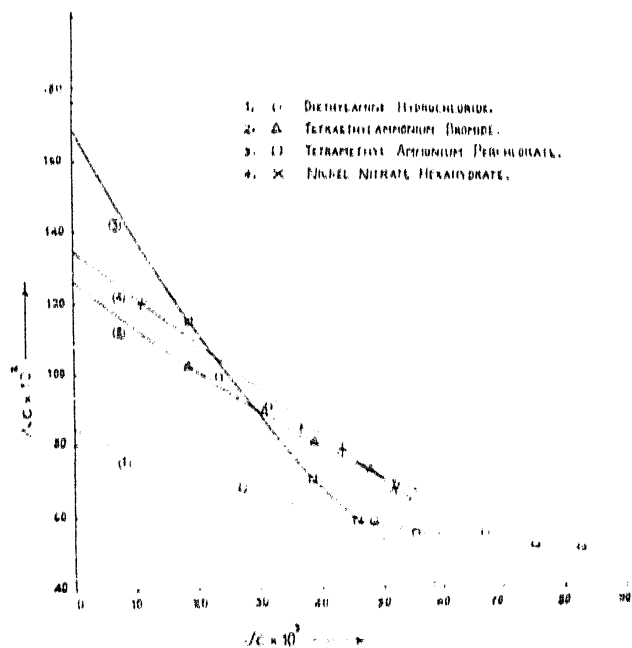


CONDUCTANCE OF SALTS IN DI-ETHANOLAMINE AS A NON-AQUEOUS SOLVENT

THE study of conductance in non-aqueous solvents has been made by a number of workers both for understanding the nature of these solutions and also for testing the various theories of conductance that have been developed in this field. But for systems where the solvent is very viscous and also where solvent molecules are large or of the same order of magnitude as the solute molecules, little work has been done.<sup>1</sup> In this note data for the electrical conductivity of solutions of a number of organic and inorganic electrolytes, e.g., tetraethylammonium bromide, tetramethyl ammonium perchlorate, diethylamine hydrochloride and nickel nitrate in a very viscous solvent, diethanolamine (C<sub>2</sub>H<sub>5</sub>OII), NH<sub>2</sub>, have been recorded. Diethanolamine should behave both as an alcoholic solvent as well as a strong ammoniacal base and has a viscosity,  $\eta = 3.676$  poise at 30° C.

The Debye-Hückel-Onsager's equation<sup>2</sup>  $\lambda_c = \lambda_0 - x\sqrt{c}$  (where  $\lambda_0 =$  equivalent conductivity at infinite dilution,  $\lambda_c =$  equivalent conductivity at concentration  $c$  and  $x =$  Onsager's slope), has been applied to get an approximate value of  $\lambda_0$  in every case. For this,  $\lambda_c$  was plotted as ordinate against  $\sqrt{c}$  and a freehand curve or a straight line as the case may be was drawn as shown in the figure. From these



graphs  $\lambda_0$  was obtained by extrapolating to zero-concentration of the electrolyte and the values are recorded in the following table.

Temperature 30°C.	
Solvent = Diethanolamine ( $\eta = 3.676$ poise)	
Electrolyte	$\lambda_0 \cdot 10^2$
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N Br	126.0
(CH <sub>3</sub> ) <sub>4</sub> N ClO <sub>4</sub>	168.0
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH.HCl	84.5
Ni(NO <sub>3</sub> ) <sub>2</sub> ·6 H <sub>2</sub> O	134.5

Our best thanks are due to Sir J. C. Ghosh,

kt., D.Sc., F.N.I., for the interest he has taken during the course of this investigation. Further work is in progress.

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ON THE SUITABILITY OF THE DIELECTRIC CONSTANT METHOD FOR THE DETERMINATION OF MOISTURE IN LAC

THE moisture content of lac usually varies from about 1 to 3 per cent. depending mostly on the humidity of the atmosphere. Although the range of variation may appear to be small, its determination is often necessary since it influences some of the important physical properties, such as fluidity,<sup>1</sup> solubility,<sup>2</sup> polymerizability, etc. The usual method of drying a substance to constant weight at 100° C. or above is not applicable to lac since it easily gives off its combined water at such high temperatures resulting in a partially polymerised product. Other methods<sup>3</sup> involve the employment of vacuum desiccation at lower temperatures. But as all these methods are cumbersome and time-consuming, the need for a rapid, reproducible and accurate method for the determination of moisture in lac, has always been felt.

The results of experiments with a specially designed cylindrical condenser showed, however, that there is practically no increase in capacitance till the moisture content rises from zero to about 1.4 per cent. (moisture determinations being made by the I.L.R.I. method<sup>4</sup>). A further increase in the quantity of moisture in lac results in a slow but gradual rise in the value of capacitance of the experimental condenser till almost the saturation point of moisture is reached, when, however, a rapid increase in capacitance can be observed. The following table embodying the results of measurement on a sample of powdered kusum lac illustrates this.

Moisture content of lac (percentages after conditioning at different humidities)	Capacitance of the condenser in micro micro-farad at the frequency of	
	100 kc/s	1 kc/s
0.00	56.0	72.0
0.75	56.0	72.5
0.88	56.0	72.0
1.26	56.5	72.0
1.43	56.0	72.5
1.52	56.5	73.0
1.70	57.0	74.0
2.25	60.5	76.0
2.62	66.0	82.5

This anomalous increase in capacitance due to gradual absorption of moisture is to be expected from our previous finding on the role and nature of moisture based on the study of the dielectric properties of different mixtures of hard and soft lac.<sup>5</sup> The moisture that is first taken up by dry lac enters into some sort of combination with it being adsorbed on the surface in such a way that the water molecules become more or less fixed and, therefore, incapable of orientation in the alternating electric fields. As the moisture content gradually increases, layers of water molecules following upon those strongly adsorbed on the surface have more and more freedom for orientation and as a consequence an increase in dielectric constant or capacitance is noticed. The results obtained for lac by the dielectric constant method, therefore, cannot be correlated with those obtained by the existing methods of moisture determination, since the increase in capacitance, which is too small to be observed at the initial stages, is also not proportional to the moisture content when it increases to a measurable magnitude later.

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#### PHOTOCHEMICAL AFTER-EFFECT IN THE DECOMPOSITION OF HYDROGEN PEROXIDE BY POTASSIUM FERRO- CYANIDE

It is well known that a pre-illuminated solution of potassium ferrocyanide decomposes hydrogen peroxide in the dark at a much higher rate than a solution which has not been exposed to light.<sup>1,2</sup> In the course of a systematic investigation of this marked photochemical after-effect it was found that a dilute, freshly prepared aqueous solution of pure potassium ferrocyanide decomposes hydrogen peroxide at a fairly constant unimolecular rate in the dark, but the same reaction employing aqueous ferrocyanide which has been kept in the dark for a few days, or heated to 80-90° C. before use, shows an appreciable and distinct fall in the rate of decomposition in the initial stage of the reaction. A solution of potassium ferrocyanide which is used a few minutes after an hour's insolation shows a similar behaviour. When, however, pre-illuminated solution of ferrocyanide is added to hydrogen peroxide in the dark immediately after darkening, the decomposition of the latter continues with a uniformly high velocity to the end. Further it has been established that one minute's insolation of ferrocyanide produces the maximum reaction acceleration.

In the following experiments, which were performed at  $40 \pm 1^\circ \text{C}$ ., M/64 potassium

ferrocyanide (10 c.c.) was insolated for various time intervals and mixed with hydrogen peroxide in the dark as soon as practicable after darkening. The strengths of ferrocyanide and hydrogen peroxide were M/320 and N/6 respectively. The total volume of the reaction mixture was 50 c.c. In the following table, 'T' indicates the time of pre-illumination by direct sunlight of potassium ferrocyanide before it was added to hydrogen peroxide in the dark:—

T	K. 10 <sup>5</sup>
10 sec.	168
30 sec.	250
1 mt.	449
2 mts.	348
5 mts.	274
10 mts.	167
30 mts.	105
60 mts.	87

K. 10<sup>5</sup> for the reaction in the dark with unilluminated ferrocyanide = 35.

These experiments show that there is a well-marked increase in the photochemical after-effect in the beginning, with a subsequent rise to a maximum, followed by a gradual decrease with increasing periods of pre-illumination of ferrocyanide. Experiments with higher concentrations of the latter give similar results, although the effect of long exposure on concentrated solutions is not as pronounced as on dilute solutions.

In the course of these investigations, it was discovered that the activity of pre-illuminated ferrocyanide vanishes completely within a short time after darkening. It has been remarked earlier that the reactions performed with pre-illuminated solutions of ferrocyanide a short time (five minutes) after darkening give in the initial stage of decomposition a distinctly lower value of the velocity constant than with unilluminated solutions. It has been observed that there is a measurable interval between the cessation of illumination and the complete disappearance of activity in the pre-illuminated solutions of ferrocyanide. Below are given some figures showing the fall in the photochemical after-effect with increasing time intervals (T) between the cessation of illumination of ferrocyanide and its addition to hydrogen peroxide in the dark. The period of pre-illumination was one minute.

T	K. 10 <sup>5</sup>
30 sec.	229
1 mt.	119
2 mts.	74
5 mts.	39

The diminution of activity with time is very sharp, but a measurable after-effect of illumination is detectable even in solutions used two minutes after illumination.

In view of the above observations, the author is led to the conclusion that the dark reaction between hydrogen peroxide and a pure aqueous solution of potassium ferrocyanide is really due to the action of the former on potassium aquopentacyanoferrite, which exists as a substitution product in very slight concentration in the aqueous solution of potassium ferrocyanide in the dark.