

density of adsorbed acid molecules is reduced by dipping in hexadecane, may be explained as a result of the reverse process taking place, hexadecane replacing stearic acid which has been dissolved away. These authors do point out that a surface may become oleophobic before the adsorption process is complete.

Identical observations have been made on retracted monolayers of long-chain aliphatic alcohols and primary amines. It has not been possible to observe any island structure when the mica has not been immersed in solution long enough for it to become oleophobic, although Bigelow and Brockway were able to obtain faint layer lines in electron diffraction pictures. It may well be that any clusters of molecules oriented on the surface are too small to be replicated satisfactorily.

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<sup>1</sup> Bigelow, W. C., Pickett, D. L., and Zisman, W. A., *J. Coll. Sci.*, **1**, 513 (1946).

<sup>2</sup> Epstein, H. T., *J. Phys. and Colloid Chem.*, **54**, 1053 (1950).

<sup>3</sup> Bigelow, W. C., Glass, E., and Zisman, W. A., *J. Coll. Sci.*, **2**, 563 (1947).

<sup>4</sup> Sobotka, H., and Rosenberg, S., *J. Coll. Sci.*, **5**, 581 (1950).

<sup>5</sup> Bigelow, W. C., and Brockway, L. O., *J. Coll. Sci.*, **11**, 60 (1956).

### Magnetometric Titration: a New Method of Chemical Analysis

It is well known that the addition of paramagnetic solutes to water brings about a marked reduction in the nuclear spin-lattice relaxation time of solvent protons<sup>1</sup>, the inverse of the relaxation time being linearly related to solute concentration according to the equation:

$$(T_1^{-1} - T_0^{-1}) = \alpha \mu_N^2 C$$

where  $T_1$  and  $T_0$  are spin-lattice relaxation times in the presence and absence of added solute, respectively;  $\alpha$  is a proportionality constant;  $\mu_N$  is a parameter expressing the effectiveness of a particular solute in this phenomenon, sometimes called the 'effective' paramagnetic moment of the solute;  $C$  is the concentration of the solute. In the case of solutions of paramagnetic complex ions, the magnitude of the effect (that is, the value of  $\mu_N$ ) depends on the nature of the co-ordinated groups<sup>2</sup>. We find that the phenomenon enables the replacement of one ligand by another in solution to be followed with sufficient precision to form the basis for a method of determining the concentration of metal ions, and it is now suggested that this method of analysis should be widely applicable in cases where the addition of a complexing agent to the solution of a paramagnetic ion in solution causes the formation of a new complex ion of different  $\mu_N$  and of high stability in solution. The analyses can conveniently be carried out by use of a low-resolution nuclear magnetic-resonance spectrometer.

The application of the method to the titration of nickel(II) is illustrated in Fig. 1. The breaks in the curve correspond to equivalence points, in a manner somewhat reminiscent of conductimetric titrations. Nickel(II) represents a particularly favourable and

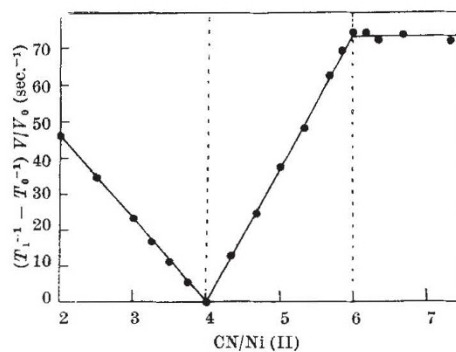


Fig. 1

interesting case for this method, since the diamagnetic species  $[\text{Ni}(\text{CN})_4]^{2-}$  does not catalyse the spin-lattice relaxation at all. Values of  $(T_1^{-1} - T_0^{-1})$ , corrected for the dilution effect which accompanies addition of titrating agent, are plotted against the amount of potassium cyanide added to an ammoniacal solution of nickel cyanide, that is, a solution of  $[\text{Ni}(\text{NH}_3)_6]^{2+}[\text{Ni}(\text{CN})_4]^{2-}$ .

The curve is interesting in that two equivalence points are observed. These occur after addition of four and six moles of cyanide per mole of nickel(II) respectively, and demonstrate the formation of stable species  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{Ni}(\text{CN})_6]^{4-}$ . Since present indications from other experimental methods are that  $[\text{Ni}(\text{CN})_6]^{4-}$  (in aqueous solution) is not paramagnetic, this particular result raises other problems, because only paramagnetic solutes are thought to be effective in catalysing spin-lattice relaxation.

A feature which makes the technique attractive in analytical chemistry is the small amount of solute required. In our apparatus sample volumes of 0.23 c.c. and concentrations of nickel(II) in the range 0.01–0.1 M were convenient, but both these values could be substantially reduced. The dilution during titration can be kept low by using a concentrated solution of titrating agent, but is easily allowed for by multiplying the values of  $(T_1^{-1} - T_0^{-1})$  by  $V/V_0$ , where  $V_0$  is the initial volume of the solution and  $V$  the volume after addition of titrating agent.

Other applications of the titration technique, for example, to the study of relative stability constants of different complexes in solution, readily suggest themselves.

It is hoped to publish more detailed accounts of the technique and experimental results elsewhere.

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<sup>1</sup> Bloembergen, Purcell and Pound, *Phys. Rev.*, **73**, 679 (1948).

<sup>2</sup> For example, Morgan, Nolle, Hull and Murphy, *J. Chem. Phys.*, **25**, 206 (1956).

### A Dose Test for Irradiated Polyethylene

ALTHOUGH a large body of results has been published on the changes of physical properties induced in ethylene polymers by irradiation, no description of an actual dose test has come to our notice. It happens during electron irradiation of objects that such factors as thickness may influence the dose received at any point so that it is desirable to have available a test which can be used to assess