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Effect of a polyethoxylate surfactant on the electrodeposition of tin

A. ARAGÓN, M. G. FIGUEROA, R. E. GANA*

Departamento Química Analítica y de Electroquímica, Facultad de Química, Pontificia Universidad Católica de Chile, casilla 306 correo 22 Santiago, Chile

J. H. ZAGAL

Departamento de Química, Facultad de Ciencias, Universidad de Santiago de Chile, casilla 5659, Santiago, Chile

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The electrodeposition of tin in the presence of polyethoxylated additive TX-102 has been investigated in acid medium. The additive causes a substantial increase in the overpotential for the discharge of Sn^{2+} ions. Below $0.12\,g\,dm^{-3}$ the additive has little effect on the quality of the tin deposits. Periodic oscillations in the voltage of the cell are observed, which are associated with the initial growth of whiskers. For higher concentrations of additive, the deposits are smooth and homogeneous, and no growth of whiskers and no voltage oscillations are observed. The effect of TX-102 for concentrations below the CMC has been interpreted in terms of blockage of high energy sites of preferential growth on the tin surface. For additive concentrations above the CMC, micelles are formed. These high molecular weight aggregates also block the surface, hindering the mass transport of Sn^{2+} through a membrane-like layer that forms on the tin.

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1. Introduction

Tin is electrodeposited at relatively low overpotentials from stannous acid solutions in the absence of additives. The deposits, however, are porous, coarse and non-adherent, with formation of needles, whiskers and dendrites which cause short circuits between anode and cathode. It has been known for a long time [1] that addition of certain organic molecules to the electrolyte results in an increase in the polarization even at relatively low current densities. These additives, however, substantially improve the quality of the deposits in terms of adherence and size grain homogenization and they also inhibit the formation of whiskers and dendrites.

Figure 1 shows the different features of tin deposits obtained (a) without and (b) with the addition of $1.0\,g\,dm^{-3}$ of a polyethoxylated additive [2] keeping all the operational parameters under control. The increase in the polarization by additives is due to the adsorption of additive molecules on the electrode surface, blocking high energy sites for crystallization of the metal. In the specific case of surfactant additives, these can form micelles at the critical micelle concentration (CMC). It is very likely that these micelles also affect the deposition of tin. The increase in polarization due to the additive may be detrimental if it is excessive as the deposition reaction would require much more energy, making the process more costly.

The purpose of the present investigation was to study the effect of a polyethoxylated surfactant additive, Triton X-102 (TX-102), on the electrodeposition of tin from acid solutions, because this additive has given better results in previous studies [2, 3].

2. Experimental details

Measurements of cell voltage with large electrodes were carried out in a rectangular acrylic cell of $250\,cm^3$ capacity. The tin anodes were cast from grade A Sn (99.8%) exposing a geometric area of $16\,cm^2$. As cathodes, copper sheets of 1 mm thickness (99.99%) also of exposed area $16\,cm^2$ were employed. The electrode separation distance was 9.5 cm. A constant current density of $1.0\,A\,dm^{-2}$ was used. The electrolyte was $25\,g\,dm^{-3}$ Sn^{2+}, $60\,g\,dm^{-3}$ H_2SO_4 and $50\,g\,dm^{-3}$ phenolsulphonic acid (analytical grade Merck).

Potentiodynamic and potentiostatic measurements with small electrodes were performed in a double walled Pyrex glass cell of $300\,cm^3$ capacity. The working electrode was tin (Baker analytical grade) with an exposed area of $0.22\,cm^2$ (mounted in Araldite). The counter electrode was platinum wire (99.99%) 0.3 mm thick and 150 mm long, and the reference was a saturated calomel electrode, immersed in the electrolyte without additive. TX-102 was obtained as commercial grade material from Rohm & Haas, and the head group of this species, on average contained between 12 and 13 oxyethylene units. The surfactant was used from a stock aqueous solution containing $100\,g\,dm^{-3}$ of TX-102. The measurements were conducted at

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* Author to whom correspondence should be addressed.

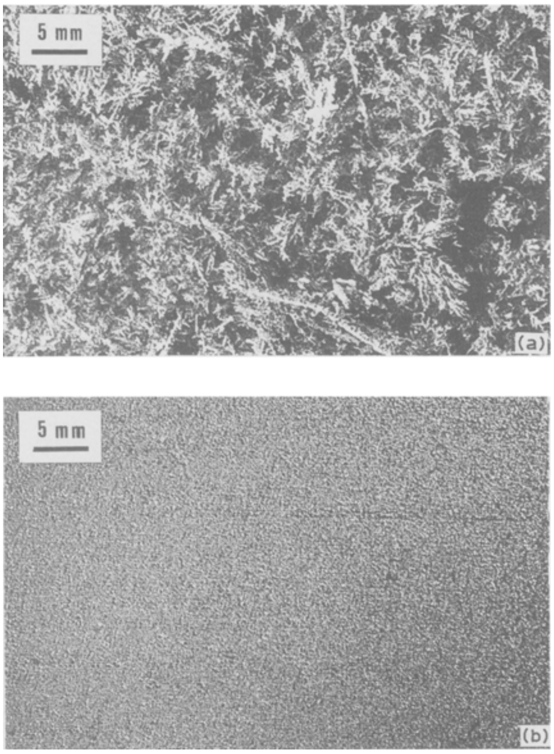

Fig. 1. Tin deposits after 4 h of electrolysis with $i = 1\,\mathrm{A\,dm^{-2}}$ and $25\,\mathrm{g\,dm^{-3}}$ of Sn^{2+}, $60\,\mathrm{g\,dm^{-3}}$ H_2SO_4 and $50\,\mathrm{g\,dm^{-3}}$ of phenol sulphonic acid at 25°C: (a) without additive and (b) with an polyethoxylated additive.

25 ± 1°C and the electrolyte was degassed with purified nitrogen. Before each experiment, the tin working electrode was polished with 600 grit emery paper and with 0.3 μm alumina, followed by degreasing with perchloroethylene and cathodic electrolytic degreasing, pickling in 10% HCl and, finally, rinsing several times with bidistilled water. The electronic equipment consisted of a Tacussel model PRT 20-X potentiostat, a Tacussel model GSTP signal generator and a Hewlett Packard 7004B recorder.

3. Results

3.1. *Cell voltage behaviour*

Figure 2 shows a graph of cell voltage against time of electrolysis for the deposition of tin under galvanostatic conditions ($i = 1\,\mathrm{A\,dm^{-2}}$) with different concentrations of surfactant TX-102 in the electrolyte. There is initially, a rapid increase of voltage with time, for concentrations of additive equal to or higher than $0.12\,\mathrm{g\,dm^{-3}}$ which suggests that for those concentrations, the adsorption of the additive on the tin surface is sufficiently high to substantially increase the overpotential for the discharge of Sn^{2+} ions.

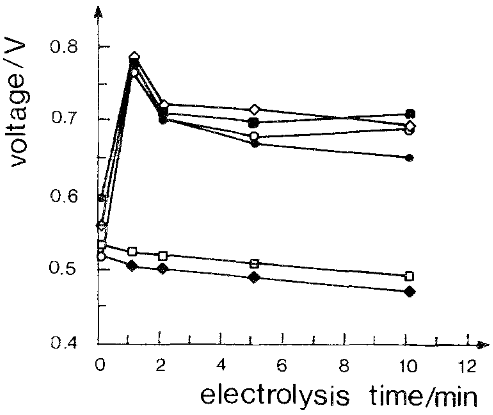

Fig. 2. Cell voltage vs time of electrolysis, $i = 1\,\mathrm{A\,dm^{-2}}$. Electrolyte: $25\,\mathrm{g\,dm^{-3}}$ Sn^{2+}, $60\,\mathrm{g\,dm^{-3}}$ H_2SO_4 and $50\,\mathrm{g\,dm^{-3}}$ phenolsulphonic acid. T = 25°C Additive conc./$\mathrm{g\,dm^{-3}}$: (◆) 0.035, (□) 0.09, (●) 0.12, (◇) 0.40, (■) 0.50 and (o) 1.0.

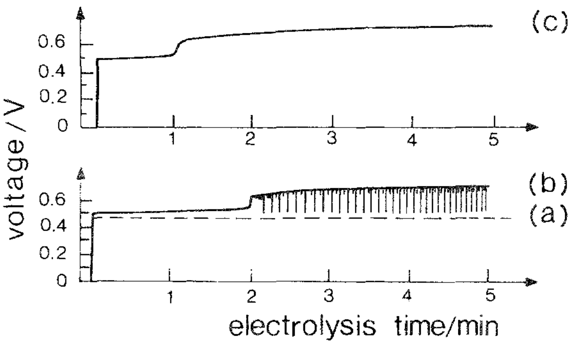

Fig. 3. Voltage evolution with time of electrolysis for $i = 1\,\mathrm{A\,dm^{-2}}$. Electrolyte composition the same as in Fig. 2 for $T = 25°\mathrm{C}$. (a) No additive, (b) with $0.04\,\mathrm{g\,dm^{-3}}$ and (c) with $0.12\,\mathrm{g\,dm^{-3}}$ of TX-102.

Figure 3 shows a continuous recording of cell voltage vs time for the first 5 min of electrolysis at constant current density ($i = 1\,\mathrm{A\,dm^{-2}}$). Without additive, the voltage remains constant with time (curve 3a). This is also observed when small amounts ($< 0.04\,\mathrm{g\,dm^{-3}}$) of additive are present. However, when the additive concentration is $0.04\,\mathrm{g\,dm^{-3}}$, the voltage is slightly higher (curve 3b), increases gradually and, at 2 min, changes abruptly to a higher value and periodic oscillations begin to appear. It was found that these oscillations were related to a cathodic phenomenon, as corroborated by introducing a reference electrode (SCE) to the system. Such oscillations have been observed by other authors. Nezu *et al.* [4] observed cathodic oscillations of about 150 mV amplitude and periods of 3.6 min during deposition of tin in the presence of crown ethers. They attributed these oscillations to periodic changes in the concentration of the crown ether at the electrode surface. This explanation may also be valid in the present work. However, the oscillations detected in this work have periods smaller than those reported by Nezu but with amplitudes similar to those observed here. When the concentration of additive is equal or greater than $0{\cdot}12\,\mathrm{g\,dm^{-3}}$ keeping $i = 1\,\mathrm{A\,cm^{-2}}$, the voltage increases gradually (curve 3c) up to a point where it rises suddenly (about 150 mV) and then it continues to increase gradually without any detectable oscillations.

The influence of current density on the voltage oscillations was studied by conducting experiments using $0.04\,\mathrm{g\,dm^{-3}}$ of additive and varying the current density between 0.5 and $2.0\,\mathrm{A\,dm^{-2}}$. Voltage oscillations appear at $i = 1\,\mathrm{A\,dm^{-2}}$. As the current density increases the oscillations become more intense (greater amplitude) and the frequency decreases. (Fig. 4). For this additive concentration, when oscillations are detected whiskers were observed at some sites on the

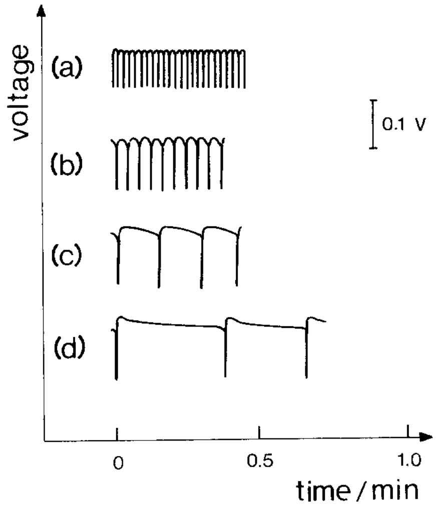

Fig. 4. Influence of the current density on the type of voltage oscillations. Electrolyte composition the same as in Fig. 2. Additive concentration = 0.04 g dm^{-3} at current densities/A dm^{-2}: (a) 1.0, (b) 1.1, (c) 1.2 and (d) 1.3.

electrode surface (Fig. 5). In some experiments a rapid growth of whiskers took place and caused an increase in the oscillation frequency. The oscillations disappeared completely when the "whisker" becomes a dendrite with long ramifications (20–30 mm). If these dentrites were mechanically removed from the electrode surface without interrupting the electrolysis, the whole process was reproduced, with voltage oscillations and growth of whiskers. With additive concentration 0.12 g dm^{-3}, no oscillations were observed with $i = 1$ A dm^{-2} but they appeared at low current density (0.4 A dm^{-2}) and then again at high current density (2 A dm^{-2}). Similarly to those experiences with 0.04 g dm^{-3} of additive, the recording of voltage oscillation coincides with the appearance of whiskers on the tin cathode. Once these oscillations are present they gradually disappear when the current density is increased or decreased without stopping the electrolysis. These observations are interesting since they correlate the oscillation phenomena to the current density and explain why they appear when a whisker that has grown very rapidly becomes long and branched (dendrite). There is little doubt that the "point effect" causes very uneven current distribution, producing an "explosive" growth of the dendrite as a result of a high local current distribution, the latter being low on the rest of the flat portions of the electrode surface. This observation is associated with a voltage cell decrease.

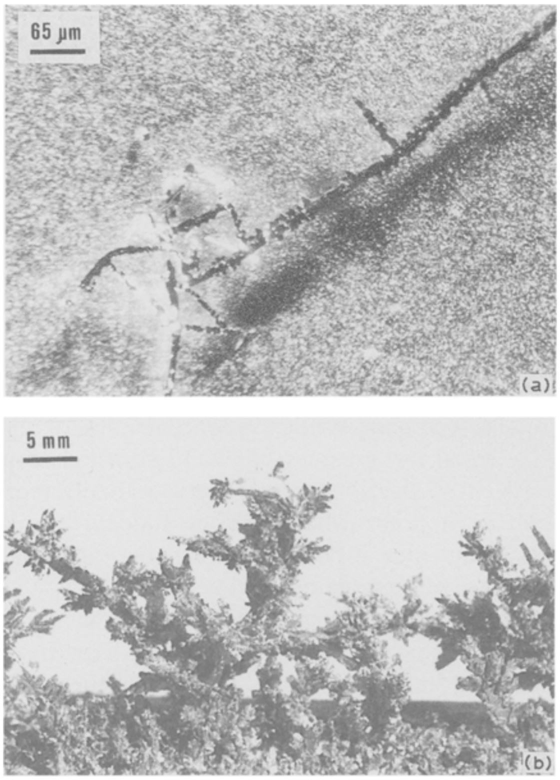

Fig. 5. Tin deposits at $i = 1$ A dm^{-2}. Same electrolyte composition as on Fig. 2 for $T = 25°C$; 0.04 g dm^{-3} of TX-102 added. (a) Growth of whiskers after 5 min of electrolysis and (b) dendritic growth after continuous 4 h of electrolysis.

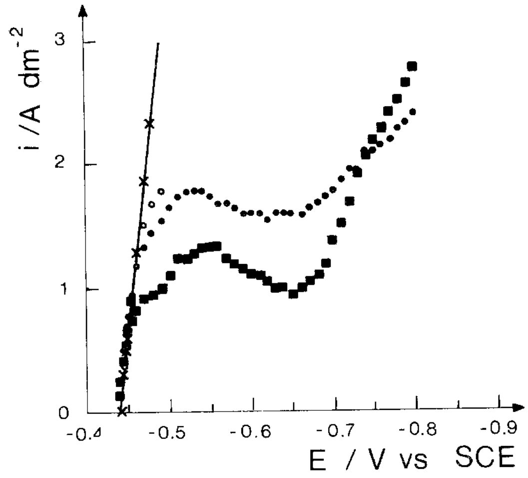

Fig. 6. Polarization curves for tin deposition at 25° C. Same electrolyte composition as Fig. 2. Without additive, (○) with 0.04, (■) 0.20 and (●) 1.0 g dm^{-3} TX-102.

3.2. *Current potential curves under potentiostatic conditions*

Figure 6 illustrates polarization curves obtained with and without additive TX-102 added. These curves were obtained under steady state conditions. In the absence of additive the current increases rapidly starting at $E = -0.44$ V. The presence of a relatively low concentration of additive (0.04 g dm^{-3}) causes no changes at the foot of the wave but for higher overpotentials the currents are lower than those without additive. Increasing additive concentration (>0.12 g dm^{-3} and more) causes the appearance of well defined limiting currents, probably due to a mass transfer-controlled process of Sn^{2+} ions through a barrier of molecules of additive and micelles. It may be noted that the limiting current has its lowest value for an additive concentration of 0.2 g dm^{-3}, which is close to the CMC [5].

3.3. *Potentiodynamic response*

Figure 7 illustrates the potentiodynamic response of a small area tin electrode (0.22 cm^2) in the presence of additive. The first scan gives a higher current

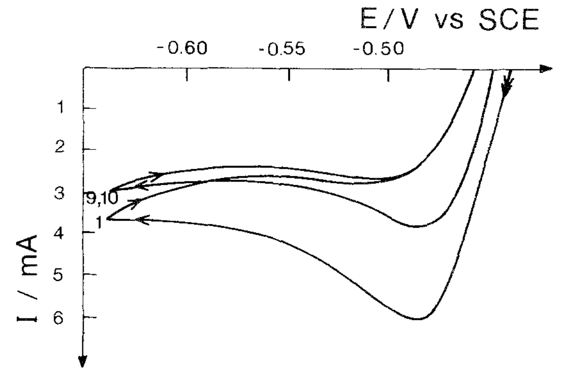

Fig. 7. Linear voltammogram of Sn in the electrolyte described in Fig. 2 for $T = 25°C$. Potential scan rate $0.01\,V\,s^{-1}$ with $1.0\,g\,dm^{-3}$ of TX-102. (1) First scan, and (9, 10) ninth and tenth scans.

which gradually decreases with further sweeps until it reaches a steady value after the 9th scan. If the potential scan is interrupted at the initial potential (-0.44 V/SCE, which is the rest potential of the system) the solution stirred for about 30 s and the potential scan restarted, the peak current is equal to that obtained previously after 9 sweeps. It is possible that after the 9th sweep, the electrode reaches a steady state condition involving a relatively stable Sn^{2+} concentration profile. Since these currents were reproducible they were used for purpose of comparison rather than the peak current obtained for the first scan.

Figure 8 illustrates the effect of varying the additive concentration on the peak current of the cyclic voltammograms. The peak current decreases abruptly in the lower concentration range (0–0.1 $g\,dm^{-3}$). A minimum is observed over the range 0.15 to 0.20 $g\,dm^{-3}$. At higher additive concentrations the peak currents increase gradually reaching a stable value for concentrations higher than 0.6 $g\,dm^{-3}$.

Figure 9 shows curves of peak currents against additive concentration for three different temperatures. The minimum obtained for a given temperature is probably correlated to the CMC since it has been found in the literature [5] that the CMC in a given electrolyte can be determined using cyclic voltammetry by plotting peak current vs. concentration of surfactant. According to these findings, the minimum in the plots of peak current vs. surfactant concentration corresponds to the CMC and the values compare well with those determined using other techniques. The same reasoning can be applied to the system discussed in Fig. 8. The CMC might be expected to shift to lower values with temperature since the surfactant used in this work is non-ionic [6]. However, in Fig. 9 there is practically no effect of temperature on the CMC in the range studied.

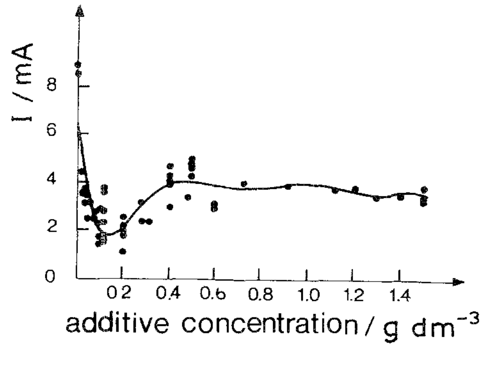

Fig. 8. Variation of peak current of the 10th scan against additive concentration.

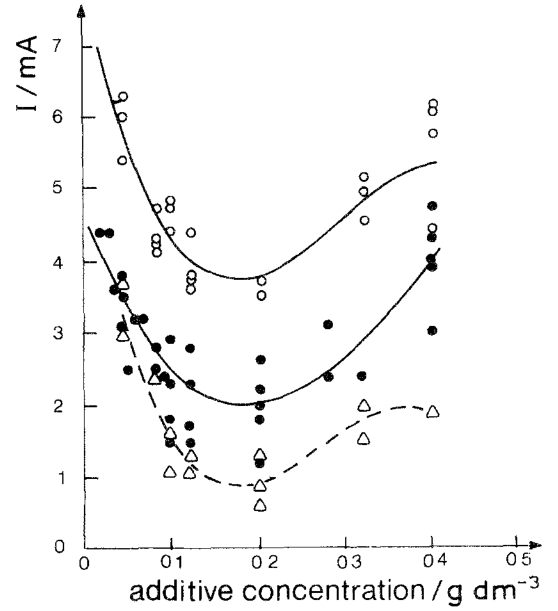

Fig. 9. Effect of temperature on the variation of peak current of the 10th scan with additive concentration at temperatures/°C: (△) 10, (●) 25 and (○) 40.

4. Discussion

One interpretation of the action of additives on the electrocrystallization of metals is via the blocking of preferential growth sites. The additive molecules are thought to adsorb on those sites. This phenomenon increases the overpotential for the reaction by decreasing the sites available for discharge of metal ions. Another interpretation postulates the formation of a permeable barrier that hinders the transport of cations to the surface of the electrode. The formation of a thin film of adsorbed molecules on the electrode surface constitutes a simple energy barrier. A linear dependence of overpotential on log i would then be expected.

The additive used in this study is an octylphenol, with 12–13 units of ethylene oxide per molecule and with an average molecular weight of 750 $g\,mol^{-1}$. According to studies on similar compounds [7–9], it may be assumed that this compound forms micelles with an aggregation number equal to or higher than 100. For additive concentrations below the CMC (about 0.2–0.3 $g\,dm^{-3}$) it is likely that a mechanism of blockage of active sites with adsorption-desorption of individual molecules takes place. However, when additive concentrations are equal to or higher than the CMC, high molecular weight micelles are formed. These micelles form a thick layer constituting a membrane, anchored on the sites of highest energy on the electrode. It is possible that, as the crystallization process progresses, on sites neighboring the blocked sites, the anchoring of the micelle shifts to other sites of high energy as they are generated. This is possible since the half-life of micelles is rather short (in some cases in the order of 10^{-7}s [9]). The surface thus obtained is then constituted by many small crystals rather than a few large ones. Further, due to the thickness of this micellar layer, the ionic transport to the electrode surface is hindered, causing mass-transport control at higher current densities. For additive concentrations below the CMC, the growth of tin can take place at such a rate that only partial blockage by additive occurs, since its bulk concentration is too low. Whiskers, and then dendrites, start to form. The additive molecules probably jump from one site to the next blocking and unblocking high current density sites. This may explain the oscillations observed in this work. At higher additive concentrations, this type of growth does not occur and oscillations are not observed. However, if the electrolysis is carried out at high current densities (2 A dm^{-2}), some whiskers may grow so fast that they disrupt or break through the layer of additive molecules and micelles, causing the observed oscillations.

5. Conclusion

From this work we conclude that the appearance of voltage oscillations during electrolysis as an indication of irregular tin deposits with dendrite or whisker growth. In order to obtain deposits with uniform grain size without dendrite growth, the critical parameters are (a) the current density and (b) the additive concentration. These parameters must be maintained in a certain range for practical application in plating or electrolytic refining of tin.

Acknowledgements

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References

[1] S. Meibuhr, E. Yeager, A. Kosawa and F. Hovorka, *J. Electrochem. Soc.* **110** (1963) 190.
[2] B. Donoso, Tesis de pregrado, Facultad de Química, Pontificia Universidad Católica de Chile (1990).
[3] A. Aragón, M. T. San Martín, M. Figueroa and R. Gana, XVIII Congreso Latinoamericano de Química y XVII Jornadas Chilenas de Química. Santiago, **2** (1988) 529.
[4] H. Nezu, N. Kaneko, and N. Shinohara, *Denki Kagaku* **54** (1986) 1027.
[5] A. Baran Mandal, B. Unni Nair and D. Ramaswamy, *Lamgmuir* **4** (1988) 736.
[6] M. E. Ginn, F. B. Kinney and J. C. Harris, *J. Am. Oil Chem. Soc.* **37** (1960) 183.
[7] M. J. Schick, S. M. Atlas and F. R. Eirich, *J. Phys. Chem.* **66** (1962) 1326.
[8] B. Andersson and G. Olofsson, *J. Chem. Soc., Faraday Trans. 1*, **84** (1988) 4087.
[9] R. H. Ottewill, *in* 'Surfactants', Academic Press, London (edited by Th. F. Tadros), (1984) pp. 15.