

# A NEW POLAROGRAPHIC METHOD FOR ESTIMATION OF ANIONIC SURFACE ACTIVE COMPOUNDS IN TECHNICAL SUGAR SOLUTIONS USING CATION-EXCHANGE RESIN

S. K. D. AGARWAL AND R. K. GUPTA

[ *National Sugar Institute, Kanpur (India)* ]

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## ABSTRACT

Solutions of white consumption and khandsari sugar, jaggery and molasses were passed through cation-exchange resins, to eliminate the possibility of reduction of cationic substances during polarographic analysis. The solution thus obtained showed well-defined polarograms. The half-wave potential of all such technical sugar solutions was found to be  $\approx 1.5$  volt. The straight lines obtained between diffusion current and concentration showed the possibility of quantitative estimation of the substance reduced, which appeared to be some anionic surface active compound present in the systems. The irreversible nature of reductions of the surface active compounds was established. The importance of the reduction with similar half-wave potential in establishing the role of anionic substances in many sugar technological problems are expected to be established by this approach. The white consumption sugars were characterised by absence of any polarographic wave. The concentration of the reducible substance was found more in molasses than in jaggery and still less in khandsari.

## INTRODUCTION

BEHAVIOUR of technical sugar solutions including juices, syrups, molasses and even white sugars whether prepared by the vacuum pan process known as white consumption sugar or the khandsari sugar of the open pan process contains a series of impurities which when present in small quantities, sometimes even in traces, markedly affect the substances both in their chemical and physico-chemical properties. It is well recognised that the anionic impurities have more pronounced effect than cationic during processing. The rate of inversion<sup>1</sup> of sucrose is markedly affected by the presence of anionic impurities and so the viscosity of molasses and massecuites. This has led to the marketing of a series of viscosity reducing compounds which

as far as known are of anionic nature and include such commercial preparations as  $\alpha$ -methyl glycoside ester ( $\alpha$ -MGE) known in the trade name as Hodag<sup>2</sup> CB-6, Pan Aid<sup>3</sup>, Pan Aid concentrate<sup>4</sup>, Instol<sup>5</sup> (a product made and developed at the N.S.I., Kanpur) Coutol, Teepol B-300, Prorex D-oil, Avalon-50 and Veedol the details of which are not available.

Work done so far has shown that the surfactants are mainly responsible for the formation of floc produced during preparation or processing of technical sugar solutions. The importance of the subject has led it to be dealt mainly in the subject 19 of White Sugars of the International Commission for Uniform Methods of Sugar Analysis (ICUMSA), where the sediment and floc forming impurities have especially been dealt in the 14th and 15th Sessions. The 15th Session of ICUMSA held in 1970 recommended tentative adoption of Coca-Cola floc test<sup>6</sup> and further studies on rapid test for carbonated beverages and completion of the details of the foam test<sup>7</sup>.

The floc forming tendency was investigated polarographically by Hibbert<sup>8</sup> *et al.* and Schiweck<sup>9</sup> in a quantitative manner. Moroz<sup>10</sup> developed another method depending on the suppression of oxygen maximum by the floc forming impurities with dilute KI as supporting electrolyte. Ramaiah and Trevedi<sup>11</sup> also developed a similar method based on characteristics of the two reduction waves of oxygen having half-wave potentials 0.2 and -0.8 volt vs S.C.E. The second wave was shown to be affected by the presence of surface active compounds in a quantitative manner for cationic, anionic and non-ionic constituents. It was shown to be dependent only on the nature and concentration of the supporting electrolyte and was thus utilized for quantitative estimation of floc forming impurities. Gupta and Agarwal<sup>12</sup> have shown by alternating current polarography technique that the surface active compounds give two types of peaks (*a*) the desorption peak and (*b*) chemical peak. The summit potential of chemical peak does not vary with the concentration of the surface active compounds while that of desorption peak markedly changed. These methods are, however, influenced by many variables and interfering substances.

The present method though confined to estimation of anionic impurities is expected to be of better utility in the study of characteristics of anionic substances which control various processing conditions to a great extent.

#### EXPERIMENTAL

A manual polarograph<sup>13</sup> with all variable controls was used. The instrument was standardized by polarographic reduction of standard cationic substances.

The cation exchange resin IR-120 (Rohm and Hass Co., U.S.A.) was used. This was regenerated every time by recycling 2N-HCl and finally by making it free from traces of HCl with distilled water before use.

The technical sugar solutions used were of carbonation and sulphitation molasses, refined and white consumption sugars and open pan khandsari sugars and jaggery. The concentrations used were as under:—

(1) White consumption sugar	.. 10-25%
(2) Khandsari sugar	.. 1-10%
(3) Jaggery	.. 0.2-2.0%
(4) Molasses	.. 0.2-0.6%

A known volume of the solutions of desired concentrations was passed through the cation-exchange column and only the latter portion was utilised. The concentration of supporting electrolyte KCl (E. Merck) was kept at 1 N.

The solutions of sugar house product(s) were first passed through the cation-exchange resin to be sure of absence of any cationic constituent and the effluent taken in the polarographic cell for recording the polarogram. The pH of effluent was noted in each case.

#### RESULTS AND DISCUSSIONS

Figure 1 gives the typical set of the polarograms obtained from ordinary white consumption sugar at different concentrations thereof. The polarograms showed an increasing trend without any saturation current indicating therefrom the absence of any reducible ions in the voltage range scanned. It is well known that most of the cations have their reduction waves in this potential range whereas anions, if present, are not reduced ordinarily. The sugars which are invariably left intact through the resin are reduced at higher negative potentials for which KCl as supporting electrolyte cannot be employed. It may, therefore, be easily taken that under present conditions, the sugars do not interfere in the work. This was again established by taking polarograms of analytically pure samples of sucrose, fructose and glucose (results not given). Different concentrations of white consumption sugars were examined. The absence of any saturation potential at any concentration of the white consumption sugar indicated the non-existence of any reducible impurity under the analytical conditions. This was examined for a large number of samples of sugars produced from vacuum pan factories corresponding to 29 and 30 Indian Sugar standard grade.

Khandsari sugars produced by the open pan factories after clarification by the sulphitation process are apparently as white as the white consumption sugars of the vacuum pan process in many cases. The only departure in the manufacturing technique that can be envisaged lies in the use of certain compounds of surface active nature, both of chemical and vegetable origin, which are meant to suppress the foam generation during concentration in the open pans, *i.e.*, in the use of antifoaming agent. The possibility of these in such sugars getting embedded in the crystal lattice are very high. A large number of samples when examined polarographically under the

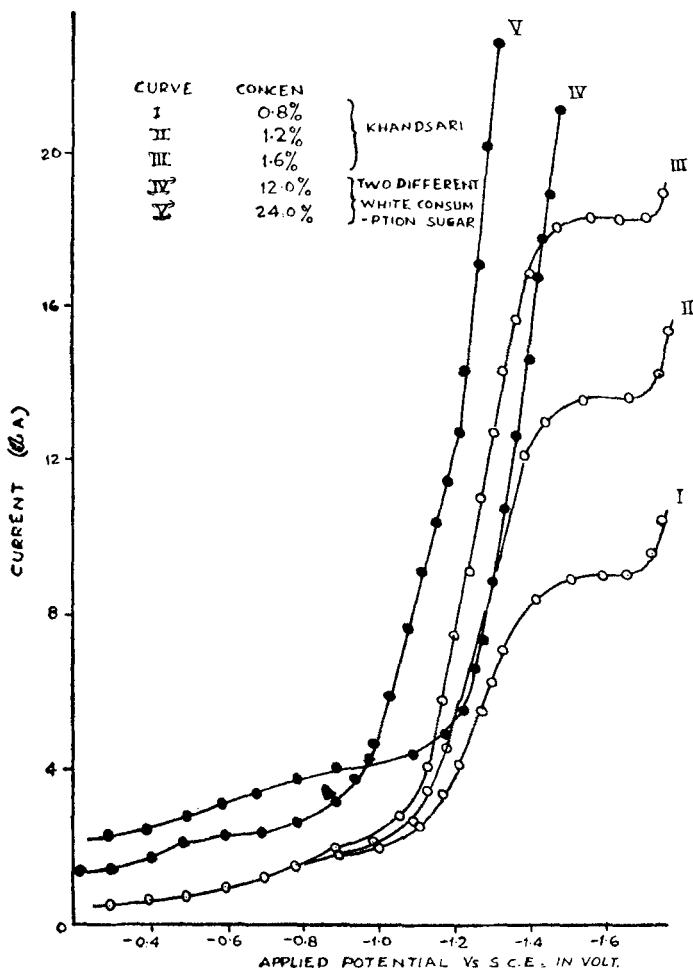


FIG. 1. Polarograms showing the cathodic reduction in khandsari sugar and non-reduction of white consumption sugar.

above conditions showed well-defined polarograms (see Figs. 1 and 2). These had a slight trend of increase of current at a potential of  $-0.9$  to  $-1.1$ , whose magnitude did not differ with the concentrations of sugars. In sample 1, a concentration of 0.8, 1.2 and 1.6% of khandsari sugar was taken, while in sample 2 the same was 4, 6 and 8% respectively. Apparently the quality of sugar sample 2 was superior. The well-defined polarograms showed the reduction of some surface active compounds which are not cationic, since these were isolated by passing of the sugar solutions through cation exchange resin. This was got confirmed by passing the sugar solutions under examination through an anion-exchange resin as well and then examining it polarographically, this showed the non-existence of any polarogram. The

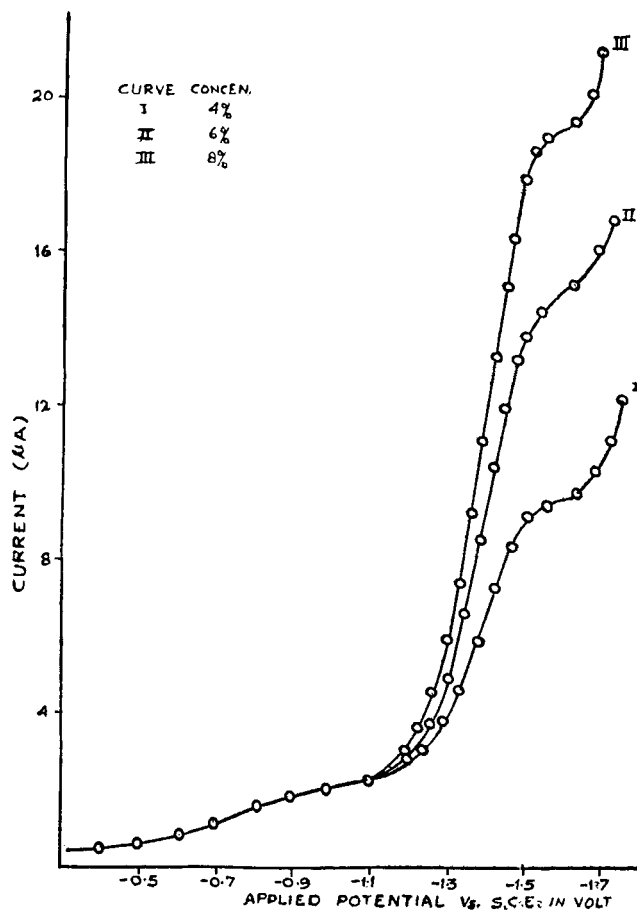


FIG. 2. Polarograms showing the cathodic reduction in khandsari sugar.

extent of presence of anionic surface active compounds was found to vary from sample to sample. It may, however, be seen from Fig. 3 showing the relationship between concentration and diffusion current for five types of khandsari sugar samples that the relationship was linear as per Ilkovic's standard equation.

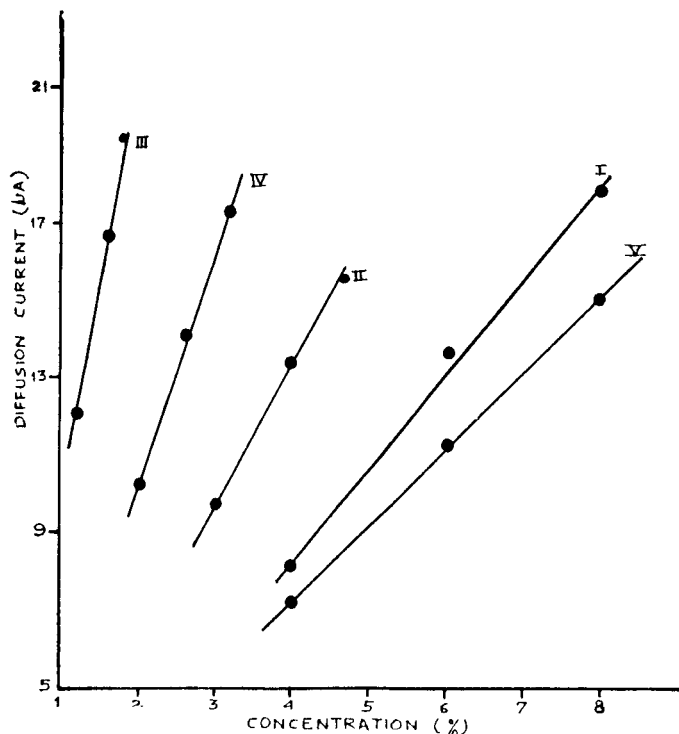


FIG. 3. Showing the linear relationship between diffusion current and concentration in khandsari sugar.

It has been shown by Authors<sup>14</sup> earlier that the vacuum pan and open pan sugars have various characteristics differences especially in their calcium content, conductivity, filtration impeding impurities and in crystal shape<sup>15</sup>. The present difference in their characteristics is therefore an important criterion in their differential nature and could well be utilised to differentiate the two types of sugars.

Jaggery, which is produced in large quantities in India in open pans in an indigenous fashion by small manufacturers, is made by utilising vegetable mucilages as antifoaming agents during concentration of the clarified syrup to final yellowish-brown material of solid consistency, was examined

under similar conditions. Because of the conversion of clarified juice directly into solid mass, all the constituents of juice are converted to solidified form. Jaggery therefore contains a large amount of cationic and anionic impurities. A series of jaggery samples were examined polarographically by preparing a 5% solution, and passing through the resin column as discussed before.

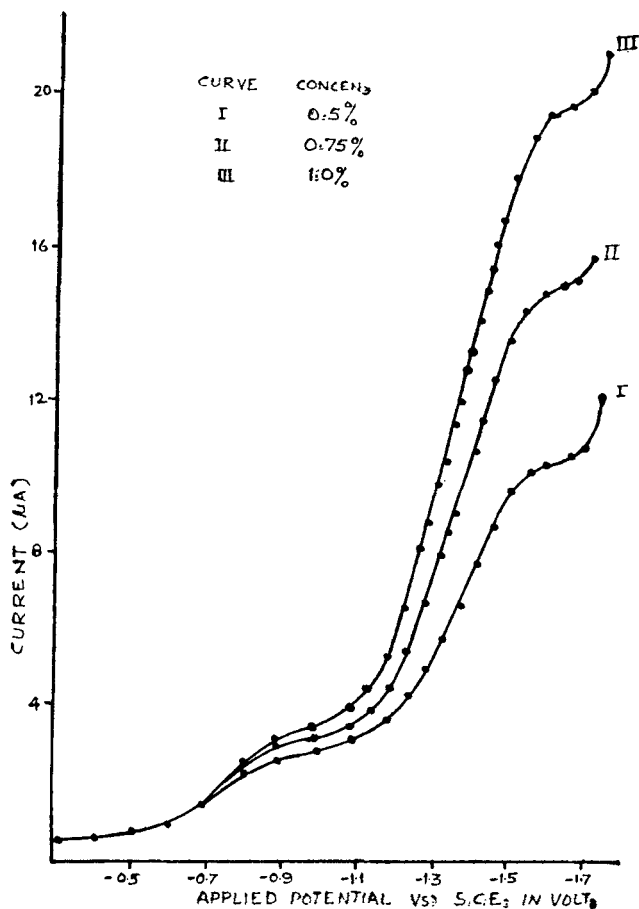


FIG. 4. Polarograms showing the cathodic reduction in Jaggery.

Typical sets of polarograms obtained in two samples were given in Figs. 4 and 5. Curves 1, 2 and 3 in Fig. 4 corresponded to the concentration of 0.5, 0.75 and 1%, while curves 1, 2 and 3 in Fig. 5 to the concentrations of 1, 1.4 and 1.8%. The polarograms showed well-defined nature with  $E_{\frac{1}{2}} \simeq -1.5$  volt vs S.C.E. It may be seen from Fig. 6 showing the relationship between concentration of the jaggery of different types and the diffusion

current, that a linear relationship followed, indicating the reduction of some specific substance present in the jaggery samples. The extent of anionic surface active compounds that has been supposed to be reduced vary widely from sample to sample, but was invariably higher than the amount present in khandsari sugar. It may be seen also that the bent or inclination of the curves was different in all the samples because of the presence of particular substance(s) to different extents. Apparently no generalisation was possible.

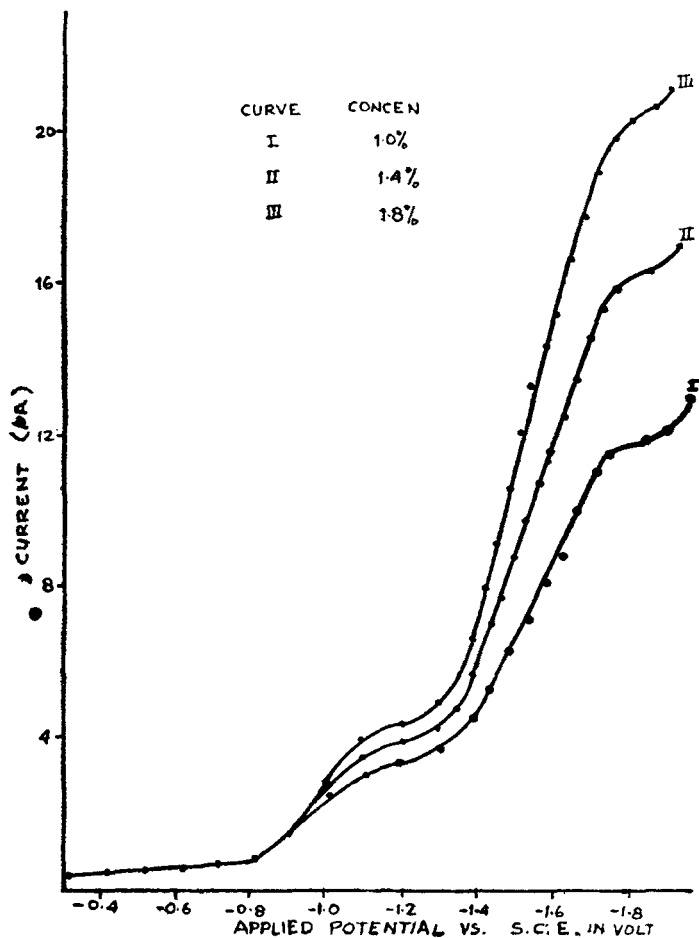


FIG. 5. Polarograms showing the cathodic reduction in jaggery.

Results obtained with molasses produced with different carbonation and sulphitation factories were examined under similar experimental conditions by following the concentration range in Figs. 7 and 8 at known con-



concentrations of 0.1 to 0.6%. The reduction was indicated at the same potential as with khandsari sugar and jaggery. It can be seen from the curves that the polarograms were very well-defined S-shaped curves as are generally observed with any other reducible compounds. The concentrations of molasses used was much smaller indicating the presence of higher amounts of surfactants in the concentrations range studied in khandsari sugar and jaggery. Apparently no generalization was possible between the concentration used (extent of surface active compounds present) and the diffusion current, as may be seen from Fig. 9 where the bent was different in all the molasses samples examined which naturally related to the quantity of molasses which is different in all cases.

The irreversible nature of the reductions of the surface active compounds left after passing through cation-exchange resin was established by following

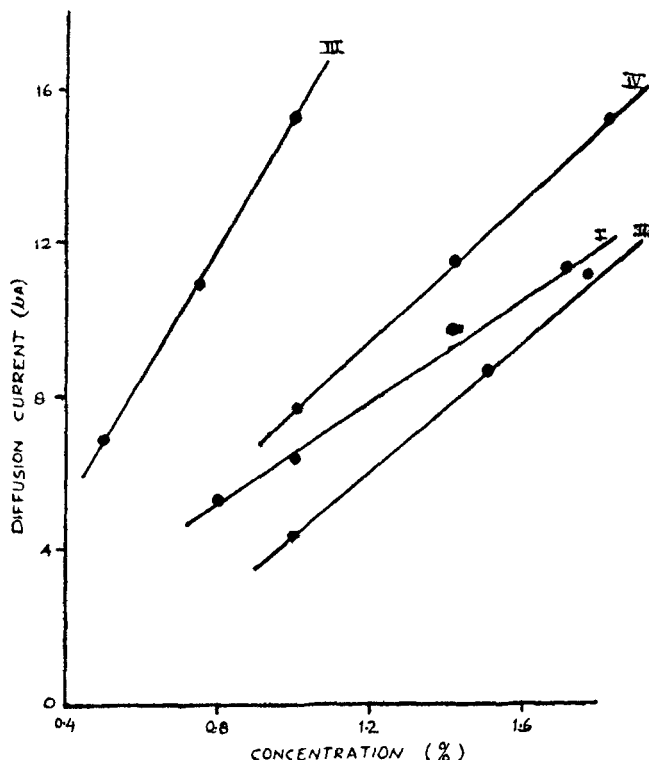


FIG. 6. Showing the linear relationship between diffusion current and concentration in jaggery,

Curve II shifted down by 2  $\mu$  A on the Y-axis.

the fundamental equation of Heyrovsky and Ilkovic. This equation is generally employed for testing the irreversible nature of reduction or oxidation process occurring at dropping mercury electrode. The equation is:

$$E_{d.e.} = E_{\frac{1}{2}} - 0.0591/n \log i/id - i$$

where  $E_{d.e.}$  and  $i$  are corresponding values at any point on the wave,  $E_{\frac{1}{2}}$  is the half-wave potential of the wave,  $id$  is the diffusion current.

The plots of  $\log i/id - i$  vs  $E_{d.e.}$  giving the value of  $n$ , the slope of which is equal to  $-0.0591/n$  volt was utilized for testing the irreversible

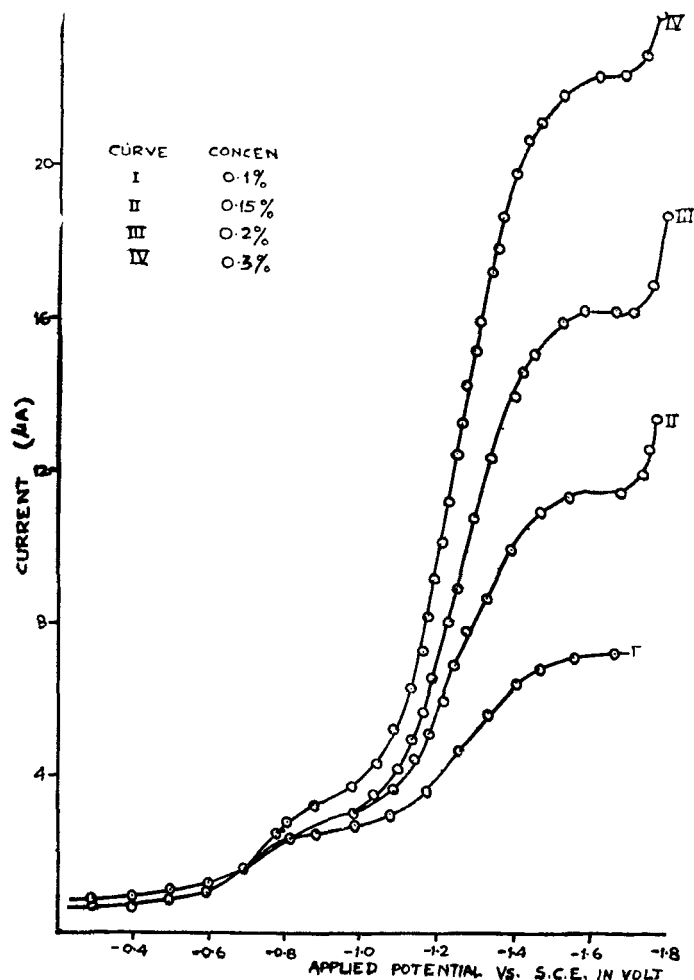


Fig. 7. Polarograms showing the cathodic reduction in molasses.

nature of the process when  $n$  a value less than 1 was indicated. The irreversible reduction was established from the above criterion for the open pan khandsari sugars, jaggery and molasses (see Fig. 10). The value of  $n$  for above three systems were found to be 0.32, 0.36 and 0.28 respectively on an average.

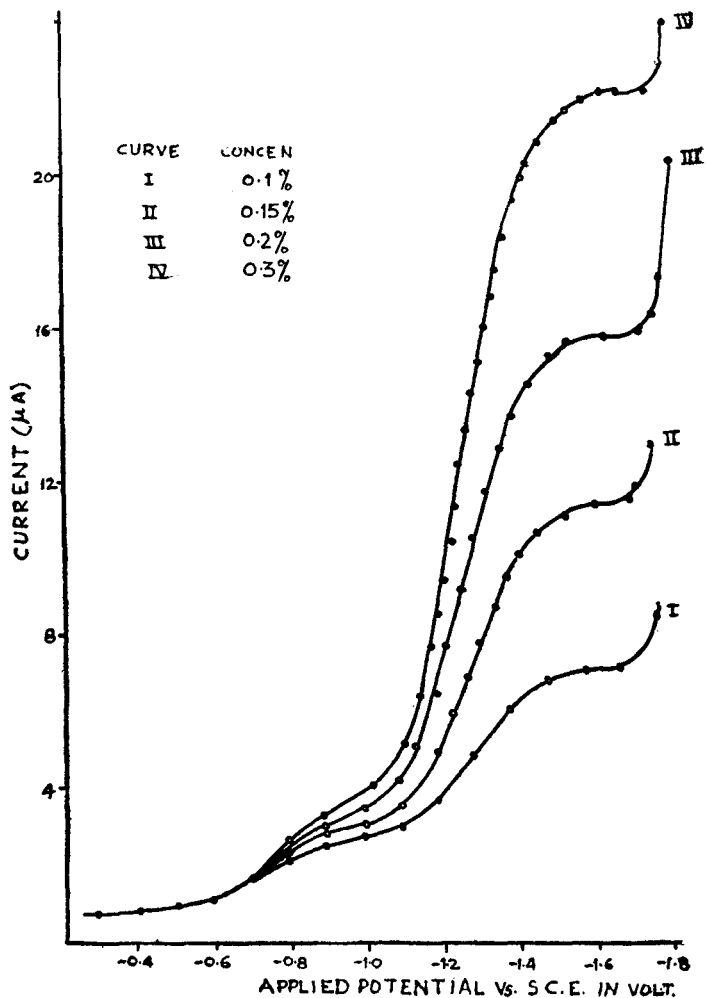


FIG. 8. Polarograms showing the cathodic reduction in molasses.

The irreversibility was established by another criterion based on the measurement of  $E_{\frac{3}{4}}$  and  $E_{\frac{1}{4}}$  from the polarograms which corresponded to three-fourth and one-fourth of the diffusion current, i.e.,

$$E_{\frac{3}{4}} - E_{\frac{1}{4}} = -0.0591/n \quad \log 9 = -0.0564/n.$$

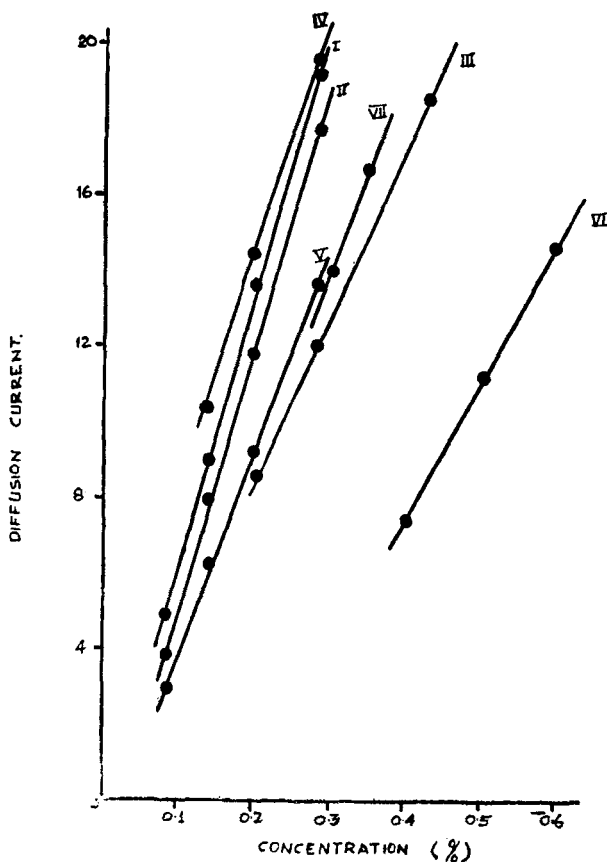


FIG. 9. Showing the linear relationship between diffusion current and concentration in molasses. Curves I, VII and IV shifted up by 1, 2 and 3  $\mu$ A respectively on the Y-axis.

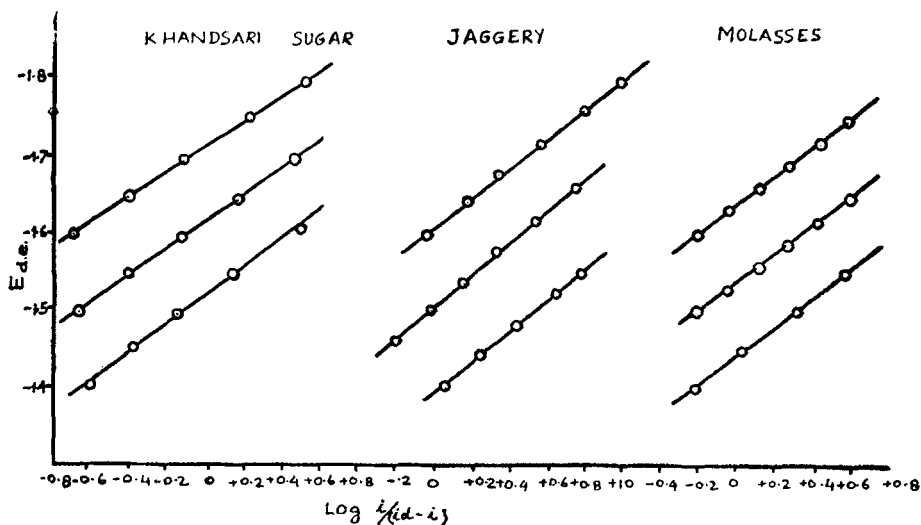


FIG. 10. Showing the irreversible reduction of sugar house products.

The compilation of the data for khandsari sugars, jaggery and molasses was given in Table I. The value of  $n$  at different concentrations of the systems were of the order of 0.37, 0.31 and 0.33 on an average respectively.

TABLE I

*Determination of value of number of electrons involved in the polarographic reduction*

Sl. No.	Nature of the Sugar house product	Sample No.	Concentration of solutions %	$E_{\frac{1}{2}}$	$E_{\frac{2}{2}}$	$E_{\frac{3}{2}}$	$n$
1.	Khandsari sugar	1	0.8	-1.47	-1.515	-1.36	.361
			1.2	-1.46	-1.53	-1.38	.376
			1.6	-1.45	-1.52	-1.365	.361
		2	4.0	-1.56	-1.62	-1.455	.341
			6.0	-1.57	-1.63	-1.49	.403
			8.0	-1.57	-1.63	-1.49	.403
		3	3.0	-1.45	-1.525	-1.36	.341
			4.0	-1.445	-1.52	-1.37	.376
		4	2.0	-1.535	-1.6	-1.45	.376
	2.6		-1.53	-1.61	-1.45	.352	
	3.2		-1.53	-1.6	-1.445	.361	
	5	4.0	-1.54	-1.61	-1.41	.282	
		6.0	-1.55	-1.62	-1.44	.313	
		8.0	-1.56	-1.62	-1.47	.376	
	2.	Jaggery	1	0.5	-1.585	-1.655	-1.5
0.75				-1.565	-1.65	-1.475	.322
1.0				-1.55	-1.65	-1.46	.296
2			1.0	-1.545	-1.64	-1.45	.296
			1.4	-1.53	-1.64	-1.43	.268
			1.8	-1.52	-1.64	-1.425	.262
3		0.8	-1.585	-1.65	-1.5	.376	
		1.0	-1.58	-1.65	-1.485	.341	
		1.4	-1.58	-1.655	-1.475	.313	
		1.7	-1.57	-1.66	-1.47	.296	

TABLE I—*Contd.*

Sl. No.	Nature of the Sugar house product	Sam- ple No.	Concen- tration of solu- tions %	$E_{\frac{1}{2}}$	$E_{\frac{1}{4}}$	$E_{\frac{3}{4}}$	$n$
		4	1.0	-1.58	-1.66	-1.49	.331
			1.5	-1.565	-1.665	-1.47	.289
			1.75	-1.56	-1.66	-1.46	.282
			2.0	-1.56	-1.655	-1.46	.289
3.	Molasses	1	0.1	-1.51	-1.595	-1.44	.361
			0.15	-1.475	-1.57	-1.4	.331
			0.2	-1.47	-1.565	-1.395	.331
			0.3	-1.455	-1.545	-1.385	.352
		2	0.1	-1.505	-1.575	-1.425	.376
			0.15	-1.475	-1.56	-1.4	.352
			0.2	-1.45	-1.535	-1.385	.376
			0.3	-1.45	-1.54	-1.385	.361
		3	0.1	-1.52	-1.61	-1.44	.331
			0.15	-1.475	-1.57	-1.405	.341
			0.2	-1.45	-1.55	-1.38	.331
			0.3	-1.445	-1.55	-1.38	.331
		4	0.4	-1.53	-1.615	-1.45	.341
			0.5	-1.515	-1.6	-1.43	.331
			0.6	-1.505	-1.595	-1.425	.331
		5	0.3	-1.43	-1.51	-1.37	.403
			0.45	-1.43	-1.515	-1.365	.376
		6	0.2	-1.46	-1.55	-1.385	.341
			0.3	-1.455	-1.54	-1.38	.352
		7	0.3	-1.37	-1.44	-1.29	.376
			0.35	-1.365	-1.43	-1.29	.403

The polarographic characteristics of the substances left after passing through the cation-exchange resin, where the common anions have hardly any possibility of reduction, established the possibility of determination of anionic surface active compounds in the khandsari sugars, jaggery and molasses. The evaluation though not completely conforming to the flocc forming potentiality led to the establishment of procedure for quantitatively analysing the extent of anionic surface active compounds in various sugar

house products. The fact that the half-wave potential was well marked and was at  $\approx -1.5$  volt is very significant and is likely to have utilisation in devising methods for their quantitative impact and on such processing conditions in the sugar factories, where anionic components have major role.

Though actual concentration of the surfactants could not be obtained in any technical sugar product by the above method by now, it was apparent that the method had potentiality of quantitative evaluation, the work on which is still under progress.

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