is very small, many times smaller than that of salts with univalent
ions, and at least 20 times smaller than in water. It is for this reason
that we have thought proper to disregard the influence of the ionic
dissociation on the results given in the preceding communication,
Moreover, this influence would only strengthen the conclusion arrived
at in that paper.

Amsterdam, June 1903.   _ *Organ. Chem. Lab. University.*

Chemistry. — *"Do the Ions carry the solvent with them in electro-
lysis?"* By Prof. C. A. LOBRY DE BRUYN.

It is generally known that the behaviour of electrolytes in solu-
tion has in many respects not yet been elucidated. We know, for
instance, that strongly dissociated electrolytes do not conform to
OSTWALD's law of dilution. In view of this, H. JÁHN [1]) some time
ago developed a theory in which he attributes this "deviation" to a
mutual interaction of the ions, whilst NERNST [2]) also assumes interac-
tion between the ions and the non-dissociated molecules.

A priori it did not appear to be impossible that the ions might exert an
action on the molecules of the solvent which would cause them to
carry the solvent with them during the electrolysis. If this were found
to be the case, it would have to be taken into account in the study
of the phenomena of electrolysis.

The question whether the ions carry with them during electro-
lysis one or more molecules of the solvent cannot as a matter of
fact be studied by using purely aqueous solutions, but it can be done
by means of solutions of an electrolyte, say, in mixtures of water
and methylalcohol. Then if one of the ions carried with it one of
the solvents, this would be found out by the difference in the pro-
portion of the two solvents at the cathode and the anode both by
comparing them with each other and with the original solution [3]).

In the research an apparatus of the usual kind was employed
such as is used for the determination of the transport numbers of

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[1]) Z. ph. Ch. **36.** 458, **37.** 490, **38.** 125. [2]) Ibid. **38.** 487.

[3]) When the experiments were already in progress Prof. ABEGG told me that
Prof. NERNST had already made similar experiments using water + mannitol as sol-
vent. These experiments, which only appeared in the Göttinger Nachrichten [1900. 68]
had not led to a definite conclusion; Prof. NERNST confirmed this statement. J.
TRAUBE (Chem. Zt. 1902, 90) also thinks it probable that each ion is in unstable
combination with one molecule of the solvent.

7*

ions (capacity 150 cc.); a few experiments were made with a larger pattern (capacity 450 cc.) As solvent a mixture of methylalcohol and water was used of three different concentrations.

As electrolyte, cuprichloride was first used; when this substance appeared to be unsuitable for the purpose (owing to formation of cuprouschloride) silvernitrate was taken. This salt was sufficiently soluble in the diluted methylalcohol and did not seem to affect it during the electrolysis. The electrodes were made of silver, the cathode was placed in the uppermost limb of the apparatus and the anode, around which the increase of concentration of the silvernitrate takes place, in the other. After placing the apparatus in the waterbath a current of 70 volts was passed for 3 to 4 hours; the strength of the current was determined by means of a milli-ampère-meter.

Separate experiments had shown that the methylalcohol could be very accurately determined by distillation. The liquid to be analysed (25 cc. of the cathode- and anode solutions) was mixed with 25 cc. of water and of this mixture 25 cc. were very carefully redistilled into a weighed measuring flask. The amount of silvernitrate was found by titration and the silver deposited on the cathode was weighed. From the following particulars of the experiments, we may draw the conclusion that under the circumstances of the experiments there is no question of a transference of the solvent along with one of the ions.

It was found previously that on dissolving $AgNO_3$ in dilute methylalcohol the volume of the liquid is scarcely affected. Methylalcohol of 25 pCt. by weight.

Weight of measuring flask after distillation from solvent   36.838

// // // // // // solution n. $AgNO_3$ $\begin{cases} 36.872 \\ 36.879 \end{cases}$

I. Meth. alc. of 25 pCt. by weight. Small apparat. Curr. 0.36 ampéres.
    Time: $3^{1}/_{2}$ hours. Silver on the cathode: 4.50 grams.
    Conc. Ag NO_3 before the experiment: normal.
    Conc. Ag NO_3 after // // $\begin{cases} \text{anode 1.30 normal} \\ \text{cathode 0.54 } // \end{cases}$
    Weight of measuring flask after the distill. $\begin{cases} \text{solution at anode 36.876} \\ // \quad // \text{ cathode. 36.875} \end{cases}$

II. Meth. alc. 35pCt. by weight. Large apparatus. Current 0.32 ampère.
    Time : 4 hours. Silver at cathode: 4.1 grams.

Conc. of $AgNO_3$ before the experiment: normal.

$\quad$ // $\quad$ // $\quad$ // $\quad$ after $\quad$ // $\quad$ // $\quad$ { anode 1.37 normal
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ { cathode 0.94 //

Weight of measuring flask after the distill. { original solution 36.498
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ { solution at anode 36.508
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ { // // cathode 36.503

III. Meth. alc. of 64 $^o/_o$ by weight. Small apparatus. Current 0.15 ampère. Time : $3^1/_2$ hours. Silver on the cathode : 1.80 gr. Conc. of silver before the experim. : normal.

$\quad$ // $\quad$ // $\quad$ // $\quad$ after $\quad$ // $\quad$ // $\quad$ { anode : $AgNO_3$ crystal. out
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ { cathode : 0.73 normal.

Weight of measuring flask after the distil. { original solution 35.100
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ { solution at anode 35.100
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ { // at cathode 35.094

By an easy calculation we now find ·that if for instance, the Ag- or NO_3-ion had carried with it one molecule of the solvent, for every 4 grams of silver an increase or decrease of 0,6 to 0,7 gr. of water or of about 1.2 grams of methylalcohol at the anode or cathode would have been stated. This would have been plainly detected by the analysis even though the amount had been largely diminished by diffusion [1]).

I have to thank my assistants Messrs. C. L. JUNGIUS and S. TYMSTRA for their assistance rendered in these experiments.

Chemistry. — Prof. C. A. LOBRY DE BRUYN presents communication N°. 5 on Intramolecular Migrations : C. L. JUNGIUS. "*The mutual transformation of the two stereo-isomeric methyl-d-glucosides.*"

1. When in 1893 EMIL FISCHER [2]) discovered the glucosides of the alcohols and proposed for these substances a formula deduced by him from the glucose-formula of TOLLENS, namely

$$CH_3O—CH—CHOH—CHOH—CH—CHOH—CH_2OH,$$
$$|\underline{\qquad\qquad O\qquad\qquad}|$$
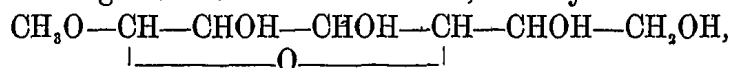
he suggested that on account of the appearance of a new asymmetric

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[1]) It is possible of course that the two ions act in the same manner and carry with them equal quantities of one of the solvents or of both.

[2]) Ber. **26**. 2400.