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SOME PROPERTIES OF LITHIUM CHLORIDE
IN MIXED SOLVENTS.

by

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INTRODUCTION.

A satisfactory theory of electrolytes must take into account not only the effects of the ions on each other, but also the interaction between ions and the solvent molecules. This interaction may be of two kinds (1) definite compound formation between ions and solvent molecules, (2) physical effects due to the action of the electric forces of the ions on the solvent molecules. According to electrostatic theory, the molecules of a polarisable medium will be attracted into the vicinity of the ions and held by considerable forces, giving rise to an apparent hydration. It is not yet possible to distinguish with certainty the effects of such a physical interaction from definite compound formation.

If two kinds of solvent molecules are present in the solution it is to be expected that the more polarisable will be attracted by the ions to a greater extent than the other, and that the solvent in the immediate vicinity of the ions will always contain a greater proportion of these molecules than other parts. The less polarisable molecules will thus have a greater apparent concentration in the bulk of the solution when ions are present. This phenomenon has been extensively studied as the "salting out" effect.

The/

The salting out effect has been studied almost exclusively in the dilute aqueous solution, either by the effect of various salts on the solubility of slightly soluble non electrolytes, or by distribution measurements between the aqueous solution and an immiscible solvent in which the electrolyte is insoluble.

Rothmund (Zeit. Physk. Chem. 33, 401, 1900), carried out a number of experiments showing that the solubility of phenyl thiocarbamide is smaller in salt solutions than in pure water and the decrease is dependant on the nature of the salt and also on its concentration. An exception was found with ammonium nitrate which increased the solubility.

By finding the difference in the number of gram moles of water required for the solution of one gram molecule of ethyl acetate in the absence and presence of certain salts Glasstone and Pound (J.C.S. 127, 2660, 1925), calculated certain hydration values on the assumption that the water molecules attached to the ions were no longer available for the solvation of the ethyl acetate and more must therefore be added when a salt is present. These values, undoubtedly, do not represent quantitatively the number of water molecules attached to the ions, but may be some measure of it and their salting out power. In some of their experiments these workers found, however, that/

that certain salts, notably lithium iodide, seemed to be combining chemically with the ethyl acetate and hence the results had no special significance from the standpoint of the salting out effect.

In a later paper Glasstone, Dimond and Jones (J.C.S. 29, 2935, 1926) suggested that the addition of the salt increased the already large internal pressure of water and hence reduced its power of solvation of a non polar substance.

Sudgen (J.C.S. 129, 174, 1926) has suggested that, since the difference in the molar hydration of sodium and potassium salts is constant and independent of the anion, it is only cations which are hydrated. The anion may, however, exert a depolymerising effect on the associated water molecules, an effect which will oppose the hydration effect. Moreover, he remarks that since the electronic field decreases rapidly with ionic radius, hydration effects should be most evident with small ions like that of lithium.

Shaw and Butler (Proc. Royal Soc. A. 129, 519, 1930), studied the effect of lithium chloride on the partial vapour pressures of water and alcohol when the proportions of the latter varied from 0% to 100%. In solutions containing a small proportion of alcohol its vapour pressure was increased by the presence of the salt and in solutions containing a large proportion of alcohol it was decreased, but it was found that in all/

all such solutions the fractional lowering of the vapour pressure of water was greater than that of alcohol, indicating that the ions attracted water molecules more than those of alcohol even when the latter was present in great excess.

The problem of interaction of ion and solvent molecule may be studied from another angle, namely, consideration of the molecular refractivity of the salt in solution.

Before discussing the present ideas on refractivity it may be well to give a short historical account of the various formulae which have been suggested as a measure of this quantity.

H.A. Lorentz (Wied. Ann. Phys. 9, 641, 1880), and L.V. Lorenz (Wied. Ann. Phys. 11, 70, 1880), have deduced in several ways that the expression:-

$$\frac{n^2 - 1}{n + 2} \cdot \frac{1}{d}$$

where n is the refractive index and d is the density under the same conditions, shall have for every substance a value independent of temperature, pressure or state. This value is known as the specific refractivity and has created the real theoretical basis for refractivity work.

Attempts had been made before this to deduce some expression for refractivity linking up density and refractive index which would fit all cases.

Laplace (Traité de Mécanique céleste t. iv. libr./

libr. X, 32), using the Newtonian theory of light deduced the formula:-

$$r = \frac{n^2 - 1}{d} \quad \text{where } r \text{ is the specific refractivity.}$$

This had a theoretical basis at the time, which it lost when the electromagnetic theory of light displaced the old Newtonian corpuscular theory.

Biot and Arago (Mem. Int. France 7, 301, 1806), confirmed its validity in gases and stated empirically their law of mixtures:-

$$100r_{ab} = pr_a + (100 - p) r_b$$

where r_{ab} = refractivity of the mixture
 r_a = " of constituent a
 r_b = " of constituent b
 p = % weight of a in the mixture

or the refractivity of a mixture is equal to the sum of the refractivities of the constituent parts.

Gladstone and Dale (Phil. Trans. 153, 317, 1863), propounded their empirical formula:-

$r = \frac{n - 1}{d}$ which, notwithstanding its lack of theoretical support, accomplished such good service that it could hold its own for a time even against the later Lorentz-Lorenz expression.

These earlier formulae are now no longer used and/

and in what follows the Lorentz-Lorenz expression is the basis of calculation. It is customary in present work to discuss, not the specific refractivity, but rather the molecular refractivity:-

$$R = \frac{n^2 - 1}{n^2 + 2} \frac{M}{d}$$

where M is the molecular weight of the substance.

Since the later part of the Nineteenth Century a great many investigations have been carried out whose object has been to calculate the molecular refractivity of various salts and acids in solution, mostly aqueous.

The mode of calculation is an application of the above mentioned law of mixtures.

$$R = \frac{M}{\bar{m}} \left[\frac{n_1^2 - 1}{n_1^2 + 2} \cdot \frac{w - m}{d_1} - \frac{n_0^2 - 1}{n_0^2 + 2} \cdot \frac{w}{d_0} \right]$$

Where n_1 = refractive index of the solution

n_0 = " " " " solvent

d_1 = density of the solution

d_0 = " " " solvent

w = wt. of solvent present

m = " " solute in w gms. solvent

M = mol. wt. of the salt

The first term in the bracket represents the refractivity of $w + m$ gms. of solution and the second the refractivity of w gms. of solvent alone. The difference/

Fig. 1.

Comparison of Various Authors' Results for NaNO_3

x Chéneveau
• Steffken

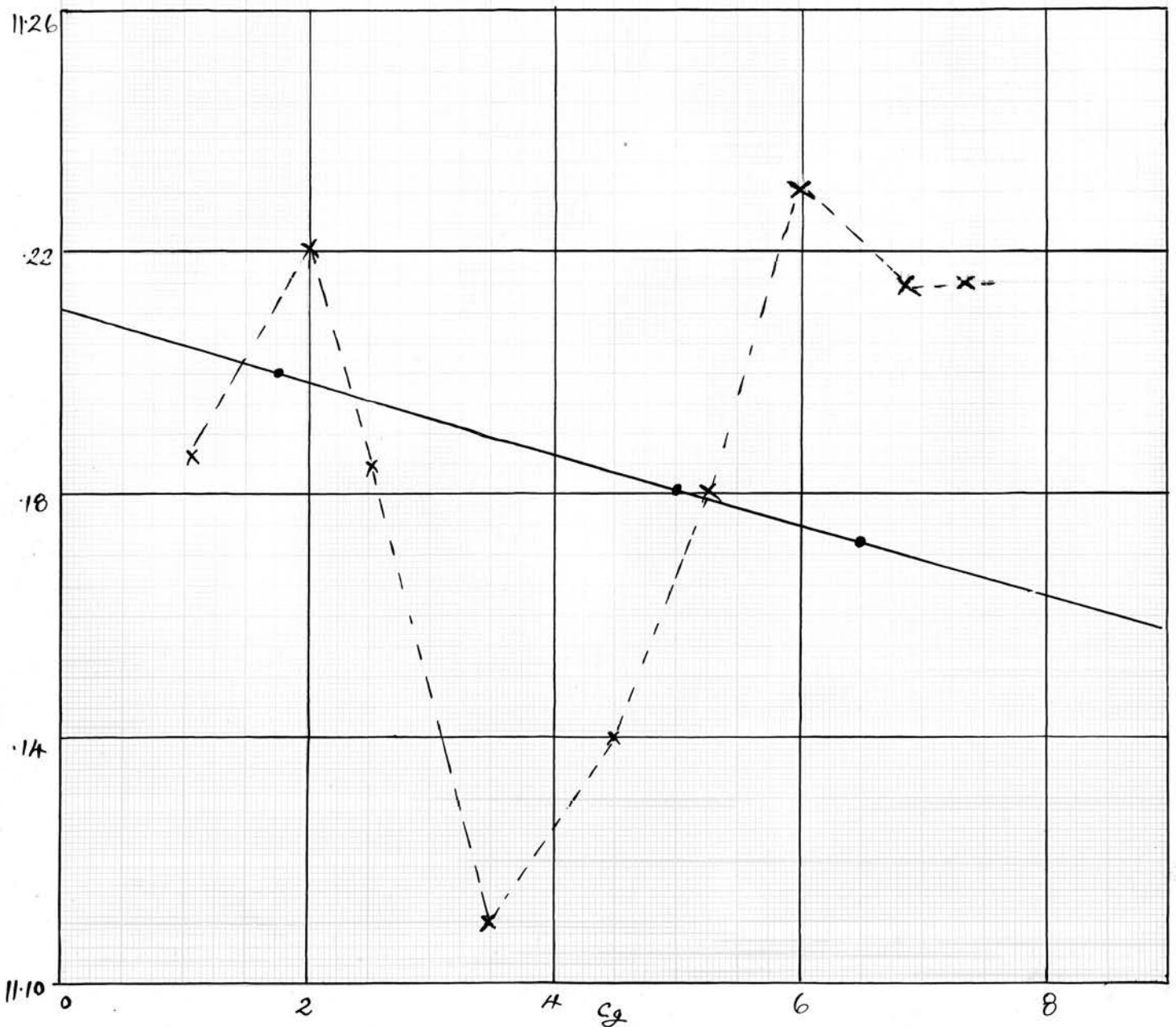
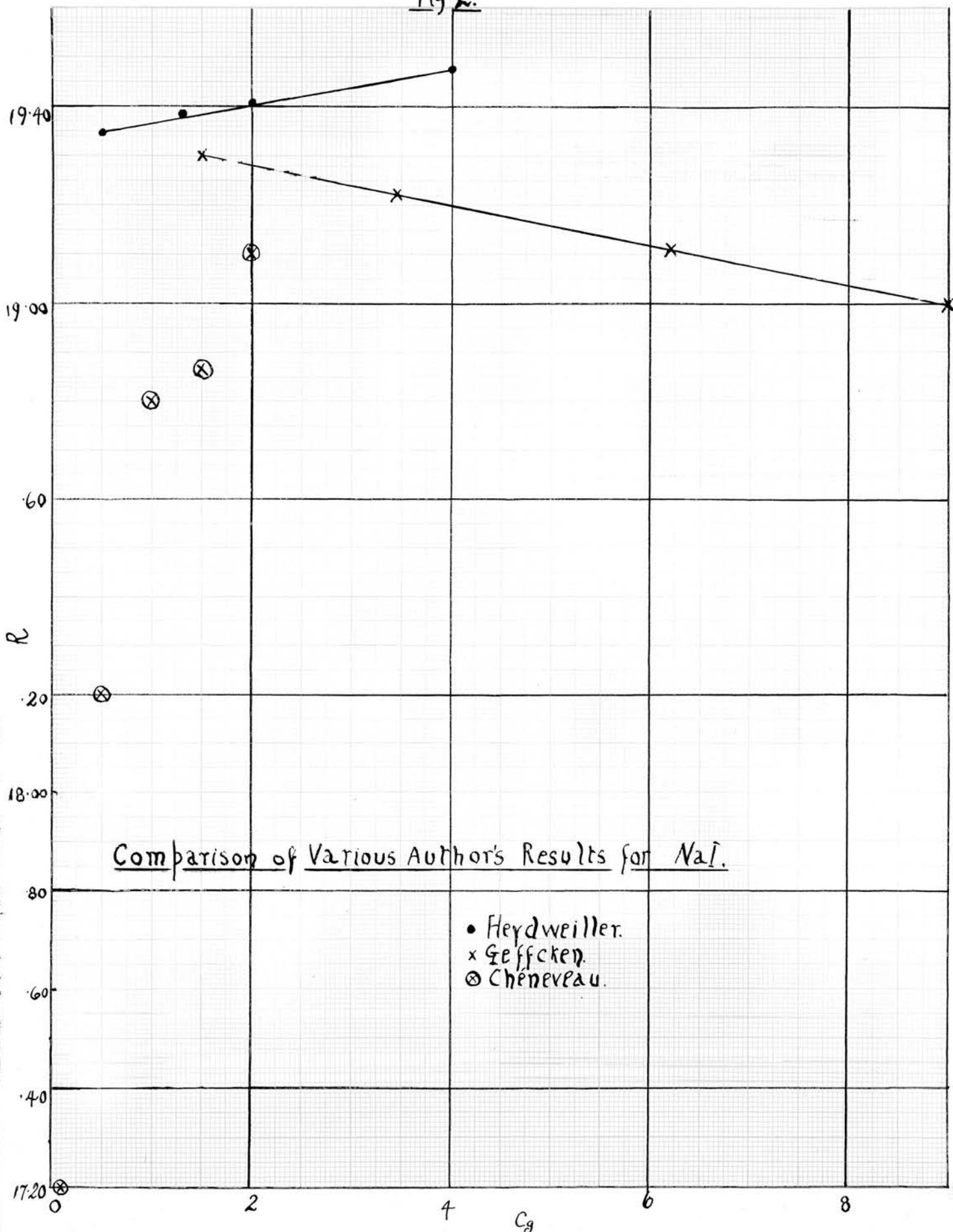


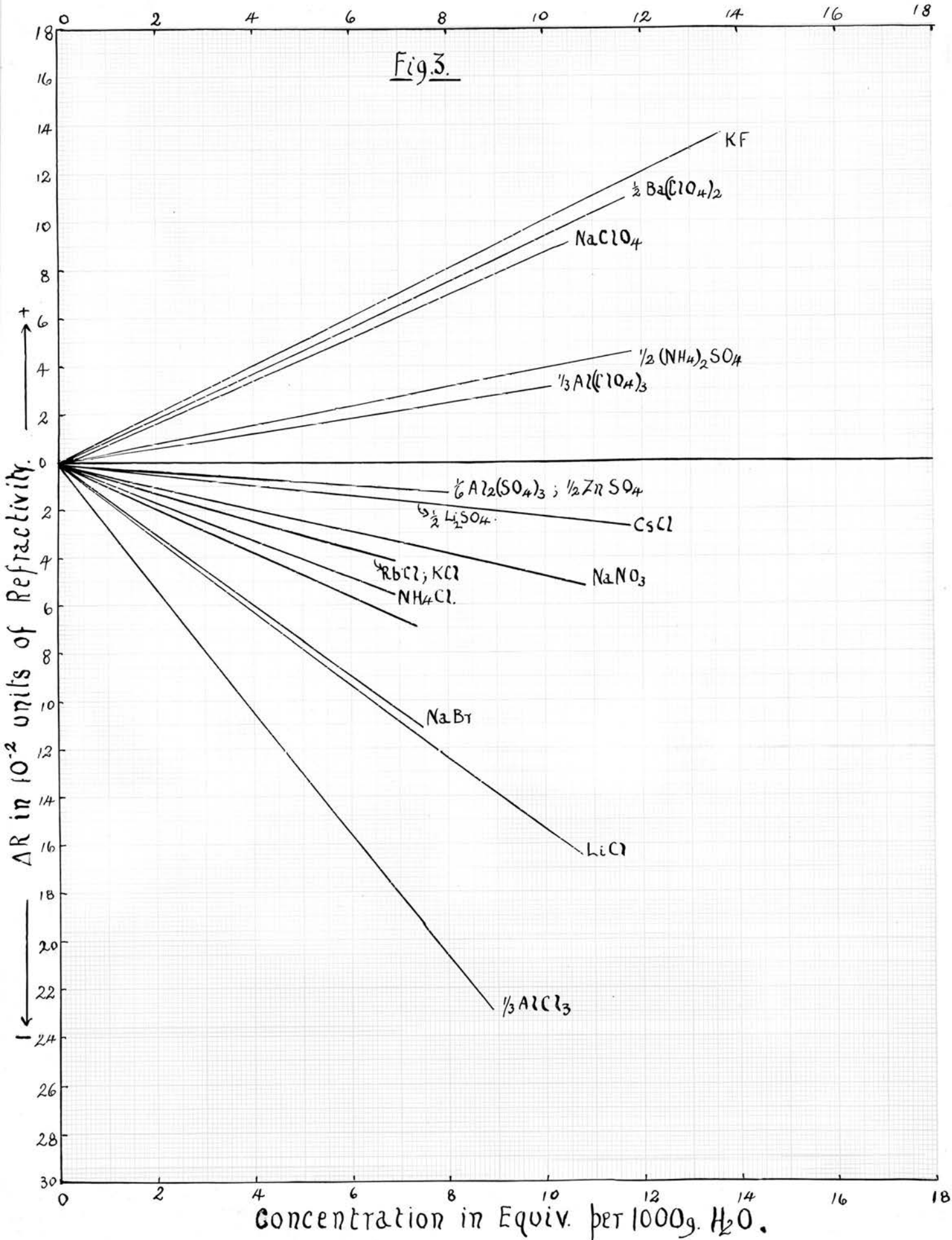
Fig 2.



Comparison of Various Author's Results for NaI.

- Heydweiller.
- x Geffcken.
- ⊗ Cheneveau.

Fig. 3.



difference yields the refractivity of the solute present, and knowing the concentration the molecular refractivity can be found.

The first important worker in this field was Cheneveau (Ann. Chim. (8), 12, 123, 1905) who applied this relation to a great variety of salts at various concentrations. His results in comparison with those of recent workers are very inaccurate. He was led to believe, notwithstanding, that the refractivity of any salt as calculated in this manner was constant and independent of concentration. Two graphs taken from the paper by Fajans and Kohner (Zeit. Physk. Chem. 147, 241, 1903), will show how Cheneveau's results compare with other workers and also that even contemporary workers using the greatest accuracy have not always obtained the same values.

It has now been shown in a great number of cases that the refractivity of a salt in solution is not exactly independent of concentration, but that in general there are slight deviations from constancy. These deviations are shown in fig.3 where the change in equivalent refractivity is plotted against concentration. There is, moreover, another apparent discrepancy. The value of the molecular refractivity of a salt in solution does not agree with the value for the solid crystal, in fact differs materially from it. In view of these two divergences from a constant/

constant value we must either reject the values for the molecular refractivity as so found, or assume that on solution extensive changes take place which have not been taken into account in the calculation. Such changes are separation into ions and the effect of those ions on the solvent molecules. This latter course seems the more probable and a study of refractivity values should yield interesting information regarding those changes.

Fajans (Trans. Far. Soc. 23, 359, 1923), discusses the values for the molecular refractivity of a large number of salts and acids in various states on the basis that the differences between these values must be regarded as some indication of the influence of the various components on each other. In conjunction with Joos he has come to certain conclusions. The refractivity of the anion is lowered by the neighbouring cation and the more so the greater the electric field set up by the latter. Conversely, the refractivity of the cation is increased by the anion.

The physical meaning of the molecular refractivity may be represented by:-

$$R = \frac{4}{3} \pi N \alpha$$

where N is Avogadro's number, and α is the coefficient of polarisation of one molecule, or a measure of the deformability of the molecule. The deformability may be regarded as the ease of displacement of the electron shells with respect to the nucleus./

nucleus. When to the positive change of the nucleus of the anion there is added the effect due to the positive change of the cation, the outer electrons of the anion will be more firmly held and their ability to be displaced decreased. This will result in a decrease of polarisability and hence of the refractivity. The electron sheaths of the cation on the other hand will suffer a repulsion from the nucleus as a result of the negative field of the anion. The outer electron sheaths of the cation will therefore be more readily displaced, hence increasing the refractivity. The union of ions into molecules will therefore be accompanied by a net diminution in the refractivity if the consolidating effect of the cation outweighs the loosening effect of the anion and vice versa.

Having seen the fundamental ideas underlying refractivity we can now turn to Fajans' conception of the effect of the ions on the refractivity of the water molecules in their immediate vicinity. The cation just as it decreases the refractivity of the anion will depress the refractivity of the water molecules attached to it. The anion will raise the refractivity of the water molecules in its vicinity since it will increase their polarisability due to its negative charge.

Fajans and Joos (Zeit. Physik. 23, 1, 1924) have deduced certain hypothetical values for the refractivity of various ions in the gaseous state.

For/

For example:-

$$R_D \text{ of } \text{Li}^+ = 0.2$$

$$R_D \text{ of } \text{Cl}^- = 9.00$$

Hence assuming that the lithium and chlorine ions have the same refractivity in the gaseous state as in solution one would expect that for lithium chloride at infinite dilution R_D should be 9.20. It is, however, only 8.76 a lowering of 0.44 units. Clearly too much has been subtracted for the refractivity of the water which has evidently been affected by the presence of the ions.

The following are the values given by Fajans for the effect of various ions on the refractivity of water.

H^+	Li^+	Na^+	Al^{+++}	F^-
- 0.67	- 0.62	- 0.30	- 2.58	+0.30

This effect is considerable only in the case of small ions, e.g. Li^+ or those ions which have a high charge, e.g. Al^{+++} , for the deformability of water is small as seen by its low refractivity. These ions would be expected to have the greatest effect since from other data they are known to be highly hydrated. It is evident that any variation either in the number or the nature of the solvent molecules round the ions should make itself evident in the refractivity of the salt.

The/

The question as to whether the molecular refractivity of a salt in solution varies according to the solvent was first studied by Walden (Zeit. Physk. Chem. 59, 385, 1907), who examined solutions of tetraethyl ammonium iodide. The atom of iodine has a refractivity of 14.12 whilst that of the ion is 16.6. Hence one might expect that the refractivity in solution of one mole of the salt would vary according to the degree of dissociation into ions brought about either by change in concentration or change of solvent. There was found to be no appreciable change due to concentration, but, by varying the solvent, changes in the refractivity were produced. The greatest variation from the value in pure water being 2% in nitromethane.

E. Schreiner (Zeit. Phys. Chem. 133, 420, 1928 and 135, 461, 1929) has measured the molecular refractivities of hydrochloric acid and lithium chloride in water, methyl alcohol and ethyl alcohol. The following are the values for R_D^{18} for lithium chloride.

H ₂ O	MeOH	EtOH.
8.73	8.58	8.38

The values in each solvent for both lithium chloride and hydrochloric acid decreased with concentration. Fajans and co-workers had already favoured/

favoured the existence of the monohydrated ions

H^+H_2O , and similarly H^+MeOH and H^+EtOH a view supported by the catalysis experiments of H. Goldschmidt. Schreiner agrees with this and suggests similar formations for the lithium ion, Li^+H_2O , Li^+MeOH and Li^+EtOH the presence of which causes the lowering of the refractivity with concentration increase.

Besides this stoichiometrical chemical hydration there also appears to be a hydration of a statical physical kind in which these monohydrated ions have further interaction with the solvent molecules. Whether it is necessary to introduce the conception of these complexes to explain the changes is difficult to say since the observed phenomena might be equally well explained on a purely physical basis.

The difference between R_D for lithium chloride in water and alcohol was not great. But it was thought that an investigation of the manner in which the value in water changed to that in alcohol in various water-alcohol mixtures might give some idea of the relative quantities of alcohol and water molecules in the vicinity of the ions.

The refractivity of lithium chloride in both alcohol and water may be considered as constant from 0 to 2 molal concentration of the salt. No attempt was made to study concentration changes, but simply the change in molecular refractivity with change of water and alcohol proportions.

EXPERIMENTAL.I. PREPARATION OF MATERIALS.

(a) ALCOHOL. Commercial absolute alcohol was allowed to stand for at least eight days over freshly burnt quick lime in a stoppered flask and afterwards refluxed for eight hours on the water bath. The flask was then fitted with a fractionating column and water condenser and the contents slowly distilled rejecting the first and last distillates, (Danner J. A.C.S. 44, 2832, 1922). During these operations all corks were covered with tin foil and calcium chloride tubes were attached where necessary in order that moisture be excluded. That portion of the distillate distilling at the correct temperature was stored in an amber coloured Winchester having a tightly fitting stopper. The contents were further protected from atmospheric moisture by means of a rubber cap tied over the stopper.

The alcohol so obtained had a density of $D_4^{18.1} = .79085$. Another preparation used for surface tension work had a density of $D_4^{25} = .7849$.

(b) LITHIUM CHLORIDE. This salt was prepared from Kalbaum's preparation which was dissolved in alcohol and filtered till free from sediment and a clear liquid./

liquid obtained. The sediment consists chiefly of the other alkali chlorides which are insoluble in alcohol. Most of the alcohol was evaporated off above 50°C under reduced pressure. The anhydrous lithium chloride which appeared was quickly filtered at the pump whilst the syrupy saturated solution was still hot. It was then transferred to a flask and dried according to Pearce and Hart (J. A.C.S. 44, 2411, 1922) by heating in a stream of hydrochloric acid gas on an oil bath at 170°C . When dry, the hydrochloric acid gas was replaced by a stream of hydrogen which was kept up till the gas issuing from the flask no longer gave an acid reaction with litmus paper. The hydrochloric acid gas was generated from "AR" sulphuric and hydrochloric acids and dried by first bubbling through concentrated sulphuric acid and then passing through a long tube containing phosphoric oxide. The hydrogen was generated in the usual way from "AR" materials and dried in the same manner.

The lithium chloride so obtained was kept in a vacuum dessicator over phosphoric oxide. On analysis for chlorine content it gave 83.51%.

In preparing a later sample it was found to be more convenient to estimate the purity by comparing the drum reading on the interferometer for an aqueous solution with the readings taken for aqueous solutions prepared from the first sample.

II. APPARATUS AND PROCEDURE.

Kohner (Zeit. Phys. Chem. (B) 1, 427, 1928), has given a very exhaustive account of the effect of errors in the data required for calculation of the refractivity of the salt, namely refractive index, density and concentration. The greatest accuracy is essential, especially in the first named which appears as a square in the Lorenz-Lorentz formula.

(a) REFRACTIVE INDICES. These were measured with a Pulfrich refractometer. At first a single cell was used, fitted with a water jacket through which flowed a stream of water at the required temperature.

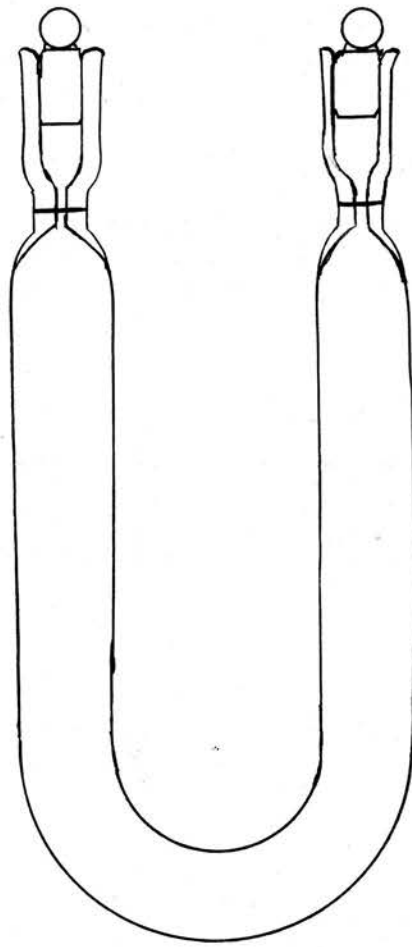
This method was found, however, not to be sufficiently accurate and a Zeiss Interferometer was tried with a view to obtaining greater accuracy. Using a 10 m.m. cell it was proposed to measure the refractive indices of the alcohol-water solvents by the above method, and the change caused by the addition of the lithium chloride by the interferometer by comparing solvent against solution in the two chambers of the cell. This method would have been highly successful but for the fact that the drum reading was a function, not only of the change in refractive index, but also of the difference in the dispersions of solvent and solution. As no other way of measuring the dispersions than by the Pulfrich refractometer /

refractometer, using a divided cell, presented itself, this method was also unsuitable.

The investigation with the divided cell of the Pulfrich refractometer had shown that it was possible to measure small differences of refractive index very accurately, and this was the method finally adopted. The absolute values of the refractive indices for the alcohol-water solvents were obtained with the single cell at 18°C. The solvent was then put in one half of the divided cell and the solution in the other. As a source of light a mercury arc lamp of the Kromayer pattern was used and all readings were for the green line ($\lambda = 5461 \text{ \AA.U.}$). The prism of the refractometer was set such that the lines for solution and solvent were seen at the same time through the eye piece. The reading for the solvent was taken approximately and the difference in reading between it and the solution was obtained on the small drum with great accuracy. From the conversion tables the difference in refractive index was obtained. By addition of this value to the refractive index of the alcohol-water solvent the refractive index of the solution was obtained.

In this method the temperature of the divided cell is, within limits, of small importance. It is essential, however, to have both sides at the same temperature. To secure this the cell was covered during/

Fig. 4



PYKNO METER.

during the reading with a small cardboard box lined with cotton wool.

A consideration of the manner of calculation of the refractivity of the salt will show that it is not so important to know the absolute values of the refractive indices as the change produced as a result of the addition of the salt.

The accuracy in the refractive index difference measurement is ± 0.00002 .

(b) DENSITIES. The densities were measured in a U shaped pyknometer made of silica and capacity of about 15c.c. A sketch is shown (actual size). The liquid whose density was being taken was brought to the correct temperature by placing the filled pyknometer in a small glass thermostat such that the marks etched on the capillaries were at eye level. The liquid was adjusted to the marks by small needle shaped pieces of filter paper. The calibration was performed by weighing the pyknometer empty and filled with distilled water. Assuming the density of water at 18.1°C to be $.99860$ (International Critical Tables value) the capacity was found to be 14.9133c.c. (1)

The/

(1) When the measurements were completed it was found that an error in the calibration of the thermometer had been made and that the density measurements had been made at 18.1°C and not at 18.0°C , as was intended. The molecular refractivity depends ultimately on the difference of refractive index and of density between the solvent and the solution and so long as the differences are measured when the solvent and the solution have the same temperature, a small difference between the temperature at which the densities and the refractive index differences are measured does not affect the value of R.

The same procedure as to drying and weighing the pyknometer was adhered to throughout.

(c) THE SOLUTIONS. The various molar fractions of alcohol and water were prepared and from them the lithium chloride solutions. All the solutions of lithium chloride in a particular alcohol-water mixture were prepared from the same sample of that solvent since it is difficult to reproduce another sample having the same refractive index and density to the required accuracy.

RESULTS.

The method of calculation of the molecular refractivity is that mentioned earlier in the work. Since the concentrations are expressed as moles per 1000 gms. solvent, $w = 1000$ gms. and $m = Mc$ where c is the concentration.

Having the densities of solvent and solution it is possible to calculate the apparent increase in volume of the solution on the addition of the lithium chloride.

$$\Delta V = V_1 - V_0 = \frac{1000 - Mc}{d_1} - \frac{1000}{d_0}$$

Where ΔV is the apparent increase in volume.

V_1 = volume of 1000 + Mc gms solution.

V_0 = " " 1000 gms. solvent.

In Table I are given the various alcohol-water mixtures used and the concentrations of the lithium chloride dissolved in them together with their densities and refractive indices. The molecular refractivities and values of ΔV are also shown.

The molecular refractivities for the weaker solutions have not been calculated since the percentage error is so great. The densities of all solutions have been used to calculate the ΔV values.

TABLE I.

TABLE I.

Refractive indices and densities of solutions of lithium chloride
in water-alcohol mixtures.

Molar fraction of Alcohol	Concentration of lithium chloride	18·1 d 4	18 n 5461	R 5461	$\Delta V = V - V_0$
0·00	0·000	0·99860	1·33410	-	-
	0·3980	1·00814	1·33762	8·81	7·34 Mls
	0·4611	1·00972	1·33824	8·81	8·33 "
	0·6839	1·01494	1·34021	8·81	12·45 "
	0·7264	1·01597	1·34055	8·81	13·28 "
	0·9554	1·02123	1·34250	8·78	17·48 "
	1·1235	1·02500	1·24392	8·79	20·69 "
0·20	0·0000	0·93817	1·35911	-	-
	0·1432	0·94173	-	-	2·42 "
	0·2206	0·94352	-	-	3·87 "
	0·3559	0·94672	1·36208	8·82	6·31 "
	0·6318	0·95306	1·36426	8·81	11·46 "
	0·7989	0·95692	1·36556	8·79	14·51 "
	1·2812	0·96801	1·36936	8·77	23·26 "
0·40	0·0000	0·88633	1·36538	-	-
	0·2402	0·89220	-	-	3·98 "
	0·3456	0·89470	1·36813	8·74	5·82 "
	0·4747	0·89757	1·36905	8·74	8·30 "
	0·5098	0·89840	1·36932	8·75	8·91 "
	1·2312	0·91484	1·37472	8·75	21·90 "
0·60	0·1022	0·84713	1·36696	-	-
	0·1893	0·85217	-	-	2·44 "
	0·3800	0·85699	1·37013	(8·50)	5·21 "
	0·6436	0·86326	1·37225	8·69	9·57 "
	0·9056	0·86919	1·37411	8·68	14·19 "
	1·5207	0·88330	1·37857	8·66	24·55 "
	1·9770	0·89212	1·38108	8·64	34·43 "
0·70	0·0000	0·83097	1·36678	-	-
	0·0833	0·83324	-	-	1·02 "
	0·1361	0·83481	-	-	1·38 "
	0·2442	0·83754	1·36896	8·60	2·92 "
	0·6830	0·84869	1·37264	8·65	9·00 "
	1·0173	0·85679	1·37522	8·63	14·08 "

Fig. 5.

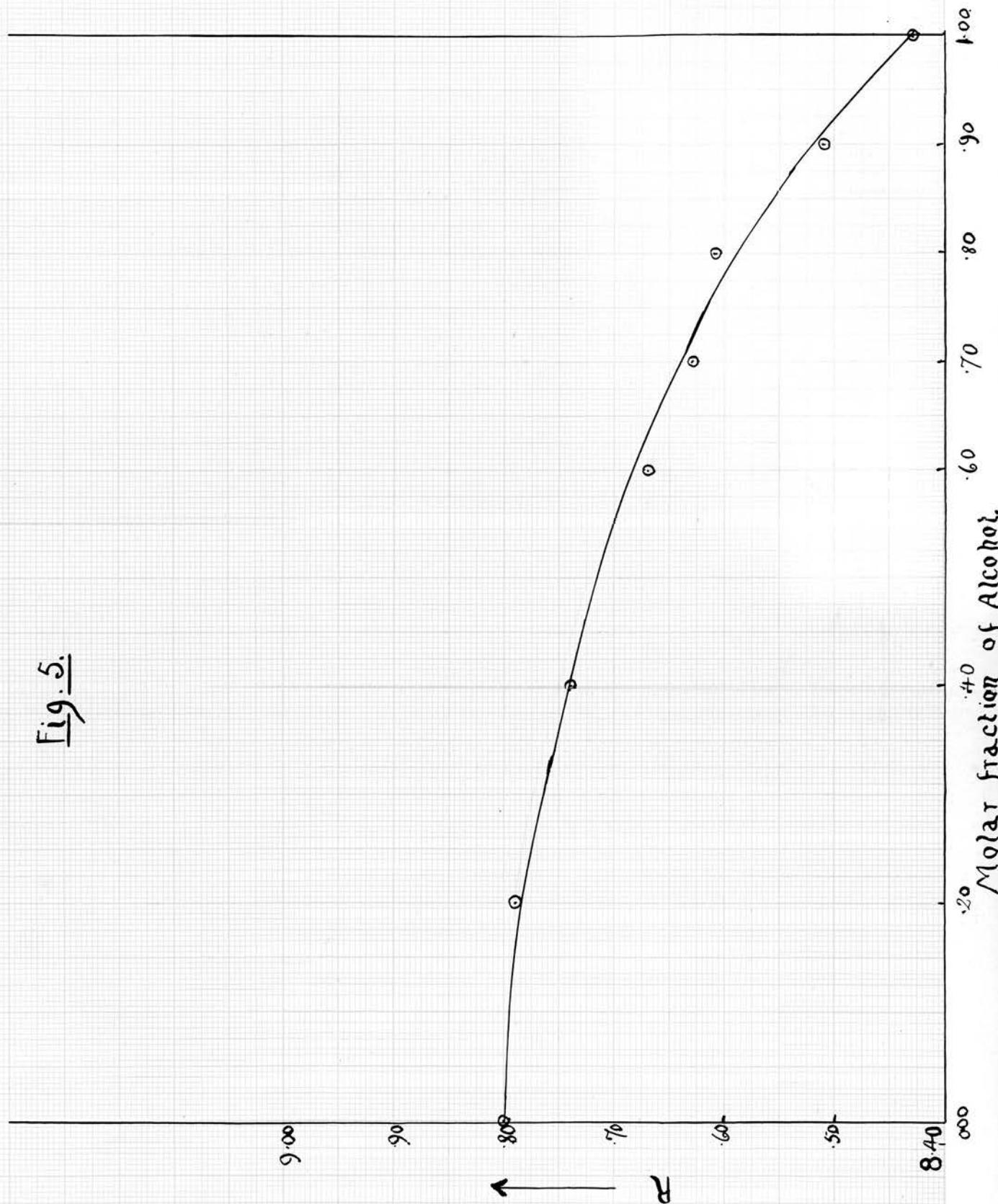


Fig. 6.

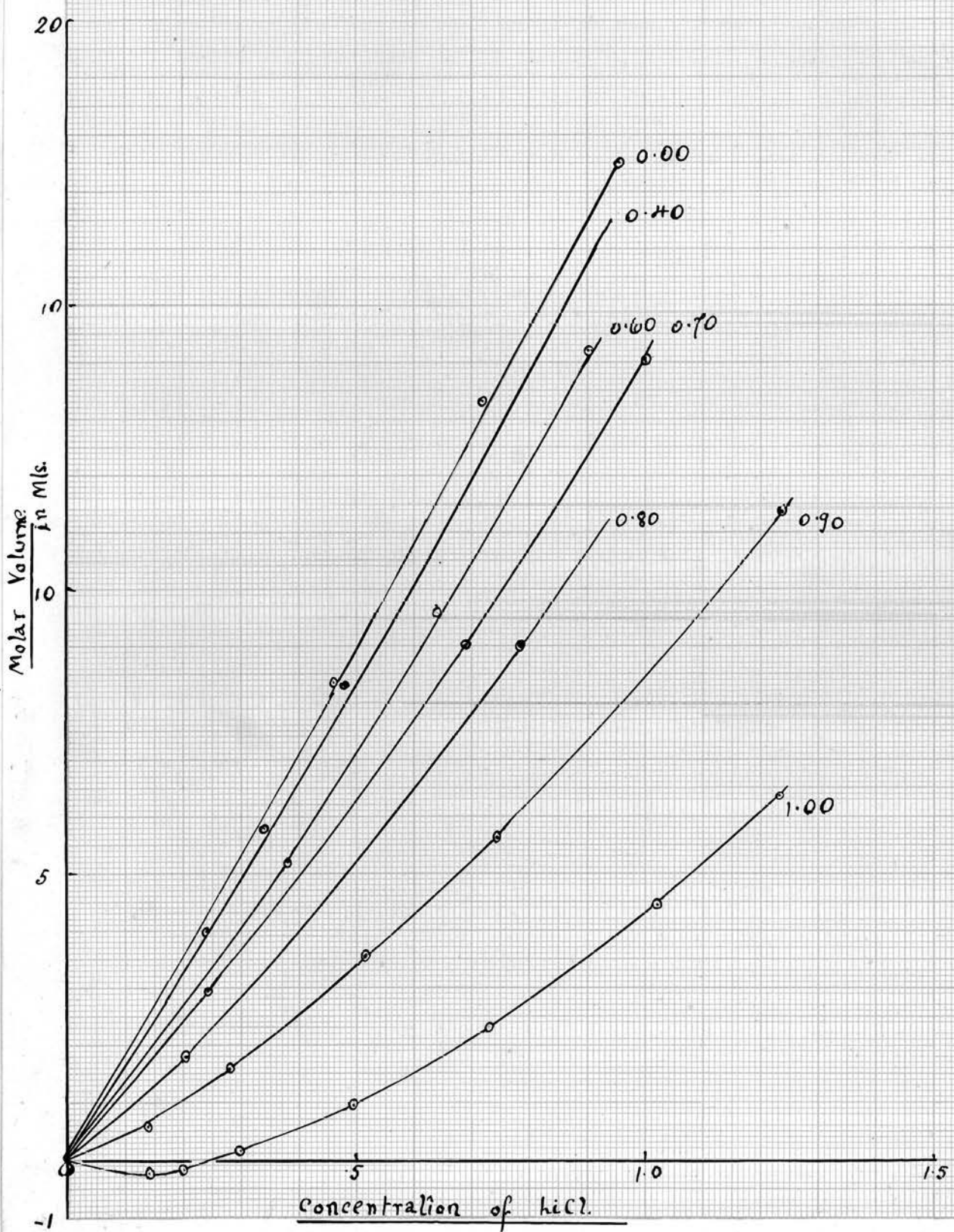


TABLE I. (Contd).

Molar fraction of Alcohol	Concentration of lithium chloride	18°1 d 4	18 n 5461	R 5461	$\Delta V = V - V_0$
0.80	0.0000	0.81664	1.36601	-	-
	0.2093	0.82267	-	-	1.81 Mls
	0.3786	0.82714	1.36958	8.64	3.85 "
	0.6023	0.83839	1.37330	8.60	8.81 "
	1.7392	0.86164	1.38078	8.59	21.66 "
0.90	0.0000	0.80321	1.36485	-	-
	0.1359	0.80745	-	-	0.60 "
	0.2800	0.81168	1.36780	8.50	1.63 "
	0.5188	0.81854	1.37013	8.50	3.56 "
	0.7426	0.82476	1.37225	8.53	5.66 "
	1.2301	0.83751	1.37645	8.52	11.30 "
1.00	0.0000	0.79084	1.36322	-	-
	0.1450	0.79584	-	-	-0.22 "
	0.2030	0.79776	-	-	-0.18 "
	0.3008	0.80082	-	-	+0.17 "
	0.4954	0.80683	1.36893	8.44	+0.98 "
	0.7334	0.81397	1.37140	8.43	+2.31 "
	1.0230	0.82224	1.37422	8.44	+4.47 "
	1.2339	0.82808	1.37615	8.42	+6.32 "

Taking the mean values for the molecular refractivity for each alcohol-water mixture, Fig.5 was obtained by plotting R against molar fraction of alcohol.

Fig.6 represents change of ΔV with concentration for the various alcohol-water mixture.

DISCUSSION.THE REFRACTIVITIES.

From the variation of refractivity of one mole of salt as shown by Fig.5. we can obtain some information concerning the relative amounts of alcohol and water molecules in the immediate vicinity of the ions.

The observed molecular refractivity of a salt in solution is dependant on:-

- (1) the polarisability of the ions themselves, and
- (2) the change in polarisability produced in the solvent molecules by their presence.

Remembering the expression $R = \frac{4}{3} \pi N \alpha$,

and referring to the mode of calculation of the refractivity of a salt in solution we can write.

$$\frac{n_i^2 - 1}{n_i^2 + 2} \cdot \frac{w + m}{d_i} = \frac{4}{3} \pi \left[\sum N_i \alpha_i + \sum N_s \alpha_s \right]$$

Where N_s is the number of solvent molecules in w gms. solvent for which the coefficient of polarisability for externally applied fields is α_s and N_i is the number of ions in m gms. of lithium chloride having the coefficient of polarisability α_i .

So also

$$\frac{n_o^2 - 1}{n_o^2 + 2} \cdot \frac{w}{d_o} = \frac{4}{3} \pi \sum N_s' \alpha_s'$$

Where α_s' is the coefficient of polarisability of the/

the solvent molecules in the absence of any ionic field.

So we may write:- $R = R_{\text{ions}} - R(\text{solvent})$

$$\text{where } R_{\text{ions}} = \frac{4}{3} \pi \frac{M}{m} \sum N_i \alpha_i$$

$$\text{and } \Delta R(\text{solvent}) = \frac{4}{3} \pi \left[\sum N_s' \alpha_s' - \sum N_s \alpha_s \right]$$

The molecular refractivity (R_D) of lithium chloride when completely ionised in the gaseous state according to Fajans and Joos (loc. cit.) is 9.20 ($\text{Cl}^- = 9.00$, $\text{Li}^+ = 0.2$).

Since the observed refractivities in water and alcohol (R_D) are 8.76 and 8.38 respectively, then

$$\Delta R(\text{solvent}) = 0.44 \text{ for water and } 0.82 \text{ for alcohol.}$$

Without laying any stress on those values it is evident that since the molecular refractivities of alcohol and water are 12.8 and 3.7 respectively,

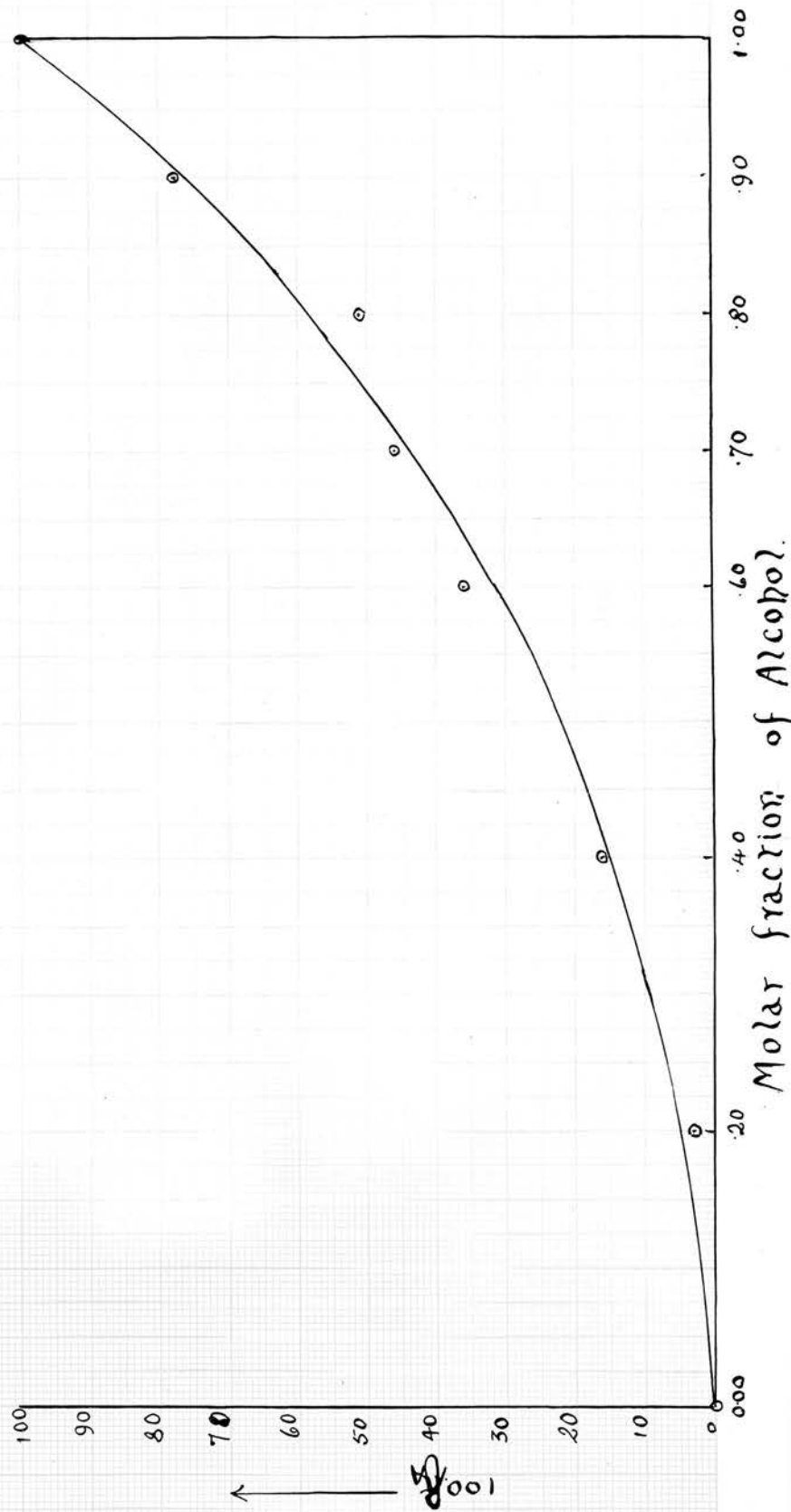
$\Delta R(\text{solvent})$ is only a small fraction of the total refractivity of the molecules which are in actual contact with the ions. Since the electric field decreases rapidly with distance from any ion it is reasonable to assume that only those molecules which are in actual contact with an ion have a lower polarisability than those which are not so situated.

In the case of a solvent containing two kinds of molecules we shall have:-

$$\Delta R(\text{solvent}) = \frac{4}{3} \pi \left[n_1 (\alpha_1' - \alpha_1) + n_2 (\alpha_2' - \alpha_2) \right]$$

where n_1 and n_2 are the numbers of the molecules of the two/

Fig. 7.



two kinds which are in contact with one gram molecule of the salt, and $\alpha'_1 - \alpha_1$, and $\alpha'_2 - \alpha_2$ the average difference in polarisability produced by the ions in those molecules.

Thus if we write:-

$$\Delta R_A = \frac{4}{3} \pi n_{o1} (\alpha'_1 - \alpha_1)$$

and

$$\Delta R_W = \frac{4}{3} \pi n_{o2} (\alpha'_2 - \alpha_2)$$

for the solvent effect of a gram molecule of the ions in alcohol and water respectively, we have:-

$$\frac{R_W - R_S}{R_W - R_A} = \frac{\Delta R_W - \Delta R_S}{\Delta R_W - \Delta R_A} = f_A$$

where the suffixes W, A and s refer to solutions in water alcohol and a mixed solvent respectively and

$f_A = \frac{n_2}{n_{o2}}$ is the ratio of the number of alcohol

molecules in contact with the ions in the given solvent to the corresponding number in pure alcohol.

The values so obtained for f_A are tabulated in Table II and Fig.7 is obtained by showing the change in this quantity with variation of mole fraction of alcohol.

TABLE II.

Values of f_A .

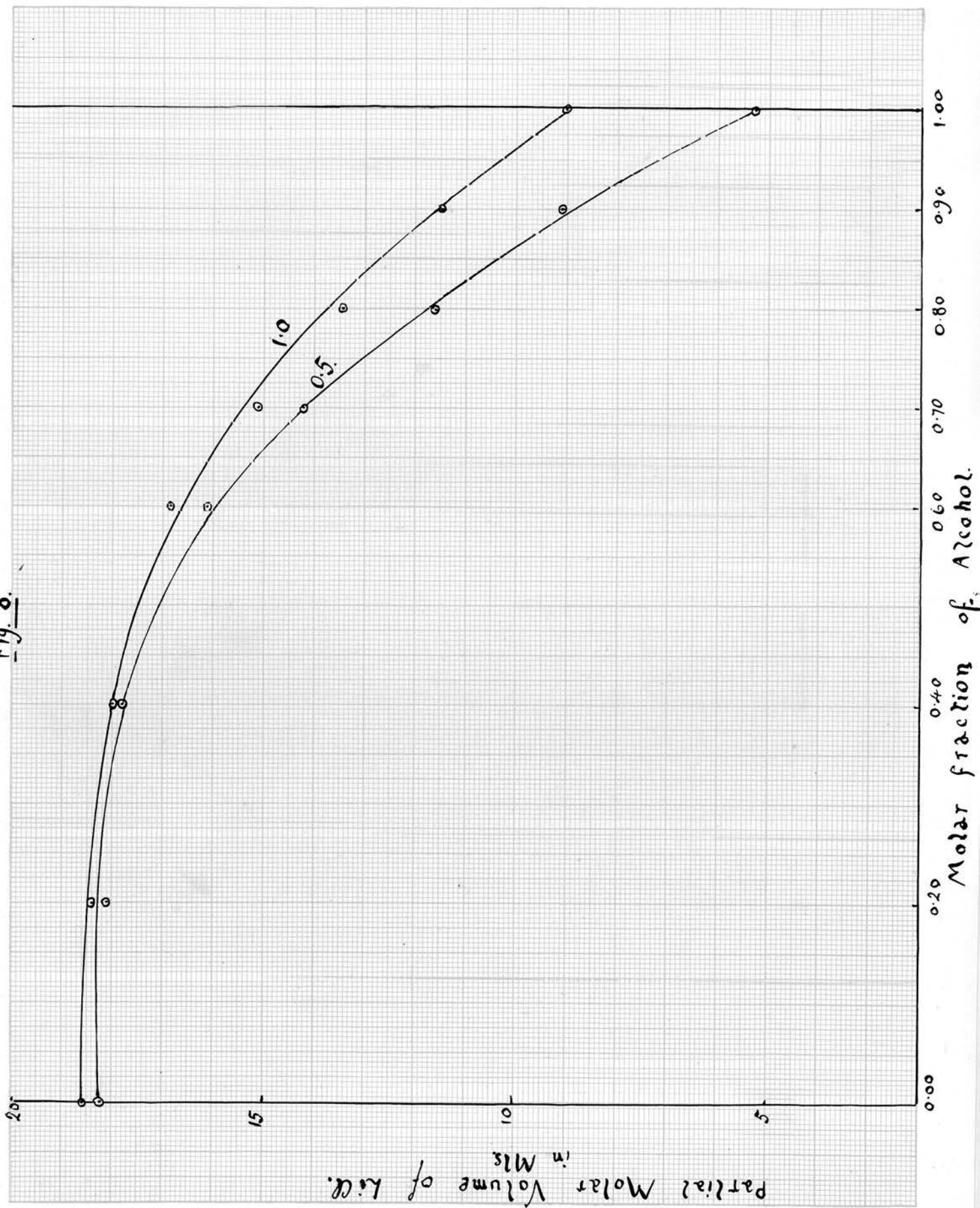
Molar fraction of alcohol	R	$100 \cdot \frac{R_W - R_S}{R_W - R_A}$
	5461	
0.00	8.80	0
0.20	8.79	3
0.40	8.74	16
0.60	8.67	36
0.70	8.63	46
0.80	8.61	51
0.90	8.51	78
1.00	8.43	100

Studying Figs.5 and 7 together it can be seen there is little change in R until the molar fraction of alcohol is greater than 0.20. Beyond this point it falls off steadily as the proportion of alcohol is increased, to the value for pure alcohol. We may therefore conclude that the ions are surrounded almost entirely by water molecules until the molar fraction of alcohol in the solvent reaches about 0.2. From this region the number of alcohol molecules in contact with the ions increases steadily as the proportion of alcohol is increased. These conclusions have been shown graphically in Fig.3, and are in agreement with those drawn by Shaw and Butler (loc. cit.) from a study of the vapour pressures of the same system.

THE PARTIAL MOLAR VOLUMES.

The variation of the densities of the solutions with lithium chloride concentration is greatly affected by the proportion of alcohol present. This may be illustrated by Fig.6 which shows the change of volume produced by the addition of the lithium chloride. Whereas the addition of lithium chloride to water gives rise to a nearly linear increase of volume, in alcohol it causes a decrease in the total volume at small concentrations and an increase at greater concentrations.

Fig. 8.



A more important quantity than the apparent volume in solution is the partial molar volume \bar{v} , defined as:-

$$\bar{v} = \frac{dV}{dc}$$

or the increase in volume caused by the addition of one gram mole of the substance to the solution assuming that the concentration of the various constituents do not change.

It may be obtained at any desired concentration by taking the slope of the curve ΔV against C at that concentration. The values so obtained for $C = 0.5$ and $C = 1.0$ are given in Table III and shown graphically in Fig.8.

TABLE III.

Partial Molar Volumes of Lithium Chloride.

Molar Fraction of alcohol	\bar{v}	
	$C = 0.5$	$C = 1.0$
0.00	18.3 Mls.	18.6 Mls.
0.20	18.1 "	18.4 "
0.40	17.8 "	17.9 "
0.60	16.1 "	16.8 "
0.70	14.2 "	15.1 "
0.80	11.6 "	13.5 "
0.90	9.1 "	11.6 "
1.00	5.2 "	8.1 "

We may first observe that the partial molar volumes of the salt in 100% alcohol are much smaller than in water. The molecular volume of solid lithium/

lithium chloride at 18°C is 20.5 mls (Baxter and Wallace (J. Amer. C.S. 38, 70, 1916)) Its partial molar volume at $C = 1$ is 18.6 mls. in water and 8.1 mls. in 100% alcohol. Referring to the definition of partial molar volume the difference between the molecular volume of the solid and its partial molar volume represents the contraction, per gram molecule of the salt when a small quantity is added to the given solution. There is a contraction of 1.9 mls. per gram molecule when lithium chloride is added to the solution in water where $C = 1$, and of 12.4 mls. per gram molecule when added to a solution in alcohol of the same strength. We have no means of determining how much of this change of volume is due to a change in the intrinsic volume of the lithium chloride and how much is due to the contraction of the solvent caused by the presence of the salt. But since it is entirely improbable that the intrinsic volume of lithium chloride in alcoholic solution is little more than one third of the volume of the solid salt, we must conclude that the contraction of the solvent (electrostriction) produced by the salt is considerably greater in alcohol than in water. It is possible that the determination of the partial molar volumes of a salt in a series of solvents would reveal some interesting effects.

Secondly, whereas in water an increase in concentration/

concentration of the salt causes only a small increase in the partial molar volume, in 100% alcohol it produces a very great change. The partial molar volume of lithium chloride in 100% alcohol as can be seen from Fig.6 is negative at small concentrations and increases rapidly with concentration, becoming 5.2 mls at $C = 0.5$ and 8.1 mls at $C = 1.0$.

Baxter and Wallace (loc. cit.) who determined the apparent molar volumes of the halogen salts of all the alkali metals in aqueous solution have advanced a theory to explain the increase in this quantity with increasing concentration. They postulate two opposing effects. One, that on solution in water there will be an increase in volume due to the ions so produced having a greater volume than the molecules of the solid salt. The second, that there will be a contraction in volume due to the electric forces set up between water molecule and charged ion. Whether there is an increase or decrease of the salt on solution will depend on the relative magnitude of these two effects.

It is clear that the changes in the partial molar volume of the lithium chloride in alcohol cannot be explained on the assumption of a great increase in the proportion of unionised molecules between $C = 0.5$ and $C = 1$. Such a change would be expected to cause variations in the molecular refractivity, unless the undissociated salt and its ions/

ions have the same molecular refractivity, which is unlikely. These variations have not been observed. The explanation must lie in the interaction of ions and alcohol molecules. It may be suggested that collisions between two ions, which become more frequent as the concentration is increased, cause a certain amount of disorientation of the sheaths of solvent molecules carried by them, and thus give rise to an increase of volume. This effect would be greater when the ions are surrounded by alcohol molecules, than those of water. A more detailed discussion, however, would be unprofitable with the data at present available.

Thirdly, one may consider the change in the partial molar volume with composition of the solvent, at constant concentration of lithium chloride. The form of the curves of Fig.8 is very similar to the variation of the molecular refractivities with composition of the solvent. The presence of alcohol up to a molar fraction of about 0.4 causes only a small change in the partial molar volume, but in solvents containing a greater proportion of alcohol the value decreases steadily. Similar conclusions may be drawn to those considered from the refractivity data.

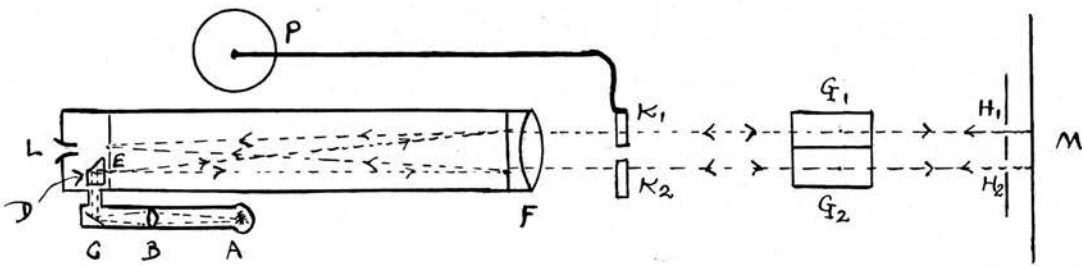
It is noteworthy that whereas Walden (loc. cit.) found that the refractivity of tetraethyl ammonium iodide/

iodide varied inversely as its apparent molecular volume in a series of solvents, in the case of lithium chloride the refractivity decreases in the same direction as but to a much smaller extent than the change in volume. Walden's relation, therefore, cannot be generally true.

SUMMARY.

- (1) The molecular refractivities and partial molar volumes of lithium chloride have been determined in a series of water-alcohol mixtures.
- (2) The molecular refractivity in each solvent is constant over the range of concentrations investigated. It is hardly affected by the presence of alcohol until the molar fraction of the latter is over 0.20. With greater proportions of alcohol it falls off steadily to the value for pure alcohol.
- (3) On certain assumptions, the proportions of water and alcohol molecules in contact with the ions have been calculated. The proportion of water molecules in contact with the ions is always greater than their proportion in the solvent.
- (4) The partial molar volumes of lithium chloride is much smaller in 100% alcohol than in water and increases rapidly with the concentration. Its variation with the composition of the solvent, at a constant concentration of the salt, is similar to the refractivity.

Fig. 9.



Essential Parts of the Interferometer.

THE INTERFEROMETER.

As mentioned in the experimental section it was intended to measure the refractive indices by means of the interferometer. It is proposed to give here, a brief account of the use of the instrument and explain how the "apparent refractive index" as measured on it differs from the true refractive index as measured on the Pulfrich refractometer.

The interferometer was of the Zeiss pattern which is a modification of the Rayleigh interferometer. A detailed description of the instrument and the theory underlying its use has been given by L.H. Adams (J.A.C.S. 37, 1189, 1915).

A sketch of the instrument is shown.

After passing through the lens B, the mirror C, and the totally reflecting prism D, the light from the lamp A after being focussed at the slit E passes through the collimating lens F and thence through the two chambers G_1 , G_2 , composing the cell which can be removed. The two beams thus produced then pass through the rectangular slits H_1 and H_2 , and are reflected back on themselves by means of the mirror M to meet at N, forming a set of interference fringes which are viewed through the eyepiece L.

Besides/

Besides this pair of interfering beams another pair start from E in the same way and pursue similar paths to the first pair except that they pass underneath the cell containing the two chambers. The set of fringes produced by the second pair of interfering beams is fixed in position, its purpose being to furnish a set of fiduciary lines on which the other set of fringes may be measured. In fact these fringes may be regarded as taking the place of the cross wires in optical instruments. The first pair of beams also pass through two compensating plates K_1 , K_2 , one of which K_2 is fixed whilst the other K_1 may be inclined to the beam of light by turning the drum P, thereby increasing the optical path.

Using monochromatic light the two beams of the first pair reinforce each other when the optical path difference corresponds to 0, 1, 2, 3 etc., complete wave lengths and interfere when it corresponds to $\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, etc., wave lengths difference. The centre of the series of fringes is thus bright when the wave length difference of the two paths differ by a whole number. Turning the drum we therefore get a bright fringe every time this condition is satisfied.

We may therefore calibrate the drum to give directly the displacement in wave lengths caused by turning the drum through any number of divisions.

The/

The source of monochromatic light was a mercury arc lamp using the violet and green lines ($\lambda = 4359 \text{ \AA}.$ and $5461 \text{ \AA}.$). The small electric lamp and holder were removed and by an arrangement of lenses and mirror the light from the arc lamp allowed to replace it, appropriate light filters being interposed to give monochromatic light of the wave length desired. A continuous series of fringes was seen in the upper half of the field of view. A fringe about zero was taken as starting point and the drum readings taken at intervals of five fringes for each wave length. The cell was removed during the calibration.

Table IV gives the result of this calibration.

TABLE IV.

TABLE IV.

CALIBRATION.

$\lambda = 5461 \text{ \AA. U.}$		$\lambda = 4359 \text{ \AA. U.}$	
DRUM READING	FRINGES	DRUM READING	FRINGES
0	0	105	0
66	5	157	5
132	10	210	10
198	15	262	15
264	20	318	20
331	25	370	25
339	30	423	30
466	35	477	35
534	40	530	40
602	45	583	45
670	50	638	50
739	55	693	55
809	60	748	60
879	65	804	65
950	70	860	70
1021	75	913	75
1092	80	968	80
1163	85	1025	85
1234	90	1093	90
1306	95	1149	95
1378	100	1205	100
1451	105	1263	105
1525	110	1321	110
1600	115	1378	115
1675	120	1437	120
1750	125	1496	125
1825	130	1553	130
1900	135	1613	135
1976	140	1671	140
2052	145	1730	145
2129	150	1790	150
2207	155	1850	155
2286	160	1910	160
2365	165	1970	165
2444	170	2031	170
2524	175	2091	175
2604	180	2153	180
2684	185	2217	185
2765	190	2280	190
2847	195	2215	195
		2400	200
		2465	205
		2530	210
		2592	215
		2658	220
		2722	225
		2787	230
		2852	235
		2919	240
		2983	245

Now suppose that the cell is in position and the refractive indices of the liquids in the two halves are n_2 and n_1 . The change in the optical paths of the beams, as a result of the interposition of the two liquids in the paths of the beams, will be

$$\frac{n_1 l}{\lambda} \text{ and } \frac{n_0 l}{\lambda} \text{ wave lengths.}$$

Where λ is the wave length of the light used and l is $2 \times$ the length of the chambers, since each chamber is traversed twice by each beam.

The optical path difference between the beams is $\frac{(n_1 - n_0) l}{\lambda}$ wave lengths.

If we turn the drum until this difference is compensated and knowing the optical path difference corresponding to the drum reading we find:-

$$\frac{(n_1 - n_0) l}{\lambda} = N$$

Where N is the number of fringes corresponding to the drum reading, after subtracting the zero error.

In practice it is impossible to work with monochromatic light for there is no means of knowing which bright fringe corresponds to zero path difference. Using a continuous source of light the fringes of the different colours are confused and so produce a continuous illumination, but there is in general one position of the drum where bands are produced, namely when fringes of all colours fall on the same, or nearly the same position. The fringe which is pure/

pure white should correspond to zero path difference whilst those on either side of it will be tinged with blue on the side nearer the centre fringe and red on the side away from it. This position may, however, differ from the position of equal optical path for each beam due to a wandering of the true achromatic fringe, so that while $\frac{(n_1 - n_0) l}{\lambda} = N$

holds approximately it cannot be used for the determination of the precise value of $n_1 - n_0$. The following table will illustrate this.

Zero of instrument = 108 drum divisions.

Length of chambers = 0.995 cm.

$$l = 1.99 \text{ cm.}$$

"g" and "v" refer to the green and violet lines respectively.

$$\therefore \Delta n_g = (n_1 - n_0)_g = \frac{N \times 5461 \times 10^{-8}}{1.99}$$

The two liquids compared are water and dilute aqueous solutions of lithium chloride.

TABLE.

Solution	Δn_g (Pulfrich)	Apparent Δn_g (Interfer)
.0585 M	0.00057	0.00059
.2040 M	0.00188	0.00204
.3173 M	0.00289	0.00310

This/

This wandering of the true achromatic fringe has been explained by Adams, but the following theory which is new is simpler, and also permits the calculation of the dispersion difference between the liquids for two wave lengths when the optical calibration of the instrument has been carried out for these wave lengths.

Consider two wave lengths λ_v and λ_g . Let the optical path difference of the solutions be

$$\frac{(n_1 - n_0)_v l}{\lambda_v} \quad \text{and} \quad \frac{(n_1 - n_0)_g l}{\lambda_g}$$

Let the optical path introduced by the compensator in the two cases be N_v and N_g wave lengths. Here the condition for superposition of the fringes of each wave length is:-

$$\frac{(n_1 - n_0)_v l}{\lambda_v} - N_v = \frac{(n_1 - n_0)_g l}{\lambda_g} - N_g$$

Let the dispersion difference for the two wave lengths:-

$$(n_1 - n_0)_v - (n_1 - n_0)_g \text{ be equal to } D.$$

Let/

Let n (glass) be the refractive index of the glass of the compensator and d its thickness.

Then,

$$\left[\frac{(n_i - n_o)_v}{\lambda_v} - \frac{(n_i - n_o)_g}{\lambda_g} \right] \cdot l = N_v - N_g$$

$$= \frac{n_v(\text{glass})}{\lambda_v} - \frac{n_g(\text{glass})}{\lambda_g}$$

since $N \cdot \lambda = n_{\text{glass}} \cdot d$.

$$\left[\frac{(n_i - n_o)_v}{\lambda_v} - \frac{(n_i - n_o)_g}{\lambda_g} \right] \cdot l = \left[\frac{(n_i - n_o)_g}{\lambda_g} - \frac{(n_i - n_o)_g}{\lambda_v} \right] \cdot l$$

$$+ \left[\frac{n_v(\text{glass})}{\lambda_v} - \frac{n_g(\text{glass})}{\lambda_v} \right] \cdot d$$

$$+ \left[\frac{n_g(\text{glass})}{\lambda_v} - \frac{n_g(\text{glass})}{\lambda_g} \right] \cdot d$$

$$(n_i - n_o)_g \left[\frac{1}{\lambda_g} - \frac{1}{\lambda_v} \right] \cdot l = \frac{D \cdot l}{\lambda_v} - n_g(\text{glass}) \left[\frac{1}{\lambda_v} - \frac{1}{\lambda_g} \right] \cdot d$$

$$- \frac{d}{\lambda_v} \left[\frac{n_v(\text{glass}) - n_g(\text{glass})}{\lambda_g - \lambda_v} \right]$$

$$\frac{(n_i - n_o)_g}{\lambda_g} \cdot l = \frac{n_g(\text{glass}) \cdot d}{\lambda_g} - \frac{D \cdot l}{\lambda_g - \lambda_v}$$

$$+ d \cdot \left[\frac{n_g(\text{glass}) - n_v(\text{glass})}{\lambda_g - \lambda_v} \right]$$

$$= N_g - \frac{D \cdot l}{\lambda_g - \lambda_v}$$

$$+ \frac{N_g \lambda_g - N_v \lambda_v}{\lambda_g - \lambda_v}$$

$$(n_i - n_o)_g = \frac{N_g \lambda_g}{l} - \frac{\lambda_g}{\lambda_g - \lambda_v} \cdot D$$

$$+ \frac{\lambda_g}{l(\lambda_g - \lambda_v)} [N_g \lambda_g - N_v \lambda_v]$$

That/

That is to say, the original simpler expression,

$$(n_1 - n_0)_g = \frac{N_g \lambda_g}{l}$$

is subject to two correcting factors,

Firstly,
$$- \frac{\lambda_g}{\lambda_g - \lambda_v} \cdot D.$$

due to the difference in the dispersions of the two liquids,

and secondly,
$$+ \frac{\lambda_g}{l(\lambda_g - \lambda_v)} (N_g \lambda_g - N_v \lambda_v)$$

which corrects for the dispersion effect of the glass of the compensator plate.

Modifying the calibration table slightly so that zero fringe for each wave length occurred at zero of the instrument, $N_g \lambda_g$, and $N_v \lambda_v$, were respectively plotted against drum reading. Their graphs were found to lie very close together. It appears that while the dispersion effect of the glass is not negligible the main discrepancy is caused by the difference in the dispersions of the two liquids.

D may be found accurately as follows:-

$$\begin{aligned} & \left[\frac{(n_1 - n_0)_v}{\lambda_v} - \frac{(n_1 - n_0)_g}{\lambda_g} \right] \cdot l = N_v - N_g \\ & \left[\frac{(n_1 - n_0)_v}{\lambda_v} - \frac{(n_1 - n_0)_g}{\lambda_v} \right] \cdot l \\ & = \left[\frac{(n_1 - n_0)_g}{\lambda_g} - \frac{(n_1 - n_0)_g}{\lambda_v} \right] l + N_v - N_g \end{aligned}$$

$$\frac{D \cdot l}{\lambda_v} = (n_1 - n_0)_g \left[\frac{l}{\lambda_g} - \frac{l}{\lambda_v} \right] + N_v - N_g$$

$$D = (n_1 - n_0)_g \cdot \frac{\lambda_v - \lambda_g}{\lambda_g} + \frac{N_v - N_g}{l} \cdot \lambda_v$$

$$D = -0.201 \Delta n_g + 0.0000219 (N_v - N_g)$$

Δn_g is got from the Pulfrich.

N_v and N_g are obtained from the calibration table.

In this method the value of Δn_g is not used itself, but one fifth of it. The error in the Pulfrich readings is reduced therefore to one fifth. In the reading of the interferometer an error of one fringe is possible, in fact probable when the reading is high on the drum. This affects the absolute values of N_g and N_v , but in $(N_v - N_g)$ the error is much smaller. The error in D probably does not exceed $\pm .000005$, an accuracy greater than that obtainable by the Pulfrich alone.

A few determinations of D were made and are shown in the table.

TABLE VI./

TABLE VI.

Mol. fract. of alcohol	Conc. of Lithium Chloride	Drum Reading	N_g	N_v	$N_v - N_g$	ng	D
0.00	0.2040	1130	74.5	93.0	18.5	0.00188	0.000029
0.00	0.3173	1694	113.1	141.8	28.7	.00289	.000047
0.20	0.2206	1082	71.1	88.8	17.7	.00180	0.000025
0.20	0.3559	1705	113.8	142.7	28.9	.00291	.000045
0.60	0.1893	992	64.8	81.9	17.1	.00167	0.000038
0.60	0.3800	1880	125.5	157.3	31.8	.00317	.000059
1.00	0.2030	1444	96.3	120.3	24.0	.00238	0.000046
1.00	0.3008	2100	139.9	175.6	35.7	.00358	.000062

S U M M A R Y.

- (1) The Zeiss Interferometer is not suitable for the determination of the absolute values of refractive index differences. This is due to the "wandering" of the true achromatic fringe. An explanation of this phenomenon has been given.

 - (2) In conjunction with the Pulfrich refractometer it is possible to obtain very accurately the dispersion change for two given wave lengths, as a result of adding a salt to a solvent.
-

The Effect of Lithium Chloride
on the Surface Tension of Water-Alcohol Mixtures.

Introduction.

A number of investigations of the effect of salts on the surface tensions of substances has been made, e.g., Freundlich and Schnell (Zeit.f.physik.Chem. 133, 1928, 151.) and Palitzsch (Zeit. f. physik. Chem., 147, 1930, 51.), and attempts have been made to determine the adsorptions by the Gibbs equation :

$$\frac{d\rho}{du_B} = - \Gamma'_B \dots \dots \dots (1).$$

where ρ is the surface tension, u_B is the partial free energy of the substance B, and Γ'_B , its excess at the surface. This equation can not be applied to a three component system for the complete equation of Gibbs for a ternary system having the components A, B, and S,

$$\text{is : } \Gamma'_A \cdot du_A + \Gamma'_B \cdot du_B + \Gamma'_S \cdot du_S + d\rho = 0 \dots \dots (2).$$

but since the dividing surface up to which the solution is perfectly homogeneous is not fixed, it may be so defined that $\Gamma'_A = 0$ and (2) becomes :

$$\Gamma'_B \cdot du_B + \Gamma'_S \cdot du_S + d\rho = 0 \dots \dots \dots (3).$$

This equation only reduces to (1) when the variation of u_S is negligible compared with the variation of u_B . This will be the case when the concentration of B is very small, but it ceases to hold when this condition is not fulfilled. It will also cease to be the case when $\Gamma'_S = 0$ for the same dividing surface.

In the case of a solution of two substances

A and B and a salt S, it is more convenient to fix the dividing surface so that Π_S is zero, i.e., in such a position that the quantity of salt present would reach this surface if the composition of the solution remained unchanged up to it. The values of Π_A and Π_B are then equal to the differences between the actual amounts of these substances present, at or near the surface, and their amounts if the solution remained homogeneous up to the dividing surface previously defined. Equation (2) then becomes :

$$\Pi_A \cdot du_A + \Pi_B \cdot du_B + d\phi = 0 \dots \dots \dots (4).$$

This equation is thermodynamically exact, but it contains two unknown quantities, Π_A and Π_B , so that, even if the variation of $d\phi$ for known variations of du_1 and du_2 is known, these can not be evaluated. But the composition of a ternary solution, e.g., of water, alcohol and salt, can be varied in two distinct ways, (i) by varying the proportion of alcohol, keeping the amount of salt constant, (ii) by varying the salt concentration in solvents of fixed composition. For any given solution we may thus obtain two equations similar to (3), corresponding to variations of these two kinds, viz.,

$$\left. \begin{aligned} \Pi_A \cdot du_A + \Pi_B \cdot du_B + d\phi &= 0 \dots \dots \dots \\ \Pi_A \cdot du'_A + \Pi_B \cdot du'_B + d\phi' &= 0 \dots \dots \dots \end{aligned} \right\} \dots \dots \dots (5).$$

Knowing the corresponding values of $d\phi$, du_A , du_B and $d\phi'$, du'_A , du'_B , Π_A and Π_B can now be evaluated.

The partial free energies of the substances per mole are given by the equations :

$$\left. \begin{aligned} u_A &= u_A^\circ + RT \cdot \log p_A \cdot \cdot \\ u_B &= u_B^\circ + RT \cdot \log p_B \cdot \cdot \end{aligned} \right\} \dots (6).$$

where p_A and p_B are the partial vapour pressures of A and B respectively. Hence, if we take variations for which $d\rho = d\rho'$ we have

$$\bar{\Gamma}'_A \cdot d \log p_A + \bar{\Gamma}'_B \cdot d \log p_B = \bar{\Gamma}'_A \cdot \log p'_A + \bar{\Gamma}'_B \cdot \log p'_B$$

$$\text{or } \frac{\bar{\Gamma}'_B}{\bar{\Gamma}'_A} = - \frac{d \log p_A - d \log p'_A}{d \log p_B - d \log p'_B} \dots (7).$$

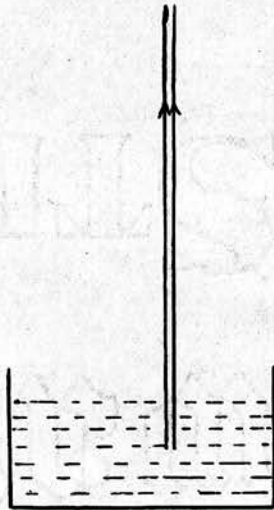
While the excess of a substance which is present in very dilute solution can be identified with the actual amount adsorbed at the interface, this is not the case in concentrated solutions. In the case of alcohol and water, it has been shown by Schofield and Rideal that as the proportion of alcohol is increased the excess of alcohol at the interface rises to a maximum and then decreases. The cause of this phenomenon and the actual state of the interface are still unknown. It is evident that the method outlined above, if sufficient data were available, permits the determination of $\bar{\Gamma}'_A$ and $\bar{\Gamma}'_B$ with reference to a third substance.

The partial vapour pressures of water and alcohol in solutions containing lithium chloride have been determined by Shaw and Butler (loc.cit.) and this is the only system for which this information is available. The measurements given below were undertaken as a preliminary test of the feasibility of the

method outlined above. It is not at present possible to include the whole range of compositions, for the surface tension lowering of the alcohol is already vary great in the most dilute solution investigated by Shaw and Butler. Further vapour pressure measurements are in progress in the laboratory and it is hoped that it will be possible eventually to deal with the complete range of composition of the alcohol-water solvents.



Fig. 10.



Experimental.

The capillary rise method was employed in the measurement of the surface tensions of the liquids.

If a capillary tube dips into a liquid which wets glass, such as alcohol or water, the liquid will tend to rise up the tube in its effort to spread over the glass surface, as shown by the arrows in the diagram. This upward force due to surface tension is, however, opposed by the weight of the column of liquid raised. Equilibrium will be established when the two forces balance.

The force acting upwards due to surface tension is

$$2\pi r\rho$$

and the force acting downwards due to the weight of the liquid raised is

$$\pi r^2 h d g,$$

where r = the radius of the capillary,

ρ = the surface tension of the liquid,

h = the capillary rise observed,

d = the density of the liquid and

g = the acceleration due to gravity.

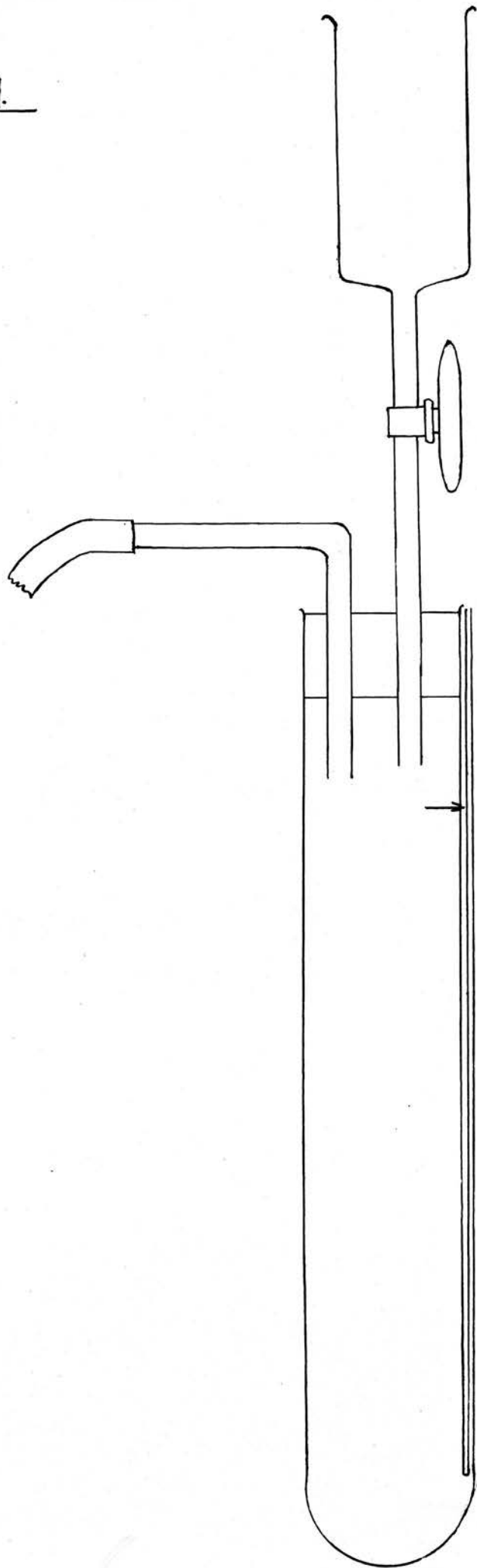
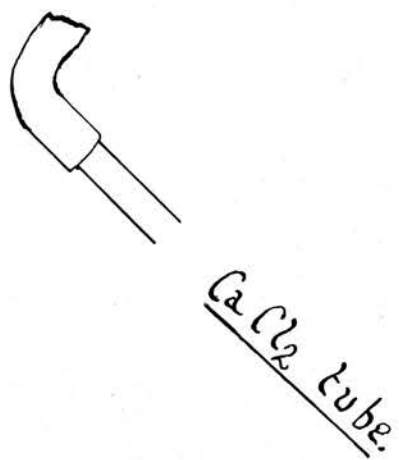
Hence,

$$\rho = 1/2 r h d g.$$

In the actual determination of the capillary rise, the procedure of Richards and Coombs (J.A.C.S., 37, 1915, 1656.) was adhered to.

By drawing out a piece of capillary tubing in a fish-tail flame, a capillary was obtained after

Fig. 11.



several attempts in which alcohol showed a rise of about 8 cm. It was sealed on a wide tube of about 2 cm. diameter to form a U-tube.

After being well cleaned with a mixture of sulphuric acid and potassium dichromate, a few preliminary experiments were carried through with the apparatus. Pure alcohol was used and varying amounts put into the wide tube by the method about to be described and a part of the capillary tube selected where the radius appeared to be constant over a short length, as was shown by the regularity of the distance between the two menisci. A fine mark was made on the wide tube opposite this place.

In measuring the capillary rise for the various liquids the wide tube was fitted with a double-bored stopper through which passed a small dropping-funnel with tap and a tube with a length of rubber tubing and calcium chloride tube for blowing. By means of this arrangement it was possible to measure the capillary rise with a falling capillary by blowing and also by adding the liquid drop by drop to arrange that the capillary meniscus was always measured at the same part of the capillary tube.

The U-tube was placed in a small thermostat with plate-glass windows behind and in front. A sheet of white paper covered the rear window and illumination was supplied with two electric lamps. The difference in the heights of the two menisci was measured with a carefully levelled cathetometer-telescope.

In defining the lower meniscus, a device of Richards and Coombs was used. A moveable screen made of black cardboard and having a sharp upper edge was hung over the back of the thermostat. In reading the level of the lower meniscus, this upper edge was arranged to be tangential to the meniscus, which then became sharply defined.

The densities of the liquids were obtained as before.

Solutions of lithium chloride in alcohol-water mixtures of 1.00, 0.80, 0.50, 0.25, 0.064, and 0.00 molar fraction of alcohol were prepared.

One U-tube was found to be sufficient for all the solutions except those in aqueous solution, where another U-tube was used with a wider capillary. These tubes were calibrated with alcohol and water respectively, assuming the surface tension of alcohol to be 21.85 dynes/cm. and that of water to be 71.97 dynes/cm. (International Critical Tables values.)

The method of calculation given is not strictly correct since the formula:-

$$\rho = \frac{h d g}{2 \left(\frac{1}{b_1} - \frac{1}{b_2} \right)}$$

Where b_1 and b_2 are the radii of curvature at the lowest points of the menisci in the narrow and wide tubes respectively, has been shown to be more correct than the simpler expression.

$$\rho = \frac{1}{2} r h d g$$

Sudgen (J.C.S., 119, 1921, 1483) has evolved a method of obtaining the correct values in surface tension measurements and also produced tables used in the calculations.

The method will be more easily explained by actually working out examples.

A quantity much used in surface tension work is the "capillary constant" denoted by " a^2 " such that

$$a^2 = rh \quad \text{or} \\ = h / (1/b_1 - 1/b_2) ,$$

according to which formula is used.

Let r_1 and r_2 be the radii of the narrow and wide tubes respectively. Consider the calibration with pure alcohol. In the case of the wide tube, to a first approximation,

$$a^2 = \frac{\sqrt{2 \cdot \rho}}{g \cdot d} = 5.676 \text{ sq. mm.} \\ = 2.382 \text{ mm.}$$

r_2 was found to be 9.7 mm. by actual measurement.

$$\text{Thus } r_2/a = 9.7 / 2.382 \\ = 4.072.$$

Now, knowing r/a , we can obtain r/b from Sudgen's table. Thus,

$$r_2 / b_2 = 0.054.$$

$$\text{Therefore, } b_2 = 9.7 / 0.054 \\ = 180 \text{ mm.}$$

$$\text{Since } a_2 = h / (1/b_1 - 1/b_2) \\ h = 76.2 \text{ mm.}$$

$$\text{we obtain } 5.676 = 76.2 / (1/b_1 - 1/180)$$

$$\text{giving } b_1 = 0.07446 \text{ mm.}$$

Putting $r_1 = b_1$ and repeating the process,

$$\begin{aligned} r_1 / a &= 0.07446 / 2.382 \\ &= 0.03128. \end{aligned}$$

From the table,

$$r_1 / b_1 = 0.9997.$$

Therefore,

$$r_1 = 0.07444 \text{ mm.}$$

Let us take as a typical solution, say, that with 0.25 mole fraction of alcohol.

The observed height (h) = 84.7 mm.

So that $a^2 = rh = 84.7 \times 0.07444 = 6.31 \text{ sq. mm.}$

Thus, $a = 2.51 \text{ mm.}$

Therefore,

$$r_2 / a = 9.7 / 2.51 = 3.87.$$

And, from the table,

$$r_2 / b_2 = 0.063.$$

Therefore,

$$b_2 = 154 \text{ mm.}$$

Also,

$$\begin{aligned} r_1 / a &= 0.07444 / 2.51 \\ &= 0.03966. \end{aligned}$$

From the table,

$$r_1 / b_1 = 0.9997.$$

Therefore,

$$b_1 = 0.07446 \text{ mm.}$$

Since,

$$\rho = \frac{h d g.}{2 \left(\frac{1}{b_1} - \frac{1}{b_2} \right)} \quad (d = 0.9185)$$

Therefore,

$$\rho = 28.45 \text{ dynes/cm.}$$

Using the simpler formula:-

$$\frac{\rho_1}{\rho_0} = \frac{\frac{1}{2} r h_1 d_1 g}{\frac{1}{2} r h_2 d_0 g}$$

$$\rho_1 = \frac{h_1 d_1}{h_0 d_0} \times 21.85$$

Where ρ_1 , d_1 , b_1 and ρ_0 , d_0 , b_0 refer to the mixed solvent and alcohol respectively

$$\begin{aligned} \rho_1 &= \frac{8.47 \times 0.9}{8.72 \times 0.7849} \times 21.85 \\ &= 28.42 \text{ dynes./cm.} \end{aligned}$$

It can be seen that the error incurred is very small for this particular tube. It was not, therefore, considered necessary to make any corrections since the error involved is no greater than the experimental error. A similar statement can be made concerning the other tube used for the pure water solutions.

TABLE VII./

RESULTS.

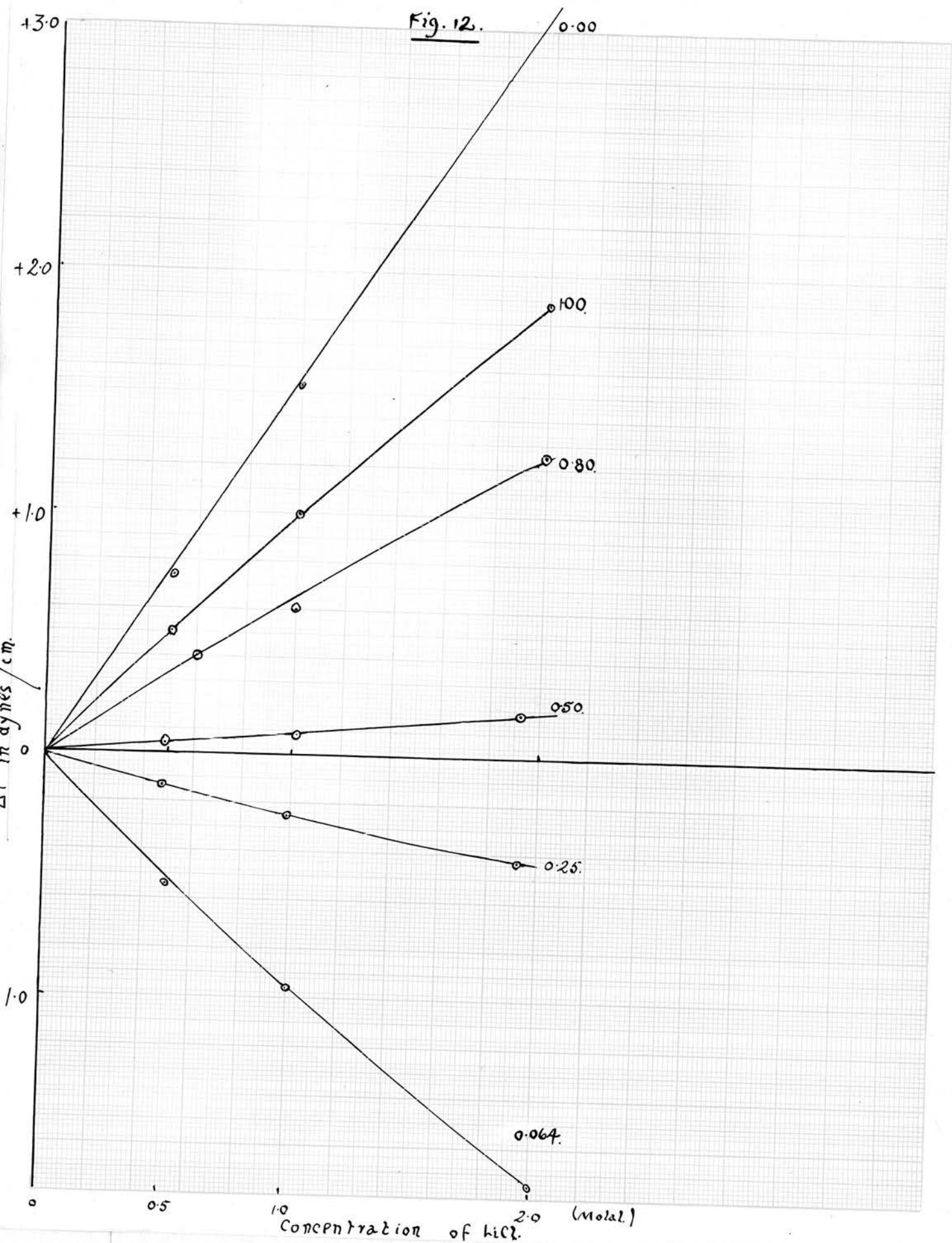
The following table gives the observed capillary rises together with the surface tensions derived from them for the various solutions. The changes in surface tension as a result of the addition of lithium chloride are also shown.

TABLE VII.

Molar fract. of alcohol.	Concentration of LiCl	D_4^{25}	h (Cms.)	ρ dynes/Cm.	$\Delta\rho$
1.00	-	0.7849	7.62	21.85	-
	0.500	0.8013	7.64	22.36	+ 0.51
	1.000	0.8164	7.66	22.85	+ 1.00
	1.995	0.8425	7.710	23.75	+ 1.88
0.80	-	0.8109	7.83	23.19	-
	0.608	0.8273	7.81	23.59	+ 0.40
	1.000	0.8373	7.78	23.79	+ 0.60
	2.000	0.8632	7.75	24.44	+ 1.25
0.50	-	0.8652	8.12	25.65	-
	0.465	0.8761	8.03	25.69	+ 0.04
	1.025	0.8887	7.797	25.73	+ 0.08
	1.890	0.9077	7.79	25.83	+ 0.18
0.25	-	0.9185	8.47	28.42	-
	0.474	0.9294	8.33	28.28	- 0.14
	0.985	0.9405	8.20	28.17	- 0.25
	1.934	0.9600	7.98	27.99	- 0.43
0.064	-	0.9735	11.81	42.00	-
	0.500	0.9852	11.52	41.46	- 0.54
	1.000	0.9960	11.28	41.04	- 0.96
	2.000	0.0180	11.82	40.23	- 1.77
0.00	-	0.9970	13.48	71.97	-
	0.500	1.0082	13.47	72.71	+ 0.74
	1.000	1.0191	13.47	73.50	+ 1.53
	2.000	1.0411	13.51	75.31	+ 3.24

Fig.12 shows the manner in which $\Delta\rho$ varies in the various alcohol-water mixtures.

Fig. 12.



DISCUSSION.

It can be seen from Fig.12 that the rise in surface tension caused by the addition of lithium chloride decreases and actually becomes negative in solvents containing 0.25 and 0.064 molar fractions of alcohol. Between the change produced in this last solvent and that in pure water there is a remarkable difference. Incidentally the addition of lithium chloride to a solvent of composition about 0.40 molar fraction of alcohol should cause no change in the surface tension of the solvent.

These results are to be expected from a study of the partial vapour pressures of alcohol and water in these solutions. In these solutions the lithium chloride may be considered as having two effects:-

(1) Like most other inorganic salts, lithium chloride raises the surface tension of pure alcohol and pure water.

(2) In some of the solutions considered it increases the partial vapour pressure of the alcohol and in all the solutions it lowers the partial vapour pressure of the water more than the alcohol. In general, therefore, it causes a relative increase in the activity of the alcohol and this produces a lowering of the surface tension, since the presence of alcohol in the surface layer/

layer is favoured. In mixed solutions, then, the change in surface tension caused by the salt is always less than in the pure solvents.

In order to evaluate $\frac{T_B}{T_A}$ equation 7 was used. The data required have been summarised in table VIII.

Let p_B and p_A denote the partial vapour pressures of alcohol and water, respectively, obtained from the results of Shaw and Butlen.

Values not obtained directly have been interpolated.

TABLE VIII.

Molar fract. of alcohol.	Concentration of Li Cl.	ρ dynes/Cms.	$\log p_A$	$\log p_B$
0.80	0.500	23.19	0.992	1.682
	1.000	23.51	0.929	1.680
	2.000	23.79	0.865	1.672
		24.44	0.403	1.631
0.50	-	25.65	1.236	1.564
	0.500	25.69	1.198	1.578
	1.000	25.73	1.162	1.581
	2.000	25.85	0.884	1.575
0.25	-	28.42	1.341	1.464
	0.500	28.27	1.336	1.480
	1.000	28.16	1.324	1.490
	2.000	27.97	1.104	1.502
0.064	-	42.00	1.341	1.086
	0.500	41.46	1.335	1.117
	1.000	41.04	1.324	1.142
	2.000	40.23	1.223	1.190

In the application of equation (7) a graphical method was employed. The values of $\log p_A$ for various concentrations of lithium chloride in each alcohol-water solvent were plotted on the same graph against the surface tensions for a single concentration of lithium chloride, namely 1 molal. By taking the difference in slopes of the series of graphs so obtained for equal values of $\Delta \rho$, values of $(d \log p_A - d \log p'_A)$ at 1 molal lithium chloride were obtained for the various mixed solvents.

A similar process was carried out for values of $\log p_B$.

Values of $\frac{\pi_B}{\pi_A}$ were obtained as shown below:-

TABLE IX.

Molar fract. of alcohol	$du_A - du_A^I$	$du_B - du_B^I$	$-\frac{\pi_B}{\pi_A}$	$\frac{\pi_B}{\pi_A}$
0.80	.53 - (-.35) = 0.88	-.12 - (-.03)	-10	10
0.50	.18 - (-00) = +00	-.0.08 -(-large qty.)	?	?
0.25	0.02 - 0.11 = -0.09	-0.06 - (-0.2) = 0.14	- 0.6	0.6
0.064	.004 - (-.036) = 0.03	-0.04 - (-.14) = 0.10	- 0.3	0.3

In water-alcohol mixtures, as the proportion of alcohol is increased, the adsorption of alcohol by the Gibbs equation rises to a maximum and then falls. It has been suggested that this is due to the formation of a film of water under a surface film of alcohol. (Schofield and Rideal, Proc. Roy. Soc. (A) 109, 57, 1925). The preliminary measurements obtained above seem to dispose of this idea, for, if it were the case we should find $\frac{\pi_{alc}}{\pi_{H_2O}}$ decreasing in solutions in which this phenomenon is observed. However, further measurements are required before any definite conclusions can be drawn.

S U M M A R Y.

The effect of lithium chloride on the surface tension of a series of alcohol-water mixtures has been determined. By means of the method outlined information has been obtained regarding the surface layer. Approximate values of $\frac{\pi}{\pi}$ alcohol.
water
have been obtained.

In conclusion, I wish to thank Dr J.A.V. Butler for his encouragement and valuable guidance throughout the research.
