

Chemistry. — *Electrophoresis of Amino Compounds.* By H. R. KRUYT and G. E. VAN GILS.

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During an investigation on the function of the NH_2 -group particularly with a view to the electrokinetic behaviour of proteins, KRUYT and WENT¹⁾ performed electrophoresis measurements on a number of suspensions of amines.

In these measurements, where a flat cuvette constructed by the authors was used, the electro-endosmotic flow of liquid in the cuvette was not taken into account. The velocities of the particles were, namely, measured at half the height of the cuvette and not at the place where the liquid stands still.

For our new measurements we made use of a tubular cuvette, as was already described by one of us²⁾, and the electro-endosmotic flow of liquid was taken into consideration.

The organic preparations used were once more purified by recrystallization or by sublimation (anthracene). Aniline could not be obtained sufficiently pure by vacuum distillation only. For this reason acetanilide was prepared first and, after recrystallization from water, out of this aniline was formed, which finally was distilled in vacuum. Thus a colourless product was obtained which could be preserved for months, when kept in the dark.

The suspensions were prepared in the same way as was described by KRUYT and WENT. Aniline could simply be shaken with water, diphenylamine as well, but above its melting-point, the liquid subsequently being rapidly cooled, β naphthylamine by cooling of a hot saturated solution. All other sols were obtained by dissolving the organic substance in alcohol and afterwards pouring into water (Alcohol concentration maximally 1 %). Consequently we shall have to pay regard to the influence which in these cases the alcohol with its very active OH-group may exert on the electrophoretic behaviour of the micells.

The sols were on the whole but slightly stable and the less so according as the substances were purer. Mostly „sols” could not really be spoken of. They were suspensions, the particles of which became coarser after a shorter or longer time and subsequently separated above or below in the liquid. For each measurement, therefore, we had to make new suspensions,

¹⁾ H. R. KRUYT and J. J. WENT, Proc. Royal Acad. Amsterdam, **34**, 1007 (1931).

²⁾ G. E. VAN GILS, Doctor Thesis, Utrecht 1936.

which then had to be measured as quickly as possible. The reproducibility of the measurements sometimes was very bad, so that only after a large number of measurements a conclusion could be drawn concerning the mean electrophoretic velocity. The measurements on suspensions of diphenylamine and β amino naphthalene in pure water showed a strong progress. For diphenylamine in water we even could not record a numerical value.

Results of the measurements.

Table 1 gives the results of the measurements, all performed at 20° C and expressed in μ /sec. per volt/cm. Taking into consideration the limited accuracy, we have given the results in one decimal only. Of the 1.5 diamino naphthalene measured by KRUYT and WENT we have not been able to make suspensions suiting our purpose. On the other hand, we had at our disposal a preparation octadecylamine, which we were so fortunate to receive from the organic-chemical laboratory at Leyden.

TABLE 1.

	m. molecules HCl/L.				
	0	1	3	5	10
Anthracene	-1.7	-0.6	f. neg.	0	0
Naphthalene	-2.8	-0.6	f. neg.	f. neg.	f. neg.
Aniline	-3.0	-2.1	-1.2		-0.5
Diphenylamine	neg.	+3.8	+5.4	+3.0	+2.1
β Naphthylamine	(-1.1)	+1.5	+2.1	+1.8	+1.3
β Amino anthracene	+1.1	+2.8		+2.7	+2.6
9 Amino anthracene	+0.7	+1.5	+1.2	+1.1	
Octadecylamine	+4.6	+5.5	+5.4	+4.9	+4.9

Discussion of the results.

On the whole, therefore, the conclusion of KRUYT and WENT is confirmed, that the NH_2 -group is the carrier of a positive charge. Whereas the hydrocarbons naphthalene and anthracene by addition of HCl lose their original negative potential but cannot be reversed in charge, the substances containing an NH_2 -group may become positive (Diphenylamine and β naphthylamine).

However, now we find that the NH_2 -group is so strongly positive that many amines even in *pure water* already have a positive electrophoretic velocity. This is particularly the case with the aliphatic octadecylamine.

On further addition of HCl the positive amines become still more strongly positive, and subsequently decrease in potential at a higher concentration of the acid.

All this becomes comprehensible, if we attribute two functions to the hydrochloric acid:

1. the acid will promote the dissociation of the NH_2 -groups turned to the water and consequently cause the positive charge and with it also the electrokinetic potential of the micells to increase.
2. the added ions will compress the electric double-layer and consequently bring about a decrease of the electrokinetic potential.

Aniline shows a seemingly deviating behaviour, since it cannot be positively charged. However, this may be easily understood, if it is borne in mind that aniline as well as aniline chloride fairly readily dissolve in water, so that a strongly buffering solution is formed. Addition of HCl will, therefore, exert but little influence on the pH of the surroundings, and after all it is the pH which determines the dissociation of the NH_2 -groups.

Diphenylamine, on the other hand, dissolves very badly in water, so that addition of small amounts of HCl already greatly alters the pH of the surroundings.

In support of what was remarked above, we performed pH measurements (with the glass electrode) of suspensions in pure water and in a 1 m.mol HCl solution (Table 2).

TABLE 2.

	pH of the suspension	
	in water	in 1 m. mol HCl
Without any addition	(c. 6.0)	3.0
Aniline	8.1	7.1
Diphenylamine	5.6	2.8
β Naphtylamine	6.2	4.3
β Amino anthracene	5.6	2.9
9 Amino anthracene	6.0	3.1

The water used was twice distilled and „free of CO_2 ”, but nevertheless had a pH of about 6.0. A solution of 1 m. mol HCl has a $\text{pH}=3$. In table 2 it is seen that the three last mentioned substances hardly change the pH of the surroundings, whereas aniline does it very strongly indeed. Never will such a pH be attained with aniline as to give rise to a positive charge of the particles.

It is a well-known fact that the hydrocarbons are negatively charged (Flow potential measurements on paraffin capillaries¹).

The stronger basic character of the aliphatic amines, in comparison to

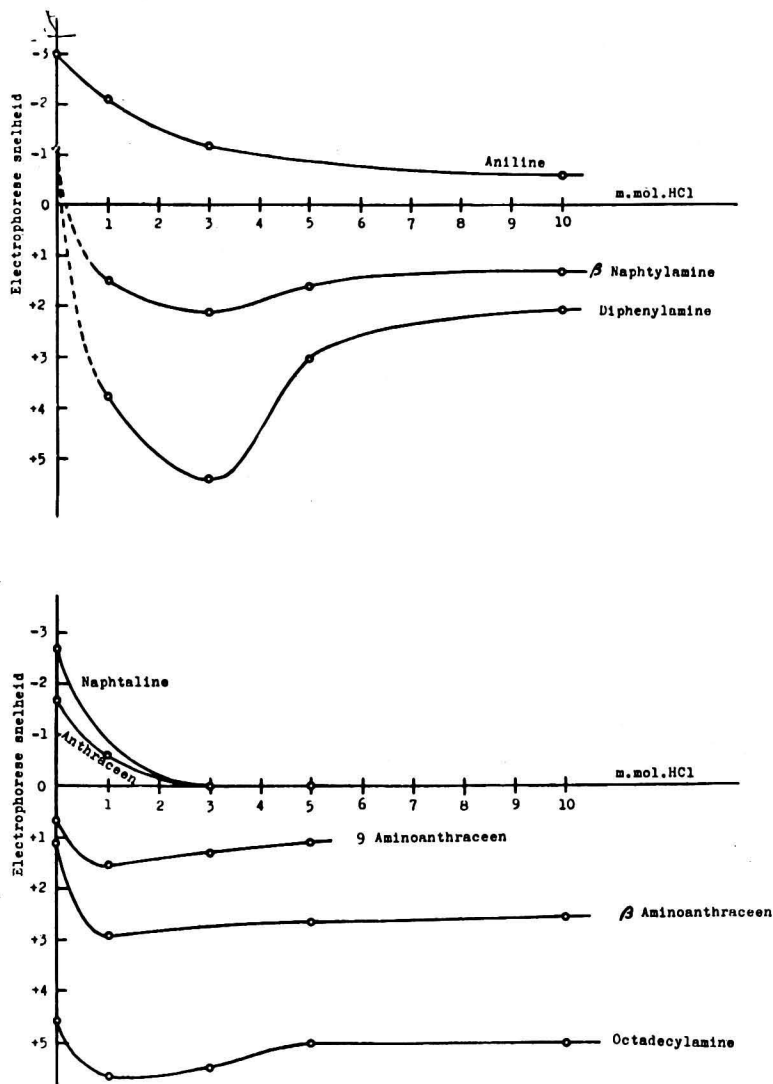


Fig. 1.

the aromatic amines, is also manifest in their electrophoretic behaviour. On determination of the degrees of dissociation of the various amines, undoubtedly a closer correlation would be found between these magnitudes and the electrophoretic behaviour.

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¹) H. R. KRUYT and R. RUYSSSEN, Proc. Royal Acad. Amsterdam, 37, 498 (1934).