The Effect of Some Surface Active Substances on the Polarographic Reduction Process of Metallic Ions[1]

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Introduction

The use of some surface active substances such as gelatin and some sorts of organic dyes to suppress the so-called maximum has been widely known in polarography. The effect of such substances on the polarographic current-voltage (*c-v*) curve is of great importance from both the theoretical and practical standpoints. As the electrode process generally takes place at the interface between two separate phases, it is expected to have a close relation to the surface phenomena like adsorption of surface active substances. The structure of the electrical double layer at the electrode interface is evidently changed by the adsorption of such substances, and such an effect will appear on the electrode

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processes. In the polarographic method with the dropping mercury electrode (DME), it is possible to study both the electrode process and the electrocapillary phenomena at the same interface, which seems to be a great advantage in the study of the effect of surface active substances on the electrode process.

Some studies along this line have been published in the literature[3]. J. Heyrovsky mentioned the effect of the films of adsorbed molecules such as pyridine in the discussion on the mechanism of electrodeposition of metals[4], and J. E. B. Randles reported that the addition of small amounts of gelatin or methyl red changed the rate of some electrochemical processes[5]. The formation of micelles of some surface active substances and its effect on the polarographic reduction waves were discussed by E. L. Colichman, who proposed a new method for the determination of the critical micelle concentration (CMC) by the polarographic method[6]. To our best knowledge, however, there have been only few studies which concern the relation between the electrode processes and the electrocapillary phenomena at the DME. Furthermore, the recent rapid development in the synthetic detergents makes it possible to get some sorts of surface active substances with similar main aliphatic parts but different electrical property, which will be very desirable in such studies as mentioned above. Under these circumstances, we have planned to study the effect of three kinds of synthetic detergtnes on the polarographic reduction process of metallic ions and their electrocapillary (E-C) curves by using the DME[7].

Experiments

Materials.—The detergents used in this study are listed in the following table. These detergents, which were kindly given by the Nezu Chemical Laboratory, Tokyo, were of the highest purity available and free from impurities which were reducible at the DME. All other chemicals were of reagent grade and used without further purification. The mercury of the DME was washed several times with dil. HNO_3 solution and distilled water, and was distilled three times under vacuum.

Apparatus and Procedure.—Both pen-recording polarograph (POL-I, Yokogawa Electric Works, Co.) and manually operating polarograph were used to obtain the c-v curve. The polarographic cell used throughout the present study is shown in Fig. 1, the resistance of which was about 40 Ω in 0.1 N KCl solution. The capillary constant of the DME was 2.060 mg$^{2/3}$ sec$^{-1/2}$ in 0.1 N KCl solution without applied potential. A specially designed mercury reservoir using the principle of the Mariotte flask[8] was used to keep the level of the mercury column of the DME constant. The potential of the reference electrode (Ag-AgCl electrode) was occasionally checked against the normal calomel electrode (N. C. E.). Because the height of the polarographic maximum is very sensitive to a slight change in the condition of the system, the maximum suppression point (MSP) of the detergents was determined by observing the change of the maximum current with the successive addition of the solution of detergents from a microburette in Fig. 1, in order to maintain the condition of the system as constant as possible. The E-C curve was obtained in 0.1 N KCl solution with the various concentrations of the detergents by measuring the drop-time of 10 drops of mercury from the DME at each electrode potential under the assumption that the interfacial tension is approximately proportional to the drop-time[9]. All measurements were carried out at 25.0 ±0.1°C, and the dissolved oxygen in the solution was expelled by bubbling nitrogen through the solution.

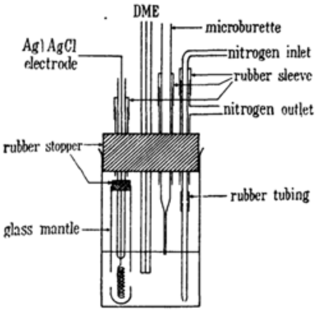

Fig. 1. Polarographic cell assembly.

TABLE I

Detergent			Molecular Weight
Sodium dodecyl sulfate (SDS)	$C_{12}H_{25}SO_4Na$	anionic	288.4
Dodecyl pyridinium bromide (DPB)	$C_5H_5NBrC_{12}H_{25}$	cationic	328.3
Polyoxyethylene lauryl ether (LEO)	$C_{12}H_{25}O(C_2H_4O)_{15}OH$	non-ionic	862

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3) For example: L. Meites and T. Meites, *J. Am. Chem. Soc.*, **73**, 177 (1951); N. Tanaka and M. Kobayashi, This Bulletin, **24**, 132 (1951); M. Dratovsky and M. Ebert, *Chem. Listy*, **45**, 88 (1951); J.E. Strassner and P. Delahay, *J. Am. Chem. Soc.*, **74**, 6232 (1952).

4) J. Heyrovsky, *Discussions Faraday Soc.*, **1947**, 212.

5) J.E.B. Randles, ibid., **1947**, 11.

6) E. L. Colichman, *J. Am. Chem. Soc.*, **72**, 4036 (1950).

7) Recently, a similar study was independently carried out by Sj. L. Bonting and B.S. Aussen, which appeared in *Rec. trav. chim. pays-bas*, 73, 455 (1954).

8) E.F. Mueller, *Ind. Eng. Chem. Anal. Ed.*, **12**, 171 (1940).

9) I.M. Kolthoff and J.J. Lingane, "Polarography" Vol. I, p. 84, 1952, Interscience Pub.

Experimental Results

Maximum Suppression Point.—The effect of the detergents on the polarographic maximum was studied with the reduction waves of Pb^{2+}– and Ni^{2+}– ions in the medium of 0.1 N KCl solution. The MSP is defined as the minimum concentration of the detergents which is necessary to make i_m/i_l equal to 1⁶⁾, where i_m means the maximum current and i_l the limiting current. It was determined graphically by plotting i_m/i_l against the logarithm of the concentration of the detergents, $\log C$ (Fig. 2 and Table II).

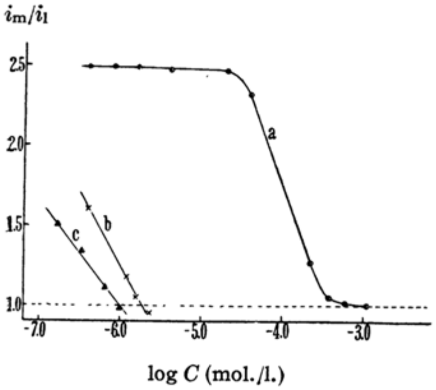

Fig. 2. The relation between i_m/i_l and the logarithm of the concentration of detergents in the systems of 3mM Ni^{2+}-detergents in 0.1 N KCl solution.
a, SDS; b, DPB; c, LEO.

TABLE II
THE MSP OF THE DETERGENTS

Detergent	MSP	
	Pb^{2+}-max.	Ni^{3+}-max.
SDS	2.3×10^{-6}M	1.1×10^{-3}M
DPB	2.3×10^{-6}M	1.9×10^{-6}M
LEO	1.3×10^{-6}M	1.0×10^{-6}M
(Gelatin	1.1×10^{-3}%	1.2×10^{-3}%)

The Effect of Detergents on the C-V Curve.—The half-wave potential and the relation between the electrode potential, V, and $\log i/(i_l\text{-}i)$ (the log-plot analysis) were investigated with the reduction processes of Tl^{+}–, Pb^{2+}– and Ni^{2+}– ions in 0.1 N KCl solution with the various concentrations of the detergents. In general, the half-wave potential shifted to the more negative and the shape of the c-v curve was gradually distorted with the increase of the concentration of detergents. These tendencies were most clearly seen in the systems of Ni^{2+}-LEO and Ni^{2+}-DBP, then in the systems of Pb^{2+}-LEO and Pb^{2+}-SDS, and least in the system of Tl^{+}-DPB. If we plot the half-wave potential of the metallic ions in the systems of Ni^{2+}-LEO and Pb^{2+}-LEO against the logarithm of the concentration of detergents, an interesting relation is obtained as in Fig. 3, which shows a sudden change in the half-wave potential in a certain concentration range of the detergent.

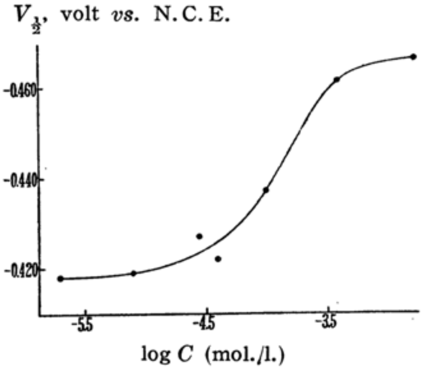

Fig. 3. The relation between the half-wave potential of Pb^{2+}-reduction wave and the logarithm of the concentration of LEO in 0.1 N KCl solution.

There was practically no effect of the presence of DPB or LEO on the shape of the c-v curve of Tl^{+}-ion, but it was slightly affected by the presence of SDS. In the case of Pb^{2+}-ion, an apparent change in the c-v curve was detected by the addition of a certain amount of SDS or LEO. The symmetrical property of the c-v curve of Ni^{2+}-ion was extensively disturbed by the presence of LEO or DPB in the system. The effect of DPB, however, could not be studied at its higher concentrations, because of the interference of the reduction wave of DPB itself on the c-v curve of Ni^{2+}-ion.

The limiting current of the metallic ions was approximately kept unchanged over a relatively wide concentration range of the detergents in each of the present systems.

Some of the typical experimental data are summarized in Table III. α in the third column of the table is a fractional number between zero and one, which appeared in the equation for the polarographic c-v curve of the activation-controlled type¹⁰⁾:

$$V=const-\frac{RT}{n\alpha F}\ln\frac{i}{i_l\text{-}i} \qquad (1)$$

where n is the number of electrons which participate in the redox reaction of the reducible substances at the DME. The value of α was calculated from the tangent of the

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10) R. Tamamushi and N. Tanaka, This Bulletin, 22, 227 (1949).

TABLE III

THE EFFECTS OF DETERGENTS ON THE POLAROGRAPHIC REDUCTION WAVES

Concn., mol./l	$V_{\frac{1}{2}}$, volt *vs.* N. C. E.			log-plot analysis (α)			$\partial t/\partial \log C$		*E-C* max. volt. *vs.* N. C. E.
	Tl^+	Pb^{2+}	Ni^{2+}	Tl^+	Pb^{2+}	Ni^{2+}	E-C max.	−1.12v.	
SDS									
4.0×10^{-6}	*	−.417	*	*	.66	*	− .10	−.09	−.49
8.0 〃	*	—	*	*	—	*	− .10	−.09	—
2.0×10^{-5}	−.481	−.442	*	.79	unsym(S)	*	− .10	.05	−.49
4.0 〃	−.494	−.447	*	unsym(S)	〃 (S)	*	− .65	−.01	−.57
8.0 〃	−.487	−.439	*	.74	〃 (S)	*	−1.24	0	ca. −.4 −.7
1.2×10^{-4}	−.490	−.429	*	.68	〃 (S)	*	− .14	.73	ca. −.3 −.8
1.6 〃	−.497	−.442	*	unsym(S)	〃 (S)	*	− .47	.23	ca. −.3 −.8
2.7 〃	−.503	−.441	*	〃 (S)	〃 (L)	*	− .97	0	ca. −.3 −.8
DPB									
8.0×10^{-6}	−.477	−.417	×	1.02	.76	×	− .02	×	−.48
2.8×10^{-5}	—	−.419	×	—	.74	×	− .36	×	ca. −.4 −.6
4.0 〃	−.484	−.419	×	.92	.76	×	−1.46	×	ca. −.4
1.0×10^{-4}	−.482	−.424	×	.95	.76	×	− .74	×	ca. −.3 −.4
2.0 〃	—	−.423	×	—	.74	×	− .32	×	−.3 −.4
4.0 〃	−.483	−.427	×	.90	.61	×	− .66	×	−.3 −.4
1.0×10^{-3}	—	−.412	×	—	.72	×	− .33	×	−.3
1.9 〃	−.461	−.397	×	.87	.80	×	− .07	×	−.3
LEO									
2.0×10^{-6}	—	−.418	—	—	.59	—	—	—	—
8.0 〃	−.474	−.419	−1.055	.94	.60	.40	0	0	−.49
2.0×10^{-5}	—	—	−1.111	—	—	unsym(L)	− .63	− .33	−.45
2.8 〃	−.492	−.427	−1.209	.74	unsym(L)	〃 (S)	−4.78	−3.68	ca. −.2 −.5
4.0 〃	−.493	−.422	−1.375	.78	〃 (L)	〃 (S)	−2.14	−2.03	ca. −.1 −.4
1.0×10^{-4}	−.493	−.437	—	.74	〃 (L)	—	−1.14	− .69	ca. −.1 −.3
2.0 〃	—	—	−1.576	—	—	unsym(U)	− .78	− .40	ca. −.1 −.3
4.0 〃	−.487	−.461	—	.80	unsym(L)	—	− .46	− .37	ca. −.1 −.3
1.9×10^{-3}	−.489	−.465	—	.73	〃 (L)	—	− .10	− .12	ca. −.1 −.3

* Can not be determined because of the presence of maximum.

× Can not be determined because of the interference due to the reduction wave of DPB.

unsym(S): The log-plot shows a S-shaped curve.

unsym(U); The upper half of the polarographic wave is steeper than the lower half.

unsym(L): The lower half of the polarographic wave is steeper than the upper half.

log-plots by assuming that $n=1$ in the case of Tl^+-ion and $n=2$ in the case of Pb^{2+}-or Ni^{2+}-ion.

Electrocapillary Curve.—The presence of a certain amount of these detergents changed both the position of the electrocapillary maximum (*E-C* max.) and the shape of the *E-C* curve as shown in Fig. 4. The addition of SDS more than 1×10^{-4} M in its cocentration greatly flattened the curve and lowered the interfacial tension at the potential of the *E-C* max., the latter effect of which, however, was quite small at any potential more negative than about −1.2 volts. In the case of DPB, the *E-C* max. was shifted to the more positive and the interfacial tension was mainly lowered in the potential region of the negative branch. The presence of LEO lowered the interfacial tension over the whole potential region from 0 to −1.8 volts with the gradual shift of the *E-C* max. to the more

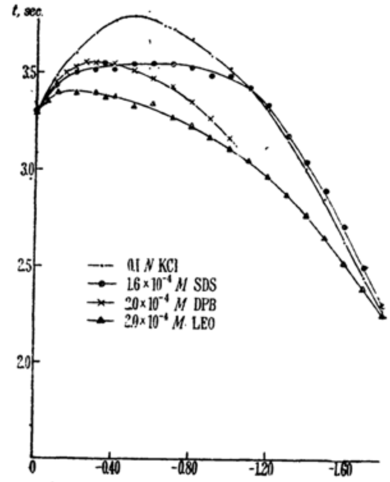

Fig. 4. The electrocapillary curves of detergents in 0.1 N KCl solution.

positive potential. This suggests that LEO will be polarized at a polarized electrode surface, the positive end of the induced dipole being surface active.

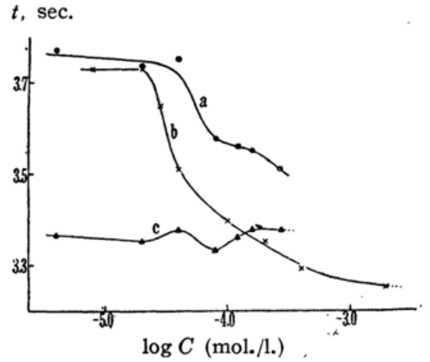

Fig. 5. The relation between the drop-time and the logarithm of the concentration of detergents in 0.1 N KCl solution. a, SDS at *E-C* max.; b, LEO at *E-C* max.; c, SDS at -1.12 volts *vs.* N.C.E.

If the drop-time at the *E-C* max., t_{max},. is plotted against the logarithm of the concentration of detergents, log *C*, the curves as shown in Fig. 5 are obtained. The tangent of the relation between $t_{\text{max.}}$ and log *C* is shown to be approximately proportional to the surface excess of the neutral detergent molecule at the electrode surface at the potential of the *E-C* max., $\Gamma_{\text{det.}}^{\text{max.}}$, because, under the assumption that the surface excess of solvent is equal to zero,

$$\frac{d\sigma^{\text{max.}}}{d\mu_{\text{det.}}} = -\Gamma_{\text{det.}}^{\text{max.}}$$

is derived from the Gibbs adsorption equation applied to an ideal polarized electrode at constant temperature and pressure:

$$d\sigma = -q dE - q d(\Delta\psi) - \Sigma \Gamma_i d\mu_i \qquad (2)^{11)}$$

σ: The interfacial tension of phases between the electrode and the solution.
μ_i: The chemical potential of a component represented by its subscript.
Γ_i: The surface excess of that component.
q: The surface charge density of electricity on the metallic phase.
E: The total applied potential difference between the working electrode and the reference electrode measured by a potentiometer.
$\Delta\psi$: The potential difference between the solution phase and the reference electrode.

It is also assumed in the present discussion that the activity coefficient of detergents in our systems is equal to one. This relation can be used in the discussion of the effect of the detergents on the reduction process of Tl^+- or Pb^{2+}- ion which is reduced at the electrode potential near the *E-C* max.

In the very low concentration range of the detergents, the value of the tangent is very small, which indicates a negligible amount of adsorption. Such a low concentration range is followed by the region of the almost constant inclination corresponding to the constant value of Γ. With the further increase of the concentration of the detergents, however, the drop-time is not decreased markedly, which does not necessarily mean the decrease in Γ of the simple detergent molecule but will be interpreted by the change in the state of the system such as the micelle formation of the detergent molecules[12]. It must be mentioned here, with regard to the usual method of the determination of CMC from the data of the surface tension, that, in the relation between $t_{\text{max.}}$ and log *C*, non-ionic detergent LEO shows only one relatively smooth step but ionic detergents have a tendency to show two steps provided that the determination is carried out over a wide concentration range (Fig. 5).

The drop-time was also plotted against log *C* at a constant electrode potential of -1.12 volts, the result of which will be useful in the discussion of the effect of detergents on the reduction process of Ni^{2+}-ion which is reduced at this potential. It is shown from Eq. (2) that the tangent of such a relation is approximately proportional to the surface excess of detergent at this potential as in the case of the *E-C* max., i.e.,

$$\frac{d\sigma^{-1.12}}{d\mu_{\text{det.}}} = -\Gamma_{\text{det.}}^{-1.12}$$

provided that the value of $\Delta\psi$ in Eq. (2) is assumed unchanged with the change in $\mu_{\text{det.}}$. This assumption seems plausible because of the presence of KCl in excess as the indifferent electrolyte. In the case of LEO and DPB, the result at -1.12 volts was qualitatively similar to that at the *E-C* max., but SDS showed a quite different curve as in Fig. 5-c indicating a negligible adsorption of SDS at -1.12 voluts over the whole concentration range of SDS. This can be explained by considering the desorption of SDS at such a negative potential, which has been once adsorbed at the more positive potentials.

Discussion

E. L. Colichman stated that the usual CMC "seems to be equal to the concentration

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[11] D.C. Grahame, *Chem. Revs.*, **41**, 441 (1947).

[12] C.P. Roe and P.D. Brass, *J. Am. Chem. Soc.*, **76**, 4703 (1954).

of colloidal agent just sufficient to suppress maxima, the maximum suppression point (MSP)"[3]. However, Table II shows that the MSP of the detergents in our present systems, except one of SDS and Ni^{2+}-ion, are in the order of 10^{-6} mol./l. which is much lower than the generally accepted value of CMC of these detergents[13]. The very poor ability of SDS to suppress the maximum of Ni^{2+}-ion will be at first sight explained by considering that the adsorption of SDS on the DME is almost absent at such a negative potential as that of Ni^{2+}-maximum (Fig. 5-c and Table III). However, in the case of LEO or DPB, which are very active to both of Pb^{2+}- and Ni^{2+}-maxima, the lowering of the interfacial tension and the adsorption of these detergents are also shown to be quite small at such a low concentration range as their MSP from the result of the *E-C* curve. These experimental results suggest that the suppression of the polarographic maximum will not only concern the adsorption or the change in the interfacial tension due to the presence of surface active substances but also the slight change in the structure of the electrical double layer. At any rate, it can be concluded that these detergents are generally very effective to suppress the polarographic maximum and are preferable to gelatin in the following respects: 1) these detergents do not seem to have any tendency of complex-formation with metallic ions; 2) the viscosity of the solution does not change makedly by the addition of their small amount enough to suppress the maximum; 3) they are completely free from deterioration.

With regard to the difference in the electrical property of the detergents, which appears in their effect on the polarographic *c-v* curve, it can be said from the experimental results that the anionic detergent generally has a larger effect than the cationic one on the reduction process with the half-wave potential more positive than the *E-C* max., and *vice versa.* It must be mentioned that the non-ionic detergent, LEO, gives a relatively large influence to the polarographic *c-v* curve in all cases. The result of the *E-C* curve also reflects the difference in the electrical property of the detergents.

The apparent value of α in Table III, which should be equal to one under the simplest condition if the overall electrode process were diffusion-controlled[10], the distortion of the *c-v* curve, and the shift of the half-wave potential to the more negative suggest that the overall electrode process becomes more and more activation-controlled[10] and the reduction process is retarded with the increase in the concentration of the detergents. Such a tendency is the largest in the case of the so-called irreversible reduction process of Ni^{2+}-ion, then in the case of reversible reduction process of Pb^{2+}-ion, and the least in the case of completely reversible reduction process of Tl^{+}-ion in the present systems, which is in good agreement with Heyrovsky's theory on the mechanism of the reduction process of metallic ions[4]. It should be mentioned here, however, that even the reduction process of Tl^{+}-ion, which had been expected to be completely reversible and not influenced by the adsorption of the surface active substances according to J. Heyrovsky, was shown to be affected, although to a relatively small extent, by the presence of a certain amount of SDS (or LEO).

The relation between the effect of the detergents on the *c-v* curve and the results of the *E-C* curve must be emphasized at the end of the present discussion. Generally speaking, the concentration range of the detergents, in which the shift of the half-wave potential and the distortion of the *c-v* curve of the reduction process of the metallic ions clearly appear, almost coincides with the concentration range corresponding to the constant value of the surface excess of the detergents as shown in Fig. 5. Such a relation is most clearly seen in the one to one correspondence between the relation of half-wave potential *vs.* log *C* and that of the drop-time *vs.* log *C* in the system of Ni^{2+}-LEO or Pb^{2+}-LEO (Figs. 3. and 5-c).

It can be said from all these experimental results that the effect of the surface active substances on the electrode process of metallic ions at the DME has a very close relation to the adsorption phenomena of the surface active substances and the structure of the electrical double layer at the electrode interface. The difference in the effect, which was given to the polarographic *c-v* curve by the presence of the surface active substances with the different electrical property, will suggest, as pointed out by J. Heyrovsky[4], that the adsorption layer of these substances mainly affects the transfer of electrons at the electrode interface and not the diffusion process of metallic ions. The results of the present study are expected to provide some new experimental facts to the study of the polarographic maximum and the mechanism of the electrode processes.

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[13] For example, C.P. Roe and P.D. Brass gave the value of 1.45×10^{-3} mol./l. for the CMC of SDS at *p*H 6.5 and Na^{+} -ion concentration of 0.1 mol./l.[12].

Summary

The effect of three detergents on the polarographic electrode reduction processes of Tl^{+}-, Pb^{2+}- and Ni^{2+}-ions was studied together with the *E-C* curve of these detergents. It was shown that these detergents were very effective to suppress the polarographic maximum and their surface excess was shown to be very small at the concentration range of their MSP from the study of the *E-C* curve. The half-wave potential was shifted to the more negative and the shape of the *c-v* curve was distorted by the presence of these detergents, the degree of which was the largest in the case of Ni^{2+}-ion and the least in the case of Tl^{+}-ion. The anionic detergent seemed to have a larger effect than the cationic one on the electrode process with the half-wave potential more positive than the *E-C* max., and *vice versa.* It was shown that the effect of the detergents on the polarographic *c-v* curve was parallel to the result on their adsorption phenomena obtained from the *E-C* curve. From these results it was concluded that the polarographic electrode process is greatly influenced by the change in the structure of the electrical double layer and that it will be the electron-transfer process which is mainly affected by the presence of the adsorption layer of the surface active substances.

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