

The Electrokinetic Potential at Gas-Solution Interfaces.

II. Cataphoresis of gas bubbles in solutions of capillary-active organic electrolytes

By *A. Gilman* and *Natalie Bach*

It has already been noted in Part 1¹ that data on electrokinetic phenomena at liquid-gas interfaces are extremely scarce. The influence of organic substances on the electrokinetic potential, for instance, has not been studied at all.

The only data to be found in the literature on the influence of organic substances on cataphoretic velocity, those of Mac Taggart², are questionable inasmuch as his measurements do not take into account the motion of the liquid in the apparatus as a result of electroosmosis. Furthermore, the measurements were conducted using concentrations at which the dielectric constant and viscosity of the solutions varied materially as compared with water.

It is the purpose of this paper to determine the influence of capillary-active substances on the electrokinetic potential at the liquid-gas interface and to compare the results obtained with the total potential drop at the same interface.

We were not able to use the results obtained by previous investigators for purposes of comparison with our experimental data inasmuch as they measured the total potential drop at higher concentrations of the dissolved substances, at which electrokinetic phenomena are no longer conveniently observed. Only the measure-

¹ N. Bach and A. Gilman, *Acta Physicochimica URSS*, **9**, 1 (1938).

² Mac Taggart, *Phil. Mag.*, **28**, 367 (1914).

ments of the total potential drops in dilute solutions of tetra-substituted ammonium salts, which were recently made by Gerowitsch³ in the Electrochemical Laboratory of the Moscow University, cover the concentration range which is of interest to us.

Inasmuch as the possibility of a spatial division of the charges of a double electric layer is a necessary condition for the appearance of electrokinetic phenomena, organic salts containing capillary-active anions or cations are most suitable for investigations in this field. We carried out measurements of the cataphoretic velocity of hydrogen bubbles in water solutions of the following compounds:

(1) Tetrabutylammonium chloride $N(C_4H_9)_4Cl$, and tetraisoamylammonium chloride $N(C_5H_{11})_4Cl$. These salts were prepared by shaking the corresponding tetra-substituted ammonium iodides obtained from Fraenkel and Landau (Berlin) with freshly precipitated silver chloride. They were used without further purification for the measurements of electrokinetic potentials, whereas for the total p. d. they had to be recrystallised twice from hot water with ethyl alcohol. The cations of these salts are very active, and it may be presumed that, in their presence, the bubbles, charged negatively in pure water, have their charges reversed.

(2) Sodium palmitate $C_{16}H_{31}O_2Na$. The salt was a Kahlbaum reagent and was not otherwise purified. In contradistinction to the tetrasubstituted ammonium salts, the orientation of sodium palmitate is such that its anion is located on the outside. It might have been expected that such an anion with a long chain would raise the negative charge at the liquid-gas interface.

The method of measurement and the apparatus used were the same as in measuring the velocity of bubbles in inorganic solutions; they are described in detail in Part 1¹.

Results of measurements

Table 1 gives the summarized results of all measurements in solutions of tetrabutylammonium chloride.

³ Unpublished data.

Table 1

$\alpha = 0,4$

c mols/litre	S μ /sec. per V/cm.	u μ /sec. per V/cm.	ζ_e mV	$\Delta u = -au$ μ /sec. per V/cm.	$v = s - \Delta u$ μ /sec. per V/cm.	ζ_g mV	Apparent sign of charge of bubble	True sign of charge of bubble
10^{-6}	-0,7	+3,2	-73	-1,3	+0,6	+13	—	+
10^{-5}	+0,5	+3,3	-75	-1,3	+1,8	+41	+	+
10^{-4}	+1,8	+3,5	-80	-1,4	+3,2	+74	+	+

The following symbols have been used in this table: α , constant of the apparatus (see Part 1); s , displacement of the bubble during the first second per V/cm.; ζ_e , electrokinetic potential at the

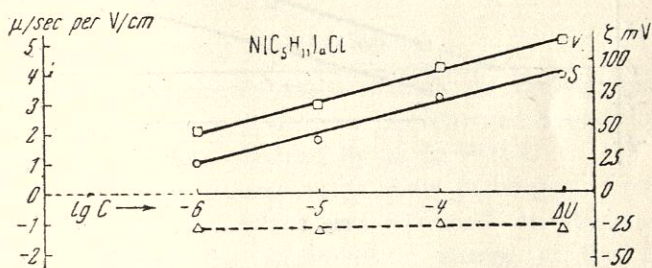


Fig. 1.

liquid-glass interface; u , electroosmotic mobility; Δu , displacement of liquid along the axis of the apparatus during the first second; v , true mobility of bubble; ζ_g , electrokinetic potential at the gas-liquid interface.

The results obtained are plotted in Fig. 1.

The results of the measurements of the velocity of bubbles in solutions of tetraisoamylammonium chloride, $N(C_5H_{11})_4Cl$, are given in Table 2 and Fig. 2.

The curves in Fig. 2 are similar to the corresponding curves obtained for solutions of $N(C_4H_9)_4Cl$.

Table 2

$\alpha = 0,4$

c gr. mols/litre	s μ /sec. per V/cm.	u μ /sec. per V/cm.	ζ_e mV	$\Delta u = -su$ μ /sec. per V/cm.	$v = s - \Delta u$ μ /sec. per V/cm.	ζ_g mV	Apparent sign of charge of bubble	True sign of charge of bubble
10^{-6}	+1,1	+2,7	-62	-1,1	+2,2	+ 49	+	+
10^{-5}	+1,8	+3,0	-70	-1,2	+3,0	+ 68	+	+
10^{-4}	+3,2	+2,6	-58	-1,0	+4,2	+ 96	+	+
10^{-3}	+3,9	+3,1	-70	-1,2	+5,1	+115	+	+

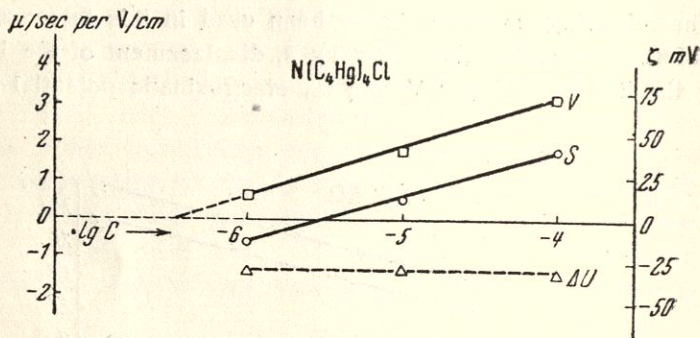


Fig. 2.

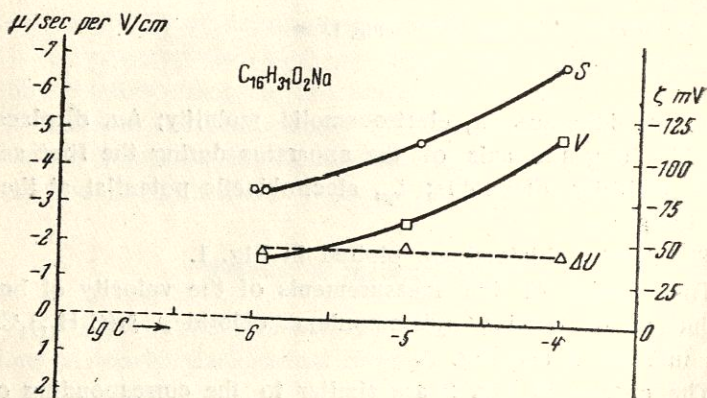


Fig. 3.

Table 3

$$\alpha = 0,4$$

c gr. mols/litre	s μ /sec. per V/cm.	u μ /sec. per V/cm.	ζ_e mV	$\Delta u = -au$ μ /sec. per V/cm.	$v = s - \Delta u$ μ /sec. per V/cm.	ζ_g mV	Apparent sign of charge of bubble	True sign of charge of bubble
$1,2 \cdot 10^{-6}$	-3,1	+4,6	-103	-1,8	-1,6	-36	—	—
$1,2 \cdot 10^{-5}$	-4,8	+4,9	-110	-2,0	-2,8	-64	—	—
$1,2 \cdot 10^{-4}$	-6,9	+4,7	-107	-1,9	-5,0	-113	—	—

Table 3 and Fig. 3 give the results of measurements in solutions of sodium palmitate, $C_{16}H_{31}O_2Na$.

From these data it is evident that in the presence of an active anion with a long chain both the negative charge of the bubble and the negative charge of the glass towards the liquid increase considerably.

Discussion

From the measurements made earlier by various authors, it follows that in pure water, bubbles are charged negatively. This is confirmed by the data obtained by us in Part I.

The results of our measurements show that organic compounds with capillary-active ions which are adsorbed on the surface of water materially affect the electrokinetic charge of the bubbles. As seen from Table 1 and Fig. 1, the apparent charge of the bubble in the presence of tetrabutylammoniumchloride, $N(C_4H_9)_4Cl$, at a concentration of 10^{-6} moles/litre is negative, that is, the movement of the bubble is directed towards the anode just as in the case of pure water. However, if we consider the movement of the water due to electroosmosis, it appears that the true charge of the bubble is really positive, but that during the first second its own velocity is considerably less than the speed of the water moving in the opposite direction. This readily shows to what wrong conclusions the ignorance of the electroosmotic effect can lead.

At $c = 10^{-5}$ moles/litre, the displacement, s , is positive, that is, at this concentration the electrophoretic velocity of the bubble is greater than the velocity of water Δu . As distinguished from the

solution-gas interface, at the glass-solution interface the potential remains negative for all concentrations of $N(C_4H_9)_4Cl$. Its magnitude lies within the limits 73—80 mV, that is, it differs little from the value of ζ_e in pure water. The magnitudes of u and Δu which depend on ζ_e remain almost constant for the entire series of concentrations. The observed increase in s consequently depends only on the increase in v , that is ζ_g .

The apparent mobility of the bubble for the first second in the $N(C_5H_{11})_4Cl$ -solution, even at $c = 10^{-6}$ moles/litres, corresponds to a positive charge. As in the case of $N(C_4H_9)_4Cl$ the glass remains negative at all concentrations.

By comparing the velocities of a bubble in solutions of $N(C_4H_9)_4Cl$ and $N(C_5H_{11})_4Cl$, given in column 6 of Tables 1 and 2, it is seen that similar effects are obtained in the second case with smaller concentrations than in the first.

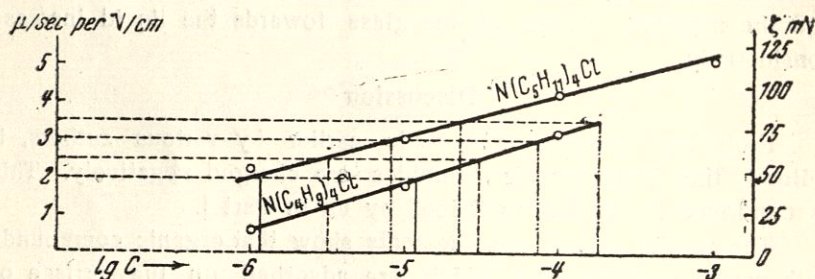


Fig. 4.

Fig. 4. gives the curves of the dependence of electrophoretic velocity (electrokinetic potential) on the logarithm of the concentration.

Tab

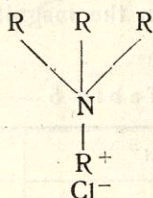
	$v=2 \mu/\text{sec. per V/cm.}$			$v=2.5 \mu/\text{sec. per V/cm.}$		
	Molality	$\frac{c_1}{c_2}$	$\sqrt[3]{\frac{c_1}{c_2}}$	Molality	$\frac{c_1}{c_2}$	$\sqrt[3]{\frac{c_1}{c_2}}$
$N(C_4H_9)_4Cl$	$1.3 \cdot 10^{-5}$	10	2.2	$3.3 \cdot 10^{-5}$	9.4	2.1
$N(C_5H_{11})_4Cl$	$1.3 \cdot 10^{-6}$			$3.5 \cdot 10^{-6}$		

As may be seen, this dependence is of an approximately linear nature. The straight line corresponding to $N(C_5H_{11})_4Cl$ lies above a similar straight line for $N(C_4H_9)_4Cl$ and is almost parallel to it, that is, the ratio of the concentrations of $N(C_4H_9)_4Cl$ and $N(C_5H_{11})_4Cl$, when the same effects are obtained, is constant.

Table 4 gives the concentrations of both salts, determined graphically, which correspond to different values of $v(\zeta_g)$, and the ratio $\frac{c_1}{c_2}$.

The ratio $\frac{c_1}{c_2}$ fluctuates around 9, and $\sqrt[3]{\frac{c_1}{c_2}} \sim 2,1$. The influence of lengthening the chain of alkyl radicals can be explained as follows.

Because of its symmetry, a molecule of a tetrasubstituted ammonium salt is orientated in such a way that only three alkyl groups are turned towards the surface, the fourth group being immersed in the liquid. The orientation of a molecule on the gas-liquid interface can be represented by the following diagram:



Inasmuch as lengthening each of the four chains of alkyl radicals by one CH_2 group produces the same effects as a ninefold increase in the concentration, it can be assumed that lengthening one of

le 4

$v=3 \mu\text{sec. per V/cm.}$			$v=3,5 \mu\text{sec. per V/cm.}$		
Molality	$\frac{c_1}{c_2}$	$\sqrt[3]{\frac{c_1}{c_2}}$	Molality	$\frac{c_1}{c_2}$	$\sqrt[3]{\frac{c_1}{c_2}}$
$8,4 \cdot 10^{-5}$	8,9	2,1	$2,1 \cdot 10^{-4}$	8,4	2
$9,4 \cdot 10^{-6}$			$2,5 \cdot 10^{-5}$		

the substituted radicals by a CH_2 group will be equivalent to an increase of the concentration by a factor of $\sqrt[3]{9} \sim 2.1$ -fold. According to Traube's rule the same effect is obtained in solutions of two successive members of a homologous series, differing by a CH_2 group, when the ratio of their concentrations is approximately equal to 1:3,4. As Frumkin⁴ pointed out, this rule is observed with respect to the total potential drop when the radical C_2H_5 is substituted successively for the three hydrogen atoms in ammonia. When substituting C_2H_5 in ammonium chloride, Traube's rule is observed for the first three hydrogen atoms but no longer holds for the fourth one, the ratio becoming < 1 , when introducing the fourth group after the third.

The constant ratio which we obtained in the case of λ is smaller than that which corresponds to Traube's rule. However, it should be borne in mind that in the tetrasubstituted salts the mutual influence of alkyl radicals lessens the influence of each group that is introduced; besides, the C_5H_{11} radicals were in this case isogroups, which also alters the value of Traube's constant. Table 5 gives Gerowitsch's data on the magnitude of the total p. d. at

Table 5

gr. mols/litre	$\text{N}(\text{C}_4\text{H}_9)_4\text{Cl}$		$\text{N}(\text{C}_5\text{H}_{11})_4\text{Cl}$	
	ϵ mV	$\zeta_g - \zeta_{\text{H}_2\text{O}}$ mV	ϵ mV	$\zeta_g - \zeta_{\text{H}_2\text{O}}$ mV
$5 \cdot 10^{-7}$			56	
10^{-6}	10	43	68	79
$2 \cdot 10^{-6}$	18			
$5 \cdot 10^{-6}$			115	
10^{-5}	45	71	154	98
$2 \cdot 10^{-5}$	63			
$5 \cdot 10^{-5}$			309	
10^{-4}	115	104	387	126
$2 \cdot 10^{-4}$	158			
10^{-3}	305			145

⁴ A. Frumkin, Z. physik. Chem., **111**, 190 (1924).

the gas-solution interfaces in the presence of $N(C_4H_9)_4Cl$ and $N(C_5H_{11})_4Cl$ against the gas-water interface measured with the usual technique using a reference air electrode covered with polonium. These values are compared with the differences, $\zeta_{\text{gas}} - \zeta_{H_2O}$, between the electrokinetic potentials at the corresponding gas-solution and gas-water interfaces.

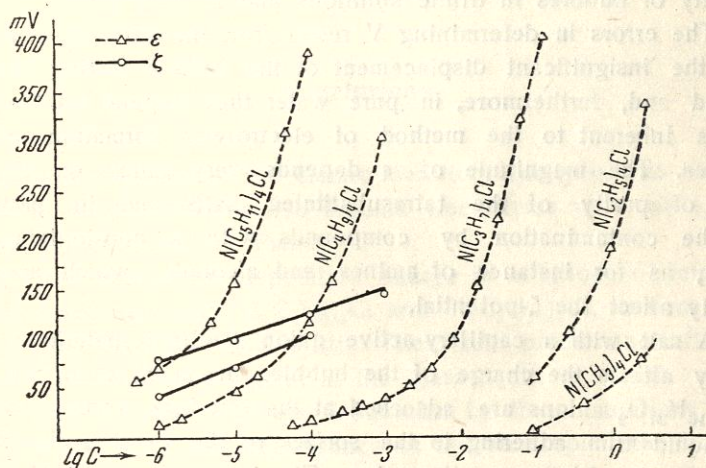


Fig. 5.

Fig. 5 gives the curves of the dependence of ε on the logarithm of concentration of $N(C_4H_9)_4Cl$ and $N(C_5H_{11})_4Cl$ obtained by Gerowitsch³, of $N(CH_3)_4Cl$, $N(C_2H_5)_4Cl$, and $N(C_3H_7)_4Cl$ obtained by Frumkin⁵, and our $\zeta - \lg C$ curves for $N(C_4H_9)_4Cl$ and $N(C_5H_{11})_4Cl$. The comparison of these curves shows that the ratio of the concentrations, corresponding to the same value of ε for two successive members of the homologous series, is much larger than in the case of ζ , and amounts to about 20. It may also be seen from these curves that, at low concentrations of $N(C_4H_9)_4Cl$ and $N(C_5H_{11})_4Cl$, the magnitudes of ε and ζ are not very different and only at higher concentrations does ζ noticeably lag behind ε .

⁵ Unpublished data.

From this fact we can draw the conclusion that in dilute solutions of capillary-active organic salts, a large part of the total potential drop ε lies in the diffuse double layer. The fact that the curve $\zeta - \lg C$ in solutions of $N(C_4H_9)_4Cl$ lies above the curve $\varepsilon - \lg C$ at concentrations lower than 10^{-4} moles/litre, that is, that at certain concentrations the measured electrokinetic potential proved to be greater than the total potential drop, must be considered as resulting from insufficient accuracy in the measurements of the electrophoretic velocity of bubbles in dilute solutions and in pure water.

The errors in determining V result from the difficulty of measuring the insignificant displacement of the bubble during the first second and, furthermore, in pure water they depend on the difficulties inherent to the method of electrolytic formation of gas bubbles. The magnitude of ε depends very much on the degree of purity of the tetrasubstituted salts and in particular on the contamination by compounds with a non-ionizing molecule, as for instance of amines and alcohols, which may but slightly affect the ζ -potential.

A salt with a capillary-active anion (sodium palmitate) also greatly affects the charge of the bubble. Inasmuch as in this case the $C_{16}H_{31}O_2$ anions are adsorbed at the interface, accumulating in the liquid film adhering to the surface of the bubble, the charge of the latter has a negative sign. The influence of the $C_{16}H_{31}O_2$ anion on the charge of the bubble is very considerable and results in an increase of the ζ -potential up to 113 mV at a concentration of $1,2 \cdot 10^{-4}$ moles/litre.

Furthermore, in contrast to solutions of tetrasubstituted salts, the ζ -potential rises greatly at the liquid-glass interface as compared with pure water.

Its magnitude changes little within the limits of concentrations from $1,2 \cdot 10^{-6}$ to $1,2 \cdot 10^{-4}$ moles/litre, and is equal to approximately 100 mV.

The results of the measurements of electrophoretic velocity of gas bubbles thus lead to the conclusion that capillary-active organic electrolytes influence the electrokinetic potential.

In the preceding paper it was pointed out that the insufficient accuracy of the method which we had developed did not permit us to solve definitely the question as to the magnitude of the

ζ -potential in pure water and in solutions of inorganic salts. In solutions of organic salts the inaccuracy of the method does not affect the results of the measurements as materially as in the preceding case, inasmuch as the correction for electroosmosis has a magnitude that is independent of the concentration. In particular, the reversal of charge of the bubble in the presence of tetrasubstituted salts is quite indisputable, for there is no reversal of charge at the glass-solution interface.

Conclusions

1. Measurements of the electrophoretic velocity of gas bubbles in solutions of capillary-active organic electrolytes were made using the method described in Part 1.

2. The bubble has a positive charge in solutions of tetrasubstituted ammonium salts $N(C_4H_9)_4Cl$ and $N(C_5H_{11})_4Cl$, at concentrations greater than 10^{-6} moles/litre. These salts produce no influence on the electrokinetic potential at the glass-liquid interface.

3. The magnitude of the ζ -potential in these solutions rises with concentration. The dependence of the electrophoretic mobility v of the bubble, and consequently of ζ on $\lg C$ is approximately linear. The ratio of the concentrations of $N(C_4H_9)_4Cl$ and $N(C_5H_{11})_4Cl$, which correspond to the same effects, is constant and equal to 9.

4. From the comparison between the total potential drop and the electrokinetic potential in the same systems it may be concluded that at concentrations lower than 10^{-4} moles/litre large part of the total potential drop lies in the diffuse double layer.

5. Sodium palmitate, $C_{16}H_{31}O_2Na$, imparts to the bubble a negative charge which grows with the concentration. At the same time the ζ -potential at the liquid-glass interface increases greatly. Its magnitude remains constant in the limits of concentrations of from $1,2 \cdot 10^{-6}$ to $1,2 \cdot 10^{-4}$ moles/litre and is equal to approximately 100 mV.

The study of the cataphoretic velocity of gas bubbles was undertaken at the suggestion of Prof. A. Frumkin. We take this

opportunity of expressing our sincere gratitude to him for his valuable advice during our work.

The Karpov-Institute for Physical Chemistry,
Laboratory of Surface Phenomena,
Moscow.

Received
April 11, 1938.