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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 28(3), 321-333
Issue Date	1981-06
Doc URL	http://hdl.handle.net/2115/25101
Type	bulletin (article)
File Information	28(3)_P321-333.pdf



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THE ADSORPTION OF SOME POLYHYDROXY AND CYCLIC COMPOUNDS AT MERCURY ELECTRODES^{*)}

By

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(Received August 11, 1980)

Abstract

Some speculations are presented about the behaviour of compounds whose adsorption behaviour at air/water and mercury/water interface differs, in particular when there is negative adsorption at the former. Some new results on sugars and related compounds are presented.

It is surprising in view of their biological importance that so little surface chemical work has been carried out with sugars and related compounds. The excellent bibliography in Jehring's book¹⁾ lists only a few rather casual studies. In fact the comprehensive study of simple sugars of Gouy²⁾ is not included. More recently Brabec *et al.*³⁾ have made a thorough investigation of the adsorption of D-ribose and 2' deoxy-D-ribose. Gouy presented 12 electrocapillary curves for eight different sugars. They are rather rounded, symmetrical curves although some differences can be noted for the different sugars indicating that there are specific effects with the different structures. Gouy's results for sucrose were reproduced and discussed by Frumkin.⁴⁾ He noted that sucrose lowered the interfacial tension at the electrocapillary maximum while it raised the surface tension of water. At the same time there was almost no shift of the point of zero charge or of the surface potential of water. Thus, sucrose is a member of a rather small group of organic compounds which contradict the general observation made by Frumkin⁴⁾ that most organic compounds behave similarly at the uncharged mercury/aqueous solution interface and at the air/aqueous solution interface. In Frumkin's article this group contains urea, thiourea and tartaric

*) This material formed the basis of a lecture given by R. Parsons at the 4th Symposium of the Electrochemical Section of the Polish Chemical Society at Jablonna in August 1977.

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acid as well as sucrose. Later work⁵⁾ shows that glycine is also a member of this group.

It is interesting first to discuss the reasons for this particular type of behaviour. Two general causes may be suggested following Frumkin's original discussion of this point.

(a) There is a specific interaction between the adsorbed compound and mercury.

(b) There is a different structure of water at the mercury/water interface from that at the air/water interface, which plays a rôle for some types of compound but is unimportant for others.

Thiourea is undoubtedly primarily an example of the first explanation on account of the strong sulphur-mercury interaction; this was made clear in Frumkin's comparison of the behaviour of urea and thiourea. However, it is not clear that the behaviour of the other compounds in this group can be explained in terms of (a). The explanation (b) is less straightforward and is more difficult to establish. In the case of glycine it is possible to invoke the high polarity of the molecule and to search an explanation in the terms of Butler's model of adsorption.⁶⁾ It was on the basis of this model that we began to study the adsorption of amino acids.⁵⁾ As predicted by Butler's model it is indeed found that the adsorption of glycine in its zwitterionic form increases with the charge on the electrode unlike other organic compounds. However the polarity is not expressed in a shift of the point of zero charge nor (probably) in a shift of the surface potential of water, since preliminary measurements of the latter made by Dr. de Valera in Bristol have shown no effect on the surface potential. The negative adsorption at the air-water interface is explicable in terms of the image force which is repulsive in this situation. However, the expected attractive image force at the mercury water interface is only weakly expressed. This is surprising in view of the large dipole moment of glycine ($p=15.5 D = 5.2 \times 10^{-29} \text{ C}\cdot\text{m}$). The behaviour at mercury is probably due to an orientation of this dipole parallel to the interface. It is interesting to recall that glycyl-glycine which has an even higher dipole moment ($p=27.6 D = 9.2 \times 10^{-29} \text{ C}\cdot\text{m}$) shows the more typical organic behaviour⁷⁾ in that it becomes desorbed as the charge on the mercury increases in either direction. Preliminary measurements made by Mr Double in Bristol indicate that the surface tension of water is lowered by glycyl-glycine so that in spite of the large dipole moment this molecule seems to be positively adsorbed at the air/water interface. If the dipole moment of these two amino acids is parallel to the interface its influence on the adsorption of each will be similar. Since

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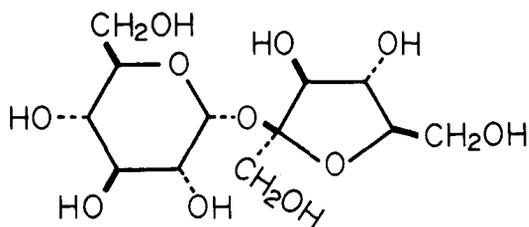
this influence is rather weak for glycine, the effect the "organic" region in the centre of the molecule of glycyglycine evidently predominates.

Another compound in the original group pointed out by Frumkin is urea which has a smaller dipole moment ($p=4.89 D=1.5 \times 10^{-29} \text{ C}\cdot\text{m}$) than the two compounds discussed above, but also less "organic" character, as it is a very small molecule. In spite of this its adsorption behaviour at mercury is that of a typical organic substance.⁸⁾ It is also notable that there must be some degree of dipole orientation at an angle to the plane of the interface because the point of zero charge is shifted by a few decivolts — a much smaller shift however than is observed with thiourea⁹⁾ which has approximately the same dipole moment.

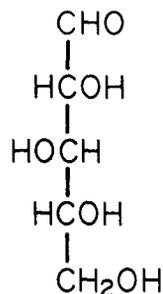
This survey suggests that imaging may play a rôle in the repulsion of some of these compounds from the air/water interface, but it seems likely that some other factor is at least as important in the adsorption at the two interfaces. The behaviour of less polar compounds suggests that interaction with water structure may provide this other factor. For example the importance of hydroxyl groups in the adsorbing molecule may be indicated by a comparison of the compounds in the series tartaric, maleic and succinic acids. The first compound having two hydroxyl groups as well as two carboxyl groups, raises the air/water surface tension while the other two having progressively fewer-OH groups lower this surface tension. On the other hand it must be noted that glycerol, which has of course 3-OH groups but no-COOH, also lowers the surface tension of water.

There is little evidence in the literature for the behaviour of sugars and other polyhydroxy compounds at the air/water interface. According to the old measurements of Traube^{10,11)} besides sucrose, lactose, glucose and mannitol are negatively adsorbed at the water surface but the information is too sparse for any quantitative conclusions. Again the dipole moment may play a rôle. Reid and Franks¹²⁾ have estimated a dipole moment of 5 to 7 D ($=1.5$ to $2 \times 10^{-29} \text{ C}\cdot\text{m}$) for several similar compounds in aqueous solution but in view of the great flexibility of these molecules it is not possible to be sure that this dipole moment is also valid at the surface.

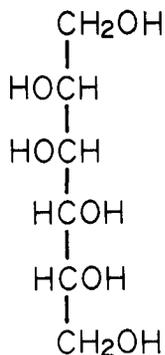
In order to investigate these interesting problems in more detail, we have recently studied the adsorption of a few sugars and related compounds some of which are shown in Figure 1. These measurements were made in the department of physical chemistry in the University of Bristol using techniques already well established. Capacity measurements over a range of concentrations in aqueous solutions of sodium fluoride at 25°C were made without any great difficulty. However the measurement of interfacial tension



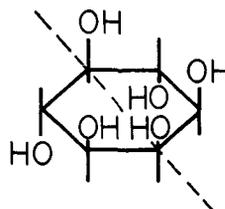
SUCROSE



D-(+)-XYLOSE



D-MANNITOL



myo-INOSITOL

Fig. 1. Schematic structures for some of the compounds discussed here.

either by the Lippmann electrometer or the maximum bubble pressure method was much more difficult. For some reason, which is not at present evident, the presence of sugar in solutions of sodium fluoride strongly enhances the tendency of the meniscus to stick in the capillary; so much so that even the maximum bubble pressure method could not be used. We therefore resorted to the following approach. Electrocapillary measurements were made in solution of sodium *chloride* of the same concentration as the sodium *fluoride* used in the capacity measurements. It is reasonable to assume that the structure of the double layer is essentially identical in these two series of solutions when the mercury is negatively charged. Consequently integration of the capacity curves may be based on integration constants derived at a potential substantially negative of the point of zero charge. It seems probable that reasonably reliable thermodynamic information may be derived in this way.

Capacity curves for five compounds of different structures are shown

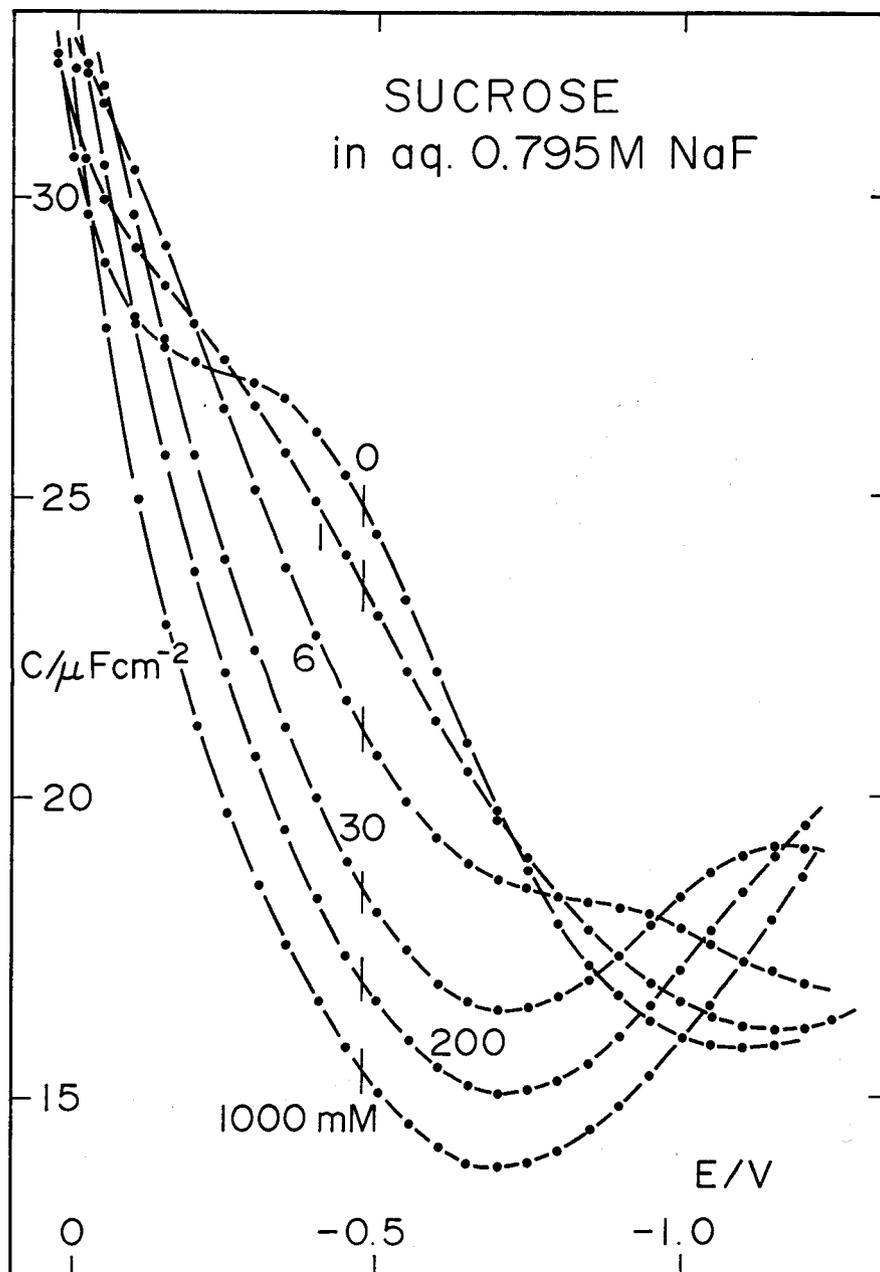
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Fig. 2. Capacity of the double layer at the mercury electrode at 250°C in solutions of 0.795 M aqueous NaF containing sucrose. The figures by each curve indicate the concentration of sucrose in mmol l^{-1} .

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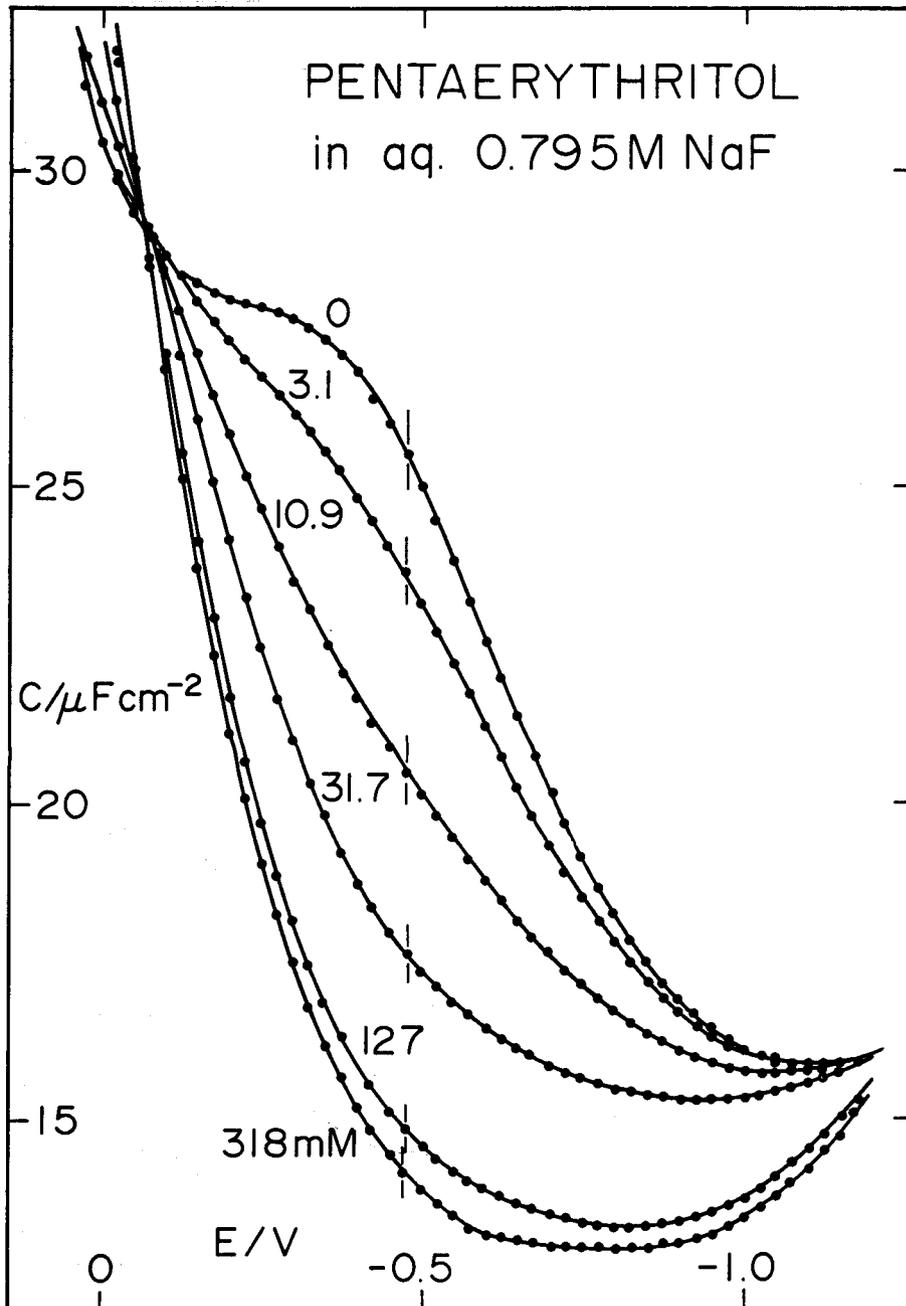


Fig. 3. As Figure 2 for pentaerythritol.

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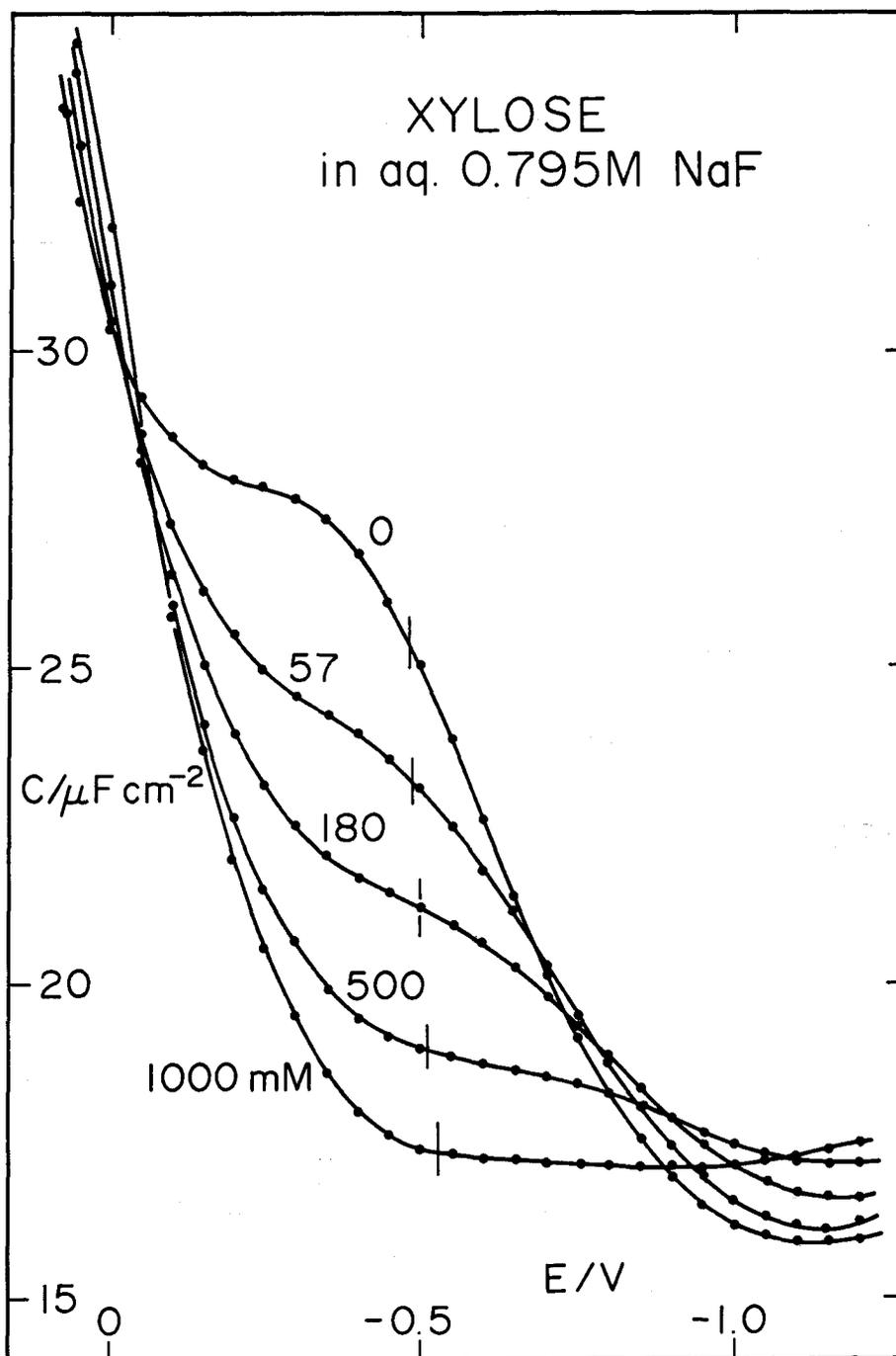


Fig. 4. As Figure 2 for xylose.

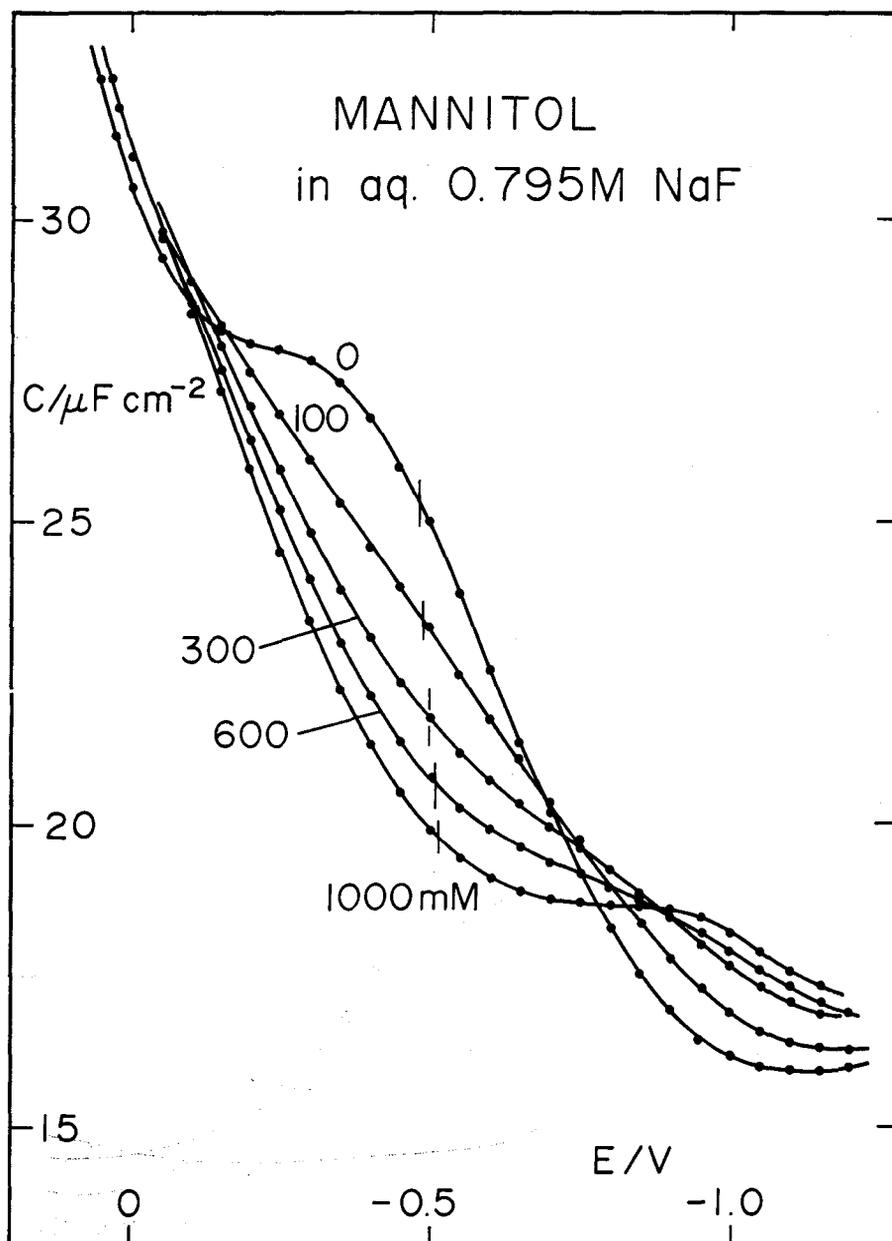
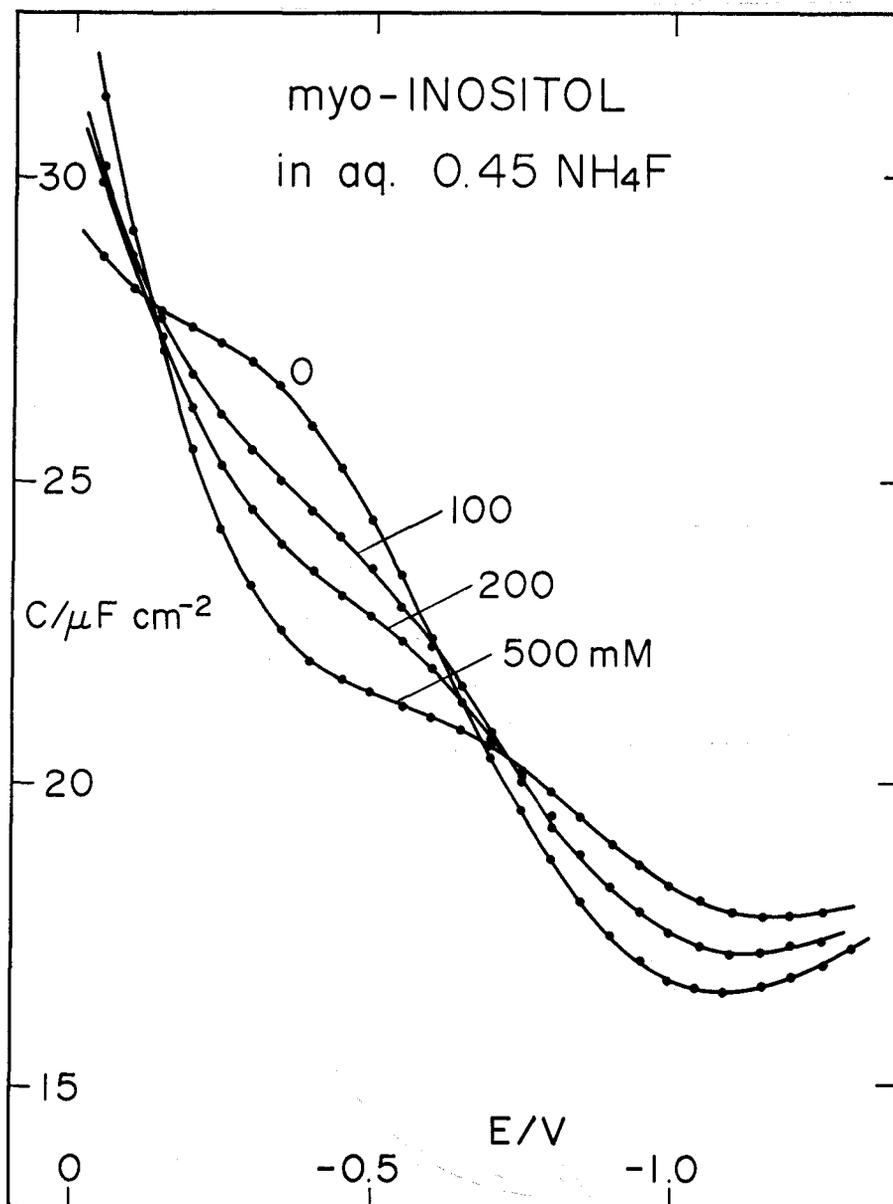


Fig. 5. As Figure 2 for mannitol.

Sugar Adsorption at Mercury ElectrodesFig. 6. As Figure 2 for *myo*-inositol.

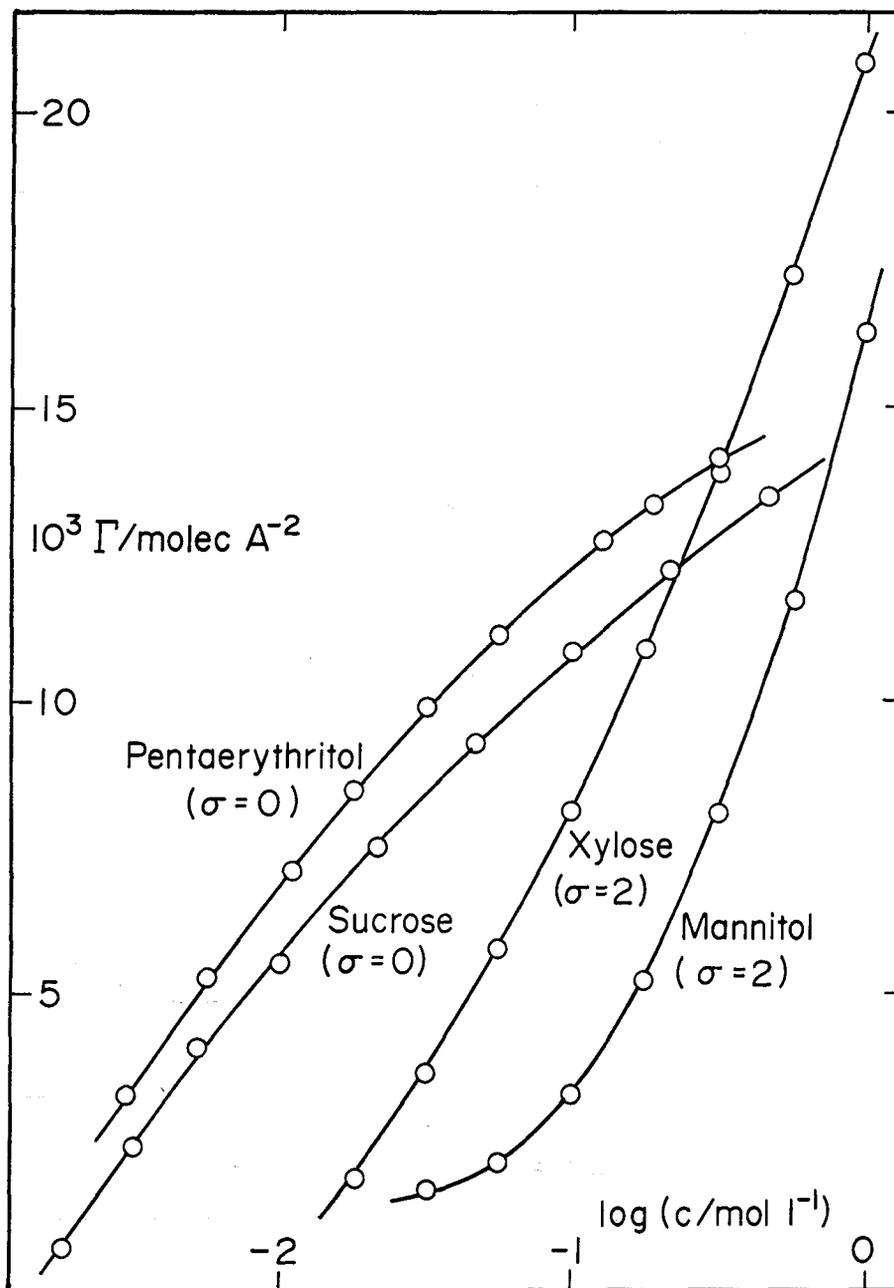


Fig. 7. Adsorption isotherms at the charge of maximum adsorption for the four compounds indicated.

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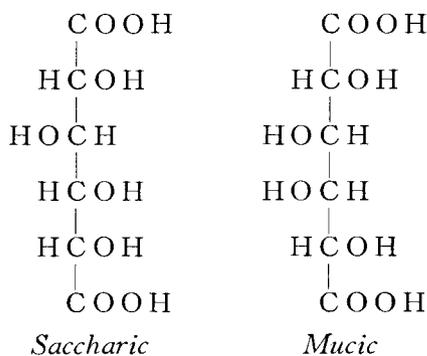
adsorption is very similar to that of urea⁸⁾ but there is no obvious intertypical "organic" behaviour: there is a marked lowering of the capacity in the region of the point of zero charge, followed by an increase of capacity as the charge is increased in either direction. The latter feature is more or less well expressed in each curve depending on the accessible range of potentials. In any case none of these curves show the sharp peaks characteristic of substances like the higher aliphatic alcohols. This is in agreement with the rounded electrocapillary curves described by Gouy.²⁾ For this type of curve frequency dispersion is usually small and in fact very little was observed. Analysis of these curves shows that maximum adsorption occurs at or close to the point of zero charge. The adsorption curves are fairly symmetrical when plotted as a function of charge on the electrode though they all tend to flatten at a higher amount adsorbed at positive charges. Closer inspection reveals two somewhat different types of behaviour. Sucrose and pentaerythritol ($C(CH_2OH)_4$) show maximum adsorption at the point of zero charge while the other three compounds show maximum adsorption at $\sigma = +2 \mu C. cm^{-2}$. (It should be noted that the limited data for myo-inositol must be regarded as only approximate as they were obtained by a less experienced worker Mr. B. Turner). This sub-classification is revealed also in the shapes of the adsorption isotherms shown in Figure 7. Sucrose and pentaerythritol at $\sigma = 0$ show isotherms which are concave towards the $\log c$ axis and thus show a tendency to approach a saturation value. In contrast xylose and mannitol are substantially less strongly adsorbed and have isotherms concave towards the Γ axis showing no tendency to approach a saturation value. These results were obtained on the basis of the usual type of thermodynamic analysis assuming that the solutions behave ideally (activity coefficients are independent of sugar concentration). This assumption seems reasonably well justified for systems of this type¹³⁾ but in any case the behaviour of the isotherms is reflected in that of the surface pressure curves and corrections for non-ideality are unlikely to lead to significant modification of the classification made above.

A more detailed analysis is in progress. At present it may be noted that subject to the above assumptions the adsorption of sucrose is found to be congruent both with respect to potential and with charge. It can be fitted to a Frumkin isotherm with interaction coefficient $A=2$ and saturation coverage (Γ_s) corresponding to an area per molecule 0.7 nm^2 . The latter suggests that the molecule is probably adsorbed in a flat position. This is consistent with the minimum capacity of $13 \mu F. cm^{-2}$ which would imply a thickness of about 0.7 nm . The potential or charge dependence of the

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in Figures 2 to 6. It is evident from these that all these compounds show pretation of this in terms of the coefficient $\frac{1}{2} \Delta x/\epsilon\Gamma_s$, where Δx is the change of thickness of the inner layer due to adsorption and ϵ is the permittivity.

The cause for the grouping of these compounds in terms of their structure is at present not clear and further interpretation must await a more detailed analysis or perhaps more experimental data. Structural effects in compounds of this type may be extremely subtle. In fact it was a remark to this effect by Franks¹⁰ which initiated this work. He called attention to pairs of closely related compounds which have considerable differences of solubility in water. One is the pair myo- and scyllo-inositol. Myo-inositol which is quite soluble is shown in Figure 1. Scyllo-inositol which is much less soluble has the sole difference that the right-hand OH group at the lower edge of the ring is below the ring instead of above. The other pair is the soluble saccharic acid and the insoluble mucic acid.



Again the difference is in the configuration at a single carbon atom. It is not clear whether the solubility differences are due to the energy of interaction in the crystal or in the solution. Whichever is the case it would seem of great interest to study the adsorption behaviour of these pairs of compounds. Up to the present we have succeeded in obtaining satisfactory samples only of one compound in each pair.

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