

Chemistry. — *The Double Layer of the Silveriodide-Sol.* By E. J. W. VERWEY. (Communicated by Prof. H. R. KRUYT).

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According to investigations by KRUYT and his collaborators¹⁾ the structure and the properties of the silver halogenide sols are given by simple laws. As a negative sol the silver iodide forms a very stable sol, and can be practically entirely liberated by dialysis of the excess of peptizing electrolyte (e.g. KI) and the electrolyte formed (KNO_3).

Accordingly, the silver iodide-sol seems a much better defined sol than e.g. the gold-sol, and a very suitable object for the study of the properties of sols of the hydrophobic type. In an inquiry into the interaction between these dialysed AgI-sols and indifferent electrolytes²⁾ it appeared, however, necessary to acquire a more accurate knowledge of the double layer in these sols. A short account of some researches in this direction will be given here.

1. In the *undialysed* sols the quantity of peptizing electrolyte taken up in the double layer has been determined; this could be done by a very accurate control of the quantities of silver nitrate and potassium iodide used in the preparation of the sols, and the subsequent determination of the quantity of free I^- (resp. Ag^+)-ions in the ultrafiltrate.

I^- and Ag^+ were determined by potentiometric titration of an aliquot part of the ultrafiltrate with greatly diluted AgNO_3 - resp. KI-solutions; I^- in some cases also colorimetrically (with PdCl_2). Besides, of the sols the "surface" per litre of sol was determined by counting the number of sub-microns of the greatly diluted sol in the ultramicroscope per volume unit, and by calculating the total surface of the particles from this on the supposition that they have all the same sizes, and are cube-shaped; to this magnitude only a relative, not an absolute significance can be assigned, the sols being both polydisperse and partly amicronic; the actual total surface of the boundary layer of the particles is always larger than the "surface" determined by counting.

It then appeared that the adsorptivity of AgI to I^- and Ag^+ was not only comparatively small, but that (e.g. expressed in meq. per m^2 of AgI,

¹⁾ H. R. KRUYT and P. C. VAN DER WILLIGEN, *Z. physik Chemie (A)* **139**, 53 (1928).

²⁾ Publication in a following communication.

and per tenth power of the concentration of the free I^- resp. Ag^+ -ions¹⁾) it did not seem to be a well-defined quantity in a single case too. From a great number of experiments some regularities could, however, be established :

a. The adsorption of I^- in the sols varies greatly with time ; an ageing of the sols manifests itself in a continual decrease of the adsorption of the I^- -ion. We find e.g. for the adsorption of I^- (in meq. per litre) after times t with the given sol-concentrations (AgI = millimol AgI per litre, KI = millimol KI added in excess in the preparation) :

AgI	10	10	50			
KI	0.087	0.307	1.32			
"Surface" (per 1. sol.)	35 (m ² /l)	41	190			
	t	ads.	t	ads.	t	ads.
	30 min.	0.064	30 min.	0.085	30 min.	0.28
	5½ hours	0.049	3 hours.	0.063	18 hours	0.18
	24 ,,	0.035	24 ,,	0.053	330 ,,	0.08
	48 ,,	0.030	800 ,,	0.032		

b. In general the adsorption is relatively smaller in more concentrated sols than in more dilute sols (Cf. also the table).

c. The decrease of the adsorption is still much more pronounced at higher temperature. For a sol (AgI = 10 millimol ; KI = 0.107 millimol ; "Surf." = 35 m^2), which after 40 min. contained 0.051 milli-eq. I^- in the double layer, and was then split up into two parts, one part of which was put at 90°, we find :

t	ads. (20°)	ads. (90°)
40 min.	(0.051)	(0.051)
1 1/2 hours	0.049	0.030
18 ..	0.040	0.011

d. Also for the positive sols this decrease of the adsorption is observed, which is, however, much smaller. In newly precipitated AgI relatively less Ag^+ is adsorbed than I^- ; the adsorption, however, only diminishing clearly in the first hours, the adsorption of Ag^+ soon exceeds that of I^- — e.g. :

¹⁾ For the potential-determining ion-adsorption probably $\Delta x = k \cdot \Delta \log c$ holds. (x = adsorption, k = constant, c = equilibrium-concentration). E. LANGE and R. BERGER, Z. Elektrochemie, 36, 171 (1930), Z. physik. Chem. (A) 147, 470 (1930).

AgI AgNO ₃ "Surf."/1	10 0.246 39 m ²	10 0.338 53	10 0.514 43			
	t	ads.	t	ads.	t	ads.
	30 min.	0.062	30 min.	0.046	45 min.	0.061
	20 hours.	0.046	27 hours.	0.041	25 hours.	0.042
	150 ..	0.049	170 ..	0.044	240 ..	0.040
			480 ..	0.038		

On heating the positive sols flocculate, with great adsorption-diminution.

e. The adsorption-diminution is *not* accompanied by a great change in the number of particles; observed changes in the number of countable particles in old sols or sols that had been heated at 90° for a long time (at first it is always found that the number of countable particles slightly increases, apparently in consequence of the growth of amicros on to the ultramicroscopically observable region, at the expense of other amicros that have gone into solution), were always quite inadequate to account for the diminished adsorption as a consequence of surface diminution through coarsening or "ripening" of the silver iodide (in the sense of diminution of the degree of dispersion).

2. In the *dialysed* sols (always electro-dialysis was applied as leading more quickly to the purpose) the quantity of adsorbed iodide will of course have decreased still more as a consequence of the decrease of concentration of the free iodide; since the relation between them is logarithmic, the diminution of the adsorption caused by the dialysis will remain comparatively small: by the dialysis the free iodide-concentration is lowered to 10^{-6} or 10^{-7} molar, i.e., as the adsorption zero-point (the point at which the adsorption of Ag^+ and I^- compensate each other) in saturate AgI-solution ($c_{\text{I}^-} = 10^{-8}$) has not yet been reached, the adsorption decreases to scarcely half in consequence of the dialysis, if c_{I^-} in the undialysed sol was, say, 10^{-4} .

As described above, during the analysis the adsorptive power of the AgI decreases continually; the velocity with which this change in the boundary surface is accomplished in dialysing or dialysed sols differs, however, from that in undialysed sols: for it appears that this velocity is dependent on the free iodide-concentration in the sol. When e.g. a newly-prepared sol was split up into two parts, and one half was dialysed for a few hours, the adsorbed quantity in the undialysed part ($\text{AgI} = 10 \text{ m. mol}$; $\text{KI} = 0.119 \text{ m. mol}$) had decreased from 0.063 to 0.057 meq. during this time, in the dialysed part (also the dialysis water was analysed for this) to 0.050 meq.; a fortnight later these values had, however, become resp. 0.037 and 0.044 meq., i.e. in the undialysed part the adsorbed quantity has

become already smaller in spite of the greater c_{I^-} in the intermicellar liquid: the ageing process is, therefore, furthered by free I^- .

In the dialysed sols the process has, however, not come to a stop; the sols contained always again free iodide after some time: a sol ($AgI = 50$ m. mol; $KI = 0.50$ m. mol) e.g. contained 0.0001 m. eq. of free iodide immediately after the dialysis, after 6 days 0.011, and after 3 months 0.060 meq./l.

The changes in the adsorptivity could also be directly measured; the determination of the adsorptive power of AgI for e.g. KI in dialysed AgI -sols could be made by potentiometric "titration" of these sols with greatly diluted KI -solutions; from the titration curves found the adsorption of KI can then be calculated for any concentration (with satisfactory accuracy only for the lowest concentrations). A sol ($AgI = 10$ m. mol; $KI = 0.134$ m. mol) was e.g. rapidly dialysed (1 day) to $c_{I^-} = 0.0005$ meq./l. and then titrated with 10^{-3} mol. KI -solution. A litre of sol then adsorbed 0.010 meq. KI per tenth power of the equilibrium concentration; the dialysed sol was then heated at 90° for 16 hours (c_{I^-} increased to 0.0195 meq./l. in consequence), and dialysed once more (to $c_{I^-} = 0.0009$ meq.); the adsorptivity for KI had now fallen to 0.003 meq. per tenth power of c_{I^-} ; it had accordingly been reduced to a third of its original value; by renewed heating the adsorptivity decreased again, and soon became immeasurably small.

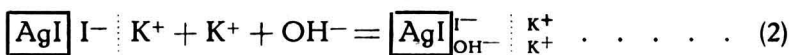
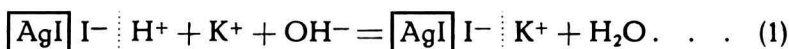
3. *The analytic concentration of dialysed sols* (the molar proportion of iodide in the double layer and AgI in the particles), in consequence of the above-mentioned phenomena, will be greatly dependent on the treatment (degree of dialysis or c_{I^-} after completion of the dialysis, duration of the dialysis, density of the current during the electro-dialysis, original KI content, etc.), which was actually observed more than once. The determination of this concentration took place chiefly according to methods described by PAULI, and applied by him, as well as by RABINOWITCH and others e.g. with the As_2S_3 -sol¹⁾). The quantity to be measured is, indeed, some orders of magnitude smaller in the AgI -sol than in a sol as that of As_2S_3 ; the methods could, however, be adopted to the greater accuracy required. The methods of analysis rest on a measurement of the counter-ions. The counter-ion in a dialysed AgI -sol, prepared e.g. from NH_4I and $AgNO_3$ by means of electro-dialysis (between two membrane filters, "Ultrafeinfilter", according to ZSIGMONDY and BACHMANN, current density 0.5 mA/cm² membrane area), is not the NH_4^+ -ion, but the H^+ -ion. The quantity of H^+ in the double layer can be determined in different ways, and with it the quantity of peptizing electrolyte, HI .

The examined sols were (in connection with the small quantities of peptizing electrolyte in the double layer), much more concentrated than the concentration of 10 m. mol/l. used by KRUYT and VAN DER WILLIGEN,

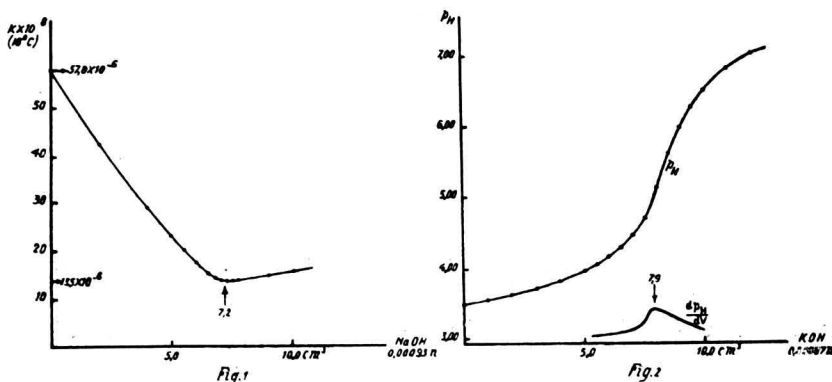
¹⁾ W. PAULI and E. VALKÓ, *Elektrochemie der Kolloide*, Wien 1929; A. J. RABINOWITCH and V. A. KARGIN, *Z. physik. Chem. (A)* 143, 21 (1929).

and in some experiments mentioned above. The AgI-sols can easily be concentrated. The greatest AgI-conc. that can be reached in the preparation (at about 10 % KI in excess) is about 100 m. mol: these sols coagulate, however, pretty rapidly, hence also already during the dialysis; mostly sols with 80 millimol AgI were made, and subjected to electro-dialysis; towards the end of the dialysis, e.g. after 4 days, the stirring was interrupted, after which the sol begins to separate into two "layers"; through the cataphoretic movement of the particles concentrated sol is formed at the positive membrane, which collects at the bottom of the dialyser on account of its greater specific gravity, the liquid above it getting entirely empty; this clear upper layer was then carefully siphoned off, the sol was again mixed with doubly distilled water etc., and at last also the concentrated sol was siphoned off ¹⁾. In this way a sol was obtained of which c_I -has diminished to about 10^{-7} mol/l., while it then contains 400 millimol (about 100 grammes) of silver iodide, or even more, per litre. Such a concentrated sol becomes stiff on flocculation with electrolytes.

In the "titration" of these dialysed sols with (e.g. 0.001 norm.) alkalis, the following boundary-surface reactions succeed each other pretty sharply:



i.e. the sol exchanges its counter-ion, and it adsorbs OH^- -ions while the charge of the particles increases; this may e.g. be inferred from the curves obtained when one follows the process conductometrically and potentiometrically (with the glass electrode). For a sol that contained 336 m mol AgI per kg sol, of which resp. 19.9 gr. was "titrated" conductometrically with NaOH 0.00093 norm. and 20.15 gr. potentiometrically with KOH 0.00087 norm., the following curves are found (fig. 1 and 2). We read from this:



¹⁾ Also PAULI mentions a similar method for the purification and concentration of gold-sols. He proposes to give to this the name of "electro-decantation". *Naturwissenschaften*, 30, 555 (1932).

a. For the reaction (1) 7.2 cm³ NaOH 0.00093 norm. are used, in which the mobile ion H⁺ is replaced by Na⁺ as counter-ion, hence the conductivity of the sol decreases. This corresponds with 0.34 meq. counter-ion per kg sol.

b. During the reaction (1) the p_H increases slowly, but gradually more rapidly, till $\frac{d p_H}{d V}$ (V = number of cm³ of alkali) reaches a maximum after 7.9 cm³ (the derived curve is also given); this point of inflection corresponds with also 0.34 meq. of counter-ion per kg. sol. Hence the sol seems to titrate like an acid; however, that the resemblance is only comparative, is seen on a closer consideration of the titration-curve: though the HI in the double layer is greatly dissociated, the curve has not the form of that for a titration of a strong acid with a strong base; the p_H of the "neutralisation point" is 5.0; from both follows that on account of the great absorbability of the OH⁻-ion the reaction (2) from the first proceeds by the side of reaction (1), and to an always greater degree, and that, therefore, the break-point resp. point of inflection only indicate the moment at which (1) and (2) interchange their rôles of principal and by-reactions, and accordingly also probably correspond only more or less to the "neutralisation-point".

c. In the second part of the curves (2) predominates, i.e. the OH⁻-ions are strongly adsorbed, through which the charge of the sol-particles and the concentration of the counter-ions increases, the p_H only slowly going beyond the value 7.

d. From the conductivity of the sol (corrected for the conductivity of the intermicellar liquid, for which the conductivity of the last electro-decantate was taken, and this was practically equal to the conductivity of the water used = $0.9 \cdot 10^{-6}$) $K = c_{H^+} (u + v) 10^{-3}$ the mobility of H⁺ in the sol is calculated to $u = 130$ ($K = 57 \cdot 10^{-6}$; c_{H^+} (per litre) = 0.00037; $u = 305$; $v = 25$); from the p_H of the sol (3.50) an activity of 0.30 meq/kg is calculated. While therefore the H⁺-ions in the double layer are still pretty much hampered in their mobility (to less than half of that in case of infinite dilution), they are, though retained there completely electrostatically, almost entirely to be measured potentiometrically: the sol behaves as a strongly dissociated acidoid.

e. As already stated above the quantity of peptizing electrolyte in the double layer is comparatively small. The total charge of a particle (average size about 40 mμ) is calculated to 900 electrons; the free charge (calculated from the conductivity) corresponds with 330 electrons per particle. (According to PAULI-VALKÓ (l.c.) these numbers are for a Fe₂O₃-sol, with an average size of 68 mμ, resp. 200000 and 65000; for a series of gold-sols of 22—29 mμ a free charge of 28000—58000 is calculated!)

4. When in this way the analytic concentration of several dialysed sols was determined, it could actually be established that in general the sols

contain the less HI in the double layer according as the sol-particles had been longer in contact with an iodide containing solution. As the size of the particles in general varied little, the proportions in the double layer are characterised by the molar relation $H^+ : AgI$, which accordingly is 0.0010 for the example given above. If the degree of dialysis is the same, this relation renders also the degree of ageing. In order to answer the question in how far this process of ageing can reach a final point, it was examined whether it is possible to prepare a sol in which this relation (with constant degree of dialysis) has reached a minimum. This question is not only of practical importance (for so far as the possibility would be opened to prepare a dialysed AgI-sol which is not, or only very slowly, going to contain again free electrolyte, and is, therefore, not continually subjected to change in its colloid chemical properties), but the answer to this question can also give an insight into the properties of the double layer of the AgI-sol. It appeared to be only very imperfectly possible to obtain such a "sol in final state". On too drastic ageing (e.g. by prolonged boiling with addition of KI), also "ripening" (coarsening) appears. When e.g. a dialysed AgI-sol ($AgI = 80$ millimol; H^+ in the double layer 0.12 meq.; adsorptivity to KI 0.04 meq. per tenth power of c_{I^-} per litre) was boiled for 24 hours at a reflux-cooler with addition of 2 m. mol HI per litre, part of it was then deposited as coarse crystals, while of the part that had remained colloidal the average size of the particles that were ultramicroscopically visible, had slightly decreased (mean length of the sides before the treatment $50\text{ m}\mu$; after it $43\text{ m}\mu$); the sol was again dialysed to the same c_{I^-} (0.0002 meq.) and analysed: AgI-content now 72 m. mol, H^+ in the double layer 0.048 meq., adsorptivity 0.02 meq./litre. Both the above-mentioned factor (here resp. 0.0015 and 0.00067) and the adsorptive power have decreased to about half by the treatment. After this the sol, indeed, gave off free I^- more slowly, but the ageing process had not yet come to an end (c_{I^-} after two months again 0.010 meq./l.).

When for the last sol, on the assumption that the particles are pure cubes, the density of HI in the double layer is calculated, it is found that there is already sufficient room for the adsorbed I^- -ions when every Ag^+ -ion on the cube-edges holds one I^- -ion bound; since on binding of the ion on the crystal edges more energy is released than on adsorption on a complete crystal face¹⁾, the I^- -ions adsorbed in excess in this sol will be adsorbed on the crystal edges and corners.

If it is assumed that the adsorption of I^- by AgI can also *only* take place at the corners and edges of the crystal, and not on the crystal faces, we have a satisfactory explanation for several properties of the AgI-sol. In the first place it is then understood why the adsorption of potential-determining electrolyte (hence the "density" of the double layer) in AgI is exceptionally much smaller than in other sols: while evidently in the

¹⁾ KOSSEL, Leipziger Vorträge 1928.

normal case the peptizing ion can be adsorbed on the whole surface of the dispersed particles, the AgI at least forms an exception to this.

In the second place, by means of the hypothesis of the edges-adsorption a good idea may be formed of the above-sketched ageing phenomena. This ageing manifested itself in a great decrease of the adsorptivity of the AgI (e.g. to a fifth or a tenth of its original value) without the degree of dispersion varying considerably. Immediately after their formation the AgI-crystals will still have a very imperfect form; they will certainly not have the form of pure cubes (as was assumed for the calculation of the "surface") or a similar simple form, but they will more likely be built up of fantastically formed smaller crystals; accordingly at their surfaces they possess projections, cracks, structural flaws and distortions or "Lockerstellen" (SMEKAL), which all are able to adsorb I^- -ions. If in consequence of the dynamic temperature equilibrium between crystal and solution, such an irregularly formed crystal, in contact with a saturate solution of AgI, begins gradually to transform to a crystal of more perfect form, the crystal loses a great part of its total edges-length, hence of its adsorptive power, its surface all the same decreasing but comparatively little¹). The ageing of AgI-sols, for so far it does not rest on coarsening of the particles, (and we have seen that this coarsening practically does not yet appear on moderate ageing) we can, therefore, consider as a consequence of the process of perfection, which the crystals undergo after the precipitation. In consequence of the circumstance that in the silver iodide sol the double layer is found only on the crystal edges, we can easily distinguish two phases of the ageing here: the perfecting of the particles to more regularly constructed crystals, which process passes so rapidly that in diluted sols (peptized with little KI) the adsorptivity has decreased already to half the value in a few hours, and the coarsening of the particles, which proceeds so slowly that these sols are not destroyed until after years.

Also other regularities found are explained by the image of the first phase of ageing given here; the process passes via the solution: in general the "perfecting" will, therefore, be promoted by all the factors that increase the solubility of AgI, hence also by rise of temperature and by increase of the concentration of free iodide. It is also to be expected that from solutions in which AgI is more readily soluble, the AgI crystallises more regularly (hence with smaller adsorptivity) in agreement with what was said under 1, *b*. Remarkable is the smaller velocity of the

¹) That the diminution of surface accompanying this is much too small to account for the decreases in adsorptivity found, may be illustrated by a schematic image. Let us for this purpose imagine a newly precipitated particle, with its distorted structure, as an aggregation of *N* smaller cubes, combined to one particle at a few points only. A decrease of the surface of this to 10% of its original value would correspond to a recrystallisation to a particle in which *N* has become 10^3 times smaller, a decrease of the total edges length to 10% requires, however, only a $10^{3/2} = 33$ times smaller value of *N*. Only the latter case furnishes a probable order of magnitude, since a sol-particle has only the length of 50—75 molecules of AgI.

process in positive sols, while AgI in dilute AgNO₃-solutions possesses about the same solubility as in dilute KI-solutions of the same molar concentration; the positive sol differs, therefore, also in this from the negative one.

Summary.

1. By different methods the adsorption of AgNO₃ and KI was measured in undialysed AgI-sols. A complete chemical and electrochemical analysis was given of a dialysed AgI-sol, and its adsorptive power to KI was measured.

2. Under different circumstances the ageing of undialysed and dialysed AgI-sols was studied, and quantitatively examined by measurement of adsorption and adsorptive power. There is an ageing without enlargement of the particles, which proceeds very rapidly, and an ageing which rests on coarsening, which proceeds much more slowly.

3. Both the absolutely very small value of the adsorption of the electrolyte forming the double layer, and the relatively considerable decrease in adsorptivity during the first stage of the ageing suggest the supposition that the adsorption of the peptizing ion takes place only at some active places of the surface of the submicroscopic crystals (corners, sides, edges); especially during the first time after the formation the number of these places decreases rapidly, in consequence of the recrystallisation of the at first irregularly built crystals to particles of more perfect forms.

In conclusion I will, already here, express my indebtedness to Prof. H. R. KRUYT for the advice and interest which I received from him in the choice and the performance of this investigation, and to Prof. F. M. JAEGER for the kind way in which he enabled me to perform this work in his laboratory.

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