

Citation:

Tijmstra Bz., S., The electrolytic conductivity of solutions of Sodium in mixtures of ethyl- or methylalcohol and water, in:

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7. With a view of ascertaining whether a transformation was also possible without HCl, the β -glucoside was kept for a long time in a fused condition. After cooling the α_D appeared to be quite unchanged.

Zincchloride in methylalcoholic solution is also incapable of causing the transformation.

8. In conclusion it may be mentioned that the rotatory power of a solution of methylmannoside [of which glucoside only one form is known as yet] in a solution of hydrochloric acid in methylalcohol gradually decreases without formation of mannose.

It seems natural to assume that this is caused by a partial change into a β -isomer which may, perhaps, also be isolated.

These investigations are being continued.

Org. Chem. Lab. University.

Amsterdam, June 1903.

Chemistry. "*The electrolytic conductivity of solutions of Sodium in mixtures of ethyl- or methylalcohol and water.*" By Mr. S. TIJMSTRA Bz. (Communicated by Prof. C. A. LOBRY DE BRUYN).

In his study of the velocity of substitution of one nitro-group in *o*- and *p*-dinitrobenzene by an oxyalkyl ¹⁾ STEGER arrives at the result that the reaction constants of *o*-dinitrobenzene and the two alcoholates Na OC₂H₅ and Na OCH₃ are not changed by dilution or by addition of a sodium salt. On the other hand, in the formation of ethers, these constants are increased by dilution, as shown by HECHT, CONRAD and BRÜCKNER, and decreased by addition of a sodium salt as demonstrated by STEGER.

LOBRY DE BRUYN pointed out that it would be necessary to investigate the conductivity of Na OC₂H₅ in alcoholic solution.

In a further investigation of the influence of water on the substitution of the NO₂-group in *o*-dinitrobenzene by an oxyalkyl ²⁾ and on the formation of ethers ³⁾ it appeared; 1st. that the velocity coefficients of these reactions remained constant when water was added up to an amount of 50 per cent by weight; 2nd. that the addition of water decreased the velocity of reaction of Na OC₂H₅ but increased that of Na OCH₃ (at least at the commencement, afterwards the velocity

¹⁾ Dissertation, Amsterdam, 1898. Recueil 18, 13. (1899).

²⁾ LOBRY DE BRUYN and ALPH. STEGER, Recueil 18, 41.

³⁾ LOBRY DE BRUYN and ALPH. STEGER, Recueil 18, 311.

diminishes again); 3rd. that in mixtures of water and alcohol in which Na is dissolved, the sodium alcoholates are still present.

This last conclusion seems at first sight strange. But previous observations had been made which justified the belief that $\text{Na OC}_2\text{H}_5$ is present in an aqueous-alcoholic solution of sodium. HENRIQUES ¹⁾ for instance showed that in the saponification of fats with aqueous-alcoholic soda the fats are not directly decomposed by the NaOH (the alcohol would then only play the part of a solvent) but that at first the ethyl esters of the fatty acids are formed. The well-known reaction of BAUMANN—SCHOTTEN leads to a similar conclusion.

Some three years after the above mentioned memoirs appeared, LULOFS ²⁾ studied the action of sodium alcoholate on chloro- (bromo- or iodo-) dinitrobenzene (1, 2, 4), and observed the influence of dilution with both absolute and dilute alcohol. It was then shown that the reaction constants are really affected by the concentration which was not the case in STEGER's experiments; decrease of the concentration increases the constant, addition of a salt with a common ion, such as NaBr , decreases the constant both in absolute and dilute ethylalcohol. Here again the water seemed to exert an influence, for in the case of ethyl alcohol a fall in the reaction constants took place whilst with methyl alcohol first a rise and then a fall was noticed. Why all this occurred could not be explained.

From the above facts it was evident (and it was repeatedly pointed out in the papers in question) that it was necessary to study the conductivity of sodiummethylate and -methylate in mixtures of water and alcohol. For this reason I decided to undertake this investigation.

A short review of the results is given in the following tables and the graphical representations connected therewith. A fuller description of the experiments will be given elsewhere.

As starting point I always used solutions which were about $\frac{1}{4}$ normal, determined their resistance and from the diluted solutions prepared therefrom, I calculated the μ 's for those dilutions and determined by interpolation the μ 's for the dilutions of 1 molecule in 1, 2, 4, 8, . . . 512 Litres. The experiments were all done at a temperature of 18° .

In the following tables, the figures are represented graphically in Fig. I, II, III and IV, where the μ 's are taken as ordinates and the logarithms of the dilutions as abscissae. By using the logarithms the scale of the drawing is reduced. The alcoholic percentages are

¹⁾ Z. f. angew. Ch., 1898, 338, 697.

²⁾ Dissertatie, Amsterdam, 1901. Recueil 20, 292. (1901).

by weight and have been determined by means of the specific gravity bottle.

[It is to be noticed that Fig. III is not reproduced on the same scale as Fig. I; since the methyl alcohol curves would intersect and the figure would therefore become confused, the scale of the abscissae has been taken four times larger].

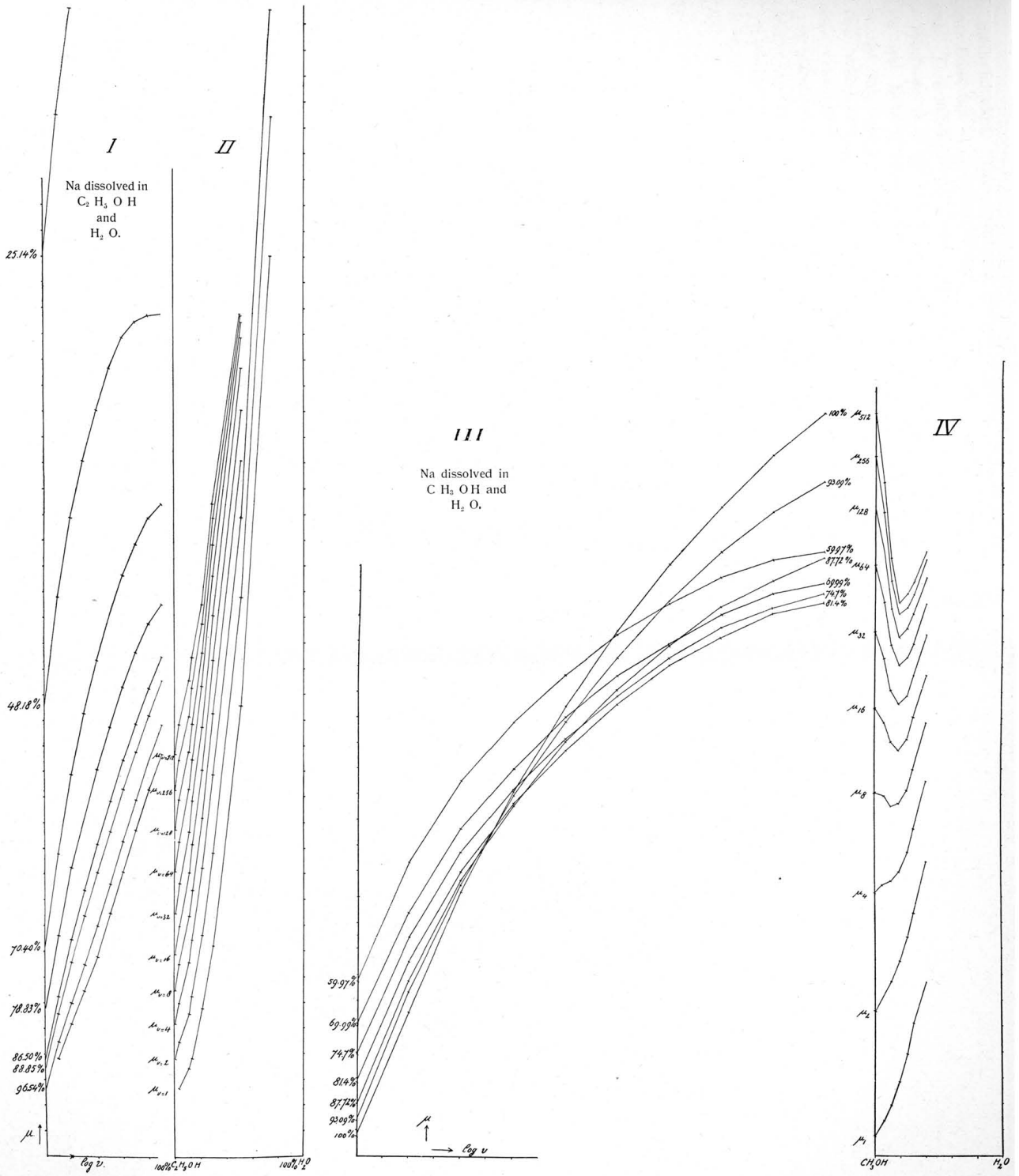
Sodium in Ethyl Alcohol + Water.

Percentage of alcohol by weight.	99.44 pCt.	96.54 pCt.	88.85 pCt.	86.50 pCt.	78.83 pCt.	70.40 pCt.	48.18 pCt.	25.14 pCt.
$\mu_{v=1}$	—	5.32	6.866	7.737	11.59	16.40	35.15	70.05
$\mu_{v=2}$	7.602	8.916	11.13	12.44	17.20	23.59	43.59	80.98
$\mu_{v=4}$	10.30	11.99	15.17	16.87	22.44	29.70	49.72	89.08
$\mu_{v=8}$	12.95	14.99	18.72	20.77	26.38	34.54	54.16	94.62
$\mu_{v=16}$	15.79	17.95	22.04	24.29	30.10	38.67	58.07	99.80
$\mu_{v=32}$	18.92	21.21	25.27	27.66	33.48	42.19	61.34	103.4
$\mu_{v=64}$	22.18	24.53	28.59	30.86	36.60	45.22	63.68	107.2
$\mu_{v=128}$	25.41	27.78	31.53	33.73	39.23	47.68	64.89	109.2
$\mu_{v=256}$	28.51	30.82	34.31	36.51	41.52	49.67	65.40	111.2
$\mu_{v=512}$	31.30	33.62	37.04	38.97	43.00	50.81	64.54	112.0

Sodium in Methylalcohol + Water.

Percentage of alcohol.	100 pCt.	93.09 pCt.	87.72 pCt.	81.40 pCt.	74.70 pCt.	69.99 pCt.	59.97 pCt.
$\mu_{v=1}$	21.49	22.77	23.89	25.72	27.85	30.21	33.48
$\mu_{v=2}$	31.18	32.66	33.59	35.02	36.92	38.80	42.75
$\mu_{v=4}$	40.38	40.97	41.21	41.97	43.43	45.26	49.01
$\mu_{v=8}$	48.13	47.90	47.03	47.24	48.36	49.93	53.60
$\mu_{v=16}$	54.78	53.63	52.07	51.41	52.37	54.04	57.33
$\mu_{v=32}$	60.77	58.65	56.15	55.03	55.73	57.30	60.47
$\mu_{v=64}$	65.97	63.08	59.64	58.13	58.68	59.79	62.87
$\mu_{v=128}$	70.42	66.98	62.62	60.28	61.00	62.07	64.99
$\mu_{v=256}$	74.50	70.09	64.73	62.12	62.60	63.57	66.40
$\mu_{v=512}$	77.92	72.44	66.49	62.99	63.72	64.55	67.01

From these figures we obtain the important result that methylalcohol differs from ethylalcohol in its behaviour. This is seen at once from the graphical representation in Fig. IV (showing the changes of the μ 's, namely of the $\mu_{v=1}$, $\mu_{v=2}$ etc. with the amount of water). At the gas concentration ($v = 22$) a minimum occurs



with methylalcohol. This minimum is not present in the higher concentrations but at the larger dilutions it becomes more and more evident. This minimum is found precisely in the neighbourhood of those dilutions ($v = 22$ and higher) at which LOBRY DE BRUYN and STEGER and LULofs have worked in the experiments referred to above and the amount of water in the alcohol is also the same as that for which these investigators have found the maximum of reaction velocity, namely in 60 to 80 per cent alcohol. There is therefore parallelism between the two phenomena; for methyl alcohol + water + sodium a maximum of the reaction velocity corresponds with a minimum of conductivity.

The experiments are being continued up to pure H_2O and also extended to mixtures of ethyl- and methylalcohol.

Amsterdam, June 1903.

Org. Chem. Lab. University.

Physiology. — *The string galvanometer and the human electrocardiogram.* By Professor W. EINTHOVEN. (Physiological laboratory at Leyden.)

In the Bosscha-celebration volume of the "Archives Néerlandaises"¹⁾ the principle of a new galvanometer was mentioned and the theory of the instrument dealt with. The practical usefulness of the instrument especially for electrophysiological measurements may be judged from what follows.

It may be remembered that the instrument consists principally of a silvered quartz thread which is stretched like a string in a strong magnetic field. When an electric current is passed through the thread, this latter deflects perpendicularly to the direction of the magnetic lines of force and the amount of the deflection can directly be measured by means of a microscope with an eye-piece micrometer.

What is the sensitiveness that can be obtained in this manner?

Since the above-mentioned publication a number of material improvements have been made in the instrument by which it is possible, for instance, to give a very feeble tension to the string, now a quartz thread 2.4μ thick, with a resistance of 10 000 Ohms. If the tension is so regulated that a deflection takes place in from 10 to 15 seconds depending on its amount, every millimetre of the displacement of the image of the string corresponds to a current of 10^{-11} Amp. when a 660-fold magnification is used. As under these circumstances a

¹⁾ W. EINTHOVEN. Un nouveau galvanomètre. Archives Néerlandaises des sciences exactes et naturelles. Sér. II. Tome VI. p. 625. 1901.