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ORIGINAL CONTRIBUTION

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Interaction between polyoxyethylene nonyl phenyl ether (n=9) and gold (III) ion in the adsorbed film and micelle

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Abstract A thermodynamic method was employed to analyze the surface tension data for studying the adsorption at the interface and micelle formation of an aqueous solution of polyoxyethylene nonyl phenyl ether having an average of nine oxyethylene units (PONPE-9) and that of PONPE-9 and gold (III) ion mixtures at pH 3, 7, and 10. The results suggested the existence of attractive interaction between PONPE-9 and gold in the adsorbed film and micelle and that the interaction strength decreases in the order pH 3, pH 10, and pH 7. This result was in accord with the percent extraction of gold obtained from the cloud point extraction method where the efficiency relies on the strength of the interaction between analytes and the surfactant. Thus, this study confirmed the usefulness of the thermodynamic equations developed.

Keywords Interaction · Nonionic surfactants · Gold (III) ion · Adsorbed film and micelle · Thermodynamics

Introduction

In our study on cloud point extraction (CPE) [1, 2, 3] of gold (III) ion by polyoxyethylene nonyl phenyl ether having an average of 9 oxyethylene units (PONPE-9), it was demonstrated that the extraction efficiency was maximum at around pH 3 and minimum at around pH 7 (see Fig. 1) [4]. We have conjectured that the extraction efficiency is dominated by the interaction between PONPE-9 and gold ($AuCl_4^-$ at pH 3 and $Au(OH)_3$ at pH 7 and 10) and therefore Fig. 1 may illustrate the pH effect on the interaction between PONPE-9 and gold.

Our previous studies on mixed surfactant systems have shown that the thermodynamic analysis of surface tension data is useful for elucidating the interaction between ionic and nonionic surfactant [5] and between nonionic surfactant and some electrolytes such as HCl and NaCl [6]. Therefore, the thermodynamic method [7, 8] has been applied in this study to examine whether there exists an interaction between PONPE-9 and gold and also to shed light on the correlation between the results from CPE and those from surface tension measurements.

The thermodynamic equations were applied to the surface tension data of the aqueous solution of PONPE-9 and $HAuCl_4$ mixtures at pH 3, pH 7, and pH 10. The results are discussed from the viewpoint of the interaction between PONPE-9 and gold, not only in the adsorbed film but also in the micelle. The results at three pH values of the solution were compared and provide satisfactory correspondence to the results of the extraction efficiency.

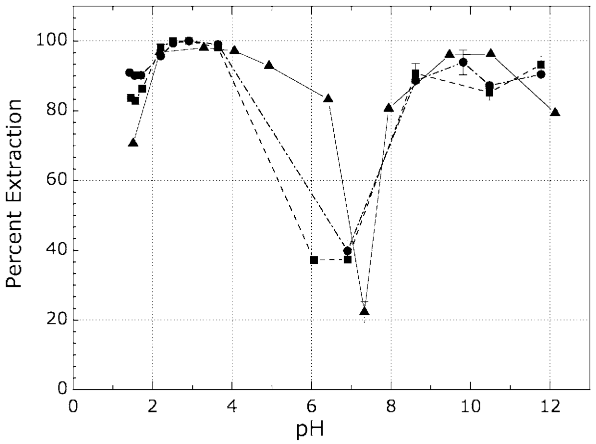


Fig. 1. The percent extraction of gold ion versus pH curves: *circles* 2.5% PONPE-9, Au^{3+} 5 ppm, 56 °C; *squares* 2.5% PONPE-9, Au^{3+} 5 ppm, 60 °C; *triangles* 2.5% PONPE-9, Au^{3+} 5 ppm, 80 °C

Experimental section

PONPE-9 was obtained from Rhodia (Thailand), and used without further purification. Hydrogen tetrachloroaurate (III) tetrahydrate ($HAuCl_4.4H_2O$) was purchased from Nacalai Tesque,, Japan. Water used in the surface tension measurement was purified by three distillations from alkaline permanganate solution. NaOH and HCl solutions were used for pH adjustment.

The systems studied were composed of PONPE-9, $HAuCl_4$, and HCl at pH 3, and of PONPE-9, $HAuCl_4$, and NaOH at pH 7 and 10, respectively. According to the potential-pH equilibrium diagram of the gold-water system [9], it is said that gold is dissolved as hydroxide $Au(OH)_3$ in the pH range 2–11. However, visual observation showed that the color of the aqueous mixture was pale yellow at pH 3 and purple at pH 7 and 10 in the presence of PONPE-9. Therefore, we took the dissolved species of gold to be $AuCl_4^-$ at pH 3 and $Au(OH)_3$ in the colloidal form stabilized by PONPE-9 molecules at pH 7 and 10, respectively. At pH 3, therefore, the total molality of the solution m defined by

$$m = m_{H^+} + m_{AUCl_4^-} + m_{PO} = 2m_{Au} + m_{PO} \tag{1}$$

and the mole fraction of PONPE-9 and gold in the mixture by

$$X_{PO} = m_{PO}/m \tag{2}$$

and

$$X_{Au} = 2m_{Au}/m \tag{3}$$

are employed as the concentration variables according to the thermodynamic viewpoints [7, 8]. Here m_{Au} and m_{PO} are the molalities of $HAuCl_4$ and PONPE-9. We employ m and X_{PO} defined above also at pH 7 and 10 for convenience, although it is not necessary to use these definitions because gold is dissolved as the nonionic hydroxide [7, 8].

The surface tension of the aqueous solution of PONPE-9 and of the mixture were measured as a function of the total molarity m at pH 3, 7, and 10 by the drop volume technique at 298.15 K under atmospheric pressure [10, 11]. The temperature was controlled within ±0.01 K by a thermostated water bath. The experimental error of the surface tension was within 0.05 mN m^{-1}.

The cloud point extraction of gold (III) ion was carried out as follows: an aqueous solution containing a given amount of PONPE-9 and gold (III) ion was prepared at the specified pH at room temperature. Then the solution was heated to a desired temperature at which the solution was separated into the water-rich and surfactant-rich phases. After the separation reached equilibrium, the concentration of gold in the water-rich phase C_w was determined by an atomic absorption instrument (AA) and then that in the surfactant-rich phase C_s was calculated on the basis of mass balance. The percent extraction E% was calculated by using the gold concentrations and the equilibration volumes of both the surfactant-rich and water-rich phases, V_s and V_w, as

$$E(\%) = 100V_sC_s/(V_sC_s + V_wC_w) \tag{4}$$

The details are given in our forthcoming paper [4].

Results and discussion

Figure 1 demonstrates the remarkable dependence of the extraction efficiency on pH: that it is very high not only in acidic conditions around pH 3 but also in basic conditions around pH 10, and is lowest around pH 7. These results motivated us to study the interaction between PONPE-9 and $HAuCl_4$ in adsorbed films and micelles at the three pH values of the solution by applying the thermodynamic method developed previously for mixed surfactant systems [5, 6, 7, 8, 12, 13].

In Fig. 2 are plotted the surface tension of PONPE-9 solution in the absence of $HAuCl_4$ and that in the presence of $HAuCl_4$ at $X_{Au} = 0.47$ against m_{PO} at three pHs. Hereafter the former and the latter are called the reference and the mixture, respectively. It is seen that the surface tension decreases with increasing the molality m_{PO} and that there is a distinct break point at the critical micelle concentrations (cmc). It should be noted that there exists an appreciable difference between the two curves at pH 3 and pH 10, but no appreciable one at pH 7.

Figure 3 shows the γ vs the total concentration m plots of the mixtures and the references at the three pH values of the solution. The cmc was determined from Figs. 2 and 3; C, C_{Au}, and C_{PO} refer to the total molality, gold molality, and surfactant molality at the cmc of the mixture and C_{PO}^orefers to the surfactant molality at the cmc of the reference. The numerical values are summarized together with the surface tension at the cmc, γ^C, in Table 1. It is important to note that the cmc of the mixtures are in the order

$$C_{PO}(\text{pH3}) < C_{PO}(\text{pH10}) < C_{PO}(\text{pH7})$$

and furthermore, $C_{PO} < C_{PO}^o$at pH 3 and pH 10, while $C_{PO} \cong C_{PO}^o$ at pH 7.

Now let us explore the interaction between gold and surfactant from the two aspects; the interaction in the adsorbed film and that in the micelle. With respect to the adsorbed films, the surface densities of components and their compositions play an important role. Taking the experimental conditions into account, at pH 3 the OH^- concentration was negligibly small and the HCl concentration for adjusting pH m_{HCl} was constant while at

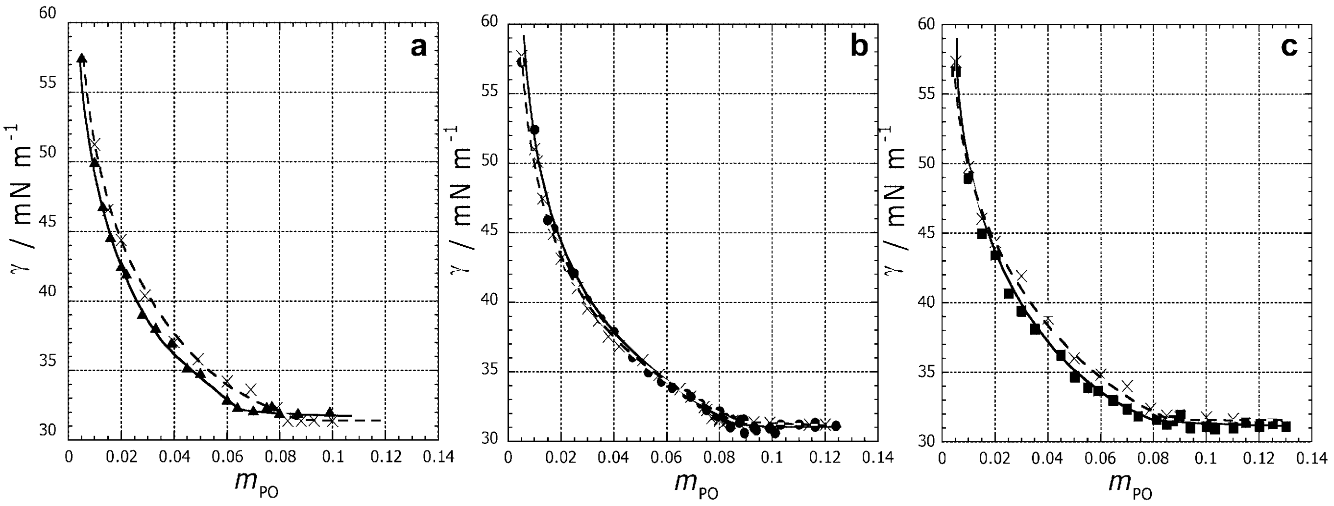


Fig. 2a–c. Surface tension versus surfactant molality curves of the mixture and reference: **a** pH 3; **b** pH 7; **c** pH 10 (*triangles, circles, squares*) mixture; (×) reference

pH 10, the H^+ concentration was negligibly small irrespective of m_{Au} and the NaOH concentration for adjusting pH m_{NaOH} was kept constant. Therefore, the total differentials of the surface tension can be expressed formally both at pH 3 and at pH 7 and 10 as

$$-\mathrm{d}\gamma/RT = (\Gamma_{Au}/m_{Au})\mathrm{d}m_{Au} + (\Gamma_{PO}/m_{PO})\mathrm{d}m_{PO} \tag{5}$$

Here Γ_{Au} is defined by

$$\Gamma_{Au} = \Gamma_{H^+}/(1 + m_{HCl}/m_{Au}) + \Gamma_{AuCl_4^-} \tag{6}$$

at pH 3 and by

$$\Gamma_{Au} = \Gamma_{Cl^-} + \Gamma_{Au(OH)_3} \tag{7}$$

at pH 7 and 10, respectively [14], and the surface density Γ_i^H of the component i is defined with reference to the two dividing planes which makes the excess number of moles of water and air to be zero [7].

In the present experiments, however, since the surface tension was measured at a fixed composition X_{PO}, it is appropriate to employ X_{PO} as the one of the thermodynamically independent variables and rewrite Eq. 5 as a function of X_{PO} and the total molality m as

$$-\mathrm{d}\gamma/RT = \left(\Gamma^H/m\right)\mathrm{d}m + \left(\Gamma^H/X_{Au}X_{PO}\right)\left(X_{PO}^H - X_{PO}\right)\mathrm{d}X_{PO} \tag{8}$$

or as a function of X_{PO} and the molality of surfactant m_{PO} as

$$\left[-\mathrm{d}\gamma/RT = \left(\Gamma^H/m_{PO}\right)\mathrm{d}m_{PO} - (1/X_{Au}X_{PO})\Gamma_{Au}^H\mathrm{d}X_{PO}\right] \tag{9}$$

The total surface density Γ^H and the mole fraction of the surfactant in the adsorbed film X_{PO}^H are defined by

Fig. 3a–c. Surface tension versus total molality curves of the mixture and reference: **a** pH 3; **b** pH 7; **c** pH 10, (*triangles, circles, squares*) mixture; (×) reference

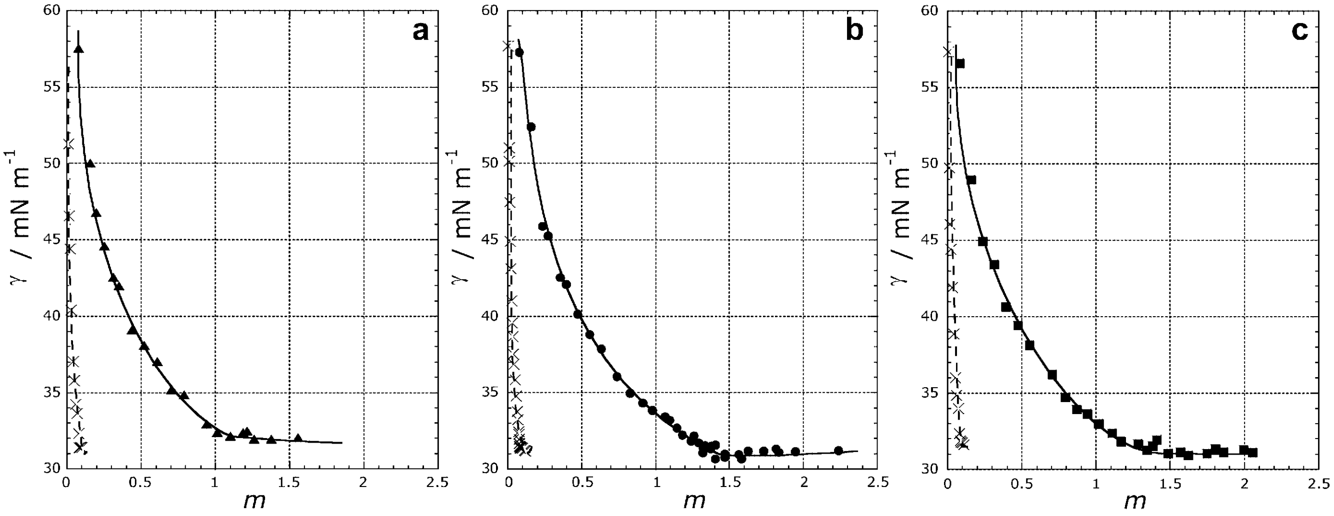


Table 1. The cmc and surface tension at the three pH values of the solution

pH		C	C_{Au}	C_{PO}	$C_{\mathrm{PO}}^{\mathrm{o}}$	γ^{C}	$\gamma^{C,o}$
		[mmol kg^{-1}]				[mN m^{-1}]	
3	mixture	1.030	0.479	0.065	–	32.1	–
	reference	–	–	–	0.083	–	31.4
7	mixture	1.350	0.620	0.084	–	31.2	–
	reference	–	–	–	0.082	–	31.4
10	mixture	1.225	0.575	0.078	–	31.3	–

$$\Gamma^{\mathrm{H}} = \Gamma_{\mathrm{Au}}^{\mathrm{H}} + \Gamma_{\mathrm{PO}}^{\mathrm{H}} \tag{10}$$

and

$$X_{\mathrm{PO}}^{\mathrm{H}} = \Gamma_{\mathrm{PO}}^{\mathrm{H}}/\Gamma^{\mathrm{H}} \tag{11}$$

respectively. Then the total surface density Γ^{H} is evaluated by applying either the equation

$$\Gamma^{\mathrm{H}} = -(m/RT)(\partial\gamma/\partial m)_{T,p,X_{\mathrm{PO}}} \tag{12}$$

to the γ-m plots in Fig 3 or the equation

$$\Gamma^{\mathrm{H}} = -(m_{\mathrm{PO}}/RT)(\partial\gamma/\partial m_{\mathrm{PO}})_{T,p,X_{\mathrm{PO}}} \tag{13}$$

to the γ-m_{PO} plots in Fig. 2. Furthermore, the mole fraction $X_{\mathrm{PO}}^{\mathrm{H}}$ and the surface density of gold are respectively evaluated from Eq. 8 by

$$X_{\mathrm{PO}}^{\mathrm{H}} = X_{\mathrm{PO}} - (X_{\mathrm{Au}}X_{\mathrm{PO}}/m)(\partial m/\partial X_{\mathrm{PO}})_{T,p,\gamma} \tag{14}$$

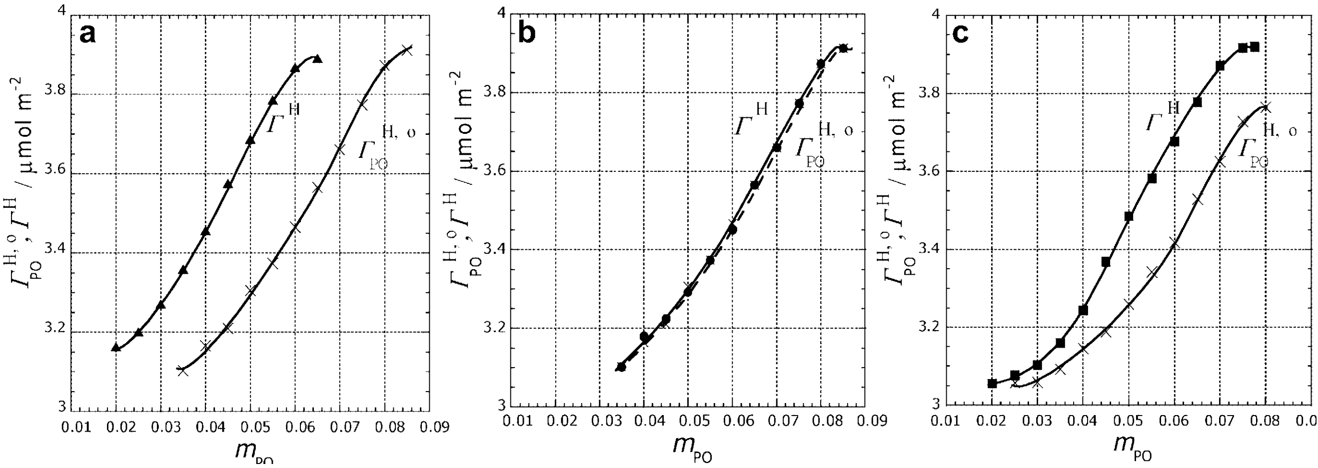
and from Eq. 9 by

$$\Gamma_{\mathrm{Au}}^{\mathrm{H}} = (X_{\mathrm{Au}}X_{\mathrm{PO}}/RT)(\partial\gamma/\partial X_{\mathrm{PO}})_{T,p,m_{\mathrm{PO}}} \tag{15}$$

The surface density of PONPE-9 of the reference $\Gamma_{\mathrm{PO}}^{\mathrm{H,o}}$ and the total surface density of the mixture Γ^{H} are plotted against the surfactant molality m_{PO} at different pH values in Fig. 4. It is clearly demonstrated that, by addition of the gold complexes to the surfactant solutions, the surface density increases both at pH 3 and 10 ($\Gamma^{\mathrm{H}} > \Gamma_{\mathrm{PO}}^{\mathrm{H,o}}$), but does not change at pH 7 ($\Gamma^{\mathrm{H}} \approx \Gamma_{\mathrm{PO}}^{\mathrm{H,o}}$). Furthermore, Figs. 5a and 5b show that the magnitude of the increase, $\Gamma^{\mathrm{H}} - \Gamma_{\mathrm{PO}}^{\mathrm{H,o}}$, goes up at pH 3 and 10, but keeps at almost zero at pH 7, with increasing not only the gold concentration m_{Au} but also the surfactant concentration m_{PO}. These findings strongly suggest the existence of an interaction between gold and PONPE-9 at pH 3 and pH 10.

Taking account of the definition $\Gamma^{\mathrm{H}} = \Gamma_{\mathrm{Au}}^{\mathrm{H}} + \Gamma_{\mathrm{PO}}^{\mathrm{H}}$ given by Eqs. 6 and 7 and that the surface densities of H^{+} and Cl^{-} are negligibly small, even in the presence of the adsorbed film of ethylene oxide groups [6], it is said that the change in $\Gamma^{\mathrm{H}} - \Gamma_{\mathrm{PO}}^{\mathrm{H,o}}$ may involve two contributions: the change in surface density of PONPE-9, $\Gamma_{\mathrm{PO}}^{\mathrm{H}}$, and that of gold, $\Gamma_{\mathrm{AuCl}_4^-}^{\mathrm{H}}$ or $\Gamma_{\mathrm{Au(OH)}_3}^{\mathrm{H}}$. The surface tension measurements confirmed that the surface density of the gold complexes was slightly negative in the absence of PONPE-9. Therefore, if the salting-out effect on the adsorption of PONPE-9 due to the presence of gold in the aqueous solution is responsible for the increase in $\Gamma^{\mathrm{H}} - \Gamma_{\mathrm{PO}}^{\mathrm{H,o}}$, the surface density of gold, $\Gamma_{\mathrm{AuCl}_4^-}^{\mathrm{H}}$ or $\Gamma_{\mathrm{Au(OH)}_3}^{\mathrm{H}}$ remains zero or even negative. On the other hand, if the interaction between PONPE-9 and gold in the adsorbed films is responsible for the increase in $\Gamma^{\mathrm{H}} - \Gamma_{\mathrm{PO}}^{\mathrm{H,o}}$, then $\Gamma_{\mathrm{AuCl}_4^-}^{\mathrm{H}}$ or $\Gamma_{\mathrm{Au(OH)}_3}^{\mathrm{H}}$ should take positive values. Looking at Fig. 2, we notice that the surface tension decreases

Fig. 4a–c. Surface density versus surfactant molality curves of the mixture and reference: **a** pH 3; **b** pH 7; **c** pH 10, (*triangles, circles, squares*) Γ^{H}; (×) $\Gamma_{\mathrm{PO}}^{\mathrm{H,o}}$



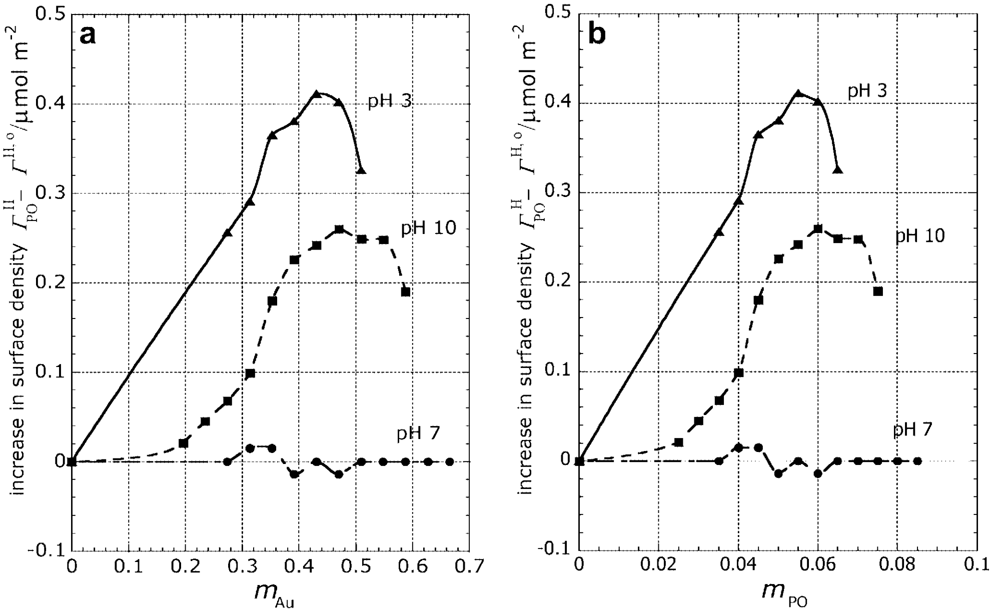


Fig. 5a, b. Increase in surface density versus molality: **a** $\Gamma^{H} - \Gamma_{PO}^{H,o}$ vs m_{Au}; **b** $\Gamma^{H} - \Gamma_{PO}^{H,o}$ vs m_{PO}, (*triangles*) pH 3; (*circles*) pH 7; (*squares*) pH 10

with decreasing X_{PO} at a given m_{PO} below the cmc at pH 3 and 10, but it does not change or even increases very slightly at pH 7. This means from Eq. 15 that the Γ_{Au}^{H} value is definitely positive at pH 3 and 10 but almost zero or very slightly negative at pH 7. Therefore, we conclude that an attractive interaction between PONPE-9 and gold in the adsorbed film is responsible for the increase of $\Gamma^{H} - \Gamma_{PO}^{H,o}$ and enhances the adsorption of PONPE-9 and gold ions at pH 3 and pH 10. Furthermore, the larger increase in $\Gamma^{H} - \Gamma_{PO}^{H,o}$ at pH 3 than at pH 10 suggests the stronger interaction at pH 3 than at pH 10.

The interaction in micelle particles is examined by using the thermodynamic relation

$$X_{PO}^{M} = \frac{1}{1 - \frac{C_{Au}}{C_{PO}}\left(\frac{\partial C_{PO}}{\partial C_{Au}}\right)_{T,p}} \qquad (16)$$

which is derived from the Gibbs-Duhem equation of the mixed micelle [7, 8]. It is noteworthy that this equation can be applied to suggest the difference in the X_{PO}^{M} value between the mixture solution and reference at each pH value of the solution. By referring to the C_{Au} and C_{PO} values in Table 1, it can be seen that C_{PO} is smaller than C_{PO}^{o} and shows the trend that $(\partial C_{PO}/\partial C_{Au}) < 0$ and $X_{PO}^{M} < 1$ consequently. Therefore, gold is incorporated into the micelle at pH 3 and pH 10. On the other hand, it is suggested that $X_{PO}^{M} \geq 1$ and therefore no gold is incorporated into the micelle at pH 7. These findings undoubtedly correspond to the extraction results demonstrated in Fig. 1. Furthermore, the equation [7, 8]

$$X_{PO}^{H,C} = X_{PO}^{M} - \left(X_{Au}X_{PO}/RT\Gamma^{H,C}\right)\left(\partial\gamma^{C}/\partial X_{PO}\right)_{T,p} \qquad (17)$$

and the γ^{C} value in Table 1 give results on the relationship between the composition of adsorbed film $X_{PO}^{H,C}$ and that of micelle X_{PO}^{M} at the cmc as $X_{PO}^{H,C} > X_{PO}^{M}$ at pH 3, $X_{PO}^{H,C} \approx X_{PO}^{M}$ at pH 7, and $X_{PO}^{H,C} < X_{PO}^{M}$ at pH 10.

It is important to note that $X_{PO}^{H,C}$ and X_{PO}^{M} are different from each other at pH 3 and pH 10, while almost the same as each other at pH 7. Although the reason for the difference between pH 3 and pH 10 is obscure, the existence of the difference itself makes it certain that there exists interaction between gold and surfactant both in the adsorbed film and in the micelle.

Let us summarize the important points about whether an attractive interaction exists or not between gold and PONPE-9 in the adsorbed film and in the micelle:

1. An appreciable difference of the γ-m_{PO} curves between the mixture and the reference was observed at pH 3 and pH 10, but it was not observed at pH 7.
2. An increase of the surface density of PONPE-9 and a decrease of the cmc through adding gold to the reference were observed at pH 3 and pH 10 and the changes were larger at pH 3 than at pH 10. They were not observed at pH 7.
3. The compositions of PONPE-9, both in adsorbed film and micelle, were smaller than unity at pH 3 and pH 10, but they were almost equal to, or even slightly larger than, unity at pH 7.
4. The composition in the adsorbed film was different from that in micelle at pH 3 and pH 10, but almost the same (unity) at pH 7.

These points make it certain that there exists attractive interaction between gold and PONPE-9 in the adsorbed film and micelle at pH 3 and pH 10 and that the interaction is stronger in the order pH 3 > pH 10 > pH 7.

The percent extraction of gold via CPE using PONPE-9 as a separation mediator was in the order pH 3 > pH 10 > pH 7 as demonstrated in Fig. 1 and coincides with the order of the interaction between gold and PONPE-9 in the adsorbed film and micelle. Therefore, although the surfactant-rich phase (under the actual extraction conditions) is not a simple spherical micellar solution but a more complex fluid containing self-organized surfactant assemblies like liquid crystals, the efficiency on CPE is probably dominated by the interaction between gold and PONPE-9 in the organized surfactant layers from which all the self-organized assemblies are constructed.

Judging from the experimental finding that the composition of the adsorbed film having a flat interface and that of the micelle having a curved one are different from each other, the structure of the assemblies is expected to influence the efficiency on CPE. Furthermore, the dissolution states of gold in the aqueous solution may change with solution conditions such as pH, concentration of surfactants, and temperature, and may therefore affect the efficiency on CPE. Actually, the color of the mixture changes from pale yellow at pH 3 to purple at pH10. Therefore, gold complex ion $AuCl_4^-$ is predominant at pH 3 and maybe gold colloidal particle stabilized by PONPE-9 molecules at pH 10. The structure of the surfactant-rich phases of the extraction experiments and the dissolution state of gold are still open questions in this study but may help in understanding the extraction process, efficiency, and mechanisms.

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