CHAPTER IV

INFLUENCE OF pH ON THE POLAROGRAPHIC BEHAVIOUR OF SURFACE ACTIVE SUBSTANCES PRESENT IN MOLASSES
CHAPTER IV

SUMMARY

Surface-active substances have at times marked influence on the polarographic maxima of the reducible or oxidizable substances by decreasing the limiting current and shifting the half-wave potential. The suppression of oxygen maxima has been used to estimate the concentration of S.A.S. in pure and impure solutions. Most of the organic compounds were studied in well buffered solutions at definite pH. The studies, when undertaken in unbuffered solutions gave split or drawn out waves. The present investigations were aimed to study the influence of pH on S.A.S. as present in molasses, which is marked by the presence of maximum impurities and non-sugar constituents. The molasses has maximum concentration of surface-active compounds and it was preferred to examine molasses alone over the entire pH range to fix the conditions for studying their polarographic behaviour.

The three different molasses samples were analysed after passing through cation exchange resin column and the concentration of all samples was kept at 0.1% for the study. When the pH was below 1.9, a continuous increase in current was observed with increasing applied potential and no polarogram could be observed. While at pH 2.0, a well defined polarogram was obtained with diffusion current of 26.5 μA.
Polarograms were obtainable at pH values of 2.0 to 3.0. At a pH of 3.2, it showed a small tendency to form a wave but above this pH no polarogram could be observed. It appeared as a general behaviour.

The variation in diffusion current with pH for the three molasses samples were examined. They showed high value of diffusion current between pH 2.0 and 2.4 and very small value above pH 2.8. The variation in wave-width of the polarograms with pH values was also examined. It was observed that the behaviour of curves varied with the nature of the molasses samples employed. In some cases, the wave-width first increased up to pH 2.5 and then fell, it was minimum between pH 2.6 to 2.9. The diffusion current values above pH 2.6 were however, quite low.

These results set a limit for polarographic studies of surfactants present in the molasses which could be worked out within the limits of pH 2.0 to 3.2. Variation of pH of the buffer either to acidic or alkaline side did not give any polarogram.

Thus the work could best be done at intermediate pH value of 2.6 when the diffusion current obtained was neither too high nor low, yet the polarograms were not drawn out and had minimum wave-width.
INTRODUCTION

Surface-active substances have at times marked influence on the polarographic waves of the substances that are reducible or oxidisable by decreasing the limiting current and shifting the half-wave potential. Sometimes the entire wave pattern is changed. These substances have found immense use for suppressing the polarographic maxima. The suppression of oxygen maxima has been used by large number of workers to estimate the concentration of S.A.S. in pure\(^1-6\) and impure\(^7-10\) solutions. Since these substances have a tendency to accumulate on the interface, they cause partitioning into phases with high concentration at the interface in the form of film having highly oriented molecules or ions. The pH of the medium had a great influence\(^11\) on the hydrophilic substances since H\(^+\) ions often participate in the electrode reaction. It is for this reason that most of the organic compounds are studied in well buffered solutions with definite pH. In an
unbuffered solution, the pH at the electrode surface changes considerably and this causes the waves to split or to be drawn out. The dropping mercury electrode which provides continuously renewed electrode surface, acquires high concentration of surfactants by preferential adsorption, will thus be the function of the total charge of the particles. It is for this reason that the S.A.S. themselves have not been so well studied by d.c. polarographic technique. The present investigations were aimed at the studies on the influence of pH on S.A.S. as present in technical sugar solutions. Since molasses has maximum concentration of such compound, it was preferred to examine molasses alone over the entire pH range to evaluate the conditions for studying the polarographic behaviour of surface-active compounds present therein.

Experimental

A polarographic circuit as discussed in earlier Chapter was employed for d.c. polarography. The cation exchange resin IR-120 (Rohm and Hass Co., U.S.A.) was used. This had polystrene matrix having -SO₃⁻H as an active group. The resin was filled in a column of 100 cm. long and 2 cm.
in diameter by first keeping glass beads and glass wool at the base. The fresh resin was washed two or three times with 2N hydrochloric acid followed by thorough rinsing with distilled water. The resin was regenerated every time after using a particular technical sugar solutions by recycling 2N-hydrochloric acid and it was ensured that the excess acid was washed off from the column by use of distilled water. The removal of acid was tested by the AgNO₃ solution for Cl⁻ ions or by the wide range indicator paper of E.D.H. make for the pH of the effluent.

Molasses pertaining to both sulphitation and carbonation processes were studied. A known volume of the solution of molasses of desired concentration was passed through the cation-exchange resin column very slowly so that the effluent was free from cationic constituents. Only the middle portion of the solution was used for the experimentation. The solution was employed only after testing its consistency with the help of the hand refractometer and only that part of the solution used whose brix of the treated and untreated solution was of the same order. The pH of the effluent was adjusted by mixing 50% of the buffer. The pH of the buffers was varied from 1.0 to 4.0. The buffers were prepared from KCl-HCl or Potassium-bi-phthalate-HCl systems.
Results and discussions -

Figs. 1-3 give the results of the polarographic analysis of three different molasses samples all at 0.1%. Fig. 1 gives the results for sample 1 in the pH range from 1.8 to 2.8. It may be observed that the curves obtained within the limits of pH 2.1 to 2.8 gave well defined polarograms. When the pH was 1.9, a trend for continuous increase in current was observed with applied potential (See Curve I) and no limiting current could be noted. Even when the applied potential was hardly -1.7V, the limiting current plateau could just be observed where after the current increased sharply. When the pH was more than 1.9, sharp polarograms of decreasing wave heights were observed. Thus at pH 1.9, 2.1, 2.3, 2.6 and 2.8, the diffusion current values were 17.0, 14.0, 12.0, 8.0 and 5.5 micro-amperes respectively. The rapid fall in current with change of pH from 1.9 to 2.8 showed that molasses could be studied within the above pH range. Fig. 2 also confirmed the same findings. In this case, the polarogram at pH 2.0 was well defined while the polarograms could not be recorded when the pH was lowered. The value of current at pH 2.9 was very small being only 4.6 μA. The molasses sample was examined at closer pH values between the range 2.0 to 3.2 and the results were given in Figs. 3A and 3B. The curves obtained at pH 2.0 showed a small saturation value pertaining to a limiting current of
Fig. 1 D. C. POLAROGRAMS OF MOLASSES AT DIFFERENT pH VALUES
Fig. 2  D. C. POLAROGRAMS OF MOLASSES AT DIFFERENT pH VALUES

<table>
<thead>
<tr>
<th>Curve</th>
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<tbody>
<tr>
<td>I</td>
<td>2.0</td>
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<tr>
<td>II</td>
<td>2.1</td>
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<td>III</td>
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<td>IV</td>
<td>2.8</td>
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<td>V</td>
<td>2.9</td>
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Applied Potential Vs. S. C. E. in Volts

Current (uA)
Fig. 3A  D. C. POLAROGRAMS OF MOLASSES AT DIFFERENT pH VALUES

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<th>Curve</th>
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<tr>
<td>I</td>
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<td>II</td>
<td>2.2</td>
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<td>III</td>
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Fig. 3B D. C. POLAROGRAMS OF MOLASSES AT DIFFERENT pH VALUES
26.5 μA, while the curves at pH 2.2 and 2.5 were well marked for the limiting current values. The curves given in Fig. 3B for pH values between 2.6 and 3.0 showed only small variation in the diffusion current. No diffusion current value was obtainable at pH 3.2 in a well defined manner. This appeared as a general characteristic and no molasses samples could give any polarogram when the pH was more than 3.2. These polarograms in different molasses were obtained after cation exchange operations which eliminated the possibility of reduction waves from the usual cationic impurities. The anionic surfactants are also retained by the resin column. The reduction of oxygen is not observed in this potential range. The only possibility of reduction is for the anionic surfactants as discussed as well in the Thesis in the subsequent Chapter in a detailed manner. Thus the results obtained as above set a limit for d.c. polarographic studies of surfactants present in molasses which could be worked out within pH limits of 2.0 to 3.2 only. These molasses samples were also analysed in different buffers over the entire pH range in the acid and alkaline ranges, but failed to give any polarographic reduction.

Fig. 4 shows the variation in diffusion current with pH for the three molasses samples examined. The variation in diffusion current with pH showed different
Fig 4 VARIATION OF DIFFUSION CURRENT WITH pH OF THE MOLASSES SOLUTION
trends in the three samples. The high value of diffusion current was observed between pH 2.0 and 2.4 and very small values above pH 2.8. Though results of only three samples were given, it was found a general pattern. This led the author to feel that the work could best be done at an intermediate pH value of say 2.6 when the influence of pH on the diffusion current obtained was neither very marked nor small. The choice of pH 2.6 was also based on the nature of the polarograms obtained under the experimental conditions, which is an important criteria for polarographic relations. It is imperative that the polarograms may be well defined S-shaped curves having lower wave-width. The narrower the limit of potential within which a polarogram exist, the better would be the shape and the possibility of its analysis. The variations in wave-width of the polarograms with the pH values given above were shown in Fig. 5 and it was observed that the behaviour varied with the nature of the molasses samples employed. In some cases (see Curve I), the wave-width first increased upto a pH of 2.5 and then fell. It was minimum between pH 2.6 to 2.9 and increased thereafter, while in others a fall or rise in wave-width with increase of pH was recorded. Interestingly at pH 2.6, the wave-width was minimum in all the three cases which was, therefore, chosen for all subsequent analysis.
Fig. 5 EFFECT OF pH ON THE POTENTIAL WIDTH OF POLAROGRAMS OF MOLASSES.

CURVE I SHIFTED UP & CURVE III SHIFTED DOWN BY 200mV ON THE 'Y' AXIS
It may be pointed out that this difference in pH values was not caused by the reduction of H+ ions themselves which showed a reversible reduction only. As discussed in a later Chapter, the polarograms of surface-active substances showed an irreversible reduction. The studies were confined within limits of pH 2.0 to 3.2, before and after which well defined curves were not given by molasses even on repeated dilutions or increasing concentrations. This sets an interesting limit for the d.c. polarographic studies of surface-active compounds and it appeared that the efforts of earlier workers for the polarographic studies on surfactants was limited for the above considerations.
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