

Nuclei of Critical Size and Silver Surface Tension

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Abstract

Analysis of the process of silver centres formation and growth in silver bromide microcrystals and in gelatin medium is a very topical problem for the theory of photographic process. Formation of new phase accompanying the development of latent image centres (LIC) can be successfully described on the concepts of the thermodynamics of new phase formation and growth.

Introduction

It is well known that, when studing the impurity silver centres, the techmigue of redox buffer solutions, proposed in [1], is widely used. It allows relating the value of overpotential created by buffer solutions to the fraction of silver centres stable in given solutions. Then according to the Gibbs-Thomson equation in the form of

$$\Delta E = \frac{4 \sigma V_m}{F d_{cr}} \qquad (1)$$

(where F is the Faraday constant, V_m is the volume occupied by one silver atom in its crystal lattice) one can determine the size of the critical nucleus, d_{cr}, for every value of overpotential ΔE. Ultimately, one can arrive at the real value for the size of latent image centres.What is necessary for this is to know the value of surface tension σ for silver particles with the critically small size and to be sure that the equation itself is applicable to them. However, in the method [1], on the one hand, the uncertainty in the choice of the σ value is preserved, and, on the other hand there is no proof that Gibbs-Thomson equation is applicable. Therefore, the estimation of LIC size performed in [1] cannot be regarded as satisfactory. The use of method presented in [1] together with electron microscopy techniques makes it possible to obtain an experimental d_{cr} vs. ΔE dependence and, therefore to verify the applicability of the Gibbs-Thomson equation and determine the σ value for such silver particles. For the first time this was done in [2] and later investigated in greater detail in [3,4]. In the region of overpotentials in equation the Gibbs-Thomson equation proved to be valid. Noted in [4] is a strong influence exerted by gelatin on σ values: for particles covered with gelatin σ = 400 mJ/m^2 and without such a covering σ = 920 mJ/m^2.

In the present work the critical size of silver particles has been investigated, depending on the overpotential, with the aim of ascertaining the specific free surface energy for these particles.Special attention was given to the influence of gelatin coating on the σ value.

Experimental

Buffer solutions based on bi- and trivalent iron salts were used in the work, as suggested in [1]. The solutions were additionally saturated with silver bromide. Solutions of the following compositions were also used: $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ - 0,2M, citric acid - 0,15M, $AgNO_3$ - 0,001 M, $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ - 0,001 to 0,15 M. The potentials were measured by the compensation technique with the use of a measure platinum electrode and silver chloride half-cell.

Silver particles of colloidal dispersity on a Formvar support, obtained by thermal evaporation from tungsten wire in 10^{-3} Pa vacuum, were investigated on a JEOC JEE-4X unit. If necessary the sprayed particles could be covered with a thin platinum film by being submerged into 0,1% solution of photographically inert gelatin in water and dried in air. Gelatin concentration was selected so that, on the one hand, it should act as an effective protective colloid and, on the other hand, the film should not reduce the electron-microscope resolution during the viewing. The electron-microscopic study of silver layers treated in buffer solutions was performed on Hitachi HU-12 and JEOL-JEM-100CX electron microscopes. Their resolution on real specimens was no less than 0,5 nm. The gelatin layer covering the silver particles was fully preserved during the preparation of specimens for electron-microscopic studies. The critical size of silver particles was determine by the minimum of the histogramme for particles size distribution, as proposed in [3].

Results and discussion.

When the treating the sprayed silver layers in buffer solutions containing $AgNO_3$ a minimum is observed to

appear already within the first few seconds. During scores of seconds the minimum is clearly observed, after which it becomes blurred and disappears. Fig.1 shows the histogrammes of sprayed silver layers without a gelatin coating before and after the treatment in the buffer containing $AgNO_3$ with ΔE = 0.068 V. The position of the minimum corresponds to the size of the critical nucleus, equal to d_{cr} = 4.0 ± 0.6 nm.

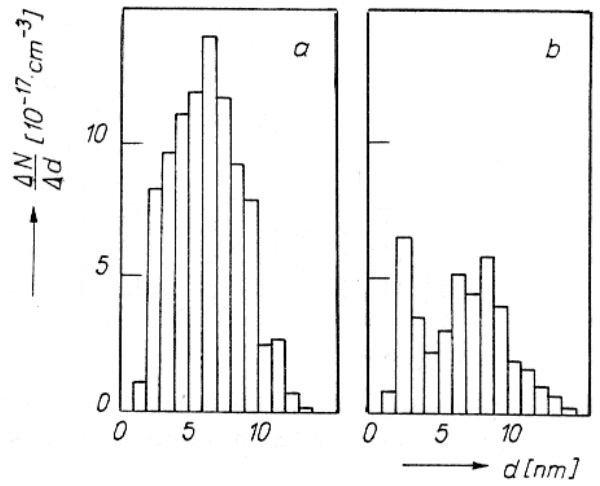

Fig.1. Size distribution of silver particles for sprayed layers treated in a redox buffer solution with ΔE = *0.068 V, treatment time 0 s (a), 30 s (b).*

The critical size values for others overpotentials are given in the Table 1. In the presence of gelatin, silver is redistributed in buffer solutions more slowly than for layers without it. However, in this case as well, a minimum appears at the initial stages, its position depending on the solution potential and corresponding to the size of critical nuclei.

Fig.2 shows the histogrammes of sprayed silver layers coated with gelatin before and after the treatment in the buffer solution with ΔE = 0.058 V. The minimum in size distribution appears only after 30 s of treatment, while for the layers without gelatin coating - not later than within 5 s. As it follows Fig. 2, with a 0.058 V overpotencial, the critical size of silver nuclei in gelatin layer is d_{cr} =4,8 ±0.6 nm. The values of d_{cr} for other overpotentials are given in the Table 1.

In buffer solutions with silver citrate as the complexing agent the process of silver redistribution goes slower than in the buffers containing $AgNO_3$. In the former case the minimum is observed to appear on the histogrammes agter longer treatment times, equal to 15 - 20 min.

Analysis of the results presented in the Table 1 showed the experimental d_{cr} and ΔE values to satisfy the equation $\Delta E = const/d_{cr}$ with the correlation coefficient of 0.969 for particles without a coating and 0.953 for particles coated with gelatin. This confirms the applicability of Gibbs-Thomson equation to silver particles of colloidal dispersity (Fig.3). Proceedings from the experimental d_{cr} vs. ΔE dependence the values of silver specific free surface energy were calculated.

Table 1. Critical size of silver nuclei (d_{cr}, i_{cr}) for different overpotentials (ΔE) values.

ΔE [V]	d_{cr} [nm]	i_{cr}
Particles without gelatine coating		
0.068	4.2±0.6	2270
0.065	4.4±0.6	2610
0.061	4.6±0.6	2990
0.055	6.2±0.6	7310
0.047	6.8±0.6	9640
0.042	6.8±0.6	9640
0.030	10.6±0.8	36500
0.023	16.0±0.8	126000
Particles coated with gelatin		
0.062	4.4±0.6	2610
0.058	4.8±0.6	3390
0.051	6.0±0.6	6630
0.042	6.8±0.6	9640

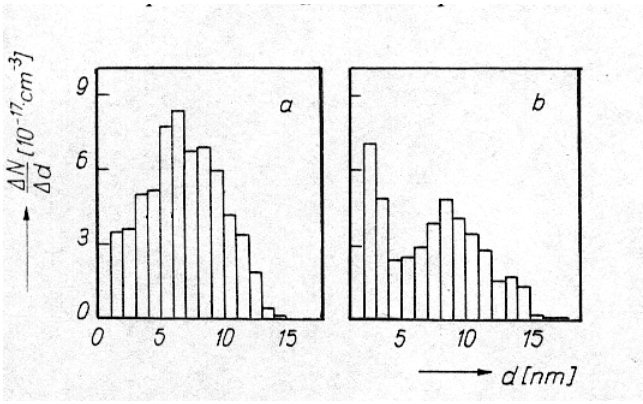

Fig.2. Size distribution of silver particles coated with gelatin after treatment in redox buffer solution with ΔE = *0.058 V, treatment time 0 s (a) and 60 s (b).*

For particles without a gelatin coating σ = 720 ± 60 mJ/m^2, and for those with the coating σ = 670 ± 20 mJ/m^2 . The coincidence, to an accuracy of the error, between the σ values for silver particles in the absence and the presence of gelatin does not agree with the results obtained in [4]. This can be due to the fact that the influence exerted by the removal of the gelatin layer, covering the silver nuclei, during the sample preparation on the particle size distribution was not taken into account in [4].

The found σ values can be used in calculating the size of critical nuclei foe different overpotentials from Gibbs-Thomson equation (1). It can be assumed that such

calculations will be valid to such silver particle values at which their metallic properties and the type of chemical bond are still preserved.

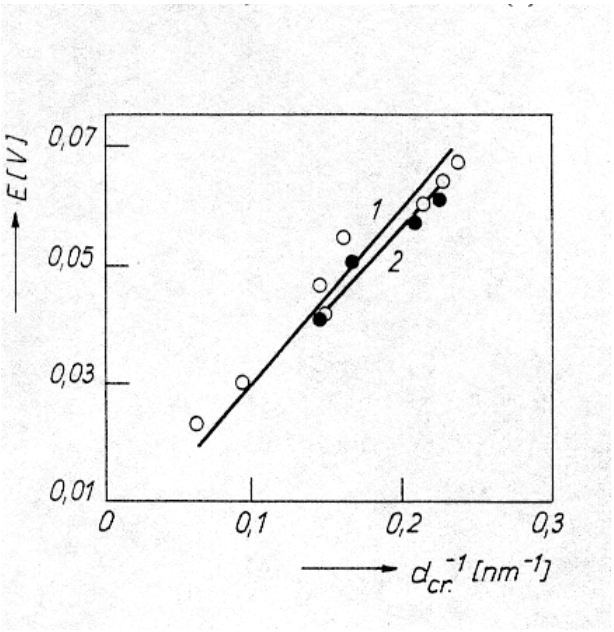

Fig.3. The value of critical-size silver particle inverse diameter vs. the overpotential.

Conclusion

The obtained experimental results fully agree with thermodynamic theory of the formation of latent image centres, developed in [5]. The electron-microscopic study of the stability of silver particles in redox buffer solutions, performed on model systems, made it possible to ascertain the experimental dependence between the critical size of nuclei and overpotential value.

References

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Acknowledgement

This work was supported in part by RFBR (grant 99-03-32373).

Biography

Valery N. Zakharov graduated from Moscow State University, Department of Chemistry, Chair of Photography in 1978. Since 1980 he has worked for the Chair of Photography and for the Laboratory of Structural Chemistry of Moscow State University. He is an author and co-author of 65 scientific papers and patents. His work has focused on ultra fine grained silver halides crystals and the components of photographic layers inside of integrated chemical systems. V. Zakharov is a member of the IS&T.