CROATICA CHEMICA ACTA CCACAA **56** (4) 553—561 (1983)

YU ISSN 0011-1643
CCA-1398 UDC 541.13/18
Invited Conference Paper

Electrochemistry/Colloid Chemistry Interaction: (a) Effect of Particle Size on Electrokinetic Phenomena and Coagulation; (b) Anodic Deposition of Colloidal Metal*

Aleksandar R. Despić

Faculty of Technology and Metallurgy, University of Beograd, Beograd, Yugoslavia

Received January 25, 1983

Thermodynamic treatement of the problem of electrochemical potential of metal particles in the colloidal range leads to a conclusion that the latter depends on particle radius. This phenomenon reflects also upon the electrokinetic potential of the colloids. Hence, in a polydisperse system particles are at different zeta-potential. The difference may be very significant towards the lower limit of the colloidal range. A quantitative treatement based on the Stern model of the electrical double layer shows the effect to be the strongest around the *pzc* and subsides towards high positive or negative potentials. As a result of this effect, the iso-electric point, rate of coagulation and electrophoretic mobility are also dependent on the particle radius.

Deposition of metal from colloidal solution has also been investigated on the example of colloidal gold. It was shown that the negatively charged gold particles deposit at the anode.

INTRODUCTION

Electrochemistry frequently runs across problems of behaviour of small particles. Thus, e. g. in electrochemical deposition of metals every new metal grain starts from an atomic cluster and in its growth, its size passes through colloidal region of dimensions; some recently developed electrocatalysts base their high activity on highly developed specific surface area, their degree of dispersion being again within colloidal range. There is, of course, a long way between the colloidal size and the true colloidal state that electrochemists cross only if interested in stabilizing their system in the particular dispersion. On the other side for contemporary colloid chemist, small metal particles are bizzare species of little or no interest. Yet, they do represent a common point at which the two disciplines meet. Hence, one could hope that electrochemical study of these systems could result in some benefit to colloid chemistry both in understanding the fundamentals of the build-up of colloid stability and solving some practical problems colloid chemists could come across. At this point three specific problems will be investigated centering around the questions:

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* Based on an invited lecture presented at the 6th »Ruđer Bošković« Institute's International Summer Conference *Chemistry of Solid/Liquid Interfaces*, Cavtat/Dubrovnik, Croatia, Yugoslavia, June 1982.

i) How does the size affect the electrical potential difference between the bulk of a metal particle and the bulk of solution;

ii) Does this dependence of the potential difference on size affect the electrokinetic potential and in which way;

iii) Is the electrochemical potential of zero charge (*pzc*) related to the iso-electric point (*iep*) of colloid chemistry and in which way.

Aside of this, some direct interaction between colloid chemistry and electrochemistry will be considered on the example of electrodeposition of a metal from a colloidal solution.

THE EFFECT OF SIZE ON THE ELECTROKINETIC POTENTIAL OF METAL PARTICLES

In principle, all metals tend to exchange ions, constituting their lattice, with the surrounding medium in a faradaic process of a definite stoichiometry. Attainement of the electrochemical equilibrium between a metal particle and the surrounding solution imposes a definite difference in inner electrical potentials of the two phases, $\Phi_o = \varphi^M - \varphi^S$. The bulk phase thermodynamics requires this to be of such a value that the electrical work of transfering a mole of the metal ions from one phase to the other $z F \Phi_o$ equals the difference in the molar chemical potentials of the exchangable species in the two phases, $\overset{M}{\mu}_{M^{z+}} - \overset{S}{\mu}_{M^{z+}}$ and the work necessary to build the interface, $\gamma \Delta A_s$, with γ — the interfacial tension and ΔA_s the increase in surface area due to exchange of one mole. From the view point of electrostatics, establishing Φ_o is tauntamount to exchange of charge, *q*, between the two phases i. e. charging the particle with a charge of one sign and the solution with equal charge of the oposite sign, in proportion to interfacial capacitance.

Hence, when electrical potential difference of relevance to colloid chemistry — the electrokinetic, or zeta-potential is considered, in the case of a metal particle it is constituted in a more complex way than that of a material phase which does not undergo such an exchange, i. e. it is a result of both an adsorptive and electrochemical interaction.

If the electrokinetic potential is (somewhat arbitrarily) taken to be equal to the potential difference between the outer Helmholtz-plane and the bulk of solution, Φ_2 (cf. Figure 1) i. e. to arise from separation of charge on the two sides of this plane, then the charge on the particle is a result of charging of both origins as shown in Figure 1. (It is only in a first approximation that it is a sum of charges the particle would carry if the electrochemical process would occur without adsorption and vice versa, since the establishment of the q^M affects also the adsorption of charged particles.)

The work of building-up the interface is insignificant in determining Φ_o when macro-dispersions are concerned. Yet, in the colloidal region of dispersion it gains in significance as it does for all other equilibrium properties. This is reflected in the well-known Kelvin effect of surface tension,[1] so that two particles of radii r_1 and r_2 are at different electrical potentials with respect to the solution, the difference being

$$\Delta \Phi = (\Phi_o)_2 - (\Phi_o)_1 = \frac{2 \gamma V_m}{z F} \left(\frac{1}{r_2} - \frac{1}{r_1} \right) \tag{1}$$

where V_m is the molar volume of the metal. If the comparison is made with a flat surface in contact with the solution ($r_2 \rightarrow \infty$).

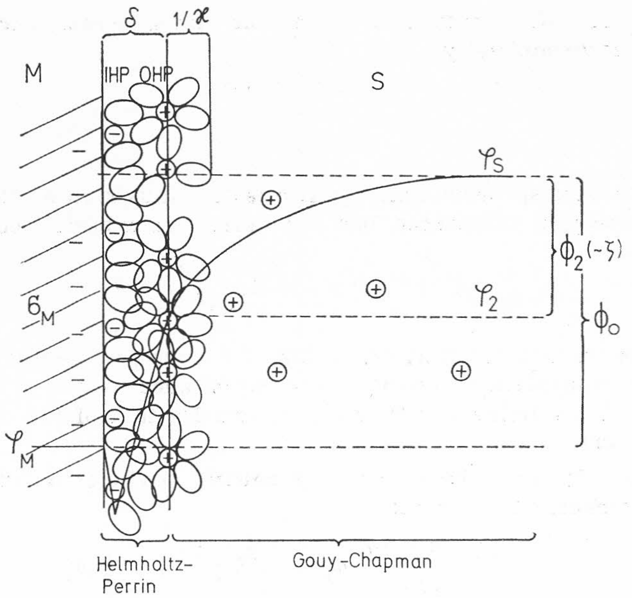

Figure 1. Model of an interface between a metal (M) and an ionic solution (S).

$$\Delta \Phi = -\frac{2 \gamma V_m}{z F r} \tag{2}$$

where r is the radius of the particle. The hyperbolic nature of this function makes the effect insignificant with coarse metal particles but gain in significance within the colloidal region. Thus, taking e. g. silver with $V_m = 10^{-5}$ m^3 mol^{-1}; $\gamma = 2.5 \cdot$ Jm^{-2} and $z = 1$, one can calculate the following series:

r (nm)	500	50	5	0.5
$\Delta \Phi$ (mV)	—1	—10	—100	—1000

Potential differences of this order between a solid piece of silver and silver particles were indeed measured by Konstantinov and Malinovsky,[2] and more recently by Hills and coworkers[3] in beautiful experiments on mononucleation of metal grains on microelectrodes.

Hence, colloidal metal particles at the lower limit of the colloidal range should have a larger negative, or lower positive relative inner potential than those at the upper limit.*

There is, however, an additional effect of the difference in the potential and, hence, the charge density on the particles: the surface tension in the case of charged particles is not a constant characteristic of materials constitut-

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* It is noteworthy that a similar reasoning based on the Kelvin effect should apply to non-metalic colloidal particles in which the charging is of a dissociative origin, since the equilibrium in heterogeneous chemical dissociation should have the same thermodynamic background (the degree of dissociation should depend on particle size in proportion with surface tension and molar volume).

ing the interface, but is known to depend on charge density according to the equation of electrocapillarity

$$d\gamma = -\sigma^M d\Phi \tag{3}$$

where

$$\sigma^M = q^M/A_s \tag{4}$$

If one considers spherical metal particles of radius r, in a solution without specifically adsorbing substances, one can derive from basic electrostatics

$$d\sigma^M = C\,d\Phi = \frac{\varepsilon_r \varepsilon_o (r^2 + \delta r)}{4\pi\delta r^2}\,d\Phi \tag{5}$$

where ε_r is the relative permitivity, ε_o that of vacuum, while δ is the thickness of a capacitor equivalent to double layer capacitance ($\delta = x_2 + (1/\varkappa)$, x_2 being the thickness of the Helmholtz-Perrin part and $1/\varkappa$ that of the diffuse part of the double layer).

Integrating (5) from the electrically neutral particle to the given inner potential difference, one obtains:

$$\sigma^M = \frac{\varepsilon_r \varepsilon_o (r^2 + \delta r)}{4\pi\delta r^2}\,\Phi_{\mathrm{o}} = \frac{\varepsilon_r \varepsilon_o}{4\pi}\left(\frac{1}{\delta} + \frac{1}{r}\right)\Phi_o \tag{6}$$

Replacing (6) into (3) one obtains:

$$d\gamma = -\frac{\varepsilon_r \varepsilon_o}{4\pi}\left(\frac{1}{\delta} + \frac{1}{r}\right)\Phi_o\,d\Phi \tag{7}$$

and integrating from the neutral state at which γ is at maximum and equal to γ_o, one obtains:

$$\gamma = \gamma_o - \frac{\varepsilon_r \varepsilon_o}{8\pi}\left(\frac{1}{\delta} + \frac{1}{r}\right)\Phi_o^2 \tag{8}$$

which accounts for the parabolic shape of the electrocapillary curve.

Replacing (9) in (2), it follows that

$$\Delta\Phi = -\frac{2\gamma_o V_m}{zFr} + \frac{V_m \varepsilon_r \varepsilon_o \Phi_o^2}{4\pi zF}\left(\frac{1}{\delta_r} + \frac{1}{r^2}\right) = -\frac{2\gamma_o V_m}{zFr} + \frac{P}{r} + \frac{Q}{r^2} \tag{9}$$

With Φ_o of the order of 1 V, δ of the order of 0.1 nm and $\varepsilon = 40$ as some average relative permitivity of water in the double-layer, the first constant is of the order of $3 \cdot 10^{-11}$ while the second one $3 \cdot 10^{-21}$. Hence, the effect on $\Delta\Phi$ for r between 0.5 and 500 nm amounts $7^0/_0$ and $6^0/_0$ respectively. Thus, the effect of charge on surface tension acts as a correction term, making the dependence of $\Delta\Phi$ on r somewhat less sharp than the Kelvin effect at constant γ_o would be.

The question arises to what extent does the change in the total electrochemical potential difference $\Delta\Phi$ affect the electrokinetic potential.

To answer this, one has to turn to the current theory of the electrical double layer. In it there is a definite relationship between the charge on the metal surface, σ^M, and the potential at the outer-Helmholtz plane, Φ_2. For a spherical particle it is best described by the equation derived by Loeb, Wiersma and Overbeek,[4] which for the Stern model of the double layer should read

$$\sigma^M = \frac{2\,z\,F\,C_o}{\varkappa}\left[2 \sin h\left(\frac{z\,F\,\Phi_2}{2\,R\,T}\right) + \frac{4}{\varkappa\,r}\tan h\left(\frac{z\,F\,\Phi_2}{4\,R\,T}\right)\right] \tag{10}$$

where $\varkappa$ iz the Debye-Hückel parameter, $1/\varkappa$ representing an equivalent thickness of the diffuse double layer.

Replacing σ^M from equation (6)

$$\Phi_o = \frac{16\,\pi\,z\,F\,C_o\,\delta\,r^2}{\varepsilon_r\,\varepsilon_o\,\varkappa\,(r^2 + \delta\,r)}\left[\sin h\left(\frac{z\,F\,\Phi_2}{2\,R\,T}\right) + \frac{4}{\varkappa\,r}\tan h\left(\frac{z\,F\,\Phi_2}{4\,R\,T}\right)\right] \tag{11}$$

The relation calculated from (11) is shown in Figure 2 for some reasonable values of the parameters ($z = 1$, $\delta = 1$ nm, $1/\varkappa = 0.8$ nm, $\varepsilon_r = 40$, $zF/RT = 40$).

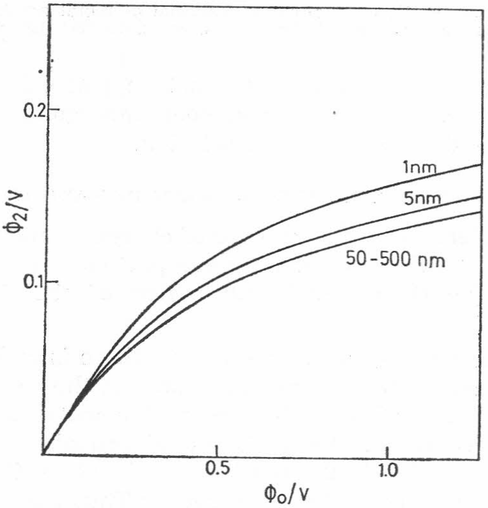

Figure 2. Relationship between the total inner potential difference (between the bulk of the metal and the bulk of solution), Φ_o and the electrokinetic potential of a metal particles of different radii.

It is seen that with increasing Φ_o, Φ_2 takes an ever smaller portion of the latter, depending to some extent on the particle radius. It is largest at $\Phi_o = 0$, i. e. at the *pzc*. To derive $\Delta\,\Phi_2$ as a function of the particle radius, but also of Φ_o, one must take the derivatives $(\partial\Phi_2/\partial\Phi_o)$ along the curves of Figure 2 for different radii, and multiply them by the $\Delta\Phi$ calculated using equation (2). In such a way the range of change of $\Delta\Phi_2$ over the colloidal region (1—100 nm) was derived as shown in Figure 3. It is seen that if coarse metal particles are e. g. at the *pzc*, the particles of 1 nm in radius should have a zeta-potential of about — 170 mV. Even at 1 V negative to *pzc* they should still have the zeta-potential some 30 mV more negative than the coarse metal, the latter having the total zeta-potential of about — 130 mV (cf. Figure 2). The effect subsides, however, very sharply with the increase in radius.

The derived dependence of the zeta-potential on particle radius is thus an additional reason to the generally accepted one, for different electrokinetic

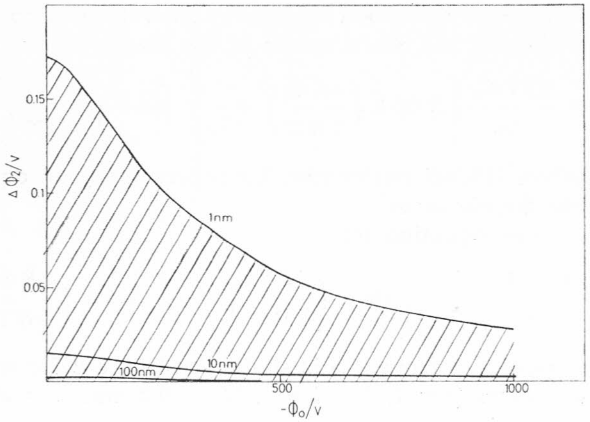

Figure 3. Range of change of the electrokinetic potential of metal particles of colloidal dimensions as a function of the total inner potential difference.

behaviour (e. g. different electrophoretic mobility) of colloidal metal particles (or non-metalic particles made of substances undergoing dissociation) of different size in a polydisperse colloidal solution.

THE RELATIONSHIP BETWEEN PZC AND IEP

The *pzc*, characterized by the absence of charge on the surface of the metal phase, should be identical to the iep only in a particular case when any separation of charge in the Helmholtz-Perrin region of the double layer is also absent.

However, in most cases, in polar solvents, there is at least the orientation of solvent dipoles, responsible for the appearance of the surface potential, which makes the first molecular layer adhering to the metal surface, act upon the solution as a charged layer. Hence, it should provoke some however small, redistribution of charge inside the solution, of the Gouy-Chapman type, acting as zeta-potential in electrokinetic phenomena. Thus, *iep* should be found at slightly different values of potential than the *pzc*.

This would be much more pronounced in the case of specific adsorption of anions, which causes the appearance of a definite potential difference between the inner- and the outer-Helmholtz plane in the absence of any charge on the metal (cf. Figure 1). Thus, the difference between *iep* and *pzc*, or else the zeta-potential at *pzc*, should be a measure of charge accumulated at the surface by adsorption, which could be assessed quantitatively if the capacitance of the system between the inner-Helmholtz plane and the bulk of solution was measured independently.

From the above derivations of the effect of size on the electrochemical potential of colloidal particles (the second section), it follows that the *pzc* of particles of different size should also differ by the same amount. This should then apply also to the *iep* and hence, one can expect a corresponding effect on the rate of coagulation, i. e. at any potential representing *iep* for particles of certain size, particles of other size would still maintain some zeta-potential and hence undergo slower coagulation.

ELECTROCHEMICAL BEHAVIOUR OF COLLOIDAL METALS

There is a large volume of knowledge on the motion of colloidal particles in an electric field in a bulk of solution, accumulated ever since the first experiments on electrophoresis. Much less definite knowledge, if at all, exists on the interaction of colloidal particles with the electrodes imposing the field. The same applies to metal deposition by discharge of ionized metal atoms versus discharge of clusters of atoms, i. e. metal particles, carrying a charge. This fact has stimulated our research in deposition of gold from colloidal gold solutions.*

EXPERIMENTAL

The solutions have been prepared following a conventional recepie,[5] so as to obtain a stock-solution with gold particle concentration of about 10^{-8} M, with particle size of the order of 5 nm. Solutions for deposition experiments have been prepared either by simple dilution of the stock-solution, or by adding the stock-solution as seed to some solution of $AuCl_3$ containing formaldehyde in order to maintain the same particle concentration but increase particle size.

Solutions have been placed into an electrolytic cell and a voltage has been placed between two graphite electrodes from a potentiostat (Stonehart BC 1200) so that the potential of the anode could be controlled vs. saturated calomel electrode. The anode was a rotating disc, so that hydrodynamics could be controlled.

The electrolysis at a constant anode potential (e. g. $+ 1$ V) was carried out for several hours. The electrode was then taken out and submitted to X-ray analysis on an electron-micro probe, scanning it across, and recording impulses. Prior to that, a blank test was run in order to record X-ray noise.

PRELIMINARY RESULTS

Typical results are shown in Figure 4 (a) and (b). Definite increase in the tracing of impulses indicated anodic deposition of gold particles. Clustering tendencies have been exhibited, expressed as accumulation of impulses at certain regions across the electrode.

Systematic investigation is being carried out of the effect of particle size, solution concentration, rotation speed, potential and time of deposition and will be reported in due course.

Likewise, it is too early to discuss possible mechanism of this deposition. It is obvious, however, that it must involve some process of production of positive charges which would help desorb the anions, being the cause of the negative charge existing on the particles, as viewed from the outside of the outer-Helmholtz-plane by virtue of the electrokinetic potential.

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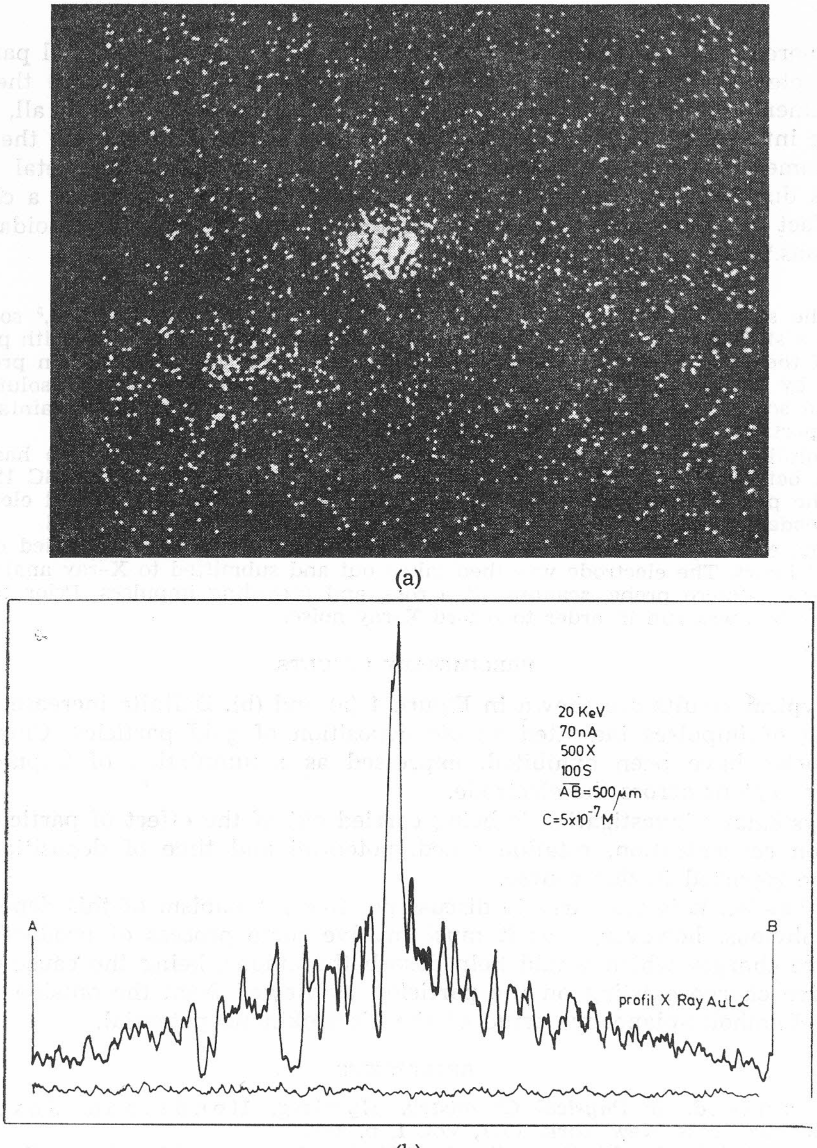
* This work has been done in collaboration with Dr. M. Pavlović, of the Institute of Electrochemistry. Acknowledgements are due to Prof. M. Pavićević and his team in the Faculty of Mining and Geology, for carrying out the micro-probe analysis of electrode samples.



(a)

(b)

Figure 4. Record of gold anodically deposited onto a graphite electrode: (a) X-ray impulses on bare graphite (b) Intensity of X-ray across the electrode.

SAŽETAK

Međuovisnost elektrohemije i koloidne hemije

A. R. Despić

Termodinamička obrada problema elektrohemijskog potencijala metalnih čestica koloidnih veličina vodi do zaključka da je taj potencijal ovisan o radijusu čestica. Taj fenomen odnosi se i na elektrokinetički potencijal koloida. Zbog toga su čestice polidisperznog sistema karakterizirane različitim zeta-potencijalima. Razlike mogu

biti osobito značajne pri donjim granicama koloidnog područja. Kvantitativno razmatranje zasnovano na Sternovom modelu električkog dvosloja pokazuje da je taj efekt najznačajniji u blizini točke nula naboja, a nestaje prema visokim bilo pozitivnim bilo negativnim potencijalima. Kao posledica tog efekta, izoelektrička tačka, brzina koagulacije i elektroforetska pokretljivost također su ovisne o radijusu čestica.

Izlučivanje metala iz koloidnih rastvora proučavano je na primeru koloidnog zlata. Pokazano je da se negativno naelektrisane čestice zlata izlučuju na anodi.