric") capacity on the basis of BREYER AND HACOBIAN'S theory. As seen from eqn. 9, at $\omega \to 0$, $C_t = C_0$ and the double-layer capacity measured approaches its equilibrium value $C_e + C_0$. At the same time, according to eqn. (54) of ref.[7] deduced by analogy with the expression for the polarization capacity of an electrochemical process limited by the diffusion rate, at $\omega \to 0$ $C_t \to \infty$. In the case of an adsorption/desorption process this result is devoid of physical sense, since at potentials lying beyond the adsorption region, the electrode charge density equal to

$$\varepsilon = \int_{\varphi\,(\varepsilon=0)}^{\varphi} (C_e + C_{t(\omega\to 0)})\,\mathrm{d}\varphi$$

has a finite, determinate value*. Thus, the application of relations deduced for the faradaic current to the adsorption/desorption process leads to erroneous results. For the same reason, the data on the kinetics of adsorption of organic compounds obtained by BREYER AND HACOBIAN[27] by means of a method developed earlier for the determination of the rates of electrochemical reactions[28] cannot be considered to be correct. Moreover, as was shown later by BAUER AND ELVING[29], the method described[28] cannot yield correct values of the rate constant for electrochemical reactions, since the results depend, to a very great extent, on the phase angle between the faradaic and the charging currents as well as on the value of the series resistance R_x. In this connection, it proved necessary, in order to study the kinetics of electrochemical processes as well as to measure the double-layer capacity[30], to supplement the measurements of the a.c. value with measurements of the phase angle[31], this being in principle equivalent to the bridge method.

* An infinite capacity is theoretically possible in the case of a two-dimensional phase transition at a certain definite value of the potential, but not within some ranges of potentials.

SUMMARY

The term "tensammetry" introduced by BREYER AND HACOBIAN as well as the mechanism proposed by them to explain the appearance of peaks on the differential capacity–voltage curves in the presence of surface-active substance have been critically discussed. The value obtained by the method developed by these authors has been shown to be identical to that determined by the comparison method used by PROSKURNIN AND FRUMKIN. The advantages of the bridge arrangement for the determination of the differential capacity of the electrode have been considered. Curves for the dependence of the differential capacity on the potential are given for the case when the desorption process is that of a two-dimensional phase transition and for that when, at some potentials there occurs a change in the structure of the adsorption layer unaccompanied by its desorption.

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