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ELECTROCAPILLARY PHENOMENA IN THE Hg, Tl, Tl^+, H_2O SYSTEM IN THE PRESENCE OF PHENOL

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The consideration of the mercury electrode behavior in solutions of thallium salts from the point of view of the applicability of the theory of electrocapillarity to reversible redox systems has shown that in the Hg, Tl, Tl^+, H_2O system two characteristic electrocapillary curves (EC) can be obtained[1–3]. The Lippmann equations describing these curves, obtained from the general equation of the EC dependence for redox systems[1,2] with a liquid–liquid interface, are of the form

$$-(\partial\sigma/\partial\varphi)_{\mu_{Tl^+}} = -\Gamma_{Tl} = \varepsilon - A_{Tl} = Q' \quad (1)$$

and

$$-(\partial\sigma/\partial\varphi)_{\mu_{Tl}} = \Gamma_{Tl^+} = \varepsilon + A_{Tl^+} = Q'' \quad (2)$$

where σ is the interfacial tension, φ the electrode potential, μ the chemical potential, Γ the Gibbs adsorption, ε the free surface charge, and A_{Tl} and A_{Tl^+} the surface excesses of thallium atoms and ions, respectively. In ref. 3 some suggestions were made regarding the adsorption phenomena in the Hg, Tl, Tl^+, H_2O system, for which EC curves were obtained at the conditions μ_{Tl^+} = const. (EC curves of the 1st kind) and μ_{Tl} = const. (EC curves of the 2nd kind). For further specification of the suggested schemes of the double layer structure, it was of interest to obtain the curves of the 1st and 2nd kind for the Hg–Tl system in the presence of surface-active neutral molecules. This paper is concerned with the investigation of the adsorption phenomena in the Hg, Tl, Tl^+, H_2O system in the presence of phenol*.

PROCEDURE AND RESULTS

The equilibrium values of σ were determined by the procedure of ref. 3 for thallium amalgams with Tl content from 0.1 to 10 at.% in x *M* $TlNO_3 + (1-x)$ *M* $KNO_3 + 0.05$ *M* HNO_3 solutions, where x varied from 0.001 to 0.1. As in ref. 3, the reference electrode was 9.9% Tl amalgam in 0.1 *M* $TlNO_3 + 0.9$ *M* KNO_3 solution. The treatment of the experimental data, however, differed somewhat from that used in ref. 3, because it had been found during the experiments that in spite of the precautions taken earlier the dilute amalgams undergo oxidation, accompanied by a

* Data on phenol adsorption on a mercury electrode from $TlNO_3 + KNO_3$ solutions were presented earlier in refs. 2 and 4, where the EC curves were obtained by the polarization of the mercury meniscus in the capillary, that is under non-equilibrium conditions.

change in the Tl content in the amalgam, when passing from the measurement of σ and φ in a solution with Tl^+ concentration x_1 M to that in a solution with a different concentration x_2 M. On the other hand, the change in the concentration of Tl^+ ions in the solution over the relatively short time of one experiment (in the solution with the same Tl^+ concentration) could be neglected. Therefore, the plotting of the EC curves of the 1st and 2nd kind for the systems in question in the presence and absence of phenol, and also the correction of the data of ref. 3 which became necessary, were carried out in this paper as follows. First, on the basis of the experimental values of σ and φ obtained, the EC curves of the 1st kind were plotted (curves 1–5 in Fig. 1)*. Then, from the experimental values of φ, obtained for the most concentrated amalgam in each solution (6.8% in ref. 3 and 9.7% in this paper) by means of the Nernst equation, the φ values were calculated for all other given amalgam concentrations. The necessary values of thallium activity in amalgams were found by the interpolation of the data of Lewis and Randall[5]. The values of φ thus obtained, marked with crosses in Fig. 1, were compared with the experimental values marked with circles. For amalgams with Tl content 0.7% and over, the experimental values coincide well with the theoretical ones. Thus, for these Tl concentrations the EC curves of the 2nd kind can be plotted, as was done in ref. 3, from the φ values obtained in the measurements of σ (curves 9–11, Fig. 1). For more dilute amalgams some discrepancies greater than the measurement errors were observed. In those cases, considering the EC curves satisfying the condition μ_{Tl^+} = const. (curves of the 1st kind) to be correct, we found for the calculated φ values the corresponding σ values from the relevant curves of the 1st kind and plotted the EC curves of the 2nd kind from the σ, φ values obtained.

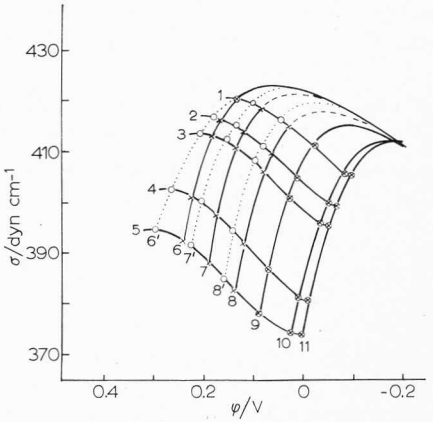

Fig. 1. EC curves of the 1st and 2nd kind plotted together (from the corrected data of ref. 3). Tl^+ concentration x in solutions x M $TlNO_3+(1-x)$ M KNO_3: (1) 0.001; (2) 0.005; (3) 0.01; (4) 0.05; (5) 0.1. Tl content in amalgams c_{Tl} in at.%: (6) 0.002; (7) 0.014; (8) 0.12; (9) 0.7; (10) 4.9; (11) 7.8. Figures with primes refer to corresponding EC curves of the 2nd kind as given in ref. 3. Potentials are referred to the electrode 9.9% Tl amalgam in 0.1 M $TlNO_3+0.9$ M KNO_3.

* The curves of Fig. 1 have been plotted from the data of ref. 3, which include the measurements on two amalgams more dilute than 0.1%. A similar figure for systems with and without phenol for somewhat different Tl concentrations, used in this investigation, is not given here.

The EC curves 6–8 of Fig. 1, thus plotted, unlike the curves 6′–8′ (dashed) really correspond to the given amalgam concentrations. From the foregoing it was found necessary to revise the values of Γ_{Tl}, Γ_{Tl^+} and $\Gamma_\Sigma = \Gamma_{Tl} + \Gamma_{Tl^+}$, which had been obtained by graphical differentiation of the EC curves at the points of intersection of curves 6′–8′ with the curves of the 1st kind (the first three lines of Table 1 in ref. 3). The values of Γ_{Tl}, Γ_{Tl^+} and Γ_Σ (in $\mu C\ cm^{-2}$) obtained by the same procedure at the points of intersection of curves 6–8 with the curves of the 1st kind are listed in Table 1.

In accordance with the values given here, the left-hand parts of the σ, φ curves 2–4 in Fig. 2 of ref. 3, corresponding to curves 6′–8′ of Fig. 1 of this paper and to curve 3 of Fig. 4 (curve 6′), as well as the left-hand part of curves 1–3 of Fig. 7 and curve 1 of Fig. 10 of ref. 3, should have a somewhat different slope. The changes in Fig. 6 of that paper associated with the corrections of Table 1 are so small that they do not affect the shape of the curve. The above-mentioned corrections, however, do not influence the qualitative conclusions made in ref. 3.

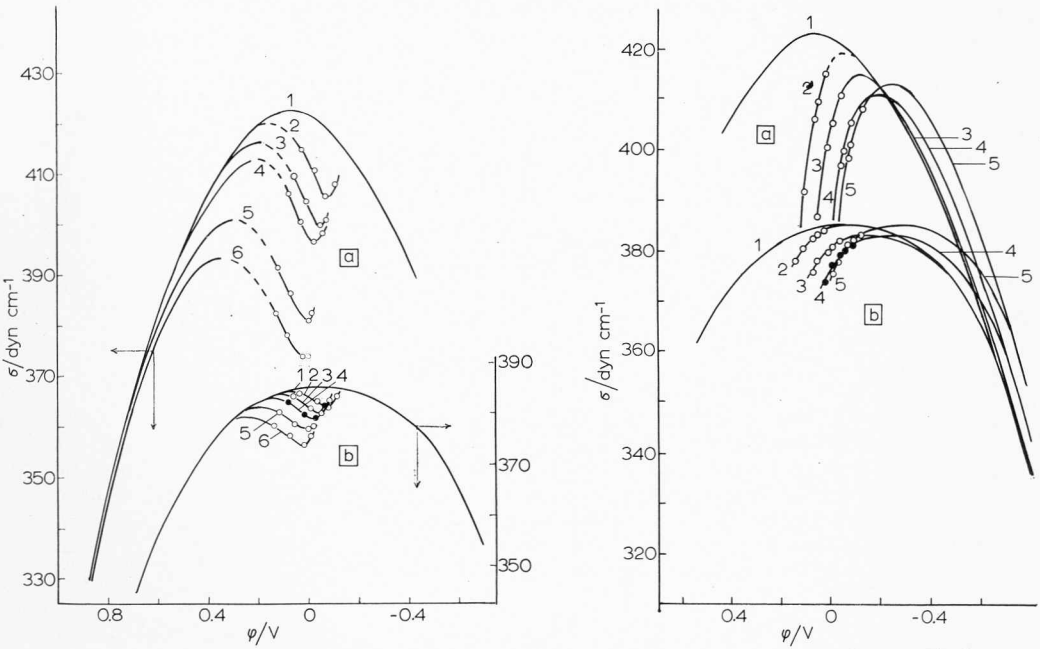

Fig. 2. Electrocapillary curves of the 1st kind. Tl^+ concentration x in solutions of x M $TlNO_3$ + $(1-x)$ M KNO_3: (1) 0; (2) 0.001; (3) 0.005; (4) 0.01; (5) 0.05; (6) 0.1. (a) in the absence of phenol; (b) in the presence of 0.2 M phenol.

Fig. 3. Electrocapillary curves of the 2nd kind. c_{Tl} in at.%: (1) 0; (2) 0.1; (3) 0.8; (4) 4.6; (5) 9.7. (a) in the absence of phenol; (b) in the presence of 0.2 M phenol.

The EC curves of the 1st and 2nd kind in $TlNO_3$ solutions (a) without, and (b) with addition of phenol in 0.2 M concentration are shown in Figs. 2 and 3. The points measured under equilibrium conditions are shown by circles. The absence of circles means that this particular part of the curve was obtained by polarization

TABLE 1

At.% of Tl in amalgam	*Molarity of Tl^+ in solution*														
	0.001			*0.005*			*0.01*			*0.05*			*0.1*		
	Γ_{Tl}	Γ_{Tl^+}	Γ_{Σ}	Γ_{Tl}	Γ_{Tl^+}	Γ_{Σ}	Γ_{Tl}	Γ_{Tl^+}	Γ_{Σ}	Γ_{Tl}	Γ_{Tl^+}	Γ_{Σ}	Γ_{Tl}	Γ_{Tl}	Γ_{Σ}
0.002	1.1	8.5	9.6	3	15	18	3.2	19.6	23	4	44	48	6.3	66	72
0.014	4.5	9.3	14	6.4	16	22	6.7	21.5	28	9.5	45	54	11	66	77
0.12	7.2	11.6	19	8.8	19.4	28	9.8	26.4	36	10.5	47	57	9.6	59	69

of the meniscus in the capillary*. As is clear from the figures, when phenol is introduced into the solution, the slopes of the descending branches of the EC curves of the 1st kind and of the ascending branches of the curves of the 2nd kind decrease significantly, and the decrease of σ with increasing Tl^+ concentration c_{Tl^+} in the solution on the ascending branch of the EC curves of the 1st kind disappears completely (compare (a) and (b) of Figs. 2 and 3). Moreover, the decrease of σ at the maximum of the EC curves of the 1st and 2nd kinds in the presence of thallium, as compared with the initial curve in KNO_3 solution at an Hg electrode, $\Delta\sigma^{max} = \sigma^{max}_{KNO_3} - \sigma^{max}_{KNO_3 + TlNO_3}$ and $\Delta\sigma^{max} = \sigma^{max}_{Hg} - \sigma^{max}_{Tl(Hg)}$, respectively, is much less when passing from solutions without phenol to those with phenol. To illustrate the mutual effects of the components adsorbed in the system Hg, Tl, Tl^+, H_2O, C_6H_5OH, the obtained data are presented as the dependence of $\Delta\sigma$ on φ for phenol, thallium, phenol in the presence of thallium and thallium in the presence of phenol (curves 1–4 of Fig. 4). Curves 2–4 were obtained from the EC curves of the 1st and 2nd kinds satisfying the conditions $c_{Tl^+} = 0.1\ M$ and $c_{Tl} = 0.8\%$, respectively, with and without phenol additions. Curve 1 shows the dependence of phenol adsorption on potential in 1 M KNO_3 solution at a mercury electrode.

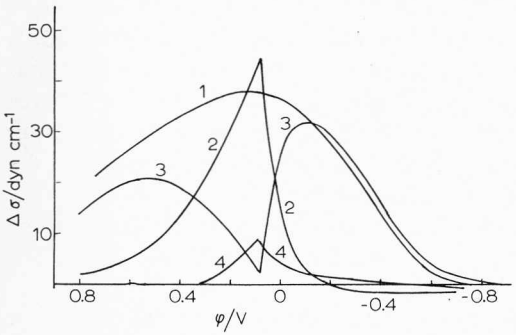

Fig. 4. $\Delta\sigma$–φ dependences: (1) $\Delta\sigma = \sigma^{1M KNO_3}_{1M KNO_3 + 0.2M C_6H_5OH}$ at a Hg electrode (from curves 1 of Figs. 2(a) and 2(b)). (2) Ascending branch: $\Delta\sigma = \sigma^{1M KNO_3}_{0.1M TlNO_3 + 0.9M KNO_3}$ (from curves 1 and 6, Fig. 2(a)); descending branch: $\Delta\sigma = \sigma^{Hg}_{0.8\% Tl(Hg)}$ in 1 M KNO_3 solution (from curves 1 and 3, Fig. 3(a)). (3) Left-hand part: $\Delta\sigma = \sigma^{0.1M TlNO_3 + 0.9M KNO_3}_{0.1M TlNO_3 + 0.9M KNO_3 + 0.2M C_6H_5OH}$ (from curves 6, Figs. 2(a) and 2(b)); right-hand part: $\Delta\sigma = \sigma^{1M KNO_3}_{1M KNO_3 + 0.2M C_6H_5OH}$ at 0.8% Tl amalgam (from curves 3, Figs. 3(a) and 3(b)). (4) Ascending branch: $\Delta\sigma = \sigma^{1M KNO_3 + 0.2M C_6H_5OH}_{0.1M TlNO_3 + 0.9M KNO_3 + 0.2M C_6H_5OH}$ (from curves 1 and 6, Fig. 3(b)); descending branch: $\Delta\sigma = \sigma^{Hg}_{0.8\% Tl(Hg)}$ in 1 M KNO_3 + 0.2 M C_6H_5OH solution (from curves 1 and 3, Fig. 3(b)).

DISCUSSION

We suggest the following interpretation of the obtained results, which agrees with the concepts of the structure of the electrode/solution interface in the Hg–Tl system set forth in ref. 3. When phenol is introduced into the system, a competition between adsorbed phenol and thallium occurs at the interface[2,4]. As is clear from curve 4, in the region $\varphi > 0.4$ V, corresponding to the ascending branch of the EC curve of the 1st kind, phenol adsorption prevails, which almost completely

* On the EC curves 2(a), 4(a) and 5(a) of Fig. 3 the lower points are omitted in order to avoid confusion of the curves (a) and (b).

suppresses the relatively low (in the absence of phenol) adsorption of thallium cations (curve 2). At φ more negative than 0.4 V, thallium adsorption becomes appreciable and with further shift of φ in the negative direction up to 0.08 V, increases gradually, remaining however quantitatively much less than for the system without phenol (curve 2). As follows from the shape of curve 3, in this region thallium adsorption markedly hinders that of phenol, which no longer completely suppresses thallium adsorption. At these potentials, corresponding to the maximum and the descending branch of the EC curve of the 1st kind to the point of its intersection with the EC curve of the 2nd kind at $\varphi = 0.08$ V, phenol adsorption can be hindered by Tl^+ cations on the negatively charged surface near the potential of zero charge* and by the anion complexes containing thallium when the sign of the surface charge changes for the positive one, as well as by thallium atoms forming dipoles with mercury (see ref. 3). Probably the greatest competition should be due to the anion complexes of thallium. In the region of φ more negative than 0.08 V, the decrease in thallium adsorption in the presence of phenol is in agreement with that observed in the system without phenol (curve 2). This fact is due to the decrease of A_{Tl^+} values caused by the drop of c_{Tl^+} in the solution when φ shifts in the negative direction, μ_{Tl} remaining constant. In accordance with the assumption made about the competition between thallium and phenol undergoing adsorption, in this range phenol adsorption increases (curve 3). In the presence of phenol the positive thallium adsorption does not change to a negative one up to the potential -0.55 V, whereas in the system Hg, Tl, Tl^+, H_2O this occurs at $\varphi = 0.2$ V (*cf.* curves 2 and 4), and to a much greater degree. This probably is the most interesting result of the investigation of the co-adsorption of thallium and phenol at the mercury/electrolyte interface. It can be supposed that the adsorbed phenol molecules, interacting with their π-electrons with the positive charges of thallium atoms (being less electronegative, the thallium atom in the dipole Hg–Tl should have a positive charge), draw these to the surface.

The sharp change in the nature of the $\Delta\sigma$, φ dependence for phenol in the presence of thallium (curve 3), as compared with that for phenol in the system without thallium (curve 1), points directly to the influence of thallium adsorption on that of phenol. It can be seen that in the presence of thallium, two regions of maximum phenol adsorption appear, corresponding to the regions of decreasing thallium adsorption in the system without phenol. On the contrary, in the region of the greatest phenol adsorption on a mercury electrode (curve 1), the maximum thallium adsorption in the Hg, Tl, Tl^+, H_2O system leads to the decrease of phenol adsorption almost to zero. It is clear from the comparison of the curves 1,3 and 4 of Fig. 4 that at a certain value of thallium adsorption in the system Hg, Tl, Tl^+, H_2O, C_6H_5OH a stronger suppression of phenol adsorption by thallium is observed on the ascending branch of curve 4, than at the same value of thallium adsorption on the descending branch of curve 4. This effect can be explained from the assumption of the existence of two forms of adsorbed thallium in the Hg, Tl, Tl^+,

* There has appeared a tendency in literature to consider the specific adsorption of inorganic cations on mercury only as a secondary phenomenon induced by specific anions adsorption[6–8]. The experimental data on the adsorption of thallium ions in the presence of fluorides and sulfates[2,3] do not fit this scheme. In the presence of NO_3^- ions, the adsorption of Tl^+ ions evidently occurs both by the direct and by the anion-induced mechanisms.

H_2O system. In the region of φ corresponding to the ascending branch of curve 4, phenol adsorption is hindered by anionic complexes of thallium present in the ionic side of the double layer. In the region of φ corresponding to the descending branch of curve 4 it is hindered by thallium atoms of the Tl–Hg dipoles, which, being located in the metal phase and oriented with their negative end inside the metal, hinder the adsorption of phenol molecules much less than the anionic complexes.

Due to the availability of experimental data for several thallium concentrations, it was possible to calculate the total thallium adsorption as atoms and ions $(\Gamma_{Tl} + \Gamma_{Tl^+}) = \Gamma_\Sigma$ in the absence and presence of phenol. Figure 5 shows the dependence of the adsorption Γ_Σ on φ calculated by two methods (see below) without and with phenol. The change of φ is carried out first along the EC curve of the 1st kind corresponding to $c_{Tl^+} = 0.05$ M, and then along the EC curve of the 2nd kind corresponding to $c_{Tl} = 0.8\%$ Tl(Hg)*. As can be seen from the figure, in the presence of 0.2 M phenol the total adsorption of thallium drops sharply, especially in the region of its maximum adsorption.

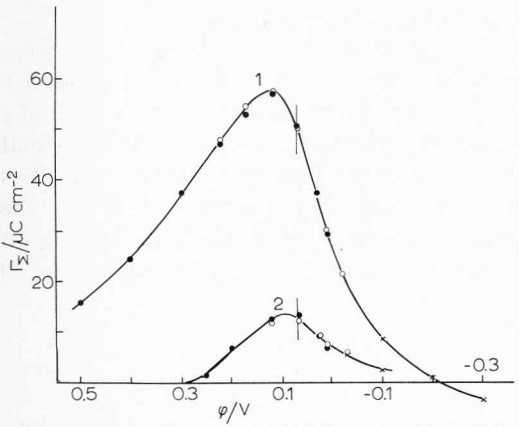

Fig. 5. Dependence of total Tl adsorption Γ_Σ on φ along the EC curves of 1st and 2nd kind, satisfying the conditions $c_{Tl^+} = 0.05$ M and $c_{Tl} = 0.8\%$, respectively, calculated from: (○) eqn. (3), (●) eqn. (5), (×) eqn. (6); (1) without phenol, (2) with 0.2 M phenol. Vertical line divides the sections of Γ_Σ–φ curves corresponding to curves of 1st and 2nd kind respectively.

The values of Γ_Σ can be obtained both by means of the equation

$$\Gamma_\Sigma = (\partial\sigma/\partial\varphi)_{\mu_{Tl}+} - (\partial\sigma/\partial\varphi)_{\mu_{Tl}} \tag{3}$$

which describes the change in the slope of the EC curves, when passing from the curves of 1st kind to those of the 2nd kind at their intersection point[3], and by the Gibbs equation. In fact, the Gibbs equation for the system in question is of the form

$$d\sigma = -\Gamma_{Hg}\, d\mu_{Hg} - \Gamma_{Tl}\, d\mu_{Tl} - \Gamma_{Tl^+}\, d\mu_{Tl^+} - \Gamma_{K^+}\, d\mu_{K^+} - \Gamma_{NO_3^-}\, d\mu_{NO_3^-} - \Gamma_{H_2O}\, d\mu_{H_2O}$$

* In calculating curve 1, the corrected data for 0.002 and 0.014% amalgams[3] were used which are not given in this paper.

By definition, $\Gamma_{Hg}=0$. For the conditions at which our measurements were carried out we can assume to a sufficient approximation that $d\mu_{H_2O}=0$, $d\mu_{K^+}=0$ and $d\mu_{NO_3^-}=0$. Thus

$$d\sigma = -\Gamma_{Tl}\,d\mu_{Tl} - \Gamma_{Tl^+}\,d\mu_{Tl^+} \tag{4}$$

From eqn. (4) and the Nernst equation

$$(1/F)d\varphi = d\mu_{Tl^+} - d\mu_{Tl}$$

it follows that

$$d\sigma = -(\Gamma_{Tl}+\Gamma_{Tl^+})d\mu_{Tl^+} + (1/F)\Gamma_{Tl}\,d\varphi = -(\Gamma_{Tl}+\Gamma_{Tl^+})d\mu_{Tl} - (1/F)\Gamma_{Tl^+}\,d\varphi$$

whence

$$\Gamma_\Sigma = -(\partial\sigma/\partial\mu_{Tl^+})_\varphi \tag{5}$$

or

$$\Gamma_\Sigma = -(\partial\sigma/\partial\mu_{Tl})_\varphi \tag{6}$$

As is clear from Fig. 5, the results of the calculations by means of eqn. (3) and of eqns. (5) or (6), which have an identical meaning, coincide.

In the treatment of the Hg, Tl, Tl^+, H_2O system, we assumed that there exist two adsorption states of thallium as ions (or ion complexes) and as atoms. Salié and Lorenz[9] treated the adsorption behavior of the above system in terms of a partial transfer of the positive charge from the adsorbed thallium ion to the metal phase, the charge transfer coefficient in the system in question being 0.7 regardless of the electrode potential. If we accept the Salié and Lorenz conclusion, the effect of thallium on phenol adsorption at constant total thallium adsorption Γ_Σ should not depend on potential. The data of this paper (see in particular Fig. 4) are at variance with this conclusion.

SUMMARY

The mutual effect of thallium and phenol adsorption in the Hg, Tl, Tl^+, H_2O system at 0.2 *M* phenol concentration has been studied. It has been shown that phenol and thallium adsorption suppress each other in a wide potential range with the result that at the potential of maximum total thallium adsorption $(\Gamma_{Tl}+\Gamma_{Tl^+})$ phenol adsorption drops nearly to zero. However, at the most negative potentials the mutual suppression changes to mutual increase of adsorption. The picture of the structure of the mercury surface layer in the presence of thallium and NO_3^- ions, developed in the previous communication, allows a qualitative explanation of the effects observed.

The results of ref. 3 obtained without taking into consideration the changes in Tl concentration in amalgam caused by its oxidation by atmospheric oxygen have been partly corrected.

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