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Application of Surface-Active Substances in Polarographic Determination of Hg(II), V(V), Fe(III), As(III), Sb(III), and Ti(IV) in the Presence of U(VI)

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The reduction of hexavalent uranium in 1 M H_2SO_4 at DME was found to be retarded by a non ionic surfactant Triton® X 100 and to shift the uranium wave to more negative potentials. Advantage was taken of this fact to determine the elements Hg(II), Fe(III), V(V), As(III), Sb(III), and Ti(IV) either individually in the presence of U(VI) or simultaneously in mixtures, a supporting electrolyte of 1 M H_2SO_4 containing 0.01% Triton® X 100 was used. The i_l/C results gave excellent correlations in each case, as was indicated from the least squares regression analysis. The outcome results suggest the method validity as a quantitative method for determination of the studied elements.

The polarographic determination of Fe(III), As(III), Cu(II), Cd(II), Sb(III), Mo(VI), U(VI) in the presence of V(V) using resorcinol or pyrogallol, which causes complete suppression of the vanadium waves, have been reported previously.[1,2] Several authors have also studied the polarographic behavior of U(VI), Fe(III), V(V), As(III), Sb(III), Hg(II), and Ti(IV) in different supporting electrolytes.[3-12] These studies were mainly either qualitative or limited to determination of each element under different conditions. Use of surface active substance (SAS) in analytical determination of metal ions has, nevertheless, attracted little attention. An attempt, however, was made by Issa[13] to study use of surfactants during the determination of Cu(II) in the presence of U(VI) adopting the rotating mercury electrode.

In the presett investigation, a trial was made to elucidate the role played by Triton® X 100 on polarographic behavior of U(VI), Hg(II), V(V), Fe(III), As(III), Sb(III), and Ti(IV). The investigation was extended to study the application of this surfactant in the analysis of the mentioned elements either individually in the presence of U(VI) or simultaneously in mixtures. The limiting current-concentration results were calculated using the method of the least-squares regression analysis.

Experimental

Chemicals and Solutions. All chemicals used were of AnalaR grade. Twice-distilled water was used in the preparation of all solutions. Stock solutions of 5×10^{-2} M (M= mol dm^{-3}) each of Hg(II), Fe(III), As(III), Sb(III), Ti(IV), V(V), and U(VI) were prepared and standardized according to the recommended procedures.[14,15] Stock solutions of 1% Triton® X 100 were also prepared. Triton® X 100 was obtained from Rohm and Haas Co., U.S.A.

Apparatus and Working Procedure. The electrolytic cell and working procedure were the same as previously described.[16] The polarograms were recorded with a Radiometer polarograph Model P04. The dropping mercury electrode has the open circuit characteristics, m=1.99 mg s^{-1} and t=4.36 s at a mercury height of 50 cm. An external saturated calomel electrode was used as a reference electrode and the cell was thermostated at 25±0.1 °C. Prior each run, N_2 gas was bubbled through the polarographic cell.

Results and Discussion

The Effects of Triton® X 100 on the Reduction Waves of U(VI). The effects of charged and uncharged surfactants (SAS) on the polarographic waves of U(VI) in sulfuric and perchloric acid solutions of various concentrations were previously investigated.[16,17] In the present work, when 1 M H_2SO_4 (M=mol dm^{-3}) is used as a supporting electrolyte, U(VI) is shown to exhibit only one wave representing the reduction of U(VI) to U(IV). The Triton® X 100, as a non ionic SAS, seems to cause retardation of the reduction process as indicated from the shifting of the whole polarogram towards more negative potentials. The $E_{1/2}$ values change from −0.18 V (in the absence of SAS) to −0.68 V (in the presence of 0.01% T. X 100), whereas the total limiting current is slightly affected (cf. Fig. 1). Accordingly, it can be concluded that, this behavior of U(VI) in T. X 100 can be utilized in determining some metal ions in the presence of U(VI) by the use of SAS.

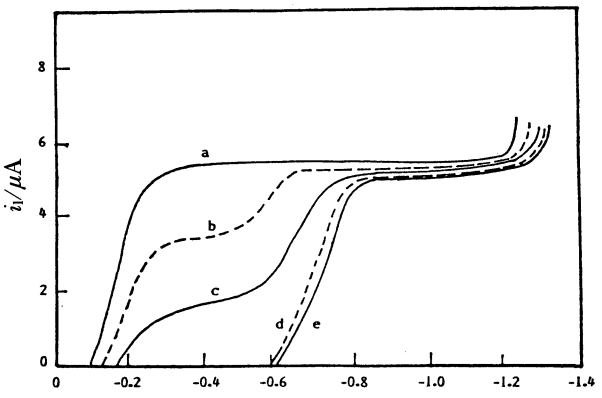

Fig. 1. The effects of Triton® X 100 on the polarographic behavior of 1×10^{-3} M U(VI) in 1 M H_2SO_4. a) No SAS, b) 0.002%, c) 0.005%, d) 0.01%, e) 0.02%.

Polarographic Determination of Hg(II), Fe(III), V(V), Sb(II), As(III), and Ti(IV) in the Presence of U(VI). Determination of Hg(II) in the Presence of U(VI). The electroreduction of 1×10^{-3} M Hg(II) in 1 M H_2SO_4 is represented by a polarogram consisting of a single reduction wave distorted by a large maximum. In the presence of 0.006% T. X 100, the maximum is eliminated and a well-developed polarogram is thus obtained with $E_{1/2}$=+0.4 V. Successive additions of T. X 100 (up to 0.02%), cause some shift in the half-wave potential to less positive values (+0.28 V), while the limiting current decreases by 13.4%. Although the difference between the reduction potential of Hg(II) and that of U(VI) is pronounced enough, viz. 0.96 V, yet the study of the behavior of this couple in the presence of Triton seems to be essential with the aim of checking the possibility of its quantitative determination in presence of a third different element, possessing a reduction wave intermediate between these two components. Thus, in the presence of 1 M H_2SO_4 and 0.01% T. X 100 as a supporting electrolyte, Hg(II) and U(VI) give two developed waves, the first one corresponding to the reduction of Hg(II) while the second wave for U(VI), $E_{1/2}$=0.28 and −0.68 V, respectively. The limiting current of each wave increases as the concentration of metal ion is increased. The applicability of the Ilkovic equation is demonstrated by the constancy of the i_l/C values shown in Fig. 2. Based on the obtained data of i_l-C, a regression analysis was applied and the derived results are summarized in Table 1. The small standard deviation attests the good reproducibility of the results.

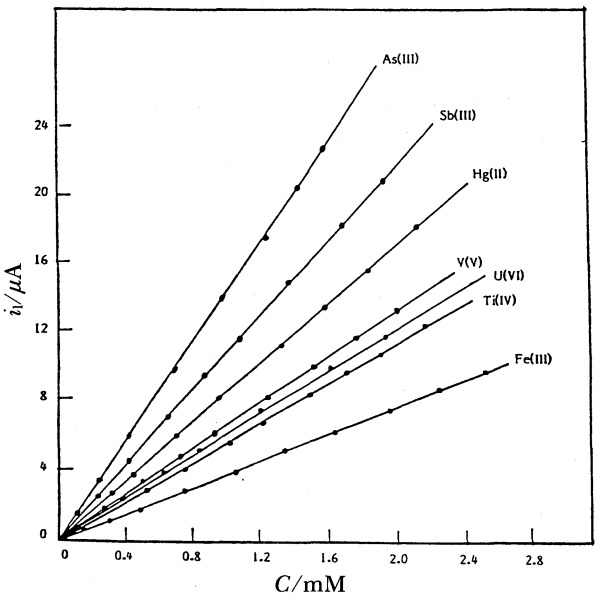

Fig. 2. Correlations of the limiting current with the concentration of the metal ions under investigation.

Determination of V(V) in the Presence of U(VI). In the absence of SAS, V(V) undergoes reduction along two steps, namely with $E_{1/2}$ values of +0.31 and −0.9 V. The first wave represents the production of tetravalent vanadium, whereas the divalent state is formed along the second wave.[18] Accordingly, V(V) and U(VI) can be determined simultaneously in presence of each other. The determination of this couple in the presence of T. X 100 is also investigated in order to increase the voltage difference between them aiming to gain a space for the possible inclusion of some other elements in the mixture, whose reduction potentials lie intermediate between vanadium and the shifted uranium wave. The effect of addition of different concentrations of T. X 100 on the electroreduction of 0.5 mM V(V) is shown clearly by shifting the whole polarogram to more negative potentials. Thus, in the presence of 0.01% T. X 100, V(V) exhibits one wave (first wave) with $E_{1/2}$ equal to +0.06 V whereas the second wave suffers a marked shifting which finally interferes with the hydrogen wave. Figure 2 and Table 1 show the results obtained with various con-

Table 1. Results of Correlation with Ilkovic Equation where; a=The slope of the regression line, C=The intercept of the regression line, S=The standard deviation, P=The population standard deviation, r=The correlation coefficient, and t=The test for the hypothesis of intercept zero

Metal	No. of Points	Range adherence to Ilkovic equation/ppm	a / μA mM^{-1}	C / μA	S	P	r	t
U (VI)	7	0.0—464.16	5.03	−0.018	0.02	0.019	1.000	Positive
Hg(II)	9	0.0—511.53	8.81	−0.027	0.052	0.048	0.999	Positive
V (V)	9	0.0—101.88	6.34	−0.017	0.021	0.02	0.998	Positive
Fe(III)	9	0.0—131.24	3.58	−0.015	0.018	0.016	0.999	Positive
Sb(III)	9	0.0—238.63	10.51	−0.005	0.008	0.008	0.999	Positive
As(III)	8	0.0—119.87	14.53	−0.014	0.04	0.036	0.999	Positive
Ti(IV)	9	0.0—100.67	5.99	−0.019	0.021	0.02	1.000	Positive
Mixture:								
U (VI)	7	0.0—559.36	5.01	−0.018	0.02	0.02	0.999	Positive
Hg(II)	9	0.0—420.26	8.33	−0.019	0.021	0.019	1.000	Positive
V (V)	7	0.0—117.16	6.29	−0.02	0.028	0.025	0.998	Positive
Fe(III)	8	0.0—134.04	3.61	−0.017	0.012	0.022	0.999	Positive
Sb(III)	7	0.0—200.89	10.11	−0.011	0.016	0.014	1.000	Positive
As(III)	6	0.0—119.87	14.02	−0.017	0.019	0.018	0.999	Positive
Ti(IV)	8	0.0—115.07	5.7	−0.021	0.023	0.02	0.999	Positive

centrations of V(V), ranging from 0.22 to 2.0 mM in the presence of 1 mM U(VI), 0.01% T. X 100, and 1 M H_2SO_4, the limiting currents being determined at −0.1 V. The suitability of the medium for V(V) determination may be inferred by considerations similar to those mentioned above for Hg(II).

Determination of Fe(III) in the Presence of U(VI). The U(VI)-Fe(III) couple behaves in a mannar similar to that of U(VI)-Hg(II) and U(VI)-V(V) couples in which they can be determined simultaneously in the presence of each other and in the absence of SAS. The Fe(III) in 1 M H_2SO_4 shows one reduction wave starting at +0.18 V which represents the production of Fe(II).[19] The presence of T. X 100 leads to a shift of the polarogram towards less positive potential (+0.05 V). From this observation and from the obtained limiting current, it may be concluded that the reduction of Fe(III) is not affected largely by the presence of SAS. Thus, it is interesting to investigate possibility of the determination of Fe(III) in the presence of uranium which is usually the case as a minor constituent. Table 1 and Fig. 2 indicate that the quantitative determination of Fe(III) in the presence of U(VI) and 0.01% T. X 100 in 1 M H_2SO_4 is quite possible.

Determination of Sb(III) in the Presence of U(VI). In the absence of SAS, Sb(III) is reduced at DME and exhibits one reduction wave with $E_{1/2}$=−0.28 V.[20] Thus Sb(III) and U(VI) cannot be determined in the presence of each other, as the potential difference between them is not largely allowed. However, in the presence of 0.01% T.X 100, the U(VI)-wave undergoes a large shift to more negative potential, whereby, two well-developed waves are observed. The first wave occurs at −0.34 V representing the reduction of Sb(III) to the metal, whereas the second wave at −0.68 V corresponds to the production of U(IV). Under these conditions, the analytical determination of Sb(III) in the presence of U(VI) is quite possible as indicated from Fig. 2 and Table 1.

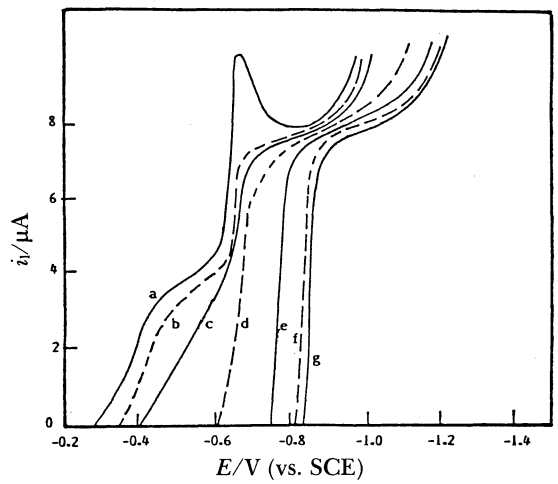

Fig. 3. The effects of Triton® X 100 on the polarographic behavior of 0.5 mM As(III) in 1 M H_2SO_4. a) No SAS, b) 0.002%, c) 0.004%, d) 0.006%, e) 0.008%, f) 0.01%, h) 0.02%.

Determination of As(III) in the Presence of U(VI). The effects of T. X 100 on the polarographic behavior of 0.5 mM As(III) in 1 M H_2SO_4 are shown in Fig. 3. In the absence of SAS, the polarogram consists of two distinct waves with $E_{1/2}$ values equal to −0.38 and −0.65 V.[2] The second wave possesses a steep rising portion and is characterized by a small maximum. At lower SAS concentrations (viz 0.005%), the first wave undergoes a marked shift to negative potential and joins with the second wave forming a single composite wave. Upon further addition of T. X 100, the whole polarogram suffers a considerable shift to more negative potential and only one wave with $E_{1/2}$= −0.85 V is observed. Figure 2 and Table 1 show that the analytical determination of As(III) of concentrations ranging from 0.1 to 1.6 mM in the presence of 1 mM U(VI), 0.01% T. X 100 and 1 M H_2SO_4, appears to be possible.

Determination of Ti(IV) in the Presence of U(VI). The electroreduction of 1 mM Ti(IV) in 1 M H_2SO_4 yields one wave with $E_{1/2}$=−0.87 V corresponding to the reduction of Ti(IV) to Ti(III).[21] The addition of T. X 100 causes a very slight decrease in the limiting current, whereas the $E_{1/2}$ of the wave becomes −1.04 V. Accordingly, the polarograms of 1 mM U(VI), 0.01% T. X 100 and 1 M H_2SO_4 in the presence of various amounts of Ti(IV) show two reduction waves with $E_{1/2}$ at −0.68 and −1.04 V respectively. The limiting current of the second wave increases quantitatively as the concentration of Ti(IV) is increased (cf. Table 1

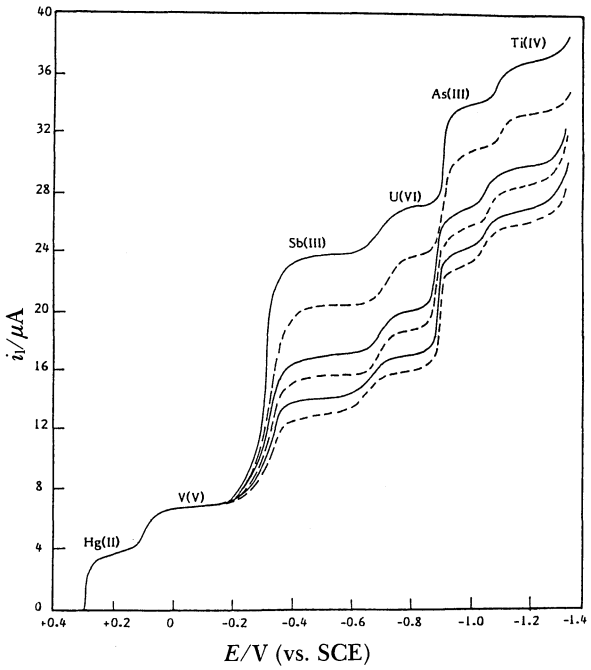

Fig. 4. Effect of Sb(III) concentration on polarographic behavior of the mixture in the presence of 0.01% T. X 100 and 1 M H_2SO_4. Run and concentration. a) 0.5, b) 0.6, c) 0.8, d) 0.95, e) 1.25, f) 1.65 mM.

and Fig. 2). Under these conditions, titanium in minerals, steel and clay can be determined quantitatively.

Determination of a Mixture of Hg(II), Fe(III), V(V), Sb(III), As(III), and Ti(IV) in the Presence of U(VI). Investigation has been carried out to determine the constituents of a mixture of Hg(II), Fe(III) (or V(V)), Sb(III), As(III), and Ti(IV) in the presence of U(VI). Thus, when a mixture of Hg(II), Fe(III) (or V(V)), Sb(III), As(III), Ti(IV), and U(VI), each at a concentration of 0.5 mM is investigated polarographically in the presence of 0.01% T. X 100 and 1 M H_2SO_4, as supporting electrolyte; a well-developed polarogram is obtained. This polarogram consists of six distinct waves. The first wave represents the reduction of Hg(II) with $E_{1/2}$=+0.28 V, the second corresponds to the electroreduction of Fe(III) (or V(V)) with $E_{1/2}$= +0.06 V, the third at −0.34 V corresponds to the reduction of Sb(III), the fourth corresponds to the electroreduction of U(VI) with $E_{1/2}$=−0.68 V, whereas the fifth and the sixth waves lie at more negative potentials $E_{1/2}$=−0.88 and −1.04 V representing the reduction of As(III) and Ti(IV) respectively. Thus, under these conditions, any one of these metal ions can be determined in the presence of each others. This is carried out by keeping the concentration of five of the constituents constant whereas the sixth one is successively increased (cf. Fig. 4). The validity of the Ilkovic equation is satisfactorily tested. The results of the correlation with the Ilkovic equation are also included in Table 1. The value of both the correlation coefficient, r, and the standard deviation, S, indicate clearly an excellent correlation. Thus, the quantitative determination of such mixture by the use of 0.01% Triton® X 100 in the presence of U(VI) is highly possible under these conditions.

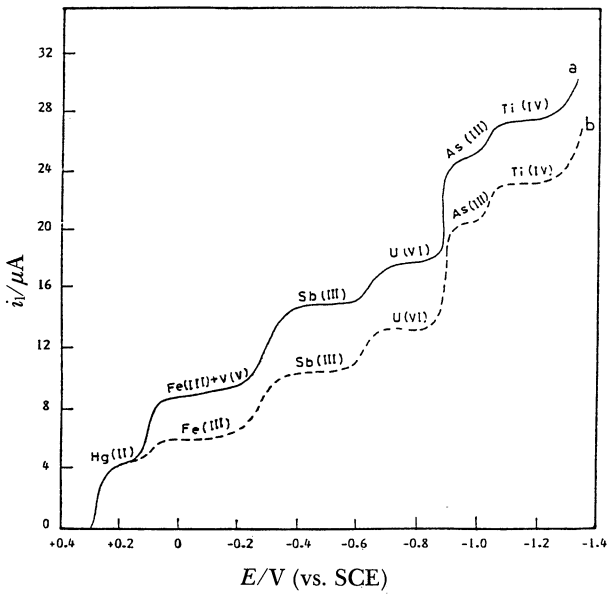

Fig. 5. Polarographic behavior of 0.5 mM Hg(II), Fe(III), V(V), Sb(III), U(VI), As(III), and Ti(IV) in 0.01% T. X 100 and 1 M H_2SO_4. a) in the absence of resorcinol, b) in the presence of 1% resorcinol.

It is to be noted that, in the presence of 0.01% T. X 100, both Fe(III) and V(V) have almost the same $E_{1/2}$ value (+0.06 V), i.e., if Fe(III) and V(V) are present in a mixture, the second wave will represent the electroreduction of Fe(III) and V(V) together. In an earlier communication,[1,2] we have noticed that, resorcinol had no effect on the limiting current of the Fe(III)-Fe(II) wave, whereas pyrogallol caused complete suppression of the wave. On the other hand, in the case of V(V), both resorcinol and pyrogallol caused a complete suppression of the vanadium wave which could be attributed to the formation of electro-inactive vanadate complex. Adopting these previously assigned conclusions, in case of presence of both Fe(III) and V(V) in the mixture, the limiting current of the second wave corresponds to the concentration of both. When 1% of resorcinol is then added, a suppression of V(V) should be expected as being confirmed experimentally in Fig. 5. The limiting current of the second wave in this case will represent only the concentration of Fe(III). The concentration of V(V), therefore, can be calculated by measuring the difference between the limiting currents of the second wave in the absence and in the presence of resorcinol. Thus, under these conditions, elements Hg(II), Fe(III), V(V), As(III), Sb(III), and Ti(IV) in the presence of U(VI) can be precisely determined at DME in the presence of each other using 1 M H_2SO_4 and 0.01% T.X 100 as a base electrolyte.

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