Chemistry. — *Cataphoresis of Amino Compounds.* By H. R. KRUYT and J. J. WENT.

(Communicated at the meeting of September 26, 1931.)

In the colloid chemistry of the proteins a positive charge is supposed to arise in a proteine particle because in an acid solution the aminogroup combines with the acid through which a kation becomes inner layer of the electric double layer [1]). In the same way arises in alkaline solution a negatively charged particle because the formed carboxyl salt furnishes a negatively charged ion as inner layer of that double layer. Meanwhile we hardly dispose of experimental data whether in fact an animo group leads to a positive electrokinetic potential.

A first attempt to provide data in this case has been made by J. J. HUIZING [2]) in his thesis. As, however, he used the technic of the cuvette according to VAN DER GRINTEN [3]) and as this technic has proved later on to produce doubtful results [4]) it was necessary to repeat and extend his experiments with an other and more certain technic. Obviously one had to choose for this a macroscopic method, but the peculiarities of the systems which are here objects of research make it impossible to follow this way. Suspensions of substances are obtained most of the time by dissolving them first in alcohol and then by pouring this solution into water. It appears that in this way generally only very diluted instable suspensions are obtained which on that account are difficult to measure according to methods in an U-shaped tube in which moreover they move with fading boundary-surfaces.

So these diluted suspensions demand a microtechnic in which separate particles are observed in their cataphoretic movement. This is why we have returned to the technic described by H. R. KRUYT and A. E. VAN ARKEL [5]). Only this cuvette has the disadvantage to be adjusted with an adhesive (picein) which can present difficulties of polluting the sols which are to be examined.

One of us (WENT) tried to give a shape to the cuvette of KRUYT and VAN ARKEL where adhesives are completely excluded and he succeeded; the following experiments have been made with that cuvette.

---

1) Cf. H. R. KRUYT, Colloids, Chapter XIV (New-York 1930).
2) J. J. HUIZING, Diss. Utrecht 1928.
3) K. VAN DER GRINTEN, J. Chim. Phys. **23**, 226 (1926).
4) H. R. KRUYT and G. S. DE KADT, Koll. Beih. **32**, 249 (1931) Vide espec. p. 273.
5) H. R. KRUYT and A. E. VAN ARKEL, Koll. Z. **32**, 91 (1923).

The Cuvette.

A number of glass pieces of about equal dimensions as were used by KRUYT and VAN ARKEL are provided with tiny holes in which pins are fitted which are soldered in a brass bottom plate *a* (see fig. 1). The glass-plates are well fixed by these pins while four clips *k* press the plates firmly
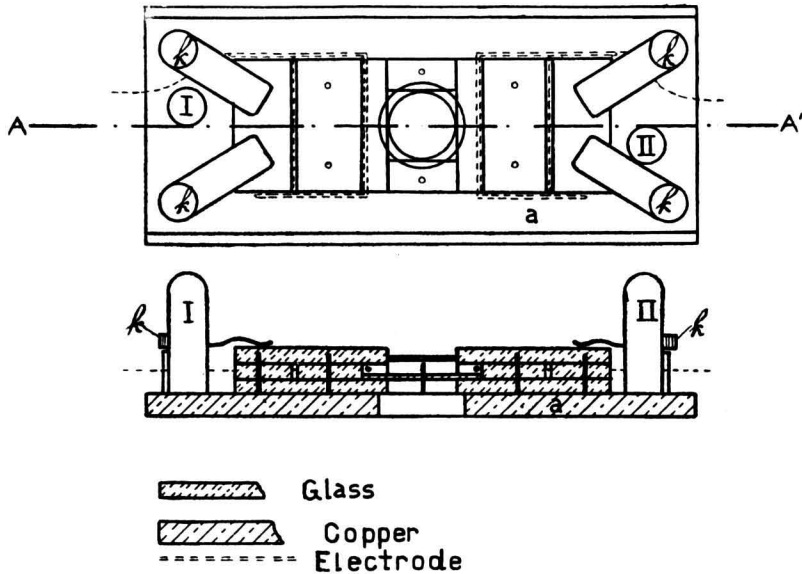

Glass
Copper
Electrode

Fig. 1.

together. The bottomplate *a* fits exactly in the slide of the object table of the microscope through which good adjustment is easely to be got.

Platinum electrodes were used. The optic system consisted of a Zeiss-paraboloid-condensor, a Reichert-objective 4c, a Zeiss-ocular 4. An ocular micrometer which had been compared with a Zeiss-object-micrometer served for measuring the distance covered by the particles. A stopwatch divided into $^1/_5$ seconds served for time-measuring. The covered distances were in the order of 0.1, 0.2, or 0.3 m.m. The light passed through a watercuvette in order to absorb as much as possible the thermic irradiation [1]).

The used voltage amounted to 10 volts in all measurements, the distance of the lectrodes to about 2 c.M. The microscope was focussed at medium height of the cuvette and all the measurements were done on this level. Provisional measurements had taught us that by this way of measuring good results are obtained. Before long we will return to the question whether the theory of the open or of the closed cuvette must be applied.

[1]) It appeared very well possible to adapt the cuvette for constant temperature. A hollow piece of brass through which water is pumped from a thermostate is placed on the two pins I and II of fig. 1. Thus a difference of some degrees with the room temperature proved to be easely compensated. For the rest this apparatus has not been used in the following experiments.

The measured sols and their preparation.

Most of the sols were obtained by dissolving the organic substances in alcohol and pouring into water. We saw to it that the final concentration of alcohol did not exceed 1 %. The choice of the substances to be examined was limited to those which lent to a sol-preparation as mentioned above. Only three sols were prepared in an other way: aniline was simply emulsionized by shaking it with water, diphenylamine likewise above its melting-temperature (the particles solidified when cooling down) and a β-naphtylamine-suspension was made in cooling down a supersaturated solution in water. After many experiments our choice has been fixed on the following substances:

a. aniline   d. naphtalene   g. anthracene
b. diphenylamine   e. β-naphtylamine h. 9 amino-anthracene
c. pseudo-basis of   f. 1.5 naphtylene-   i. β-amino-anthracene
   cristalviolet   diamine

The organic substances were carefully purified preparations. The pseudo-basis of cristal violet was obtained by treating the hydrochloric acid salt with an excess of NaOH and a prolonged washing of the precipitate which there-upon was recristallized.

Results of the measurements.

In the following table one will find the result of our measurements. The

m. mol. HCl pro litre	naphtalene	anthracene	aniline	diphenyl-amine	β-naphyl-amine	1.5 diamino naphtalene	β-amino-anthracene	9. amino anthracene	pseudo-base of cristal violet
0.00	—5.6	—8.8	—8.9	—3.7	—3.1	—1.3	—3.6	—2 0	+0.95
0.65	—3.1	—4.8	–	–	–	–	–	–	+1.57
1.27	—2.7	—4.1	—4.0	—1.2	—1.35	+0.25	—1.7	—0.8	+2.14
2.50	—1.25	–	—2.26	—0.3	+0.4	+1.36	—0.6	–	
3.10	–	–	–	–	–	+1.6	–	–	
3.68	–	–	–	–	+1.2	–	–	+1.35	
4.8	—1.0	—2.8	—1.90	very slow —	–	–	very slow —	+1.42	
5.9	–	–	–	–	+0.5	–	–	+0.68	
6.9	–	–	–	–	–	–	–	+0.48	
9.0	–	—2.5	–	–	–	–	–	–	
10.8	–	–	—1.65	–	–	–	–	+0.2	

cataphoretic velocity has been given in μ pro second for a potential gradient of one volt pro c.M. Since the measurements have been made by addition of increasing quantities of hydrochloric acid one will find in the first column of the table the HCl concentration in millimols pro litre. The mark — is meant to indicate that the particle is negatively charged, that is to say moves towards the anode; the mark + is meant to indicate that the particle is positively charged.

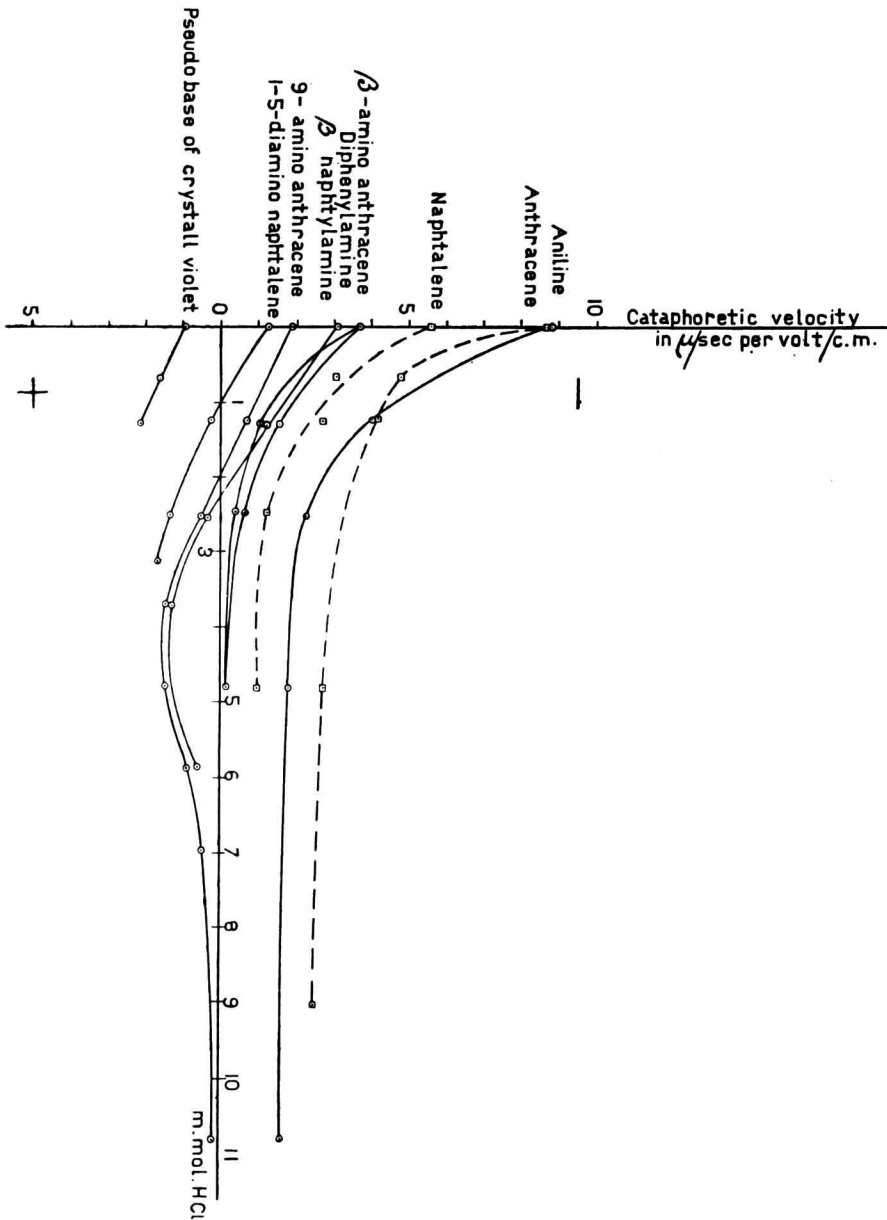The results of this table are graphically reproduced in fig. 2.

Fig. 2.

Discussion of the results.

One might think that amino-compounds when peptized in water would have to show immediately a positive charge. Our results contradict this and it is easily understood that such cannot be the case, for the hydrocarbons themselves are negatively charged in water (we have once more demonstrated this for anthracene and naphtalene [1]); we could not succeed in preparing benzene-emulsions). If one puts an amino-group in the molecule of the hydrocarbon one might expect that this group at the surface of the particle should be turned towards the water as being the polar group in the molecule. However, it is improbable that generally one amino-group should be able to call an entire reversal of charge of the surface. If however one increases the polarity of the group by turning the amino-group into a substituted ammonium ion, the positive character will have to be strongly increased by it.

Let us take the point of view which is surely allowed here, that a greater cataphoretic velocity also means a greater boundery-surface potential ("higher charge") ; then appears in fact in all the three series mentioned above, that hydrochloric acid reduces the negative charge and in many cases causes a reversal of the charge.

Naphtalene is evidently negatively charged. Addition of hydrochloric acid reduces this charge without leading to a reversal of charge. β-naphtylamine has a lower negative charge than naphtalene ; addition of HCl leads to discharge, in higher concentration occurs a reversal of the charge. When a second amino-group is put into the molecule it appears that the diamino-naphtalene in water has again a lower negative charge, is reversed in charge already at **1** millimol hydrochloric acid and shows evidently a stronger positive character.

In the series of the anthracene we observe the same fact. The hydrocarbon is only dischargeable ; also the amino-anthracene is discharged, it is true, but the one aminogroup in the large anthracene molecule is not able to achieve a reversal of the charge. Only with the 9 amino-anthracene where the amino-group is placed in the peculiar position, symmetrically in the second benzene-nucleus, reversal of the charge is possible. For the rest, the succession of the negative charges for these three substances in water is absolutely comprehensible. The mutual situation of the curves for β-naphtylamine and β-amino-anthracene is normal too.

As for the series for one single benzene-nucleus, as said before, we were not able to measure the system of benzene and water. Analine is strongly negative and it is not reversed in charge by hydrochloric acid ; this is only

---

[1]) As a matter of fact naphtalene is difficult to bring into suspension. The obtained suspensions of this substance are so instable that again and again a fresh suspension has to be prepared. With all the other suspensions the whole series of hydrochloric acid concentrations could be measured on one and the same preparation. Consequently one sees in fig. 2 that the determinations of naphtalene are affected with the greatest inaccuracy.

65

possible with diphenylamine, while the pseudo-base of cristalviolet with her numerous NH_2 groups proves to be decidedly positive, and even in pure water produces a positive sol.

As a matter of fact, the cataphoretic behaviour of the amino-compounds shows actually a great conformity with that of the so-called *positive* inorganic colloids. For THIESSEN [1]) demonstrated recently that pure Fe_2O_3 produces a negative hydrosol, which, however, is reversed in charge to a positive by very slight traces of electrolytes. Only oxydesols absolutely free from electrolytes allowed a proof of this; with the amino-compounds this conduct is much more easily to be demonstrated, only with the threefold-tertiaire amine (the pseudo-base of cristalviolet) one approaches again the case of Fe_2O_3. The suspension of that carbinol in water is either actually positive (the case of Al_2O_3) [2]), or traces of unwashed (and probably unwashable) electrolytes have caused this charge.

So we can finally state that the amino-group undoubtedly gives rise to a positive charge and consequently our results are in good harmony with the theory of the proteins which has been discussed in the beginning of this communication.

Van 't Hofflaboratorium.

Utrecht, September 1931.

[1]) P. A. THIESSEN and O. KOERNER, Z. Anorg. Chem. **180**, 115 (1929).

[2]) P. A. THIESSEN and KOERNER, Z. Anorg. Chem. **181**, 417 (1929).