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A STUDY OF THE PHYSICAL PROPERTIES OF SOLUTIONS OF LITHIUM CHLORIDE IN AMYL ALCOHOL.

BY LAUNCELOT W. ANDREWS AND CARL ENDE.

There can be no doubt that much light can be thrown upon the nature of electrolytic processes by a systematic examination of electrolytes containing no water; for the principles of the Electrolytic Dissociation Theory, if general, must be valid, not only for solutions in water, but also for all others, and conclusions derived from the study of the former can best receive independent confirmation or rebuttal by a careful investigation of the latter. The questions upon which such an investigation should bear are chiefly these: 1. Does Ostwald's Law of Dilution hold good for non-aqueous solutions? 2. In what way is the translation velocity of the ions related to the nature of the solvent? 3. Is the relatively high resistance of non-aqueous solutions of salts and acids chiefly due to higher internal friction, or to a lower grade of electrolytic dissociation? 4. Do the general physical properties of such solutions point to molecular aggregation, to dissociation, or to both?

Non-aqueous electrolytes have been subjected to investigation by Koblukoff (*Zeitschr. f. phys. Chem.* 4, 429), Wakemaun (*l. c.* 11, 49), Wildermann (*l. c.* 14, 231 and 247), Schlamp (*l. c.* 14, 272), Völlmer (*Diss\**, Halle, 1892), Bouty (*C. R.* 106, 595 [1888]), Fitzpatrick (*Phil. Mag.* (5), 24, 377 [1887]), Vicentini (*Mem. Acc. Torino* 36 [1884], from *Beibl. Phys. Chem.* 9, 131 [1885]), and Andrews (*Iowa Acad. of Science*, I, iii, 12).

For such studies it is desirable to select a solvent that can be, with relative ease, obtained and preserved free from water, and a binary salt which is freely soluble, and whose aqueous solutions have already been examined electrolytically.

Further, the solutions must be sufficiently conductive to be capable of exact measurement, and the substances employed

\* Unfortunately not accessible to us.

should be of such a character as to preclude, so far as possible, the occurrence of any chemical reaction. For these reasons solutions of lithium chloride in amyl alcohol were selected as objects of the present investigation. For each solution the following physical constants were determined: specific gravity, specific viscosity, refractive power for sodium light and electric conductivity.

#### MATERIALS AND METHODS OF RESEARCH.

The amyl alcohol employed was boiled with concentrated caustic potash to decompose any compound ethers which it might contain, then washed with water and then with a solution of phosphoric acid to remove possible traces of organic bases, then dried with fused potassium carbonate, and finally fractionally distilled and again dried with anhydrous copper sulphate and once more distilled. A sufficient amount of the distillate coming over between 130.5° and 131.0° was preserved to answer for all the measurements described in the present paper; so that the latter are strictly comparable among one another.

The amyl alcohol prepared in this way had the specific gravity  $D_{4}^{21.60} = .80949$ ,  $D_{4}^{26.40} = .80571$ ; index of refraction (D line) at 18.3° = 1.40767; specific viscosity = 3.50 at 21.1° (water = 1); resistance at 25° =  $4.524 \times 10^7$  ohms per cubic millimetre, laevo-rotary power for polarized light = 1.95 degrees.

The lithium chloride was prepared from a carefully purified sample of carbonate which showed in the spectroscope traces of sodium, but no other impurity. Its strongly acid solution was evaporated to dryness on the water bath, the residue moistened with concentrated hydrochloric acid and dried at 110°. By digestion of this salt with amyl alcohol a concentrated solution was made from which all others were prepared. After filtration, which was extremely slow, and during which the moisture of the air was, of course, carefully excluded, a knowledge of its concentration was arrived at by independent determinations of the contained chlorine and lithium, which afforded at the same time a needed guarantee that no notable amount of basic salt was present. To obtain further evidence on this point, 5 c.c. of the concentrated and perfectly clear solution was shaken up with water, colored with the methyl orange, and titrated with tenth-normal hydrochloric acid. The first 0.10 c.c. of the latter imparted an acid reaction to the mixture. Therefore basic salt was either absent or present in quantities too small to affect the quantitative results obtained.

For the analyses and for dilution, known quantities of the solution were obtained by weighing, since the high viscosity of solutions of lithium chloride in amyl alcohol, stand in the way of accurate measurement by volume.

*Determination of Cl.* I. 1.1563 grams of sol. taken. Required 17.66 c.c. Ag NO<sub>3</sub> sol. (of which 1 c.c. = 3.532 Mg Cl) = .0747 gram LiCl; ∴ 1 gram sol. contains .0646 gram LiCl. II. 1.5110 grams of sol. taken. Required 23.00 Cl; Ag NO<sub>3</sub> sol. = .0973 grams LiCl; ∴ 1 gram sol. contains .0644 gram LiCl.

*Determination of Li.* For the purpose of this determination the lithium chloride was converted into sulphate after evaporation of the alcohol, every precaution against mechanical loss by spirting being observed. III. Taken 3.3586 grams solution: obtained .2813 grams, Li<sub>2</sub> SO<sub>4</sub> = .2177 grams LiCl. ∴ 1 gram sol. contains .0648 gram LiCl. IV. Taken 5.5111 gram sol., obtained .4618 gram Li<sub>2</sub> SO<sub>4</sub> = .3574 grams LiCl. ∴ 1 gram sol. contains .0649 gram LiCl. V. Taken 5.0798 gram sol., obtained .4261 gram Li<sub>2</sub> SO<sub>4</sub> = .3298 gram LiCl. ∴ 1 gram of the sol. contains .0649 gram LiCl.

The mean of the five determinations gives .0647 grams as the amount of lithium chloride contained in each gram of the solution and the close agreement of the results as calculated from the chlorine with those as calculated from the lithium is satisfactory evidence of the absence of foreign substances and of lithium oxide. Another nearly saturated solution made and analyzed in the same way was found to contain .06681 grams LiCl per gram. According to Gooch (Fres. Zeit. 26, 356) 1 c. c. of a cold saturated solution of lithium chloride in amyl alcohol contains .066 grams of the salt.

The first solution mentioned above is of  $\frac{m}{775}$  concentration and from it was made the  $\frac{m}{1}$  solution by diluting 65.5023 grams with amyl alcohol to 100 c. c. The higher dilutions were prepared from the  $\frac{m}{1}$  by mixing, in a stoppered tube made for the purpose, having one graduation mark at 50 c. c., and another at 100 c. c. The  $\frac{m}{88}$  and  $\frac{m}{15}$  solutions only were independently made from the stronger solution mentioned above. All solutions were carefully guarded from moisture and several of those first examined were again tested at the close of the whole series of measurements and found not to have appreciably altered in conductivity.

## SPECIFIC GRAVITY.

In making the density determinations a Sprengel's pycnometer of about 10cc capacity, with thermometer fused in, was employed. The thermometer in this instrument was divided into one-tenth degrees and fiftieths could readily be estimated. The density of every solution was determined at two temperatures, from which that at 25° was calculated by interpolation. All weighings are reduced to vacuo, but no correction is applied for varying moisture of the air.

## VISCOSITY.

The determinations of fluid friction were made by the method and with the apparatus described by Ostwald (Lehrbuch, 1891, B. I, p. 549).

The observations for each solution were repeated at several different temperatures, above and below 20°C. The time of flow at the latter temperature was then calculated by means of the interpolation formula  $V_{20^{\circ}} = V_t^{\circ} \frac{k+20}{k+10}$  in which

$V_{20^{\circ}}$  = time of flow at 20°C.

$t^{\circ}$  = temperature of the observation.

$V_t^{\circ}$  = time of flow observed at  $t^{\circ}$ .

$k$  = constant for each solution, its value lying between 4 and 10 according to the concentration of the solution.

Each value for  $V_{20^{\circ}}$  obtained in this way represented the mean result of from four to fifteen independent observations, based upon the time of flow of amyl alcohol taken as 100.

To deduce from these numbers the relative viscosities, each must be multiplied by the density found for the same solution.

In spite of the care taken to secure accurate results, it is believed that those actually obtained are only approximate, in consequence of the fact that all the solutions exhibited from the time of preparation a constantly diminishing viscosity. This change was more noticeable in the more concentrated solutions, and was not noticed until the series of observations was nearly complete. The cause is entirely unknown, but the most likely supposition is that a gradual breakdown of more complex molecular aggregates at first formed occurs. The phenomenon recalls that of "birotation," which has been observed in freshly prepared solutions of many optically active compounds.

## REFRACTIVE POWER.

Pulfrich's "*Refractometer für Chemiker*" was used for the determination of the refractive index for the complete series of solutions. Three or four observations, at least, were made upon each solution; and the mean used in the calculation of the refractive power,  $N = \frac{n-1}{D}$ , for sodium light. An inspection of the tabulated results (see Table I) shows that the most highly concentrated solutions have a lower refractive power than that of the solvent, which, however, increases with the dilution until at  $v = 64$  a maximum is reached.

In the last column of the table will be found values for the refractive equivalent of the dissolved lithium chloride calculated by Landolt's formula for mixtures,

$$p N = p_1 N_1 + p_2 N_2, \text{ in which}$$

$p$  = weight of the solution.

$N$  = its refractive power.

$p_1$  = weight of the solvent.

$N_1$  = its refractive power.

$p_2$  = weight of the lithium chloride.

$N_2$  = its refractive power.

Further, for the refractive equivalent, we assume

$$R_D = 42.38 N_2.$$

The value of  $R_D$  as deduced from the more concentrated solutions is 14.9. Gladstone found (J. B., 1869, 173) for the refractive equivalent of Cl, 10.7; for the Li, 3.8; which gives 14.5 for the salt—a fair agreement. The values of  $R_D$  derived from the high dilutions are materially affected, of necessity, by accumulated experimental errors, but the latter cannot wholly account for the great increase which the table exhibits.

TABLE I.

PHYSICAL PROPERTIES OF SOLUTIONS OF LITHIUM CHLORIDE IN AMYL ALCOHOL.

DILUTION v = LITRES PER GRAM MOL.	D.	MOL. CON- DUCTIV- ITY AT 25° κ	k	RELATIVE VISCOSITY. AMYL AL- COHOL=100 AT 20°.	DENSITY D <sup>25°</sup> / <sub>4°</sub>	REFRACTIVE POWER= N = $\frac{n-1}{d}$	R <sub>D</sub> .
0.537	-.895			1.314 0			
0.775	-.368	0.14	0.00114	.....	0.84655	0.49217	14.83
0.88	.0185	0.21	0.00228	.....	0.84318	0.49348	14.95
1.00	0.000	0.28	0.00363	.....	0.83922	0.49439	14.89
1.50	.587	0.46	0.00680	.....	0.82976	0.49600	14.92
2.60	1.000	0.51	0.00634	.....	0.82438	0.49824	15.08
4.00	2.000	0.58	0.00417	.....	0.81561	0.50043	16.12
8.00	3.000	0.61	0.00232	.....	0.81147	0.50126	16.48
16.00	4.00	0.69	0.00152	.....	0.80951	0.50176	18.24
32.00	5.00	0.81	0.00108	.....	0.80813	0.50212	24.32
64.00	6.00	1.03	0.00092	.....	0.80769	0.50238	39.04
128.00	7.00	1.34	0.00085	.....	0.80726	0.50225	45
256.00	8.00	1.73	0.00080	.....	0.80704	0.50231	92
512.00	9.00	2.22	0.00078	.....	0.80700	0.50227	107
1,024.00	10.00	2.87	0.00087	.....	0.80706	0.50225	225
2,048.00	11.00	3.50	0.00037	.....	0.80699	0.50199	.....
4,096.00	12.00	4.04	0.00111	.....	0.80706	0.50190	.....
∞	∞	4.79	[.001]	100.0	0.80699	0.50200	.....

EXPLANATION.

v = number of litres which contain 42.33 grams of lithium chloride.

$$D = \frac{\log v}{\log 2}$$

k = dissociation constant (see p. 100).

n = refractive index of the solution for sodium light.

N = refractive power of the solution for sodium light.

R<sub>D</sub> = refractive equivalent of the dissolved Li Cl for sodium light.

Mean error of D = ±.00005.

Mean error of N = ±.00007.

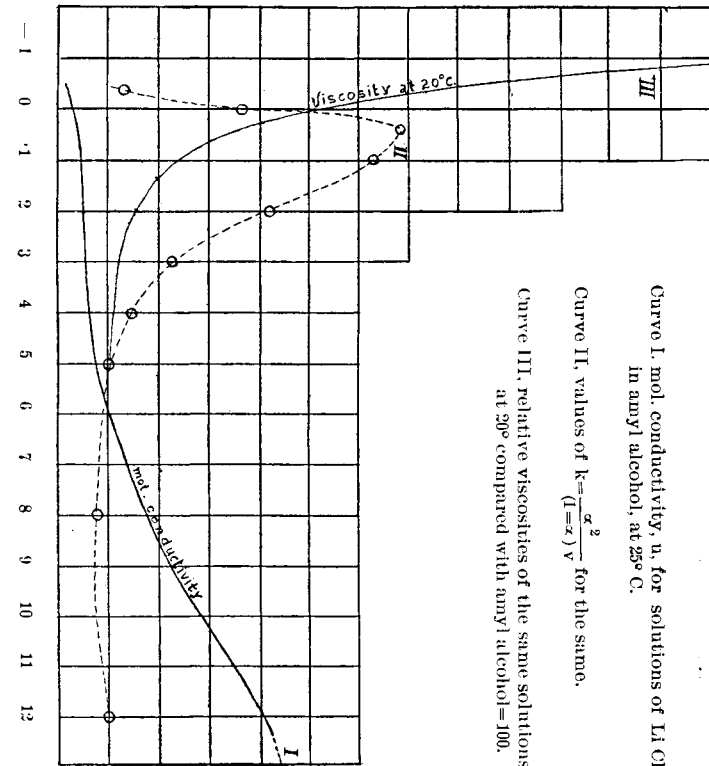
CONDUCTIVITY.

Resistances were determined by Kohlrausch's method, the arrangement being that described by Ostwald (Zeit. phys. Chem. 2, p 561). In consequence of the high resistance of the more dilute solutions, a special electrolytic cell was constructed for this research, possessing an unusually low factor of resistance. In this cell one of the electrodes of heavy sheet platinum is doubled so as to include the other between its two leaves. A number of glass rivets, passing through all three plates and fused to them, aid in preserving a constant distance between them. They stand in a vertical plane in a glass tube 5.5 c. m. in diameter. This arrangement has been found to answer very well, and the conductivity constant (k=8.44 in mercury units), showed no material alteration during a period of use covering several months.

All the molecular conductivities were corrected for the conductivity of the solvent. The corrected values are given in the following table (I.), and also in the curves (q. v.).

In order to cover the whole range of observations without drawing the curves upon too large a scale, the abscissæ are taken proportional to powers of the dilution. Thus, if  $m =$

$p = \frac{\log V}{\log 2}$	0	1.0	2.0	3.0	4.0	5.0		Mol. conductivity.	
		100	200	300	400	500		Viscosity.	
								1000	
		.001	.002	.003	.004	.005	.006	.007	Values of $k$ .



number of grams of Li Cl per litre,  $M =$  molecular weight of Li Cl = 42.37, we have  $m = M(\frac{1}{2})^p$ , in which  $p$  is the desired convenient measure of the dilution.

The molecular conductivity for infinite dilution ( $\mu_\infty$ ) was calculated from the conductivity at the three dilutions that seemed best suited to that purpose (viz.:  $v = 16$ ,  $v = 32$ ,  $v = 64$ ) by

the dissociation formula,  $k = \frac{\left\{ \frac{\mu_v}{\mu_\infty} \right\}^2}{\left\{ 1 - \frac{\mu_v}{\mu_\infty} \right\}^v}$  and the mean taken

as the nearest attainable approximation to the truth. The value



so obtained for  $u_{\infty}$  was 4.79, from which the corresponding values for  $k$  were calculated as recorded in the table. They show a fair constancy, in spite of the rather questionable calculation of the maximum conductivity, for all solutions more dilute than  $\frac{m}{16}$ . Above this point they increase rapidly, reaching a maximum at  $\frac{m}{1.5}$ , whence they fall off again very fast for the most concentrated solutions.

For the more dilute solutions the mean value of  $k$  is about .001.

The peculiar behavior of  $k$  suggests the, *a priori* very probable, supposition that in the more concentrated solutions an association of molecules takes place, resulting in the formation of  $Li_2 Cl_2$  or higher aggregates. In order to get more light upon this, a series of molecular weight determinations by the boiling point method were undertaken, Beckman's apparatus being used. The thermometer (by "Geissler's Nachfolger") was divided into  $\frac{1}{10}$  of a degree C, and  $\frac{1}{100}$  could be estimated with more or less certainty. The elevation constant for amyl alcohol was ascertained by a series of observations with solutions of salicylic acid. (*Confer.* Schlamp, Zeit. ph. Chem. 14, p. 278.)

TABLE II.

MOL. B. PT. ELEVATION OF SALICYLIC ACID IN AMYL ALCOHOL.

GRAMS PER 100 OF SOLVENT—g	RISE OF B. PT.—D	MOLECULAR RISE—S.
0.6504	0.120	25.4
1.3206	0.260	26.9
2.0218	0.400	27.1
2.7760	0.535	26.5
3.4736	0.670	26.7
		26.5 mean.

MOL. B. PT. ELEVATION OF LITHIUM CHLORIDE IN AMYL ALCOHOL

$$M = S \frac{g}{D}$$

v=LITRES PER G. MOL. OF SOLVENT.	GRAMS PER 100 OF SOLVENT—g	RISE OF B. PT.—D	M=S $\frac{g}{A}$
.88	6.060	2.298	71.5
1.00	5.333	2.660	69.2
1.50	3.536	1.872	50.
2.00	2.650	1.230	57.
4.00	1.318	.871	40.
8.00	0.653	.438	40.

These results clearly show that association occurs in the more concentrated solutions.

It is intended to extend the examination, as soon as circumstances permit, to the more dilute solutions in order to secure

further evidence as to the degree of dissociation occurring there.

The work recorded in the present paper was all completed previous to June, 1894, with the exception of the viscosity determinations.

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DISTRIBUTION OF SOME WEEDS IN THE UNITED STATES, ESPECIALLY *IVA XANTHIIFOLIA*, *LACTUCA SCARIOLA*, *SOLANUM COROLINEUM* AND *SOLANUM ROSTRATUM*.

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BY L. H. PAMMEL.

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One of the interesting parts dealing with geographical botany is the question of the distribution of plants over the earth's surface, where man has played an important part. Many changes have occurred in the character of our North American flora since it has been occupied by man. In many cases it has become quite impossible to tell when and where plants were first introduced. We have, it is true, in some cases records when plants were introduced, but in the vast majority of cases there were no records at hand. Early collectors in many cases simply mentioned vague localities with dates, but say nothing as to whether the plants are indigenous or introduced. Papers dealing with the spread of certain weeds have been made by several investigators in both Europe and America. Franz Buchenau has carefully traced the spread of *Leersia oryzoides*. L. H. Dewey that of *Salsola kali*, var. *Tragus*.\*

Who can attempt to trace the spread of *Portulacca oleracea* in the United States, or in any given state or territory, or such cosmopolitan weeds as *Polygonum aviculare* and *Plantago major*? No one has attempted to record the earliest appearance of these weeds in any part of the United States.

The writer has for several years been interested in studying the distribution of several of our weeds. I shall attempt to

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\* Russian thistle. Its history as a weed in the United States with an account of the means available for its eradication. Bulletin No. 15, Division of Botany. United States Department of Agriculture, p 26, Washington. 1894.