down to a desirable thickness, but all such methods so far used possess serious disadvantages: they do not allow a continuous control of the thickness during the grinding procedure, and wedge-shaped sections or fragments of sections are often obtained. These difficulties prompted us to seek a method for preparing ground sections based on lapping technique.

Mineralized tissue embedded in methyl methacrylate is used. The specimens are sawn into sections 3–4 mm. thick. One side of the section is lapped against cast-iron using very fine diamond abrasive, which gives the surface an extremely good quality with regard to both planarity and surface finish.

For the subsequent steps of the lapping procedure a small steel cylinder is used as a fixture for the specimen. A square-ruled area is etched on one of the plane surfaces of the cylinder, which are perpendicular to its axis. The etched lines are a few microns deep and have a width of about 50μ. On top of the etched area the lapped surface of the specimen is attached with the aid of a glue which is easy to work out to a thin film less than 0·5μ thick. When the glue is dry the specimen is cooled and ground by hand against an ordinary emery plate, down to about 1 mm. thickness.

The next step comprises grinding against a fine-grained diamond plate. The fixture is moved by hand in a V-shaped prism which is oriented perpendicularly to the rotating plane of the grinding plate. At this stage, a section of about 100μ is obtained within a few minutes. The shape of the fixture allows continuous approximate measurements of the specimen with the aid of an ordinary micrometer.

In the last step the specimen is lapped against a cast-iron plate using fine-grained diamond abrasive, the fixture being oriented with its longitudinal axis perpendicular to the lapping plane. The sections are lapped by hand to the desired thickness, checked by repeated measurements. A coarse control of the thickness of about ± 2μ can be obtained with the aid of a good micrometer. A more accurate control of thickness can be achieved with the aid of a 'microkator' (a Swedish mechanical measuring instrument, manufactured by C. E. Johansson). A complete topographical thickness-measurement, with the same lateral resolution as the light microscope can be obtained with the aid of a mechanical-optical instrument designed by Hallén[1].

Good sections have been obtained with our prototype equipment. For example, thickness measurements of a cross-section 17μ thick of the crown of a tooth was made. The thickness was measured at 100 arbitrarily distributed points within the dentin as well as the enamel. The mean thickness was 16·7μ, standard error 1·7, which gives a coefficient of variation of 10·3 per cent. The section is slightly wedge-shaped with a slope of 1/5,000.

A more detailed report will be published elsewhere.

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Aug. 27.

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Anodic Reactions of Mercury with Halide Ions in Dimethylformamide

Dimethylformamide and other organic solvents are being increasingly used for the polarography of organic substances and inorganic ions. It has been shown that a mercury pool anode in halide solutions in dimethylformamide provides a stable reference potential[1] and that this potential (and that of similar electrodes in other organic solvents[2]) differs considerably (by about − 0·5 V.) from that of the aqueous calomel electrode[1]. We have therefore studied the behaviour of iodide and chloride ion at the dropping mercury electrode in dimethylformamide in order to identify the anode reaction and ascertain why it maintains the pool at a stable potential. The results make it clear that some familiar aspects of the solution chemistry of mercury are changed when dimethylformamide is used as solvent.

We find that tetraethylammonium iodide in 0·1 *M* lithium perchlorate in dimethylformamide gives two reversible anodic waves ($E_{1/2}$ − 0·32 and + 0·10 at 20° C. at 1·96 m*M* concentration versus saturated calomel electrode; $i_d/cm^{2/3}t^{1/6}$, 1·24 and 0·50). Progressive addition of mercuric perchlorate made first one and then the other wave cathodic, with no significant change of other characteristics. Following the methods used by Kolthoff and Miller[3] in their study of mercury complexes in water we assumed the electrode reaction of the more negative wave to be:

$$\mathrm{Hg} + a\mathrm{X}' \rightleftharpoons \mathrm{HgX}^{(a-2)-} + 2\varepsilon \qquad (1)$$

for which the potential of the dropping electrode would be given by:

$$E_{de} = \text{const.} + \frac{RT}{2F} \ln \frac{i}{(i_d - i)^a} \qquad (2)$$

We plotted E_{de} for the more negative wave against the logarithmic function of equation (2) for various values of the exponent a. If one takes $a = 4$ a good straight line of slope 0·029 (= $2{\cdot}303RT/2F$) results; the electrode reaction is therefore:

$$\mathrm{Hg} + 4\mathrm{I}' \rightleftharpoons \mathrm{HgI}'' + 2\varepsilon \qquad (3)$$

When 0·1 *N* tetraethylammonium iodide is used as the supporting electrolyte in polarography in dimethylformamide the galvanometer zero is at − 0·55 V. versus standard calomel electrode; hence one is limited to the study of substances of half-wave potential more negative than this, since at less-negative potentials the mercury micro-electrode dissolves, according to equation (3). Similarly, when a diffusion current passes through the cell owing to reduction of a substance in the solution, the same reaction must occur on the mercury pool if this is used as anode. We suggest that the stability of the pool potential is to be accounted for by supposing that complex formation maintains a concentration of mercury ions in solution sufficiently high to ensure that further quantities, produced by electrolysis, do not increase the total concentration by a significant fraction. It should be borne in mind that the overall stability constant of the complex ion is high[4], and that there is a large and constant excess of iodide ions (the stability constants of the halide complexes in dimethylformamide, which we have estimated from polarographic data, will be reported elsewhere).

We do not discuss here the nature of the more positive wave given by iodide ion, because it is not relevant to the behaviour of the anode in polarography in iodide as supporting electrolyte.

The chloride ion (as lithium chloride) behaves similarly to iodide ($E_{1/2}$, $-0{\cdot}17$ and $+0{\cdot}125$ V. versus standard calomel electrode in 4·97 mM solution; $i_d/cm^{2/3}t^{1/6}$, 1·16, 0·53). Here, however, there is evidence that as well as $HgCl_4''$ another complex of mercury, with a lower ratio of halogen to metal, is formed to some extent. We have also observed that in dimethylformamide the precipitation of calomel on addition of mercury to a solution of mercuric chloride:

$$Hg + HgCl_2 = Hg_2Cl_2$$

is prevented by the presence of chloride ion (in water, precipitation does occur even if chloride is present). Moreover, calomel slowly dissolves in a dimethylformamide solution of lithium chloride (but not if the chloride is absent). It is clear, therefore, that a mercury pool in chloride solution cannot be in effect a calomel electrode as it is in aqueous chloride solutions. In fact we have found[1] that a 'calomel electrode' made up in dimethylformamide with 2 N lithium chloride has initially a potential close to that of the saturated aqueous calomel electrode, but the potential is not stable, owing no doubt to the slow dissolution of the calomel.

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A Theoretical Expression for Solubility Product

In view of the great importance of the 'solubility product' in chemistry, it was considered desirable to obtain a theoretical expression, to explain the observations described in a previous communication[1] and also to correlate the solubility product with some significant properties of the ions which combine to form the precipitates.

When two dilute aqueous solutions of electrolytes (for example, barium chloride and potassium sulphate) are mixed, the oppositely charged ions (Ba^{2+} and SO_4^{2-}) are brought into close association owing to electrical attraction and combine to form molecules of the precipitate (barium sulphate). The attraction is caused partly by Coulomb forces and partly by the mutual polarization of ions (ion–dipole interactions). The potential energy of a system consisting of oppositely charged ions is thus:

$$U = \left\{-\frac{(z_+\varepsilon).(z_-\varepsilon)}{R_0}\left(1-\frac{1}{n}\right)-\frac{\alpha_a(z_+\varepsilon)^2+\alpha_c(z_-\varepsilon)^2}{2R_0^4}\right\} \quad (1)$$

where z_+ and z_- are valencies of the cation and anion, ε is the electronic charge, α_c and α_a are polarizabilities of the positive and negative ions, R_0 the equilibrium distance between the centres of the two ions, and n, a constant (about 9) occurring in Born's repulsion-energy term.

Redispersion of these ions from the precipitate does not take place unless they possess energies exceeding E (equal to $-U$). The stronger the binding forces between the ions, the smaller is their tendency to pass out into solution as free ions, and hence the greater the insolubility of the precipitate formed.

The velocity of recombination of the oppositely charged ions in solution, which is an instantaneous process (for which the energy of activation is practically zero), is:

$$k_1.(n_{Ba^{2+}}\ n_{SO_4^{2-}}) \quad (2)$$

where $n_{Ba^{2+}}$ and $n_{SO_4^{2-}}$ are the numbers of these ions per unit volume (concentrations) and k_1 is a constant.

The velocity of the reverse process, namely, the redispersal of ions from the surface of the precipitate into solution, is:

$$k_2.A.n_0\exp(-E/RT) \quad (3)$$

where A is area of the interface of the particles of the precipitate and n_0 is the number of pairs of ions (Ba^{2+} and SO_4^{2-}) per unit area of the surface. At equilibrium:

$$k_1.(n_{Ba^{2+}}\ n_{SO_4^{2-}}) = k_2.A.n_0.\exp(-E/RT) \quad (4)$$

But by definition $(n_{Ba^{2+}}\ n_{SO_4^{2-}}) = S_P$, the solubility product of barium sulphate. Introducing the value of E given in (1) we have:

$$S_P.\left(\frac{k_1}{k_2An_0}\right)=\exp(-E/RT)=\exp\left[-\left\{\frac{z_+z_-\varepsilon^2}{R_0}\left(I-\frac{}{n}\right)+\frac{\alpha_a z_+^2\varepsilon^2+\alpha_c z_-^2\varepsilon^2}{2R_0^4}\right\}\Big/RT\right] \quad (5)$$

S_P is a constant at constant temperature if A is constant. Thus,

$$-\log_e S_P = \frac{E}{RT}+a=\left\{\frac{\alpha_a z_+^2\varepsilon^2+\alpha_c z_-^2\varepsilon^2}{2R_0^4}\right\}\Big/RT+a \quad (6)$$

since for very small values of R_0 the first term in (1), namely $\left(\frac{z_+z_-\varepsilon^2}{R_0}\right)$, can be neglected in comparison with the second term representing the mutual ion-dipole interactions. If temperature is constant, expression (6) reduces to:

$$-\log_{10}S_P = K(\alpha_a z_+^2+\alpha_c z_-^2)+a \quad (7)$$

(K_1 and a are constants. For compounds of similar chemical constitution R_0 is nearly constant.) We should therefore expect to obtain a straight line by plotting $-\log_{10}S_P$ against $(\alpha_a z_+^2+\alpha_c z_-^2)$. This is in agreement with results represented graphically in Fig. 1, obtained from known values of S_P and the polarizabilities of the constituent ions.

It is known that $\alpha = r^3$ for a spherical molecule, assumed to be a perfect conductor. Applying this to ions, we have:

$$-\log_{10}S_P = K_1\left\{\frac{r_a^3z_+^2+r_c^3z_-^2}{2R_0^4}\right\}\Big/RT+a \quad (8)$$

If we now compare salts which are chemically similar, having one common ion and the other ion having the same valency (T being constant), equation (7) becomes:

$$-\log_{10}S_P = K_1'\alpha+a = K_1'r^3+a' \quad (9)$$

This explains our previous observation[1] that the most insoluble inorganic precipitates are formed from hydrated ions having the largest size (including the hydration layer). On plotting $-\log_{10}S_P$ against $1/d^3$, where d is the distance of the diffusion front of each band from the starting point of diffusion, when we examine the bands in a chromatogram produced in an agar-gel layer containing the appropriate reagents during the diffusion of the electrolytes, then