Chemistry. — *"The Electro-viscous Effect in Rubbersol."* By Prof. H. R. KRUYT and W. A. N. EGGINK.

1. Researches on agarsol [1]) have taught that the relation [2]) between the charge of dispersed particles and the viscosity of the dispersed system manifests itself clearly in those sols in which the charge can be considerably modified without the colloid system as such being annihilated, i.e. in those systems of which the stability does not only depend on their charge, but in which also hydration (more general: solvation) protects the system. The conceptions about the stability of the lyophile sol may be applied throughout the territory of the emulsoids [3]), at least when water is taken as the substance in which the dispersion takes place. Our attention was, however, drawn by a remark on p. 570 of O. DE VRIES' Estate Rubber [4]), where it is stated that increase resp. decrease of the viscosity of a benzene rubber solution is brought about by shaking it with a few drops of a solution of alkali resp. of acid or salt.

As it seems as if this is a question of an electro-viscous effect, we have examined what influence electrolytes have on the viscosity of solutions of rubber in benzene.

2. Sols were used prepared in the following way: 1 gr. of a certain crêpe-rubber was added to 300 cm. of benzene, after 24 hours it was carefully shaken, and the sol was poured through a folded paper filter. Then benzene solutions of the electrolytes were made; the liquids which were to be examined viscosimetrically, were prepared by mixing a volume of sol with a volume of the solution of the electrolyte (resp. a volume of benzene, for the zero-standard); or as far as the measurement of rubberless liquids are concerned by diluting electrolyte solutions with benzene, as they were diluted with sol just before. At the

[1]) H. R. KRUYT and H. G. DE JONG, Z. physik. Chem. **100**, 250 (1922).

[2]) M. VON SMOLUCHOWSKI, Koll. Z. **18**, 190 (1918). We prefer the term electro-viscous to quasi-viscous, which v. SMOLUCHOWSKI uses, but which may give rise to misunderstanding.

[3]) H. R. KRUYT, Koll. Z. **31**, 338 (1922).

[4]) Batavia 1920.

beginning and at the end of every series the electrolyte-free mixture was measured, and when there was a difference, a correction was applied to the intermediate values. The measurements have been performed in an OSTWALD viscosimeter [1]) and at 25°.

In the subjoined tables the concentrations given are end-concentrations, the viscosity of benzene is put at 1.000, η_e is the viscosity of an electrolyte solution, η_{s+e} that of a rubber sol with equal electrolyte concentration. The relation of these quantities is given under $\dfrac{\eta_{s+e}}{\eta_e}$, after the said correction for the time reaction has been applied.

TABLE I.

Influence of benzoic acid on the viscosity of rubbersols.

Conc. Benzoic acid mMol p. L.	Viscosity benzene + benzoic acid η_e	Viscosity rubber + benzoic acid η_{s+e}	$\dfrac{\eta_s +}{\eta_e}$ corrected
0	1.000	1.698	1.698
6	— [2])	1.635	1.633
12	— [2])	1.601	1.598
24	— [2])	1.584	1.577
48	1.010	1.565	1.552
96	1.018	1.559	1.533
192	1.036	1.574	1.522
0	1.000	1.695	1.698

In fig. 1 these results are represented graphically. Corresponding determinations have been carried out with acetic acid, hydrochloric acid, sulphuric acid, sulphuretted hydrogen and mercury chloride. Essentially the results are the same, the viscosity reducing action alone is different; most for hydrochloric acid, in which already $1^1/_4$ mMol per litre reduces the viscosity from 1,573 to 1,486

Ammonia shows a very remarkable behaviour; the results are recorded in table II.

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[1]) With observance of all precautions according to H. G. BUNGENBERG DE JONG, Rec. Trav. chim. Pays Bas **43**, 1 (1923).

[2]) Interpolated between the values for 0 and **48** mMol per l.

The viscosity of the NH_3-benzene mixtures (η_e) did not appreciably differ from that of benzene.
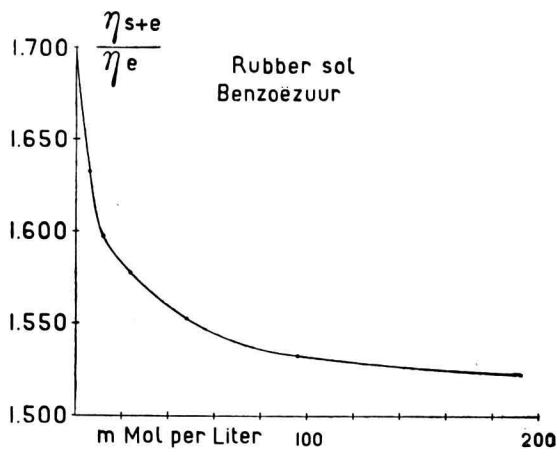

Fig. 1.

TABLE II.
Influence of ammonia on the viscosity of rubbersols.

Conc. ammonia mMol p. L.	Viscosity rubber + NH_3 η_{s+e}	$\dfrac{\eta_{s+e}}{\eta_e}$ corrected
0	1.608	1.608
0.37	1.616	1.616
0.75	1.622	1.621
1.49	1.625	1.624
2.98	1.622	1.620
5.96	1.620	1.618
11.92	1.620	1.618
23.85	1.621	1.618
0	1.611	1.608

It appears from this that the viscosity of the sols rises by addition of ammonia, reaches a maximum, and then descends.

3. The great change of viscosity by an added substance in so small a concentration as is the case with the acids, certainly makes the impression of an electro-viscous effect.

In fig. **2** a graphic representation is given of the results of all examined electrolytes, but only for concentrations below 6 mMol per litre. We have always taken the relative viscosity of the electrolyte-
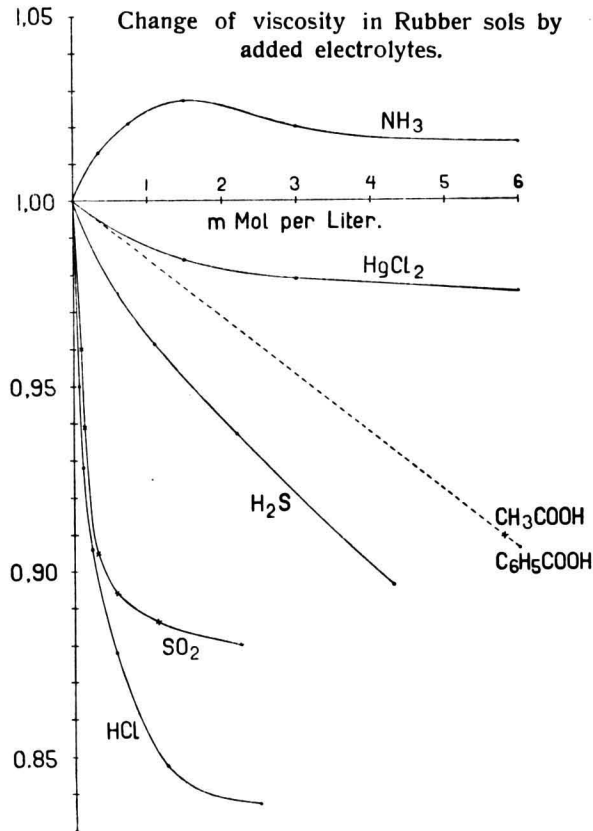

Fig. 2.

free sol as unit, and then plotted the relation $\dfrac{\eta_{s+e}-1}{\eta_{s}-1}$ as ordinates.

The behaviour of NH_3 is in striking agreement with this explanation: for it has appeared in all investigations on capillary-electric phenomena that alcalic substances give a higher potential to a negatively charged wall, lowering it again on further addition[1]). In harmony with this researches in this laboratory by Mr. Lier confirmed the occurrence of an increasing electro-viscosity by hydroxyl

[1]) See e.g. G. von Elissaffof, Z. physik. Chem. **79**, 385 (1912); R. Ellis, Z. physik. Chem. **80**, 597 (1912); H. R. Kruyt and A. E. van Arkel, Koll. Z. **32**, 29 (1923).

ions in casein, those by Dr. RUNGENBERG DE JONG did so in amylum [1]). Especially this positive effect is, therefore, a forcible argument in favour of our view.

4. Two objections may, however, be raised. The first is: is NH_3 and also is SO_2 in benzene an electrolyte? For the formation of an OH-ion from NH_4OH, resp. an H-ion from H_2SO_3 the presence of water is required. If it is, however, calculated how much water is required with the very small concentrations in question, values are found which are only a small part of the solubility of water in benzene, a quantity that is certainly always present in benzene that has not been dried with particular precautions.

A second objection might be supplied by the question whether the electrolytes in benzene are sufficiently dissociated to put these phenomena to their account. WALDEN's [2]) investigations, however, may reassure us in this respect. Equal dissociation in two solvents is attained at dilutions that are to each other as the third powers of the dielectricity constants, i.e. for the relation bezene-water $4,7 \times 10^4$. Hence the succession of the strengths is the same in two solvents. If now according to WALDEN the α is calculated for HCl in benzene, conc. 1 mMol per litre, taking into account that the constant from OSTWALD's law of dilution varies proportional to the concentration of the undissociated molecules, the value $\alpha=0,32$ is found. Here there is, therefore, a considerable ionisation. With a weak acid, as benzoic acid, the dissociation is, indeed, more greatly lowered by benzene than in the case that the substance is dissolved in water, but in the concentrations in question here, it is yet not less than $^1/_{200}$ of that in water.

There is, however, a striking difference between the electro-viscous phenomena in water and those in benzene. In water the curves for cations of equal valency coincide, but this is not the case for our curves, though they all have the H-ion as discharging ion (with the exception of $HgCl_2$). It makes the impression that the real H-ion concentration plays a part: for the anorganic acids discharge in the order of their strength. The two organic acids are, indeed, stronger than H_2S, but organic anions always counteract the discharge through their greater absorbability, the aromatic ion more strongly than the aliphatic one, thus compensating its greater strength. The exceedingly

[1]) Still unpublished; compare however for casein W. PAULI, Kolloidchemie der Eiweisskörper, 81 et seq. (Dresden-Leipzig 1920) and for amylum M. SAMEC Koll. Beih. **4**, 132 (1913), **5**, 141 (1914) etc.

[2]) P. WALDEN, Z. physik. Chem. **94**, 363 (1920).

weakly ionized HgCl, has accordingly the smallest discharging power.

5. In conclusion we wish to draw attention to a consequence of the stated electro-viscous character of part of the viscosity in the rubbersol. It has often been tried to compare the quality of different samples of rubber by measuring the viscosity of benzene solutions of the same concentration. The choice of this property for a comparison is not unlogical, as in the first instance the viscosity may be considered as a measure for the solvation, and this can be taken into account as a real colloid characteristic. Experience now actually teaches that there exists a certain correlation between the viscosity of the sol and the mechanic properties which determine the quality; it is, however, no more than a vague correlation. It has, however, appeared above, that part of the viscosity is *not* in connection with the solvation, but is of electric origin, and has, therefore, a perfectly casual character, dependent on the soluble components which accompany the rubber and which have no influence on the mechanic properties in these minimum concentrations. If it is, therefore, desired to detect a functional relation between viscosity and the properties of the quality of the rubber, it will be necessary to eliminate beforehand the electro-viscous effect by judicious addition of the electrolyte.

We consider the knowledge of these electro-viscous phenomena of importance from the standpoint of pure colloid chemistry, because they open a way to the study of the electric relations in non-aqueous sols.

Utrecht, VAN 'T HOFF-laboratory, 1922.