

The Electrokinetic Potential at Gas-Liquid Interfaces

I. The cataphoretic velocity of gas bubbles in solutions of inorganic electrolytes

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Introduction

The existence of potential differences at the gas-liquid interfaces is in some respects due to less complicated phenomena than at the liquid-liquid or solid-liquid interfaces, since in the first case there is no interchange of ions between the two phases. The total potential difference ϵ is in this case localised entirely in the liquid phase, and is due to the adsorption of ions and molecules at the interface and to their orientation¹. Its electrokinetically active part ζ depends exclusively on the adsorption of ions, since electrokinetic phenomena are only possible if the positive and negative charges of the electrical double layer can be separated.

Systems with gas-liquid interfaces are therefore of special interest for the study of the relations between the double layer structure and electrokinetic phenomena, and for the comparison between electrokinetic and thermodynamic potentials.

After Kenrick's² investigations on the total potential difference ϵ at the liquid-gas interfaces, which date from the end of the last century, Frumkin was the first to study systematically the influence of inorganic and organic substances on the value of ϵ .

¹ A. Frumkin, *Erg. exakt. Wiss.*, **7**, 235 (1928).

² Kenrick, *Z. physik. Chem.*, **19**, 625 (1896).

He found that the value of ϵ at the surface of inorganic electrolyte solutions (the negative sign of which is due to the preferential adsorption of anions) varies within large limits with the nature of the anion³.

On the other hand, no influence of the nature of the cation was noted, although it could have been expected from the influence of the valency of cations on the ζ -potential of disperse systems with negative solid phases. Frumkin's results are related, however, to concentrated solutions (from 0,3—0,5 *N* to 10 *N*) whereas the influence of cations on ζ is always observed at concentrations below 0,01 *N*—0,001 *N*.

Unpublished data obtained by Gerowitsch⁴ show that, below 0,01 *N*, solutions of salts of K⁺, La⁺⁺⁺, Th⁺⁺⁺⁺-ions differ in their behaviour towards ϵ .

At the surface of very dilute solutions of all these salts, the total p. d. is practically the same (some — 25 mV against 0,01 *N* KCl). The rate of decrease of this p. d. when the concentration increases depends, however, on the valency of the cation and is at its highest for Th⁺⁺⁺⁺ salts, but even in the latter case its sign is not reversed at concentrations above 0,01 *N*. The first attempts to measure the charge of gas bubbles were already made by Quincke⁵ in 1861, but the existing data on electrokinetic potentials at the gas-liquid interface are up to the present moment contradictory and uncertain, not only in respect to the magnitude but also in respect to the sign of the charge.

The determination of the charge of gas bubbles was made by different methods. Coehn⁶ and Mozer⁷ attempted to make use of "waterfall electricity" effects for this object, assuming that the charge appearing in the atmosphere is the same charge that can be measured by the cataphoresis of gas bubbles. Investigations made by different authors⁸ showed that the observed effect can be

³ A. Frumkin, *Z. physik. Chem.*, **109**, 34 (1924).

⁴ Experiments carried out in the electrochemical laboratory of the University of Moscow.

⁵ Quincke, *Pogg. Ann.*, **103**, 513 (1861).

⁶ A. Coehn u. H. Mozer, *Wied. Ann.*, **48**, 1005 (1915).

⁷ H. Mozer, *Diss. Göttingen*, 1916.

⁸ See a review of the latest researches by Bühl, *Koll. Z.*, **59**, 346 (1932).

explained by the tearing apart of both sheets of the electric double layer. The excess of charges of one sign is carried into the surrounding atmosphere.

The magnitude of this effect depends on the presence of electrolytes in water. The physical quantities with which this method operates are, however, not well enough defined, and the data obtained cannot be directly compared with ϵ - and ζ -potentials.

Coehn⁹ and Neumann¹⁰ attempted to determine the charge of gas bubbles assuming that the size of gas bubbles which are formed during electrolysis depends on the attraction by, or repulsion from, the electrodes; they came to the conclusion that the bubbles are negative in alkaline solutions and positive in acid ones. It was, however, shown by Kabanov and Frumkin¹¹ that the size of the bubbles which are evolved at the electrodes during electrolysis is determined by the surface tension and the contact angle at the limit bubble (electrode) solution, and that the angle itself depends on the polarization of the metal surface. The electrostatic force between the bubble and the electrode is 10^6 times smaller than it is required in order to keep the bubble from rising.

Coehn's and Neumann's conclusions concerning the sign of the bubble charge are therefore unfounded.

So also are their attempts to determine the sign of the bubble charge from the movement of minute bubble streams near the electrodes during electrolysis¹². This effect is mostly due to convection currents in the liquid and to the movement of bubbles in the non-uniform field near the electrode, owing to the fact that the dielectric constants of water and gas are very different.

Compared with all these methods the cataphoretic methods which connect the velocity of gas bubbles in an electric field with their electrokinetic potential at the gas-solution interface are more reliable.

After Quincke the first systematic investigations in that

⁹ A. Coehn, *Z. Electrochem.*, **29**, 1, 88 (1923).

¹⁰ A. Coehn u. H. Neumann, *Z. Physik*, **20**, 54 (1923).

¹¹ B. Kabanov a. A. Frumkin, *J. Phys. Chem. (Russ.)*, **1**, 538 (1933); *Z. physik. Chem.*, **A 165**, 433 (1933).

¹² A. Coehn u. H. Neumann, *Z. Physik*, **20**, 68 (1923). A. Coehn, *Z. Elektrochem.*, **31**, 552 (1925).

direction were made by MacTaggart¹³ and Alty¹⁴ who measured the cataphoresis of gas bubbles in a horizontal cylindrical tube 5—6 cm. in diameter, closed at both ends with metallic discs acting as electrodes.

Owing to a rapid and uniform rotation of the tube, the bubble remains on the axis. MacTaggart and Alty studied the influence on the cataphoretic velocity of the nature of the gas, of the presence of various inorganic electrolytes and organic surface-active substance, and of the size of the bubbles. They admitted, however, a fundamental error which invalidates all the results obtained by this method: the electroosmotic flow of the liquid in the closed tube is not taken into account. It is well known from the theory of electrokinetic phenomena that if an electric field is applied to a closed cylindrical cell, the liquid flows along the walls owing to electroosmosis and flows back in the opposite direction along the axis. At a distance equal to $\frac{R}{\sqrt{2}}$ from the axis the velocity of the liquid is zero¹⁵.

If the particle and the wall of the cell have charges of the same sign, the velocity of the particle and of the liquid are subtracted along the wall and added along the axis¹⁵.

Although it was already noted by Quincke that the observed velocity of a bubble in a liquid is equal to the sum of its true cataphoretic velocity and of the velocity of the liquid at this point, this correction was not taken into account in subsequent investigations. Whilst the repartition of velocities in the stationary state is in no way related to the dimensions of the cataphoretic cell, it was usually assumed that the electroosmotic effect must only be accounted for in very narrow tubes or very flat cells. Freundlich notes, for instance, that the velocity of the liquid in the middle of the cell may be neglected, and the observed velocity considered as the true cataphoretic velocity only in the case of cells which are not less than 2 mm. deep¹⁶. He probably assumes that the movement

¹³ MacTaggart, *Phil. Mag.*, (6) **27**, 297 (1914); **28**, 367 (1914); **44**, 386 (1922).

¹⁴ Alty, *Proc. Roy. Soc.*, **A 106**, 315 (1924); **110**, 178 (1926); **112**, 235 (1926). Currie and Alty, *Proc. Roy. Soc.*, **A 122**, 622 (1928).

¹⁵ See for instance H. Abramson, *Electrokinetic Phenomena*, p. 75, New York, 1934.

¹⁶ H. F. Freundlich, *Kapillarchemie*, **1**, 343 (1930).

of the liquid is transmitted from the walls towards the middle of the cell so slowly, that in large tubes the liquid is still motionless in the middle of the cell when the measurement is made.

The same assumption is apparently made by Mac Taggart who mentions the electroosmosis of water but does not take it into account. It will be shown later that the movement of the liquid is in reality transmitted so rapidly that it is already quite marked during the first second after closing the circuit.

The necessity of accounting for the electroosmotic flow is only considered in more recent investigations by Mooney¹⁷ and Newton¹⁸, who found that the repartition of velocities is parabolic in tubes 0.8 cm. wide, by Currie¹⁹ who also showed that the parabolic distribution in a cylindrical tube does not depend on its diameter and by Alty and Johnson²⁰ in their investigations on the cataphoresis of fatty acid particles.

The same considerations are mentioned by Abramson²¹ in his monography on electrokinetic phenomena. In the first series of our measurements the electroosmotic flow was also neglected. As will be shown further, this leads to most important errors, concerning not only the magnitude but also the sign of the charge.

The introduction of the electroosmotic correction presents considerable difficulties in the case of gas bubbles, since the usual method which consists in measuring the velocity at different definite distances from the walls of the cell cannot easily be applied in this case.

We tried various methods of accounting for, or excluding electroosmosis in our experiments. The method which was finally adopted gave the possibility of making a series of measurements in solutions of inorganic and organic substances which lead to interesting conclusions although its accuracy is by no means satisfactory.

The present paper deals with all the methodic part and the results of measurements in water and solutions of KCl and ThCl₄;

¹⁷ Mooney, *Phys. Rev.*, **23**, 396 (1924).

¹⁸ Newton, *Phil. Mag.*, **9**, 769 (1930).

¹⁹ Currie, *Phil. Mag.*, **12**, 429 (1931).

²⁰ Alty a. Johnson, *Phil. Mag.*, **20**, 129 (1935).

²¹ H. Abramson, *Electrokinetic Phenomena*, p. 249.

the data concerning organic substances constitute the object of a second paper.

Recent publications by R. Auerbach²² are concerned with disperse suspensions of gases in water. The methods described are certainly of interest, but the author has not yet published any data on the electrokinetic properties of these systems.

Method of measurement

The formation of bubbles

The cataphoretic velocity was measured by the deflection in a horizontal field of a bubble ascending freely through the liquid. The deflection was directly read on the eye-piece micrometer scale of a travelling microscope, using the vertical rack and pinion movement of the microscope tube to follow the bubble.

For the measurement to be exact, the lowest possible vertical velocity, and consequently the smallest size of the bubble is required. Very small bubbles, however, dissolve rapidly in water.

The pressure p_a at which the liquid is saturated with the gas, the pressure p_m under which is the liquid when the bubble escapes, and the radius r of the bubble in equilibrium with the solution are related by the equation

$$p_a = p_m + \frac{2\sigma}{r} \quad ^{23}$$

where σ is the surface tension of the liquid.

All the bubbles whose radius is smaller than r dissolve in the liquid, whilst all the bubbles of larger dimensions increase at the expense of the dissolved gas. Owing to the hyperbolic relation between r and p_m , it is difficult to work with very small bubbles, because minute differences in the value of r correspond to very large variations of the equilibrium pressure. Practically, it is most convenient to make measurements with bubbles from 0,01 to 0,02 mm. in diameter. It can easily be shown that such small bubbles cannot be obtained by pressing gas through a small hole

²² R. Auerbach, Koll. Z., **74**, 129 (1936); **77**, 161 (1936); **80**, 27 (1937).

²³ We were made aware of this relation by B. N. Kabanov, to whom we are happy to express our gratitude.

or a fine capillary²⁴. The bubbles were therefore originated by electrolysis in the liquid under test. The size of the bubbles evolved depends on the polarization of the electrodes and can be as small as required.

The cataphoretic cell

For our first measurements, in which the electroosmotic flow was not taken into account, we used an apparatus whose chief shortcoming was the occurrence of considerable convection currents. After different modifications we finally chose the simpler construction which is shown in Fig. 1.

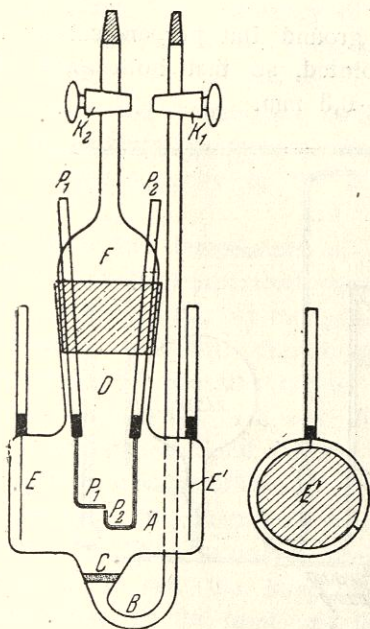


Fig. 1.

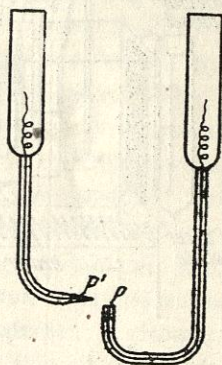


Fig. 2.

The cell consists of horizontal tube A 6—6.5 cm. in diameter and 10 cm. long. A tube B with a filter of sintered glass C and a stopcock K_1 is fused to the lower part of tube A for the saturation of the liquid with gas. At both ends of A two large platinum

²⁴ The order of magnitude of the volume of a bubble escaping from a capillary can be estimated by equating the upthrust and the surface tension along the line where the bubble is torn off. There results that for a bubble of $r=0.01$ mm. in water the radius of the capillary must be about 10^{-1} cm., i. e., the diameter of the capillary must be of molecular dimensions.

electrodes EE' , 5,6 cm. in diameter, allow of obtaining a uniform electric field. A wide neck with a ground stopper, bearing the electrodes P_1P_2 for the electrolytic evolution of gas bubbles, and a stopcock K_2 for the gas outlet are fused to the upper part of A_1 . The cell is made of Jena glass.

The electrodes for the evolution of gas bubbles are made of a platinum wire 0,05 mm. in diameter fused into glass capillaries 1—2 mm. wide (outer diameter) which were afterwards curved and mounted as shown in Fig. 2.

The end of electrode P_1 is ground flat perpendicularly to its length, whilst electrode P_2 is pointed, so that both ends of the wires can be approached to 0,2—0,3 mm.

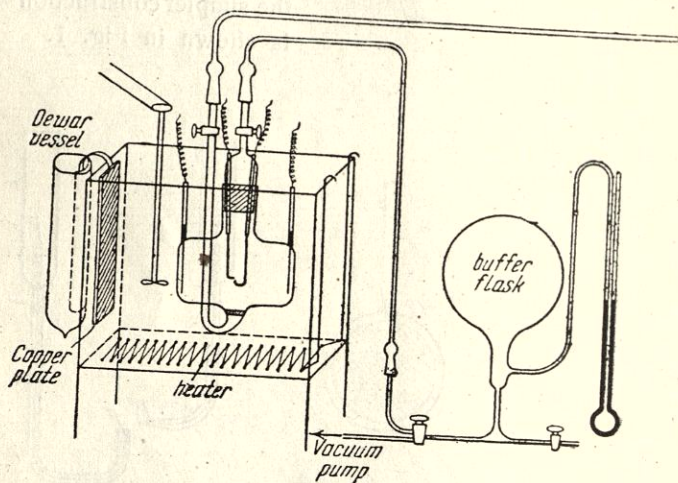


Fig. 3.

The high current density necessary for the evolution of small bubbles can readily be obtained on electrode P , where only the cross-section of the platinum wire is exposed. The exact adjustment of the electrodes in the stopper was controlled under the microscope.

The voltage applied to the electrodes for the evolution of bubbles varied in the different solutions. Up to 1000 V were necessary in pure water.

The solution was saturated with gas at atmospheric pressure; the bubbles were evolved, the liquid being under a pressure 150—250 mm. Hg below the atmospheric. For a bubble 0,01 mm.

in diameter, the equilibrium pressure p_m equals $(p_a - 222)$ mm. Hg, where p_a is the atmospheric pressure. The cell was connected with a vacuum pump, a manometer and an empty flask acting as a buffer.

The whole arrangement is shown in Fig. 3.

The water bath

The cell was kept in a water bath with plane-parallel walls of mirror glass. The constancy of temperature is most important.

At first we made the measurements at $25 \pm 0,05$; later we found $4 \pm 0,1$ more convenient because near the maximum of water density the convection currents are at a minimum. Besides at this temperature the measurements are easier because of the decrease of the velocity of the bubbles owing to the increase of viscosity.

To keep the temperature at 4° , the water was continuously cooled so that its temperature would have been $2-2,5$ without supplementary heating. At the same time it was heated by means of a nichrome coil with thermoregulator and relays. The cooling was assumed by a massive copper plate bent so that one end was immersed in the water bath and the other in a Dewar vessel containing a mixture of solid carbon dioxide and acetone. This thermostat system is a modification of Schattenstein's cryostat²⁵. On the outside the water bath was thoroughly isolated with cloth. A cooling cell with saturated alum solution was placed between the water bath and the lamp that illuminated it from behind. Scratches made on the front and the back side of the cataphoretic cell allowed of adjusting it in the water bath so that the line passing through the centre of the tube and the electrode P should be vertical.

Before each series of measurements the solution was saturated with hydrogen in the apparatus during 1—2 hours. Before switching on the field, the absence of convection currents or other accidental motions of the liquid was controlled by the free rise of gas bubbles.

The deviation from the vertical should not exceed 1—2 divi-

²⁵ A. Schattenstein, Z. Elektrochem., **40**, 653 (1934).

sions of the eyepiece scale, *i. e.*, 0,05—0,1 mm. when the microscope tube was raised over 1,5—2 cm.

The flow of the liquid in the cell

Assuming that the velocity distribution in the cell during cataphoresis must be independent of the nature of the particles, we made these measurements with emulsions of a CCl_4 — C_6H_6 mixture in water instead of gas bubbles. The proportions can easily be chosen so that the density of the mixture is equal to that of water, so that the droplets show no vertical motion.

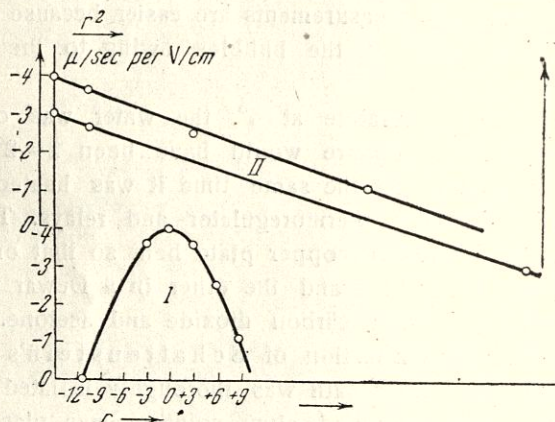


Fig. 4.

Measurements of the stationary velocity of the droplets at different distances from the axis of the cell in a horizontal plane show that the repartition is parabolic as a function of the distance (Fig. 4, curve I) and linear as a function of the square of the distance (Fig. 4, curve II).

The repartition of velocities along the vertical axis is different as can be seen from Table 1.

The velocity is constant for 3 cm. along the vertical, and its value changes only in the lower part. This is due to the form of the cell which can apparently be compared in its upper part to a flat cell with parallel walls owing to the wide neck O.

In a long cylindrical cell the velocity observed along the axis is equal to

$$V = v + u,$$

where v is the true cataphoretic velocity, and u , the electroosmotic velocity of the liquid.

In a flat cell we have

$$V = v + \frac{1}{2} u.$$

Since the form of our cell is intermediate, the correction which must be introduced to allow for the electroosmotic flow must have an intermediate value which cannot be calculated beforehand.

Several ways were tested for obtaining the true cataphoretic velocity. In order to eliminate the electroosmotic flow, we reduced the electric field along the walls to 10% of its value in the middle of the cell, by replacing the large electrodes EE' in tube A by small ones, 1 cm. in diameter. This did not, however, give satisfactory results

because of irregular motion of the droplets arising in the cell near the electrodes. A considerable increase of both the electrodes and the cell (parallel electrodes 3 cm. in diameter in a spherical tube 15 cm. in diameter) was not successful either because of convection currents.

The increase of the observed velocity along the axis of the cell after the field was applied and its decrease after it was cut off was registered as a means of determining the electroosmotic flow. In the moment the electric field is applied, the velocity of the droplet relative to the liquid becomes steady with the same value at any point of the cell. At the same moment the electroosmotic flow of the liquid sets in along the walls of the cell, but it is transmitted towards the middle of the cell owing to friction with

Table 1

Vertical distance from the middle of the tube (cm.)	Observed velocity (μ /sec. per V/cm.)
-3	1,8
-2	2,5
-1,5	2,9
-1	3,6
0 (axis of the tube)	3,6
+1	3,6
+2	3,6

a finite velocity. The curves *a* and *b* Fig. 5 represent the mean velocity per V/cm. of a droplet in the middle of the cell during successive intervals of time after the field is applied (*O*) and cut off (*P*). The observations were timed by means of a metronome. By extrapolating the curves to the moments of closing and opening the circuit it should be possible to obtain the true cataphoretic velocity of a droplet or of a gas bubble. This method could not, however, be used, because during the time required for the measurements the electric current created marked convection currents in the liquid. Besides, the adopted method of determining the velocity did not allow of noting at the beginning of the curve a number of points sufficient for the extrapolation to be reliable.

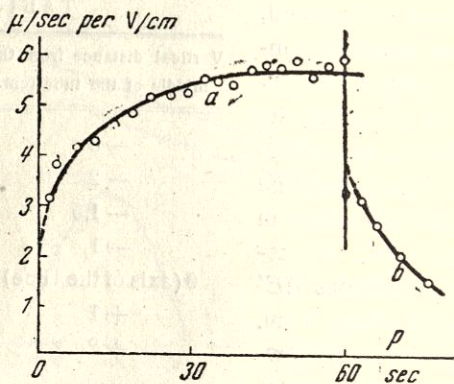


Fig. 5.

The curves in Fig. 5 show that in the middle of the cell the true velocity is established during 20–30 sec., but that already after the first seconds the liquid acquires a marked velocity.

The cell constant

The method which was finally adopted consisted in empirically determining a coefficient characteristic of the motion of the liquid in the cell during the first second after the field is applied.

If u is the electroosmotic mobility of the liquid along the walls, the displacement Δu of the liquid along the axis during the

first second per V/cm. can be expressed by αu , where $\alpha < 1$ is a constant for each cell²⁶.

If v is the real cataphoretic velocity of the particle, its observed displacement s during the first second per V/cm. is

$$s = v + \Delta u$$

α being known, if s is directly measured and u determined in an independent measurement, v can easily be calculated:

$$v = s - \Delta u = s + \alpha u.$$

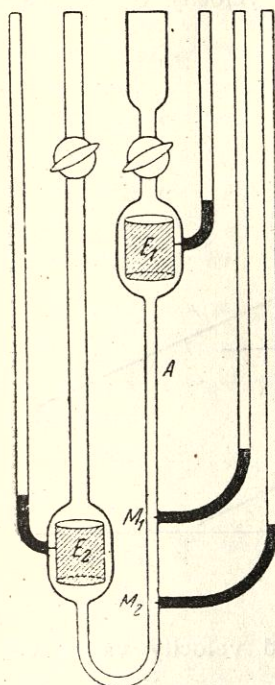


Fig. 6.

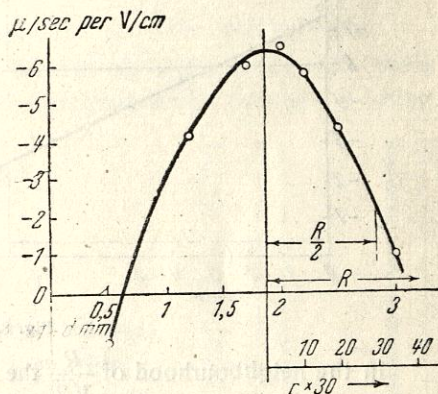


Fig. 7.

To determine α , the values of v , s and u must be measured separately for the same system.

s was measured in the cell shown in Fig. 1. The time was measured by means of a metronome striking intervals of $1/2$ sec.

v and u were determined in the microcataphoretic cell shown in Fig. 6.

The p. d. was applied to the electrodes EE' and measured on the electrodes M_1M_2 by means of an electrostatic voltmeter. The cell was placed in the water bath at $+4^\circ\text{C}$. The motion of the droplets at different distances from the walls of the cell was

²⁶ The sense of the movement of the liquid along the axis is always opposed to that of the electroosmotic velocity along the walls.

observed with a travelling microscope, using a transverse scale with a vernier adjusted to the horizontal motion of the microscope tube. Along the axis, the steady velocity is $u + v$; at a distance $\frac{R}{\sqrt{2}}$, R being the inner radius of the tube, the velocity of the liquid is zero, and the observed velocity equals v .

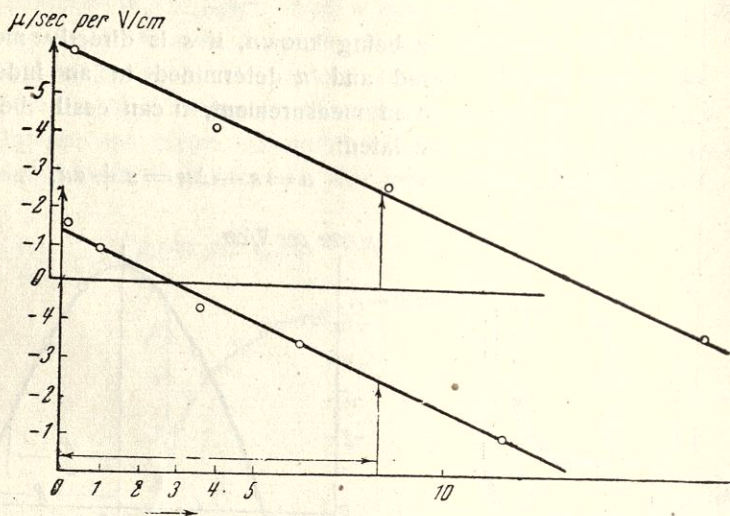


Fig. 8.

In the neighbourhood of $\frac{R}{\sqrt{2}}$ the observed velocity varies very rapidly with small variations of r , so that the measurements made at this distance often lead to considerable errors. Exact values of v were obtained from the whole curve for $V = v + u$ as a function of the distance. The variation of V with the square of the distance r from the axis must be linear. The ordinate of the point corresponding to the abscissa $\frac{R^2}{2}$ on this straight line gives the true velocity v .

The electroosmotic mobility u is the difference between v and the ordinate of the parabola on its axis; a typical parabola representing the distribution of velocities is shown in Fig. 7; the two straight lines corresponding to both branches are shown in Fig. 8.

From s , u and v we obtain $\alpha = \frac{s-v}{u}$. Considering α as a con-

stant for each cell we assume that the transmission of the motion of the liquid from the walls towards the axis depends only on hydrodynamical factors and is independent of ζ . The determination of α with different disperse systems in the same cell confirms, as it will be shown further, the correctness of this assumption.

The displacement of the gas bubble during the first second was measured in the cataphoretic cell shown in Fig. 1, as it was described for the droplets.

Twenty consecutive readings were always made, the field being reversed after each reading. The average displacement of the bubble was 1—3 divisions of the scale, fractions of a division being estimated approximately.

Electroosmotic mobility of the solution

The electroosmotic mobility of the solution along the walls of the cell was obtained from the electroosmotic pressure p using the equations

$$p = \frac{2\zeta ED}{\pi r^2} \quad \text{and} \quad u = \frac{\zeta D}{4\pi\eta},$$

whence

$$u = \frac{r^2}{8\eta} \frac{p}{E} \quad \text{or} \quad u = \frac{r^2 g}{8\eta} \cdot \frac{h}{E},$$

where p is the pressure of the water column, h its height, r the radius of the capillary; D and η have their usual meaning. p was measured in the apparatus shown in Fig. 9. The motion of the meniscus in the capillary tube b , caused by electroosmosis in the capillary tube a when a p. d. is applied to the electrodes EE' , was read on the eyepiece scale of the horizontal microscope. All readings were made several times in either direction of the field.

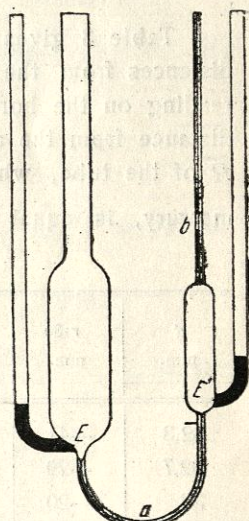


Fig. 9.

Results of experiments

The cell constant

To determine the cell constant at different ζ -potentials we used emulsions of a CCl_4 — C_6H_6 mixture in water (negative droplets) and suspensions of glass powder in solutions 10^{-5} N KCl

(negative charge of the glass) and $4 \cdot 10^{-5} N \text{ ThCl}_4$ (positive charge of the glass).

In the Tables which follow, the positive velocity corresponds to the motion of a particle or of the liquid along the axis towards the cathode; a negative velocity, to the movement towards the anode. Table 2 gives the values of the displacement of droplets (average over 20 readings in both directions of the field) at different voltages during the first second after the closing of the circuit. n is the number of divisions of the scale; E , the voltage; s , the displacement per V/cm. One division of the scale equals

Table 2

E V/cm.	n divisions	s μ
18,7	1,5	—4,4
21,4	1,7	—4,4
27,8	2,3	—4,5
28	2	—3,9

Mean value of s — 4,3 per V/cm:

$$5,5 \cdot 10^{-3} \text{ cm. } s = \frac{n \cdot 55}{E} \mu.$$

Table 3 gives the observed velocity $V = u + v$ at different distances from the walls of the microcataphoretic cell. d is the reading on the horizontal scale of the microscope in mm.; r , the distance from the axis, read on the microscope scale. The radius R of the tube, which is known from preliminary calibration with mercury, is equal to 1,81 mm., so that the distance $\frac{R}{\sqrt{2}}$ equals

Table 3

d mm.	r .30 mm.	r .9 cm. ²	n	$\left(\frac{1}{t}\right)$ average	E V/cm.	V μ /sec.
32,3	—41	16,81	5	0,085	16,9	+1,38
32,7	—29	8,41	10	0,080	16,9	—2,60
33	—20	4,00	10	0,126	16,9	—4,10
33,5	—5	0,25	20	0,092	16,9	—6,00
33,8	+4	0,16	20	0,100	16,9	—6,51
34	+10	1,00	20	0,089	16,9	—5,79
34,3	+19	3,61	10	0,133	16,9	—4,33
34,5	+25	6,25	10	0,107	16,9	—3,48
34,8	+34	11,56	5	0,062	16,9	—0,98

1,28 mm., the corresponding displacement of the microscope being $\frac{1,28}{1,33} = 0,96$ mm. Each value of V is an average from 5 readings in either sense; n is the number of divisions on the eyepiece scale, over which the droplets move during the time t ; E is the voltage.

As can be seen from the corresponding curves given in Fig. 7, the axis of the parabola corresponds to the point 33,67 mm. on the microscope scale. In the second column of Table 3 the abscissae reckoned from this axis are given; the velocity of a droplet observed at a distance of $\frac{1,28}{1,33}$ mm. from the axis, *i. e.*, at the points $d = 32,71$ and $d = 34,63$ read on the microscope scale, is the true cataphoretic velocity. The third column shows the squares of the distances from the axis. The straight lines corresponding to both branches of the parabola are given in Fig. 8.

On these straight lines the ordinates V_1 and V_2 of the points corresponding to the distance $r = \frac{1,81}{1,33 \sqrt{2}}$, *i. e.*, whose abscissae are $x = r^2 \cdot 9 = \frac{1,81^2 \cdot 9}{1,33^2 \cdot 2} = 8,33$, give the cataphoretic velocity. We used the mean value

$$v = \frac{v_1 + v_2}{2} = -2,4 \text{ } \mu/\text{sec. per V/cm.}$$

On the axis of the parabola, $V = v + u = -6,3 \text{ } \mu/\text{sec. per V/cm.}$, whence

$$u = -6,3 - (-2,4) = -3,9 \text{ } \mu/\text{sec. per V/cm.}$$

Since $s = -4,3 \text{ } \mu$, we have $\Delta u = -4,3 - (-2,4) = -1,9 \text{ } \mu/\text{sec.}$ and finally,

$$\alpha = \frac{-1,9}{-3,9} = 0,48.$$

Table 4 gives different values of α determined by this method with emulsions of carbon tetrachloride-benzene in water.

The determination of α at different ζ -potentials with different disperse systems was made in another cataphoretic cell. The results are given in Table 5. The suspensions in KCl- and ThCl_4 -solutions were made with fine powder of Jena glass, thoroughly washed

Table 4

s μ	V $\mu/\text{sec. per}$ V/cm.	v $\mu/\text{sec. per}$ V/cm.	$u = V - v$ $\mu/\text{sec.}$ per V/cm.	$\Delta u = s - v$ $\mu/\text{sec. per}$ V/cm.	$\alpha = \frac{\Delta u}{u}$
-4,2	-7,1	-2,3	-4,8	-2,4	0,40
-4,1	-6,5	-2,2	-4,3	-1,9	0,46
-4,3	-7,1	-2,3	-4,8	-2,0	0,41
-3,5	-6,5	-2,2	-4,3	-1,3	0,30
-3,8	-6,5	-2,3	-4,2	-1,5	0,40
-3,5	-5,7	-1,1	-4,6	-2,4	0,52
-3,5	-6,5	-2,3	-4,2	-1,2	0,29
Mean $0,4 \pm 0,1$					

with conductivity water, and then shaken with the respective solution until adsorption equilibrium had been attained.

It can be seen from these Tables that the value of $\frac{\Delta u}{u}$, which is characteristic for the propagation of the velocity from the walls of the cell towards its middle, is, within the limits of experimental errors, independent of the nature of the disperse system used. The difference between the values of α for two cells which had apparently the same size and form could not be explained.

Table 5

Disperse system	s	V	v	$u = V - v$	$\Delta u = s - v$	$\alpha = \frac{\Delta u}{u}$
Emulsion	-4,3	-6,3	-2,4	-3,9	-1,9	0,48
$\text{CCl}_4 + \text{C}_6\text{H}_6$ in water	-3,6	-6,0	-1,4	-4,6	-2,2	0,48
	-3,5	-5,9	-1,3	-4,6	-2,2	0,48
Suspension glass powder in $10^{-5}N \text{KCl}$	-3,0	-4,6	-1,6	-3,0	-1,4	0,46
	-3,4	-4,9	-1,4	-3,5	-2,0	0,59
	-3,5	-4,6	-1,3	-3,3	-2,1	0,63
	-3,4	-4,8	-2,0	-2,8	-1,4	0,50
Suspension glass powder in $4 \cdot 10^{-5}N \text{ThCl}_4$	+3,4	+4,9	+2,0	+2,9	+1,4	0,48
$\alpha = 0,5$						

The measurements were carried out partly in the first cell, partly in the second.

Mobility of gas bubbles in an electric field without correction for electroosmosis

Our first series of experiments were made without taking into account the electroosmotic flow. The curves corresponding to the

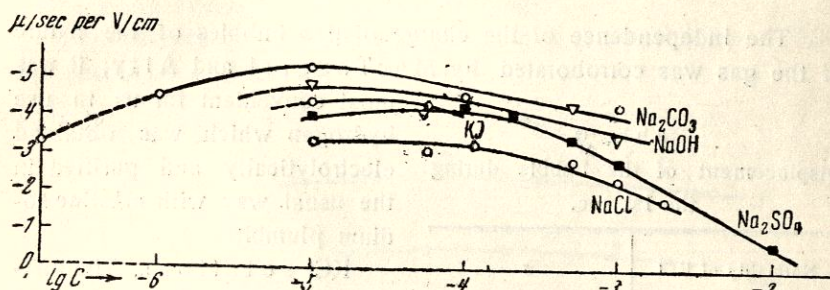


Fig. 10.

mobility of oxygen bubbles in solutions of inorganic salts with different anions and cations are shown in Figs. 10 and 11.

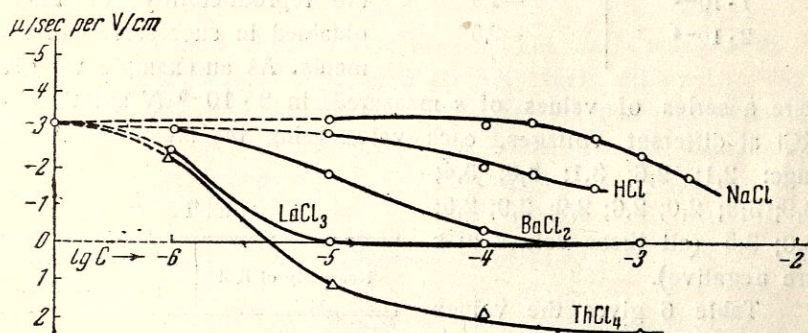


Fig. 11.

These results lead to the conclusion that gas bubbles behave in respect to the influence of different ions quite similarly to nega-

tive colloid particles. It was just this analogy with curves obtained at the glass-liquid interfaces which induced us to pay special attention to the estimation of the water motion due to electroosmosis.

True cataphoretic velocity of bubbles in solutions of inorganic salts

The independence of the charge of gas bubbles of the nature of the gas was corroborated by MacTaggart and Alty; it was most convenient for us to use hydrogen which was obtained electrolytically and purified in the usual way with alkaline sodium plumbite.

Table 6
Displacement of the bubble during the 1st sec.

Normality of KCl	s
$5 \cdot 10^{-6}$	-2,9
$1 \cdot 10^{-5}$	-2,9
$2 \cdot 10^{-5}$	-3,0
$5 \cdot 10^{-5}$	-2,9
$1 \cdot 10^{-4}$	-2,9
$2 \cdot 10^{-4}$	-2,5

here a series of values of s measured in $2 \cdot 10^{-5} N$ solutions of KCl at different voltages, each value being the mean of 20 readings: 2,1; 2,6; 3,1; 3,0; 3,4; 3,9; 3,3; 2,0; 2,6; 2,9; 2,9; 2,5; 3,0; 3,5 (all these values of s are negative).

Table 6 gives the values of s obtained in KCl-solutions of different concentrations in the cell, where $\alpha = 0,5$; each value of s is the mean of 5—10 independent measurements.

KCl solutions. The bubble usually moved within 1—3 scale divisions; fractions of a division were appreciated approximately. The exactness of the readings can be estimated by the reproducibility of results obtained in successive measurements. As an example we give

Table 7

Normality of KCl	Electroosmotic velocity $\mu/\text{sec. per V/cm.}$
10^{-5}	3,1
10^{-4}	2,6
$5 \cdot 10^{-4}$	2,5

Table 7 gives the values of the electroosmotic mobility of KCl-solutions in a cell of Jena glass.

$$u = \frac{r^2 g}{8\eta} \frac{h}{E} = \frac{r^2 g \cdot 55 \cdot 10^{-4}}{8\eta} \cdot \frac{n}{E},$$

where n is the number of scale divisions; E the applied voltage. Taking $g = 981 \text{ cm/sec}^2$, $\eta = 1,6 \cdot 10^{-2}$ and, for this particular capillary tube, $r^2 = 2,28 \cdot 10^{-4} \text{ cm}^2$ we have $u = 9 \cdot 59 \cdot \frac{n}{E}$. Each value is an average over several readings.

The curves corresponding to the values of s and $\Delta u = -0,5 u$ are shown in Fig. 12.

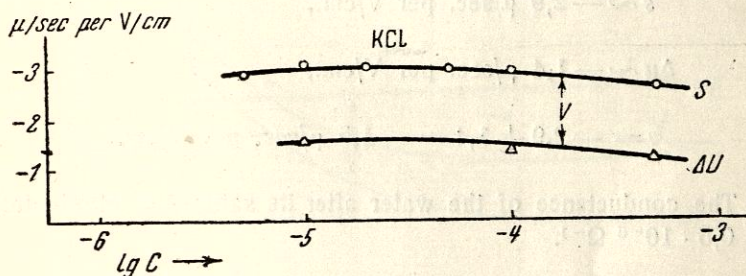


Fig. 12.

It can be seen that both values do not vary much with the concentration between $10^{-5} N$ and $10^{-3} N$; their difference, which is equal to the true cataphoretic velocity, remains approximately constant and equal to $-1,5 \mu/\text{sec. per V/cm}$. To the cataphoretic mobility v corresponds a value of ζ given by

$$\zeta = \frac{4 \cdot \pi \eta V \cdot 9 \cdot 10^4}{D} = 1,41 \eta V,$$

if V is expressed in $\mu/\text{sec. per V/cm}$. and the potential difference in volts.

For $\eta = 1,6 \cdot 10^{-2}$ and $V_4 = -1,5 \mu/\text{sec.}$ we have

$$\zeta \sim -34 \text{ mV.}$$

Water. The values of v obtained in pure water are but poorly reproducible and unreliable; the gas bubbles are evolved electrolytically with great difficulty, and their formation is apparently connected with the accumulation of electrolytes near the electrodes. In what measure the bubble surface is contaminated by these electrolytes during its formation remains unclear. Besides that, the bubbles being evolved in a very intense electric field (up to 40 000 V/cm.), at the moment they escape from the electrodes they are set in rapid motion which does not cease immediately after the field is cut off.

The values of s and u are the same as in dilute KCl-solutions:

$$s \sim -2,9 \text{ } \mu\text{/sec. per V/cm.},$$

$$\Delta u \sim -1,4 \text{ } \mu\text{/sec. per V/cm.},$$

$$v = -2,9 + 1,4 = -1,5 \text{ } \mu\text{/sec. per V/cm.}$$

The conductance of the water after its saturation with hydrogen was $0,5 \cdot 10^{-6} \Omega^{-1}$.

Table 8

ThCl₄-solutions. $\alpha = 0,4$

Normality	$s \text{ } \mu\text{/sec. per V/cm.}$	$u \text{ } \mu\text{/sec. per V/cm.}$	ζ_g mV	$\Delta u = -\alpha u$ $\mu\text{/sec. per V/cm.}$	$v = s - \Delta u$ $\mu\text{/sec. per V/cm.}$	ζ_{H_2} mV	Apparent sign of bubble charge	Real sign of bubble charge
10^{-8}	-2,5	+4,0	- 90	-1,6	-0,9	-20	—	—
$3 \cdot 10^{-6}$	-0,9	-1,3	+ 29	+0,5	-1,4	-31	—	—
$5 \cdot 10^{-6}$	-0,4	-1,5	+ 34	+0,6	-1,0	-22	—	—
10^{-5}	0	-1,9	+ 43	+0,8	-0,8	-18	0	—
$5 \cdot 10^{-5}$	+0,5	-4,2	+ 95	+1,7	-1,2	-27	+	—
10^{-4}	+0,3	-5,0	+113	+2,0	-1,7	-38	+	—
$5 \cdot 10^{-4}$	+0,4	-4,9	+110	+2,0	-1,6	-36	+	—
10^{-3}	+0,3	-4,9	+840	+2,0	-1,7	-38	+	—
10^{-2}	—	-3,7	+ 84	-1,5				

ThCl_4 -solutions. The results are given in Table 8; besides the values of s , u and v the corresponding values of ζ at the interfaces glass-solution (ζ_g) and H_2 -solution (ζ_{H_2}) are given.

Fig. 13 shows the curves representing s , u and v at different concentrations of salt.

It can be seen that the true sign of the bubble charge remains negative, and the value of its cataphoretic mobility varies but little with the concentration of the salt, fluctuating around $-1.5 \mu/\text{sec}$ per V/cm . corresponding to $\xi = -34 \text{ mV}$.

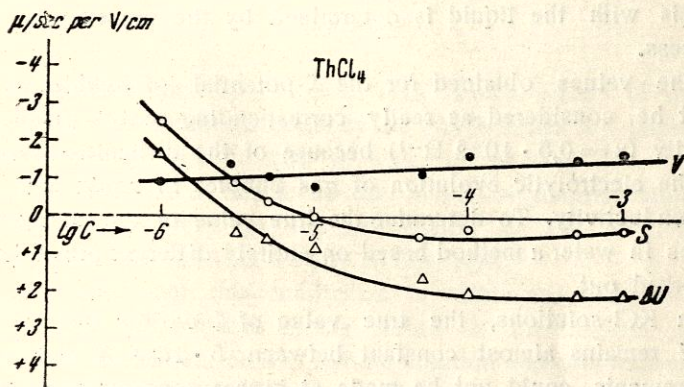


Fig. 13.

The exactness of the measurements of s is very low, especially at concentrations above 10^{-5} N . Since at high voltages at these concentrations the electric current causes marked convection currents, we were confined to fields below $30 \text{ V}/\text{cm}$. The corresponding displacements are within 1 scale division, and the errors in their estimation may reach 50% and more. The least reliable are the values $s \sim 0.3 - 0.5$; most probably the true values of s are higher, and consequently v is smaller.

Discussion

The values of the true cataphoretic mobility, obtained from the observed velocity corrected for the electroosmotic flow, show

that gas bubbles have a negative charge in water and inorganic salt.

This is what should be expected from the total p. d. at the same interfaces, which is determined by the preferential adsorption of anions on the surface of water, the corresponding cations being attracted electrostatically. During the cataphoretic movement, the gas bubble is surrounded by a liquid film which contains the anions and forms the outer sheet of the double layer with respect to the liquid, or the inner sheet with respect to the bubble. The positive sign of the other sheet which is bound during electrophoresis with the liquid is determined by the presence of cations in excess.

The values obtained for the ζ -potential of bubbles in water cannot be considered as really corresponding to the given degree of purity ($\alpha = 0,5 \cdot 10^{-6} \Omega^{-1}$) because of the difficulties associated with the electrolytic evolution of gas bubbles in liquid with a very low conductivity. To determine the true value of the charge of gas bubbles in water a method based on entirely different principles must be worked out.

In KCl-solutions, the true value of ζ on the surface of the bubble remains almost constant between $5 \cdot 10^{-6} N$ and $10^{-3} N$. Measurements could not be made at higher concentrations because of convection currents. The true cataphoretic velocity is about one half of the apparent one.

Our method allowed of definitely solving the question of the charge reversal by tetravalent cations on gas bubbles. There being no specific adsorption of cations at these interfaces, it could not be understood what accounted for the charge reversal mentioned by various authors. It appears that at a definite concentration of ThCl_4 the gas bubbles are in fact transported towards the cathode in an electric field, but that this is due to their being carried along with the water which moves towards the cathode with a velocity superior to that of the bubbles towards the anode. At this concentration of ThCl_4 the walls of the vessel become positive with respect to the liquid, and the liquid moves towards the anode along the walls and flows back towards the cathode along the axis. The real charge of the bubbles, however, remains negative at all concentrations of ThCl_4 .

The precision of our method was not sufficient to determine definitely the magnitude of the charge of the bubbles. The value of ζ may still be in error by some 10 mV, which makes it impossible to draw definite conclusions on the influence of concentration. This influence is apparently not large.

The charge of the bubbles, which is but slightly influenced by variations of the salt concentration, is relatively small, and, at any rate, essentially lower than the charge of most negative particles in disperse systems.

Summary

1. A method has been worked out, which allows of determining the true cataphoretic velocity of gas bubbles by taking into account the electroosmotic flow of water in the cell.

2. The method is based on the empirical determination of a coefficient characteristic of the propagation of the water motion from the walls towards the middle of the cell.

3. For each cell this coefficient is within the limits of experimental error independent of the nature of the disperse system, *i. e.*, of the ζ -potentials on the particle-solution and cell-wall-solution interfaces. The measurements were made with emulsions of CCl_4 — C_6H_6 mixtures in water (negative droplets and cell walls), and with suspensions of glass powder in 10^{-5} N KCl (negative particles and cell walls) and $2 \cdot 10^{-5}$ ThCl_4 (positive particles and cell walls).

4. The charge of gas bubbles is negative in water and KCl-solutions. Its true cataphoretic velocity is about one half of the apparent one, and corresponds to a ζ -potential of about — 30 mV.

5. In ThCl_4 -solutions, the true charge of a bubble also remains negative at all concentrations up to 10^{-3} N. The reversal of charge observed at 10^{-5} N is only apparent, and is caused by the carrying away of bubbles with water, with respect to which the sign of charge of the walls is reversed. The true cataphoretic velocity in ThCl_4 -solutions hardly differs from the values obtained for water and KCl-solutions.

6. The concentration of KCl and ThCl_4 is apparently of small influence on the cataphoretic velocity, but it could not be determi-

ned with sufficient accuracy to allow of drawing definite conclusions.

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