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Effect of Ionizable and Non-Ionizable Surfactants on the Polarographic Reduction of Some Metal Ions

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The effect of ionizable and non-ionizable surfactants was studied on the electrode kinetics of various metal ions such as Tl(I), Pb(II), Sb(III), U(VI), Bi(III), Cu(II), Cd(II), In(III), Cr(III), and Ti(IV) in an acetate medium. The cationic surfactant, dodecylammonium perchlorate ($DDAH^+$), causes a little enhancement effect on most metal ions studied. The non-ionic surfactant, Triton X 100 causes a marked negative shift in $E_{1/2}$ of all metal ions except Tl(I). The shift in $E_{1/2}$ can be used for the selective polarographic determination of these metal ions either individually in the presence of Tl(I) or simultaneously in a mixture. The anionic surfactant, sodium dodecylsulfate (DDS) forms an electro-inactive complex with In(III). Advantage of this behavior was taken to determine Cd(II) in the presence of In(III). Excellent linear correlations were observed between the limiting current (i_l) and the concentration (C) of metal ions.

Surface-active substances (SAS) are usually employed in polarographic analysis of metal ions to eliminate maxima of the reduction waves. The presence of SAS affects widely the $E_{1/2}$, the limiting current, the slope of the wave, the appearance of minima as well as the splitting of a wave, or a combination of all to an extent as to obliterate the wave completely. The use of SAS for electrochemical masking in selective polarographic determinations has been reported by several authors.[1-10] These studies were mainly either qualitative or limited under different conditions.

Determination of minute amounts of various metal ions in strong acidic and alkaline media in the presence of different organic electromasking agents has been investigated polarographically.[11-14] The effect of charged and uncharged SAS on the reduction waves of U(VI) in $HClO_4$ and HCl solutions[15,16] was discussed on the basis of Frumkin's theory. Recently, we reported that Triton X 100 (as non-ionic surfactant) has been considered as an electromasking agent for the polarographic determination of Hg(II), V(V), Fe(III), As(III), Sb(III), and Ti(IV) either individually in the presence of U(VI) or simultaneously in a mixture using 1 M H_2SO_4 as a supporting electrolyte.[17] As a continuation to this work, it seems worthy to investigate the effect of ionizable and non-ionizable SAS on the reduction waves of different metal ions such as Tl(I), Pb(II), and In(III) in an acetate solution. The choice of acetate medium was decided by the observation that, in its presence, the $E_{1/2}$ of the systems Tl(I)–Pb(II)–Sb(III), U(VI)–Bi(III), and In(III)–Cd(II) was inseparable[18-20] causing marked difficulties in their simultaneous determination by conventional d.c. polarographic techniques. Most of these metal ions are considered as the constituents of several ores and alloys. Accordingly, our study was undertaken to manifest the role played by SAS and its application in the analytical determination of Tl(I), Pb(II), Sb(III), U(VI), Bi(III), Cu(II), In(III), Cr(III), and Ti(IV) either individually or simultaneously in a mixture.

Experimental

Chemicals and Solutions. All chemicals used were of AnalaR grade. Redistilled water was used in the preparation of all solutions. Stock solutions of 5×10^{-2} M (1 M=1 mol dm^{-3}) of each metal ion were prepared and standardized according to the literatures.[21,22] The supporting electrolyte in all experiments was 2 M acetic acid–2 M ammonium acetate. The surfactants used in the experiments were; non-ionic surfactant, Triton X 100 provided by Rohm and Haas Co., U.S.A.; anionic surfactant, sodium dodecylsulfate (DDS), Procter and Camble Co., U.S.A.; cationic surfactant, dodecylamine (DDA), Armour Industrial Chemical Co., U.S.A. Stock solutions of 1% dodecylammonium perchlorate ($DDAH^+$) were prepared by neutralizing a calculated amount of DDA with $HClO_4$. Solutions of other SAS were prepared by direct dissolution in water.

Apparatus and Working Procedure. The electrolytic cell and working procedure were the same as described previously.[17] The limiting current–concentration results were calculated using the method of the least-squares regression analysis.

Results and Discussion

Effect of Non-Ionic Surfactant, Triton X 100. The effect of Triton X 100 on the half wave potential ($E_{1/2}$) and the limiting current (i_l) of Tl(I), Pb(II), Sb(III), U(VI), Bi(III), Cu(II), In(III), Cd(II), Cr(III), and Ti(IV) in the acetate solution as a supporting electrolyte are illustrated in Table 1, it is clear that, the successive increase in the concentration of Triton X 100 leads to a marked negative shift of $E_{1/2}$ of almost all the metal ions except Tl(I) with a slight decrease in the wave height.

Effect of Anionic Surfactants, DDS. Table 1 indicates that the reduction waves of Tl(I) and Pb(II) are not changed by the presence of anionic surfactant in the concentration range studied. On the other hand, an interesting behavior is observed for In(III) where its wave height is completely inhibited in the presence of 0.01% DDS. The half-wave potentials of the other metal ions undergo small shift to more negative poten-

Table 1. Effect of SAS on the Half-Wave Potentials [$E_{1/2}$] and Limiting Current [i] of Tl, Pb, Sb, U, Bi, Cu, In, Cd, Cr, and Ti [all 1 mM]

Surfactant concn/%	Tl(I)		Pb(II)		Sb(III)		U(VI)		Bi(III)		Cu(II)		In(III)		Cd(II)		Cr(III)		Ti(IV)	
	$-E_{1/2}$	i_l	$-E_{1/2}$	i_l	$-E_{1/2}$	i_l	$-E_{1/2}$	i_l	$-E_{1/2}$	i_l	$-E_{1/2}$	i_l	$-E_{1/2}$	i_l	$-E_{1/2}$	i_l	$-E_{1/2}$	i_l	$-E_{1/2}$	i_l
	V	μA	V	μA	V	μA	V	μA	V	μA	V	μA	V	μA	V	μA	V	μA	V	μA
Triton X 100																				
0.000	0.47	4.41	0.53	5.63	0.53	6.82	0.45	5.11	0.51	5.82	0.16	3.93	0.69	8.91	0.69	5.73	0.93	9.41	1.13	6.45
0.005	0.47	4.32	0.58	5.51	0.65	6.63	0.48	4.94	0.59	5.63	0.34	3.74	0.73	8.65	0.69	5.42	1.07	9.01	1.21	6.12
0.010	0.47	4.28	0.60	5.22	0.80	6.22	0.65	4.71	0.65	5.21	0.74	3.38	0.77	8.21	0.72	5.13	1.11	8.82	1.26	5.97
0.014	0.47	4.20	0.62	5.00	0.93	6.01	0.80	4.62	0.66	5.03	0.91	3.01	0.79	8.00	0.76	4.90	1.18	8.26	1.31	5.66
0.018	0.47	4.04	0.64	4.91	0.96	5.84	0.84	4.20	0.66	4.95	0.98	2.97	0.80	7.93	0.78	4.86	1.21	8.05	1.39	5.31
0.022	0.47	3.91	0.64	4.70	0.97	5.70	0.85	3.98	0.66	4.71	0.98	2.88	0.81	7.71	0.80	4.77	1.22	7.94	1.39	5.00
DDS																				
0.005	0.47	4.40	0.53	5.61	0.59	6.73	0.47	5.00	0.54	5.73	0.21	3.90	0.72	4.81	0.71	5.69	0.98	9.11	1.16	6.13
0.008	0.47	4.35	0.53	4.57	0.65	6.41	0.48	4.84	0.59	5.38	0.28	3.66	0.76	2.11	0.73	5.62	1.04	8.92	1.18	5.98
0.010	0.47	4.22	0.53	4.29	0.71	6.03	0.51	4.67	0.63	5.14	0.37	3.27	—	—	0.74	5.18	1.06	8.25	1.19	5.53
0.020	0.47	4.10	0.53	4.01	0.72	5.97	0.53	4.22	0.65	4.93	0.41	2.91	—	—	0.51	4.95	1.20	7.88	1.22	5.11
$DDAH^+$																				
0.005	0.47	4.41	0.53	4.61	0.58	6.77	0.45	5.00	0.52	5.83	0.16	3.91	0.67	8.91	0.69	5.18	0.93	9.21	1.13	6.16
0.010	0.47	4.35	0.53	4.48	0.62	6.25	0.45	4.91	0.50	5.66	0.16	3.56	0.64	8.35	0.66	4.77	0.91	8.75	1.15	5.87
0.015	0.47	4.26	0.53	4.17	0.67	5.72	0.45	4.31	0.47	5.19	0.16	3.01	0.61	8.11	0.61	4.16	0.88	8.22	1.18	5.11
0.020	0.47	4.18	0.53	3.98	0.69	5.29	0.45	4.04	0.47	4.87	0.16	2.97	0.60	7.72	0.61	3.88	0.88	7.89	1.21	4.79

tials by the addition of DDS.

Effect of Cationic Surfactants, $DDAH^+$. The half-wave potentials of Tl(I), Pb(II), U(VI), and Cu(II) are unchanged in the presence of $DDAH^+$, but those of In(III), Cd(II), Cr(III), and Bi(III) shifted slightly to less negative potentials with an increase in the concentration of $DDAH^+$. In contrast, the $E_{1/2}$ of Sb(III) and Ti(IV) shifted slightly towards negative potentials by adding $DDAH^+$.

The effect of charged and uncharged SAS on the electrochemical behaviors of metal ions was thus focussed on Tl(I), Pb(II), and In(III) as representative examples. Table 2 summarizes the values of the various kinetic parameters calculated from the obtained waves through the log (i/i_l-i) vs. E plots. The diffusion coefficient (D) of the depolarizer in the absence and presence of SAS was also determined experimentally by the use of Stocks–Einstein equation.[23]

From the results in Tables 1 and 2 one may conclude the following:

1. The non-ionic surfactant has, in general, a retardation effect more pronounced than that obtained for both cationic ($DDAH^+$) and anionic (DDS) surfactants. Such effect has previously been reported in the literature[24–26] which seems to be due to a very compact structure of the adsorbed layer. However, cationic and anionic surfactants are characterized by a loose structure with pores filled with solvent. If the depolarizer has a charge opposite to that of the adsorbed layer it may pass through the pores almost without any hindrance. Depolarizers with the same charge as the adsorbed layer are electrostatically repelled from the electrode surface. They have to cross a potential energy barrier before they can be reduced and therefore the waves are shifted to more negative potentials or greatly distorted. The presence of excess amounts of acetate ion as a supporting electrolyte can lead easily to the formation of a negatively charged acetate-complex with most of the metal ions. The electroreduction of these negatively charged complexes are retarded by the presence of anionic SAS whereas the presence of cationic SAS facilitates their reduction processes.

2. Tl(I) does not readily form a complex in various solutions.[27] Thus, the obtained $E_{1/2}$ and kinetic parameters are fairly constant and unaffected by the presence of different types of surfactants (Table 2). For Pb(II), the results show no marked change in $E_{1/2}$ and kinetic parameters in the presence of cationic and anionic surfactants which may be linked, similarly, to the fact that Pb(II) does not form a stable negatively charged complex.[28] So, it can easily peneterate through the adsorbed SAS layer.

3. The limiting current of In(III) drops to zero in the presence of 0.01% DDS. This indicates that the surfactant takes part in the overall electrode reaction. Such a decrease in current with an increase in the concentration of SAS cannot be explained in view of the effect of viscosity of the solution. It has been known

Table 2. Kinetic Parameters of Tl(I), Pb(II), and In(III) in Presence of SAS

Surfactant concn %	Metal	Y	αn_a	D	K_e°	ΔG^*
				$cm^2 s^{-1}$	$cm\ s^{-1}$	$kJ\ mol^{-1}$
Triton X 100	Tl(I)					
0.000		15.81	0.93	1.34×10^{-5}	6.25×10^{-3}	53.41
0.005		15.73	0.93	1.28×10^{-5}	6.58×10^{-3}	57.11
0.018		15.71	0.93	1.23×10^{-5}	7.02×10^{-3}	60.25
DDS						
0.005		15.80	0.93	1.27×10^{-5}	6.63×10^{-3}	58.35
0.010		15.66	0.92	1.22×10^{-5}	6.39×10^{-3}	54.27
$DDAH^+$						
0.005		15.64	0.92	1.31×10^{-5}	6.78×10^{-3}	54.72
0.010		15.51	0.92	1.25×10^{-5}	6.95×10^{-3}	56.69
Triton X 100	Pb(II)					
0.000		16.31	0.96	5.18×10^{-6}	3.347×10^{-5}	83.21
0.005		15.82	0.93	5.04×10^{-6}	9.21×10^{-5}	97.38
0.018		14.29	0.84	4.00×10^{-6}	1.34×10^{-6}	109.56
DDS						
0.005		16.22	0.96	5.12×10^{-6}	5.42×10^{-5}	89.75
0.010		16.10	0.95	5.09×10^{-6}	7.11×10^{-6}	94.91
$DDAH^+$						
0.005		16.31	0.96	5.16×10^{-6}	4.73×10^{-5}	84.11
0.010		16.18	0.95	5.15×10^{-6}	5.11×10^{-5}	87.84
Triton X 100	In(III)					
0.000		17.57	1.04	5.86×10^{-6}	1.35×10^{-8}	193.25
0.005		15.32	0.90	5.05×10^{-6}	3.72×10^{-9}	209.97
0.018		13.48	0.80	4.28×10^{-6}	7.96×10^{-6}	218.05
DDS						
0.005		17.45	1.03	5.78×10^{-6}	2.94×10^{-8}	198.76
0.008		17.11	1.01	5.73×10^{-6}	6.05×10^{-8}	200.56
$DDAH^+$						
0.005		17.21	1.02	5.84×10^{-6}	1.61×10^{-8}	196.11
0.010		16.19	0.96	5.16×10^{-6}	2.54×10^{-8}	198.53

Y=The slopes of the correlation of $\log i/[i_l-i]$ with E: the slopes are calculated by the least squares method. K_e°=Electron rate constant. ΔG^*=Activation energy.

that the change of viscosity of the solution taking place by the presence of lyophilic colloids does not affect the diffusion of simple electrolyte.[28,29] It is plausible that the effect of SAS on the limiting current is probably due to the interaction of the reducible ion with SAS molecule lowering the concentration of the free electroactive species in solution. The complete inhibition of the In(III)-wave may be due to the formation of an electroinactive mixed ligand complex in the bulk solution. The effect of SAS on the limiting current of Tl(I) and Pb(II) ions was shown to be slight as compared with that on the other metal ions. This finding is attributed to the low tendency of Tl(I) and Pb(II) ions to form complex ions with complex-forming substances.

4. The constancy of the $E_{1/2}$ of Tl(I) in the presence of different types of SAS seems to be of great importance from the analytical point of view, since most metals whose $E_{1/2}$ is affected by SAS can be determined in the presence of Tl(I). In the present work, when TI(I) with any one of the other metal ions are polarographed in the presence of 0.018% Triton X 100, a well-developed polarogram is obtained. This polarogram consists of two waves, the first represents the reduction

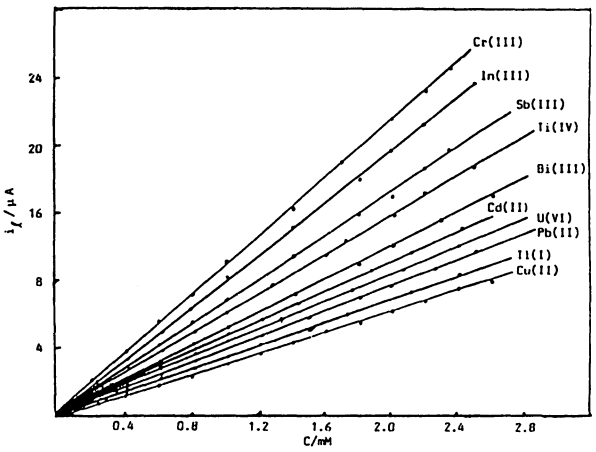

Fig. 1. Correlation of the limiting current with the concentration of metal ions.

of Tl(I) and the second wave corresponds to the reduction of the other metal ion. The limiting current of each wave increases as the concentration of the corresponding metal ion is increased. The applicability of the Ilkovic equation is well demonstrated by the con-

stancy of the i_l/C values as shown in Fig. 1.

5. Based on the above mentioned results, the nonionic surfactant, Triton X 100, can thus be used for the simultaneous determination of most metal ions in a mixture. On the contrary, cationic or anionlc surfactants cannot be used for this purpose as the shift in $E_{1/2}$ is not significant. However, in the presence of nonionic surfactant, Triton X 100, the $E_{1/2}$ values of the systems Sb(III)-Cu(II), U(VI)-In(III)-Cd(II), and Pb(II)-Bi(III) are very close to each other. Consequently, the studied metal ions, could be classified into three synthetic mixtures valid for polarographic determination:

Mixture (A): Tl(I), Pb(II), U(VI), Sb(III), Cr(III), and Ti(IV).

Mixture (B): Tl(I). Bi(III), In(III), Cu(II), Cr(III), and Ti(IV).

Mixture (C): Tl(I), Pb(II), Cd(II), In(III), Cu(II), Cr(III), and Ti(IV).

Polarograms of Mixtures (A), (B), and (C). When 0.5 mM of the mixture (A) is investigated polarographically in the presence of 0.018% Triton X 100 and 2 M acetic acid-2 M ammonium acetate as a base electrolyte, a well-developed polarogram of six waves was obtained. The first wave represents the reduction of Tl(I) with $E_{1/2}$=−0.47 V, the second wave represents the reduction of Pb(II) with $E_{1/2}$=−0.64 V, the third wave at −0.84 V corresponds to the reduction of U(VI), the fourth at −0.98 V corresponds to the reduction of Sb(III), whereas the fifth and sixth waves lie at more negative potentiais $E_{1/2}$=−1.21 and −1.39 V representing the reduction of Cr(III) and Ti(IV), respectively. The mixture (B) shows similar polarogram as the mixture (A), in which the second, third, and fourth waves correspond to Bi(III), In(III), and Cu(II), respectively. Thus, under these conditions, any one of these metal ions can be determined in the presence of other metal cations. The concentrations of five of the constituents are kept constant whereas the sixth one is successively increased. The validity of the Ilkovic equation was satistfactory as shown in Table 3. The values of both the correlation coefficient, r, and the standard deviation, S, indicate clearly an excellent correlation. Thus, the quantitative determination of such mixtures (A and B) in the acetate solution using 0.018% Triton X 100 seems possible under these conditions.

In the presence of 0.018% Triton X 100, both In(III) and Cd(II) have almost the same $E_{1/2}$ value (0.78—0.8 V): if In(III) and Cd(II) present in a mixture (C), the third wave will represent the electroreduction of In(III) and Cd(II). However, we noticed that anionic surfactant DDS served as an electrochemical masking agent for In(III), whereas $E_{1/2}$ and wave height of the other metal ions are not markedly affected by the DDS. Advantage of this behavior was taken to determine In(III) and Cd(II) simultaneously in the mixture (C). Adopting these assigned conclusions, in the presence of both In(III) and Cd(II) in the mixture (C), the limiting current of the third wave corresponds to the concentration of both. When 0.01% DDS is added, a suppression of In(III) should be expected as being confirmed experimentally in Fig. 2. The limiting current of the

Table 3. Results of Correlation with Ilkovic Equation

Metal	No. of data taken	Range adherence to Ilkovic equation/μM^{-1}	a[a] μA mM^{-1}	C[b] μA	S[c]	P[d]	r[e]	t[f]
Mixtue (A):								
Tl(I)	8	0.0—134.05	4.32	−0.018	0.011	0.021	0.998	Positive
Sb(III)	7	0.0—244.73	6.87	−0.017	0.042	0.041	0.999	Positive
U(VI)	8	0.0—546.57	6.03	0.014	0.028	0.026	0.999	Positive
Pb(II)	8	0.0—167.13	4.62	−0.009	0.018	0.016	1.000	Positive
Cr(III)	7	0.0—119.86	9.12	0.005	0.008	0.008	0.998	Positive
Ti(IV)	8	0.0—523.75	6.02	0.016	0.030	0.028	0.999	Positive
Mixture (B):								
Tl(I)	7	0.0—135.12	4.35	−0.015	0.013	0.014	0.997	Positive
Cu(II)	7	0.0—177.91	3.72	−0.006	0.005	0.004	1.000	Positive
In(III)	8	0.0—149.82	8.45	0.015	0.027	0.025	0.999	Positive
Bi(III)	6	0.0—109.91	9.01	0.016	0.034	0.031	0.998	Positive
Cr(III)	7	0.0—119.91	9.23	0.006	0.008	0.008	1.000	Positive
Ti(IV)	8	0.0—527.14	6.11	0.017	0.032	0.029	0.998	Positive
Mixture (C):								
Tl(I)	7	0.0—134.04	4.61	−0.017	0.012	0.022	0.999	Positive
Pb(II)	8	0.0—165.45	4.79	−0.011	0.009	0.010	0.998	Positive
Cd(II)	9	0.0—351.28	5.11	0.020	0.028	0.025	0.999	Positive
In(III)	9	0.0—250.12	8.61	0.016	0.027	0.024	0.998	Positive
Cu(II)	8	0.0—167.11	3.81	−0.009	0.018	0.016	1.000	Positive
Cr(III)	7	0.0—120.02	9.01	0.004	0.007	0.007	0.999	Positive
Ti(IV)	7	0.0—761.82	6.03	0.008	0.028	0.019	1.000	Positive

a) Slope of the regression line. b) Intercept of the regression line. c) Standard deviation. d) Population standard deviation. e) Correlation coefficient. f) Test for the hypothesis of intercept zero.

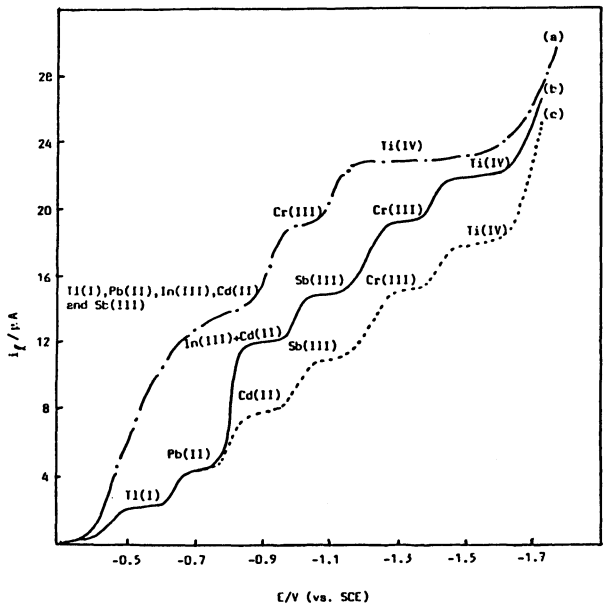

Fig. 2. Polarographic curves of 0.5 mM of mixture (C) in acetate medium (a) in absence of SAS, (b) in presence of 0.18% Triton X 100 (c) the previous solution plus 0.01% DDS.

third wave in this case will represent only the concentration of Cd(II). The concentration of In(III), therefore, can be calculated by measuring the difference in limiting currents of the third wave in the presence of DDS and its absence. Thus, under these conditions elements Tl(I), Pb(II), Cd(II), In(III), Cu(II), Cr(III), and Ti(IV): mixture C: can be precisely determined polarographically in the presence of each other using acetate solution, 0.018% Triton X 100 and 0.01% DDS as a base electrolyte.

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