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SURFACE TENSION MEASUREMENT ON DROPPING MERCURY ELECTRODE USING THIOL - COLLECTORS AND THEIR MIXTURES

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The adsorption of potassium ethyl xanthate (KETX), dithiocarbamate (DTC) and their binary mixtures on a dropping mercury electrode (d.m.e.) has been studied using electrocapillary method. The electrocapillary curves determined as a function of potential in 0.1M borate buffer with the addition of KETX and DTC indicate a reduction in surface tension. Synergistic behaviour was also studied by comparing the decrease in surface tension of individual collectors with that of their mixtures at different molar ratios and potentials of -500, -600 and -700 mv.

Key words: Surface tension, Mercury, Thiol - collectros.

Introduction

Many workers, taking advantage of its unique properties, have used mercury to study the electrochemical behaviour of surface active species in aqueous solutions. The special advantages of a mercury electrode are that one can obtain a clean, reproducible surface that does not give rise to the uncertainties due to surface roughness and oxidation that are encountered with solid electrodes. In particular, direct measurements of the electrocapillary curve and the Zero-charge potential enable one to study adsorption on the rational ϕ scale of potentials ($\phi = E - E_{(q=0)}$) as described by Antropov [1] who used mercury electrodes in the investigation of corrosion inhibitor. The surface tension measurement related to flotation collector studies using this technique have been reported by Hunter [2].

In the flotation synergistic effects between collectors and between collectors and frothers have long been recognized in plant practice [3], though little attention has been paid to these in laboratory studies. Exceptions to this are, for example, the investigations reported by Glembotskii [4] on the use of mixtures of collectors of the same type but of differing hydrocarbon chain length or degree of branching. The work of Mingione [5] on the use of dithiophosphates in conjunction with xanthates and sodium mercaptobenzothiozole in the flotation of platinum-group metals, and the work of Pomianowski and Pawlikowskizcubak [6], who have presented the results of tensammetric measurements on mercury and of flotation experiments using KETX with dodecyltrimethyl ammonium bromide.

The study of such effects between KETX and DTC on their electrocapillary curves is described in the present contribution. It is hoped that surface tension measurements carried out on a dropping mercury together with other techniques such as

cyclic voltametry and polarographic studies, could be developed into a compact method for studying synergism for the evaluation of potentially useful systems.

Experimental

The surface tension of mercury-solution interface were determined at various controlled potentials by the drop weight method using a dropping mercury electrode. This method has been used by Hunter [2] and Vanel [7] and shown to be very simple, reliable and reproducible in its operation. The dropping mercury electrode consisted of an extra long capillary and large mercury head to give as constant a mercury flow rate as possible. The lower tip of capillary was immersed in the test solution contained in the cell. The volume of the cell was 100 cm³ which houses the working electrode connected by a side tube containing a sintered glass frit and an agar-salt bridge to a side tube which formed the saturated calomel reference electrode. The potential across the cell was controlled by general purpose polarograph E.I.I cambridge model 0410 and read through the digital multimeter, Thander TM 355. All potentials were measured with respect to a saturated calomel electrode (S.C.E.) whose potential may be taken as 241.2 mv with respect to the standard hydrogen scale of potential. The electrolyte used was made from A.R. sodium tetraborate in 0.1M solution which gives a constant pH of 9.2. The solutions were deoxygenated using nitrogen that had been scrubbed in vanadous chloride. A continuous nitrogen flow was maintained through the experiments. The KETX and DTC were freshly synthesized. The xanthate was prepared according to the general method advocated by Foster [8]. The DTC was synthesized according to the method developed by Harris [9] from a procedure described by Nambury [10].

For each experiment the d.m.e. was polarized to a fixed potential relative to the S.C.E. and time taken for at least 10

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drops to form was measured with a stop watch. Measurements were made starting from the negative potentials (-1.6 V) at 100 mV intervals. All potentials were repeated at least three times to check experimental accuracy and reproducibility. The experimental determination of drop time in 0.1M borate buffer gives the reproducibility slightly better than ± 1 sec. over a time interval of about 120 sec. for the formation on 10 drops. The weight method gives only comparative values of surface tension. The calibration of the technique using standard experimental parameters was carried out by comparison of the results obtained for the borate base electrolyte with those reported by Hunter [2]. The agreement obtained was estimated at ± 2 mjm⁻².

Results and Discussion

The electrocapillary curves for mercury in the base electrolyte and with various representative additions of KEtX and DTC are shown in Figs.1 and 2. The mercury surface is initially observed as positively charged. On reducing this charge by means of applied potential, the surface tension increases, goes through maximum and then decreases. The maximum occurs at a potential at which the charge density changes from positive to negative values passing through zero. The potential at electrocapillary maximum (E.C.M.) is also known as the potential of zero charge (PZC) and given by the symbol $E_q = 0$. On either side of PZC where the surface is either positively charged or the negatively charged, counter ions are adsorbed on the surface. The variation of surface tension with potential in the absence of electroactive species, is presumably, a result of orientation effects among water dipoles due to

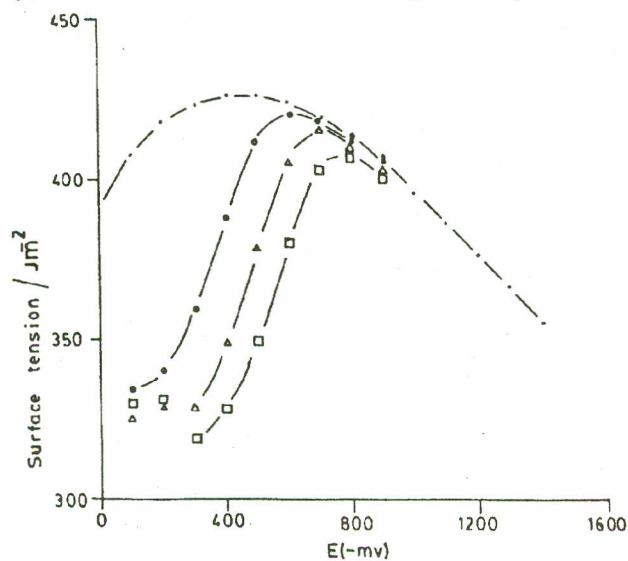


Fig. 1. Surface tension of mercury-solution interface for various KEtX concentrations in 0.1 M sodium tetraborate. Borate, 0.1M (·); KEtX, 10⁻⁴M (○); KEtX, 10⁻³M (Δ); KEtX, 10⁻²M (◻) Note. Surface tension in units of Nm is identical to surface energy. Multiplying and dividing by units of meters gives Nm^m equal to Jm².

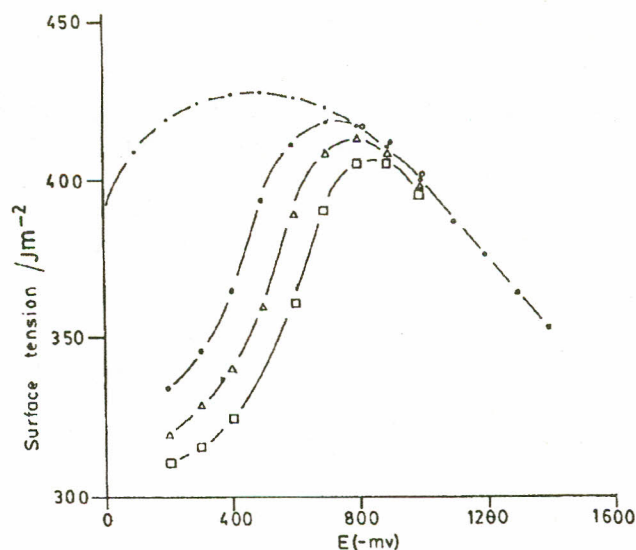


Fig. 2. Surface tension of mercury-solution interface for various DTC concentrations in 0.1M sodium tetraborate. Borate, 0.1M (·); DTC, 10⁻⁴ (●); DTC, 10⁻³M (Δ); DTC, 10⁻²M (◻).

the surface charge on the mercury as contact adsorption of sodium or borate ions is unlikely. This is supported by the observation that the point of inflexion of the curve coincides with PZC. Electrocapillary curves may be differentiated with respect to the potential to give the surface charge ($dr/dE = -q_s$) where q_s is surface charge in electrolyte and redifferentiated to give the differential surface capacitance ($dr^2/dE^2 = C$). Although in such a mathematical process any fine detail will inevitably be lost, the agreement with results obtained by direct determination [2] of surface capacitance is quite good for simple case of borate solution. With the addition of KEtX and DTC, the curves show a variation of surface tension to a varying degrees depending on the nature and concentration of collectors. The E.C.M. are shifted to more positive potentials by about 60 mV for a ten fold decrease in concentration. This is in agreement with the measurements of surface capacitance reported by Hunter [2] for different xanthate concentrations. Equating the decrease in surface tension to the extent of adsorption, it is noteworthy that measurable adsorption takes place at potentials several hundred millivolts negative to the e.c.m. where as on negatively charged surface, anion adsorption would not normally be expected to be significant. It may have been caused either by the weak affinity of sulphur, in the polar group, for mercury or by the chemisorption in which mercury atom remains a part of the metallic phase even after interaction with these collectors. The decrease in surface tension becomes greater with increasing concentration and applied potential. The magnitude of depression being proportional to the surface concentration of adsorbed xanthate and dithiocarbamate. At potentials more positive than 350 mV the formation of mercurous xanthate on the surface

caused erratic behaviour in the electrocapillary curves [2]. However, at potentials more negative than -900 mV (S.C.E.) all the curves tend to coincide with that of electrolyte.

A collector mixtures shows synergism when it can attain a greater lowering of surface tension at a given total concentration than that of separate components of the mixture at the same concentration. The lowering of surface tension for the binary mixtures of KEtX and DTC are shown in Fig. 3 as a function of molar ratio at a constant total concentration and at potentials of -500, -600 and -700 mV. Maximum synergistic effect occurs at about 7:3 molar ratio of KEtX and DTC. The observed synergistic effect could be, as a result of molecular interaction between the components of mixture or the mercury surface charge modification. From the present work, it can be suggested that the component DTC adsorbable at lower potentials, modifies the mercury surface charge for other component KEtX normally only adsorbable at higher potentials, resulting in a greater reduction of surface tension.

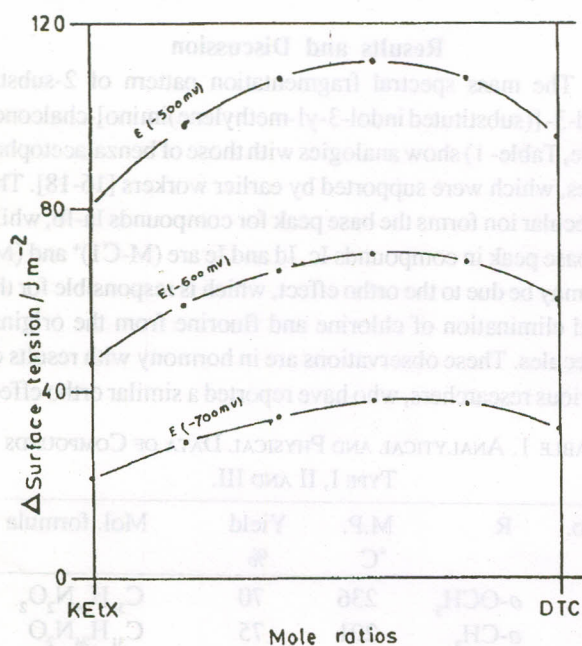


Fig. 3. Comparison of the changes in surface tension of mercury-solution interface for KEtX (10^{-2} M), DTC (10^{-2} M) and their mixtures of various mole ratios at constant total concentration (10^{-2} M) in 0.1 M sodium tetraborate.

It is evident from these experiments that synergism between collectors is an important factor in the selection of reagents in flotation. It has been demonstrated that its occurrence can be readily explored by quite simple electrocapillary measurements. In addition, experiments not reported here indicate that cyclic voltametry is another powerful method of investigation that correlate well with the technique described above. By applying these methods to other combination of collectors and mineral species it should be possible to obtain a fuller understanding of the factors that control synergism, both in general and in particular systems.

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