CHAPTER VI

USE OF ALTERNATING CURRENT POLAROGRAPHIC TECHNIQUE IN

THE ANALYSIS OF SURFACE ACTIVE SUBSTANCES PRESENT IN MOLASSES
Substances with close half-wave potentials can be resolved and analysed easily in the a.c. polarography when their summit potentials are separated by 40 mV or more and give sharp peaks whereas in d.c. polarography, a minimum half-wave potential separation of 90 to 100 mV is required. It has been reported from time to time that reversibly reducible substances give a.c. polarograms whereas irreversibly reducible substances are not amenable for analysis. Oxygen, which is irreversibly reduced, does not show any peak during the a.c. analysis, the wave character of which was made the very basis for the determination of S.A.S. in solution by the d.c. technique. The S.A.S., which as explained in earlier Chapters, are irreversibly reduced could be studied by a.c. technique because of their strong adsorption and consequent insidious influence on the electrode processes. Moreover these could be analysed polarographically for their high concentration of oriented molecules or ions. Studies made in an earlier Chapter on surface-active substances showed that the desorption peaks were in the potential range from -1.3 to -1.8 V, while the chemical peaks could be located over the entire potential span. The observance of desorption peak was thus made the basis of the presence of surface-active compounds in technical sugar solutions. The
extent of the presence of surfactants was more in molasses so that the studies were made on these samples only.

Five molasses samples from different sugar factories were analysed after passing through cation-exchange resin column and adjusting the pH with the help of buffer to 2.6. Two sulphitation molasses samples were examined in 1.0 M KCl as supporting electrolyte. The curves showed only one peak at summit potential (Eₙ) of -1.6 V vs. S.C.E. At concentrations of 0.2, 0.5 and 0.6% (for the first molasses) and corresponding currents were 33, 66 and 76 µA respectively, while the second molasses sample gave similar peaks with Eₙ at -1.63 V vs. S.C.E. at concentrations 0.4 and 0.6%. The summit current was higher to that shown by first molasses and consequently the extent of S.A.S. in this molasses was found higher. Both molasses samples showed a straight line correlation between concentration and summit current just as in d.c. polarography. A carbonation molasses sample was also examined with Eₙ at -1.64 V which was close to that given by above two sulphitation molasses samples, this indicated that the nature of S.A.S. present in such a molasses was not very different.

The other two molasses samples were analysed. The pH was kept at 2.6 but the supporting electrolyte concentration was reduced to 0.1 M KCl. This led to the appearance of a small peak at -1.0 V and shift in the Eₙ to more negative values of -1.74 and -1.80 V vs. S.C.E.
All the polarograms showed a sharp fall in base-current in the initial portion of the curve and then fast increase in current after an applied potential at -1.1V.

All the molasses samples yielded a direct correlation between concentration and summit current. The curves for all the samples showed different inclination, either because of the variation in the inherent character of the surfactants or their presence in different amounts. It is also to be specified that the aggregation of surface-active compounds could also change with concentration. A linear relationship can only be expected when the aggregation under those conditions has not altered.

Use of higher concentration of molasses in these studies was not possible because of the formation of stable mercury droplets which did not coalesce with the proceeding drops falling in the cell. The increase in current was so high and disturbances caused were so immense that the studies were not at all possible. The influence of the surfactants on the summit potential was thus more marked than was evident during d.c. studies on the diffusion current. A.C. polarographic technique offered more sensitive test for the determination of the extent of surface active compounds.
Introduction

A.C. polarographic technique has been employed with advantage over d.c. polarography. Better sensitivity is obtainable mainly because a.c. polarograms give peaks which are sharp and spread over a small potential. Substances with close half-wave potentials can be resolved and analysed when their summit (half wave) potentials are by 40 mV or more. This is in contrast to a requirement of a minimum half wave potential separation of 80 to 100 mV in d.c. polarography. The A.C. polarograms give peak currents independent of previous electrode reaction, while in the latter, the current of the previous reduction or the wave form has to be taken into account and the total current is the summation of the two reduction processes. Thus the effect of the previous electrode reaction is less marked in a.c. polarography.

It has been discussed earlier that the irreversible reduction processes are not amenable for analysis by the a.c. polarography since only reversibly reduced substances give polarograms. Oxygen, which is irreversibly reducible, therefore, does not interfere in a.c. analysis. The suppression of the oxygen wave has been the main plank of contention for the studies of surface-active substances by d.c. polarography and has
no significance in a.c. polarography. The S.A.S. are not studied on the basis of their irreversible reduction in the a.c., but for their strong and often insidious influence on the electrode process. The adsorption of S.A.S. at the electrode lead to their accumulation at the interface to form an electrical double layer having large concentration of highly oriented molecules or ions which lead to a.c. peaks of different nature which has been studied for a large number of substances.

Reilley and Stumm, Ereyer and Bauer have discussed the influence of surface-active substances on a.c. peaks in separate Chapters whereas large number of substances have been discussed individually as well. Gupta and Agarwal studied the nature of the capacity peaks observed with different surface-active compounds and showed the presence of broadly two types of peaks. One desorption peak and the other chemical peak. Studies made earlier on surface-active substances by the author (see Chapter III) showed that the desorption peaks were in the potential range -1.3 to -1.7 V. while the chemical peaks could be located over the entire potential span. Thus methylene blue gave two peaks at -0.32 and -1.41 V, while C.P.B. at -1.2V. and cerfak at -1.25 V. gave only one peak.

Doss, Gupta and Rao studied the influence of the presence of S.A.S. on the base current of the a.c. polarograms in the potential range 0 to 0.8V. The observance of desorption peak was thus made the basis of the presence of surface-active
compounds in technical sugar solutions. It was shown in the last chapter, that the extent of the presence of surfactants was more in molasses than in other technical sugar solutions. The studies were, therefore, confined to the analysis of molasses by the a.c. polarographic technique.

**Experimental**

The experimental technique and the nature of the substances examined were as described in earlier Chapters III and V.

**Results and discussions**

A large number of molasses samples were analysed for a.c. polarograms. Typical sets of results obtained with five molasses samples from different sugar factories were given in Figs. 1-5. Fig. 1 pertains to sulphitation molasses from a sugar factory in Central U.P. when molasses at 0.6, 0.5 and 0.2% concentrations was examined after passing through cation exchange resin column and adjustment of pH to 2.6 and supporting electrolyte concentration of 1.0M KCl, as used in the previous Chapters. The curves showed only one peak at summit potential of -1.60 V. vs. S.C.E. at the above concentrations. The polarograms showed a sharp fall in base current in the initial portion of the curve and then fast increase in current after an applied potential at -1.1 V. The polarograms obtained had a narrow wave-width even at higher concentrations and the peak value was well defined. The
Fig. 1 A.C. POLAROGRAMS OF SULPHITATION MOLASSES AS OBTAINED AFTER PASSING THROUGH CATION EXCHANGE RESIN COLUMN

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<th>Curve</th>
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<td>I</td>
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<td>III</td>
<td>0.2%</td>
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Fig. 2 A.C. POLAROGRAMS OF SULPHITATION MOLASSES AS OBTAINED AFTER PASSING THROUGH CATION EXCHANGE RESIN COLUMN
Fig. 3 A. C. POLAROGRAMS OF CARBONATION MOLASSES AS OBTAINED AFTER PASSING THROUGH CATION EXCHANGE RESIN COLUMN
Fig. 4 A.C. POLAROGRAMS OF MOLASSES AS OBTAINED AFTER PASSING THROUGH CATION EXCHANGE RESIN COLUMN
Fig. 5 A. C. POLAROGRAMS OF MOLASSES AS OBTAINED AFTER PASSING THROUGH CATION EXCHANGE RESIN COLUMN
current was 33, 66 and 76 μA at concentration of 0.2, 0.5 and 0.6%, respectively of the molasses solution. Just as in d.c. polarographic studies, a straight line correlation between the concentration and diffusion current of the molasses solution was obtained, similar behaviour was evident for a.c. polarograms as well (See Fig.6). The only stipulation in both the techniques that the contribution of S.A.S. in molasses amenable for analysis was identical. The polarograms of another molasses samples also from a sulphitation factory, gave similar peaks with summit potential of -1.63 V. vs. S.C.E. (see Fig.2). The pattern of the current changes with applied potential was just similar to that obtained earlier.

The summit current obtained with this molasses was, however, much higher to that given in Fig.1, which showed the extent of the presence of S.A.S. was much higher in this molasses. D.C. polarographic studies of the same molasses also showed higher diffusion current (see Chapter IV, Fig.11), which was corroborative. A molasses from a carbonation factory was also examined for the presence of S.A.S. at three different concentrations (see Fig.3). The Es was found to be -1.64 V. which was close to that given in Figs. 1 and 2. This indicated that the nature of S.A.S. present in such a molasses was not very different to that present in the sulphitation molasses samples. The concentration and summit current correlation was indicated
Fig. 6 VARIATION OF SUMMIT CURRENT (is) WITH CONCENTRATION SHOWING VARIATION EITHER IN CONCN. OR NATURE OF SURFACTANTS PRESENT IN DIFFERENT MOLASSES
by this molasses as well. The figure showed some difference in the tendency of the polarogram in not showing sharp fall in the current after attainment of the summit potential as was shown by earlier two molasses samples. This tendency of appearance of fall of current after peak potential was more evident in Figs. 4 and 5. These two figures differed in another important aspect as well. Though the pH of the solution was kept at 2.6 as in earlier cases, the concentration of KCl employed as supporting electrolyte was reduced to 0.1M. This led to the appearance of small peak at -1.0 V. Vs. S.C.E. (see Fig. 4). It was observed in some other cases not reported here that use of lower concentration of supporting electrolyte often yielded a small peak between -0.9 to -1.1 V. Use of lower concentration of supporting electrolyte also shifted the $E_s$ to more negative values of -1.74 and -1.80V. The same molasses samples yield $E_s$ of $\approx$ -1.6V with 1.0M KCl supporting electrolyte. This shift in the $E_s$ with change in concentration of supporting electrolyte has been observed by many earlier workers. The difference in the summit potentials by change of the concentrations of the supporting electrolyte did not cause any change in the current concentration relationship, which remained as was at higher concentration of the supporting electrolyte as explained in Fig.1. All the molasses samples yielded a direct correlation between concentration and current (see Fig.6). The curves for all the samples showed different inclination, either because of the variation in the
inherent character of the surfactant or their presence. It is also to be specified that the aggregation of surface-active compounds change with concentration.

A linear relationship can only be expected when the aggregation under those conditions has not altered. One of the reasons for showing non-linear relation in certain cases, not reported, can thus be caused by the nature of the macromolecules under examination.

The half-wave potentials and summit potentials of the curves obtained in case of sugar house products differed by 0.1 to 0.3V. Such differences in the potentials have been observed for many organic compounds by earlier workers 20-21 also. Sometimes the adsorption-desorption potential and the reduction potential are far apart. Since the a.c. curves give tensammetric peaks and the d.c. curves, the reduction waves which were irreversible, the basic reasons for the behaviour differed in principle in the a.c. and d.c. techniques.

Use of higher concentration of molasses in these studies was not possible. This was because of the formation of stable mercury droplets coming out from the d.m.e. which did not coalesce with the proceeding drops falling in the polarographic cell. The increase in current was so high and disturbances caused were so immense that the studies were not at all possible. It is of interest to point out here that a few molasses sample which were very viscous and tenacious
showed this behaviour even at a concentration of 0.1% of the molasses solution. Such molasses samples could not be analysed polarographically for their summit potential.

Doss, Gupta and Rao studied the effect of sugar and sugar products including molasses containing surface-active compounds on the nature of the a.c. polarograms. Their studies though confined to the applied potentials of zero to -0.8V, showed only variation in base current. They did not obtain any peak in this potential range which were akin to the polarograms given in figures 1 to 5, where the base current varied with the concentration of the molasses employed. But the difference in the current value, though small, was definite and well evident. Only at potential more negative than those employed by Doss et al, interesting variations in the nature of the curves were obtained by yielding peaks near -1.6 to -1.7 V, not observed earlier.

The influence of the surfactants on summit potential was thus more marked than was evident during d.c. polarographic studies on the diffusion current as given in earlier chapter. A.C. technique thus offer more sensitive tests for the determination of the extent of surface-active compounds.
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