

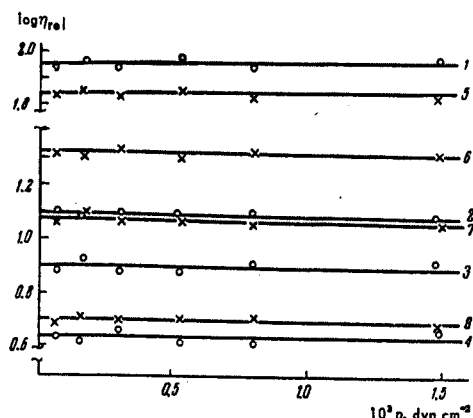


Fig. 2. Relative viscosity curves at 25° for solutions of polyisobutene and "light crepe" natural rubber at concentrations (wt.%) of — polyisobutene:

1) 1.35; 2) 0.97; 3) 0.70; 4) 0.42;

"light crepe":

5) 1.30; 6) 1.00; 7) 0.68; 8) 0.42.

friction the liquid in cylinder 2 transmits a torque to this freely floating cylinder, the magnitude of this torque depending on the shape and size of the stirrer, the viscosity of the liquid in cylinder 2, and the difference between the angular velocities of the stirrer and cylinder 2. The viscosity of the liquid under test may be determined from Margules' equation¹

$$\eta = \frac{M}{4\pi h\omega} \left(\frac{1}{R_1^3} - \frac{1}{R_2^3} \right),$$

where M is the torque on the inner cylinder 2, h the height of cylinder 2, ω the angular velocity of cylinder 2, R_1 the external radius of cylinder 2, and R_2 the internal radius of cylinder 1. The angular velocity ω is determined in the process of operation. The value M of the torque transmitted to the freely floating cylinder may be determined by calibrating the apparatus with liquids of known viscosity. In the determination of viscosity it is necessary to observe the condition for stable laminar flow²

$$\frac{u d}{\nu} < 41.3 \sqrt{\frac{r}{d}},$$

where u is the peripheral velocity of the cylinder, $d = R_2 - R_1$, r is the mean of the radii R_1 and R_2 , and ν is the kinematic viscosity.

One important advantage of this apparatus is the liquid seal 6, which makes it possible without loss of accuracy or sensitivity to examine solutions of compounds of high molecular weight in readily volatile liquids.

For testing a liquid at higher stresses the apparatus may be modified by removing the stirrer and suspending the inner cylinder from a torsion wire. This converts it into a viscometer of the Couette-Hatschek type.

As an example to illustrate the possible uses of the instrument at low stresses, Fig. 2 shows the results of measurements on toluene solutions of polyisobutene and "light crepe" natural rubber. The resultant curves of relative viscosity against stress at very low stresses are in agreement with the findings of other authors^{3,4}. Fig. 2 gives the section of the rheological curve with the maximum viscosity.

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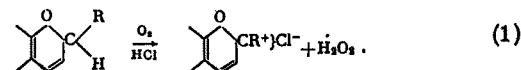
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THE MECHANISM OF THE ADSORPTION OF ELECTROLYTES ON CHARCOAL

R. Kh. Burshtein and E. A. Ponomarenko

Garten and Weiss¹⁻³ have put forward a new theory of the adsorption of electrolytes on charcoal which they believe should reconcile the views of Frumkin and coworkers⁴⁻⁹ on the one hand and those of Shilov and coworkers¹⁰⁻¹⁶ and also Steenberg¹⁷ on the other.

Garten and Weiss attribute the adsorption of acid on H-charcoal (their name¹⁻³ for charcoal activated at 800° which adsorbs acid but not alkali)³ to the presence on the surface of the charcoal of a quinone and also a chromene (benzopyran) structure, which on interaction with oxygen give rise to a carbonium ion and hydrogen peroxide:



They derived the following equation for the potential of this oxidation-reduction system:

$$E_h = \left\{ E' - \frac{RT}{2F} \ln \frac{K_R}{[H^+]} \right\} - \frac{RT}{2F} \ln \frac{1-\alpha}{\alpha}, \quad (2)$$

where E_h is the potential relative to the normal hydrogen electrode, K_R the dissociation constant of the chromene which according to Garten and Weiss is a weak base, and α the fraction of chromene which is present in the form of carbonium ions and according to Eqn. (1) is proportional to the extent of adsorption of acid. Since the expression in braces is constant at a constant concentration of hydrogen ions, Eqn. (2) may be put in the form

$$E_h = E_{1/2} + \frac{RT}{2F} \ln \frac{\alpha}{1-\alpha}, \quad (3)$$

where $E_{1/2}$ is the oxidation-reduction potential of the system for $\alpha = 1/2$.

Garten and Weiss explain the adsorption of alkali by cathodically polarised charcoal¹⁸ and by platinised H-charcoal in an atmosphere of hydrogen by the reduction of quinones to hydroquinones, which possess acid properties, according to the following schematic equation:



The problem of the hydrolytic adsorption of acid and bases from solutions of neutral salts remains open.

They propose the following equation for the reduction potential of H-charcoal:

$$E_h = E'' - \frac{RT}{2F} \ln \frac{\alpha}{C_1 - C_2 \alpha} \quad (5)$$

where C_1 and C_2 are constants and α is the fraction of the reduced form present as hydroquinone groups: the extent of adsorption of alkali is proportional to α .

Garten and Weiss believe that the validity of their theory is proved by the fact that their equations (1) and (2) are consistent with data¹⁸ on the variation with potential of the extent of adsorption of acid and alkali on a charcoal electrode. The results of the comparison are presented in the form of graphs without indicating the numerical values of the constants. The graph from Ref. 3 showing the variation with potential (relative to the normal hydrogen electrode) of the extent of adsorption of acids on positively charged charcoal is reproduced in Fig. 1. The continuous curve represents the theoretical relation according to Garten and Weiss and the circles the results of the measurements of Kuchinskii *et al.*¹⁸ for adsorption from 0.01 N H_2SO_4 (and not 0.01 N HCl as stated erroneously by Garten and Weiss³). The figure shows that, according to Garten and Weiss, the limiting adsorption for which $\alpha = 1$ should be 0.303 milliequiv. g^{-1} . The surface coverage α for any value of E_h may be represented by $A/0.303$, where A is the measured extent of adsorption. The coefficients of Eqn. (3) corresponding to the experimental data can be readily found from Fig. 2 which shows the theoretical relation of Garten and Weiss as a plot of $\log[\alpha/(1-\alpha)]$ against E_h . When these coefficients are substituted, the equation of Garten and Weiss becomes

$$E_h = 0.42 + 0.24 \log_{10} \frac{\alpha}{1-\alpha}.$$

The coefficient of $\log[\alpha/(1-\alpha)]$ is 0.24 instead of $(RT/2F) \ln 10 = 0.029$ V which follows from the theory of Garten and Weiss. Thus the theory is not completely quantitatively consistent with experiment. This is particularly evident from a comparison with experimental data of the dependence of A on E_h (shown in Fig. 1 by a dashed curve) calculated from Eqn. (3) using the theoretical coefficient of the logarithmic term. Garten and Weiss have compared their theory with the experimental data of Kichinskii *et al.*¹⁸ also for the adsorption of alkali from 0.0108 N KOH on cathodically polarised charcoal. In this case they give only part of the theoretical curve so that it is impossible to determine from the graph the theoretical limit of adsorption which follows from their theory. However, judging from the shape of the curve, in order to obtain

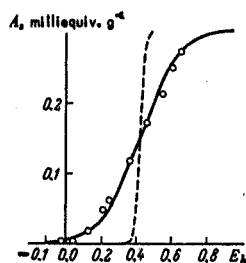


Fig. 1.

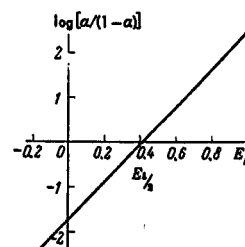
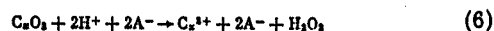


Fig. 2.

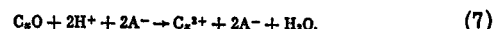
agreement with the experimental data for adsorption on reduced charcoal in an alkaline solution the coefficient of $\ln[\alpha/(C_1 - C_2 \alpha)]$ in Eqn. (5) must be given an even greater value (0.30–0.40), instead of 0.029.

The experimental values of the extent of adsorption of acid and alkali are in fact consistent with Frumkin's electrochemical theory of adsorption, lying on a straight line which bends towards the abscissa axis near the zero-charge point of carbon.

It is also of interest to examine certain other critical remarks and assertions of Garten and Weiss, which are inconsistent with the electrochemical theory. Garten and Weiss believe that there is a contradiction between the mechanism of Burshtein and Frumkin¹⁹,



and the data of Frumkin *et al.*²¹ for the ratio of adsorbed oxygen and acid, which correspond to the mechanism



In actual fact these mechanisms refer to two different processes. The process represented by mechanism (6) proceeds only in the presence of molecular oxygen in solution. Oxygen adsorbed on the surface of charcoal before the latter is placed in solution breaks down into atoms and does not form hydrogen peroxide on interaction with the acid solution. The validity of mechanism (7) has recently received fresh experimental confirmation²².

As already pointed out, Garten and Weiss attribute the adsorption of alkali on hydrogen-treated charcoal (or cathodically polarised H-charcoal) to the presence of hydroquinone groups. In this connection we undertook an experiment with a platinised charcoal electrode which was degassed at 950° for 72 h to break down the quinone or other similar oxygen-containing groups on the carbon surface (that this occurs is shown by the absence of adsorption of acids when such charcoal is placed in 0.01 N H_2SO_4). The degassed platinised charcoal was placed in a solution of alkali at room temperature in the presence of hydrogen. In an atmosphere of hydrogen such charcoal assumes the potential of the hydrogen electrode and adsorbs a considerable amount of alkali (0.473 milliequiv. g^{-1}) despite the fact that hydroquinone groups could not form on its surface.

The mechanism of the adsorption of alkali on platinised charcoal in a hydrogen atmosphere differs radically from that for the adsorption of alkali on activated charcoal heated at 400–500° in an atmosphere of oxygen. In the latter case the adsorption is a consequence of the interaction between the alkali and the surface compounds formed on the charcoal surface during oxidation.

We may mention one more phenomenon, whose explanation presented until recently certain difficulties for the electrochemical theory. Burshtein²³ observed slight adsorption of alkali on degassed carbon and suggested that the adsorption is due to the exchange of hydrogen, forming part of the hydrocarbons which did not decompose during the degassing, for cations from the solution. Garten and Weiss believe that the possibility of the exchange of hydrocarbon hydrogen for cations in the solution is doubtful. The experiments of Frumkin *et al.*²², in which adsorption measurements were combined with measurements of the potential of the charcoal, showed that, when degassed charcoal is brought into contact with a solution of alkali, some OH⁻ ions are discharged imparting a negative charge to the surface with formation of chemisorbed OH or O< groups. The negatively charged surface attracts an equivalent quantity of cations which results in the disappearance of some of the alkali from solution. Consequently the phenomenon observed by Burshtein²³ is completely consistent with the electrochemical theory, without necessity for additional hypotheses.

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THE CATALYTIC POLAROGRAPHIC CURRENT OF CERTAIN NICKEL COMPLEXES

Ya. I. Tur'yan

Mark and Reilley^{1,2} showed that addition of small amounts of pyridine (Py) to solutions containing simple (hydrated) nickel ions (Ni²⁺ in excess, $c_{\text{Ni}^{2+}}/c_{\text{Py}} = 5-1000$) results in the appearance of the so called pre-wave preceding the Ni²⁺ reduction wave. They also briefly mentioned² other nitrogen-containing complexing agents which have a similar effect. They explained the formation of the pre-wave by postulating direct reduction of the pyridine complex NiPy_x²⁺ (the reduction overvoltage of NiPy_x²⁺ is lower than that of Ni²⁺), the rate being limited by kinetic factors at the stage of complex formation.

Whilst agreeing with the conclusions of Mark and Reilley^{1,2} about the importance of the discovery of the nickel pre-wave both for the elucidation of the mechanism of the electrochemical reduction of complex nickel ions and for the solution of a number of physicochemical and analytical problems, the present author feels bound to point out that this phenomenon and its explanation, in principle completely similar to that given above, were described by him as early as 1957³ and then further developed^{4,5}. In addition similar pre-waves of thiocyanatonickel complexes were also investigated^{6,7}.

Although Mark and Reilley² quote the present author's paper³, they state that, since he used an excess of pyridine, he was allegedly unable to observe the pre-wave. This statement is completely erroneous³. Even in the presence of an excess of pyridine, with $c_{\text{Py}}/c_{\text{Ni}^{2+}} = 6-20$, the concentration of nickel ions being low ($c_{\text{Ni}^{2+}} = 2 \times 10^{-4}$ M), the author could observe the pre-wave (see Fig. 1 in Ref. 3, p. 1978) and in the same paper he explained the mechanism of the formation of this wave (see pages 1978 and 1979 in Ref. 3). Unfortunately, all this escaped the notice of Mark and Reilley^{1,2}.

In conclusion, it must be pointed out that Mark and Reilley quote the work of Ablov and Nazarova as allegedly dealing with a polarographic study of pyridine complexes of nickel. In actual fact Ablov and Nazarova⁸ described a spectrophotometric investigation of this system.

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