

The Action of Size-Selected Small Silver Clusters as Latent Image Specks and Development Centers

F. Granzer⁽¹⁾, *V. Bonacic-Koutecky*⁽²⁾, *T. Leisner*⁽³⁾,
C. Rosche⁽¹⁾, and *L. Woste*⁽³⁾

(1) Inst. Angewandte Physik, Universitat Frankfurt am Main

(2) Inst. Phys. u. Theor. Chemie, Humboldt-Universitat, Berlin

(3) Inst. Exp. Physik, Freie Universitat, Berlin

Abstract

Today we are disposing of a variety of reliable data, like binding- and dissociation energies as well as ionization potentials and electron affinities of small silver clusters. Most of these data, however, were obtained for isolated clusters in vacuum. In the following it will be shown how these properties are changing when the clusters are adsorbed on a silver bromide crystal or when they are brought into simultaneous contact with the crystal and the developer. From the results of these calculations, which are based on very simple models, it should be possible to predict the minimum sizes of latent image specks and development centers.

Properties of Free Silver Clusters

The structures, the binding- and dissociation energies, the ionization potentials and electron affinities of neutral, cationic and anionic isolated silver clusters in vacuum have been calculated using different models and methods: "The Molecules in Clusters Model" (J.W. Mitchell^{1,2}), the extended Huckel and CNDO-method (R. C. Baetzold³) and the state-of-the-art quantum mechanical methods (V. Bonacic-Koutecky et al⁴ and H. Stoll et al⁵). The results obtained by the different authors and groups will be discussed and compared with experimental data.

Silver Clusters Adsorbed on an AgBr-Surface

As a result of the elementary photographic process positively (cationic) Ag_n⁺-clusters are formed on the surface of an AgBr-microcrystal. The stability of an Ag_n⁺-cluster against dissociation, i.e. the ejection of an Ag⁺ ion into a surface near interstitial position, can be predicted by the following formula:

$$\Delta_{n,i} = D_{n/C}^+ - E_{i/S(1)} \quad (1)$$

Using the symbol: Ag_n⁺ / AgBr for an Ag_n⁺-cluster in contact with AgBr, D_{n/c}⁺ is the dissociation energy of this cluster corresponding to the reaction:



With E_{i/S(1)} we are denoting the energy released if an Ag⁺-ion is transferred from infinity into an interstitial position of the outermost surface layer S(1) of the AgBr-crystal adjacent to the cluster. Due to the broad oscillations of the point defect parameters of AgBr it is only possible to indicate the E_{i/S(1)}-values within a range from 3,13 eV to 4,05 eV. With our calculated D_{n/c}⁺-values (2nd column of TABLE I) the Δ_{n,i}-values given by Eq. 1 and listed in the last column of TABLE 1 will be always positive.

n	D _{n/c} ⁺	- E _{i/S(1)}	=	Δ _{n,i}
2	5.21	3.13...4.05		2.08...1.16
3	5.01	3.13...4.05		1.88...0.96
4	4.22	3.13...4.05		1.09...0.17
5	4.58	3.13...4.05		1.45...0.53

TABLE 1

Hence, Ag_n⁺-clusters adsorbed on AgBr-surfaces will be stable against dissociation, at least for cluster sizes 2 ≤ n ≤ 5. This result is important for practical photography since it predicts that even on the surfaces of primitive emulsion grains latent image specks (n = 4,5) as well as sub specks (n = 2,3) will survive long storage times.

Silver Clusters in Simultaneous Contact with AgBr and Developer

Ionic Component

Upon immersion in a developer a charged silver cluster adsorbed on AgBr is further stabilized by solvation (hydration). Since the adsorbed cluster is exposed only to the half space of the polarizable liquid, the gain in solvation energy will be only one half of the solvation energy released

upon immersion of a **free** cluster. Therefore, the energy needed to eject a silver ion from an adsorbed Ag_n^+ -cluster into the surrounding developer is given by:

$$(D_n)^+_{C+D} = D_{n/c}^+ + 1/2 (E_{\text{Solv}})_n - (E_{\text{Solv}})_1 \quad (2)$$

Here $(E_{\text{Solv}})_n$ is the solvation energy of a free Ag_n^+ -cluster and $(E_{\text{Solv}})_1 = 4,96$ eV is the well known solvation energy of the silver ion. With the data of TABLE 2, the dissociation energies for clusters in **simultaneous** contact with AgBr and developer will be always positive (last column), at least for cluster sizes $2 \leq n \leq 5$. Therefore, **with regard to the ionic component**, these clusters could act as **development centers**.

n	$D_{n/C}^+$	$(E_{\text{Solv}})_n$	$(E_{\text{Solv}})_1$	$(D_n)^+_{C+D}$
2	5,21	1,89	4,96	2,14
3	5,01	1,53	-"	1,58
4	4,22	1,30	-"	0,56
5	4,58	1,16	-"	0,78

TABLE 2

Electronic Component

The EMF between a cell containing a solution of Ag_n^- -clusters adsorbed on AgBr and the NHE -cell is given by:

$$|e| \cdot E(\text{Ag}_n^+ / \text{AgBr} // \text{Ag}_n^- / \text{AgBr} | \text{NHE}) = (\text{IP})_{n/C} - 1/2 (E_{\text{Solv}})_n - 4,45 \text{ eV} \quad (3)$$

Here $(\text{IP})_{n/C}$ is the ionization potential of an Ag_n^- -cluster adsorbed on AgBr. The difference:

$$(\text{IP})_{\text{Solv/n/C}}^{\text{vac}} = (\text{IP})_{n/C} - 1/2 (E_{\text{Solv}})_n \quad (4)$$

is the ionization potential of an **adsorbed cluster in solution referred to the vacuum level**.

Our calculated $(\text{IP})_{n/C}$ -values are listed in the 2nd column, the $(E_{\text{Solv}})_n$ -values, taken from literature or calculated, too, are listed in the 3rd column of TABLE 3.

n	$(\text{IP})_{n/C}$	$(E_{\text{Solv}})_n$	$(\text{IP})_{\text{Solv/n/C}}^{\text{vac}}$
1	4,66	4,96	2,18
2	4,84	3,77	2,95
3	5,11	3,05	3,58
4	5,51	2,60	4,21
5	5,33	2,31	4,18

TABLE 3

Since the ionization potentials of adsorbed Ag_n^- -clusters in solution (developer) are related to an electron at rest in vacuum they are directly comparable with the FERMI level of the developer. From its relative position to the $(\text{IP})_{\text{Solv/n/C}}$ values, listed in the last column of TABLE 3, it is possible to predict, whether an Ag_n^+ -cluster will act as a development center or not.

References

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