Indian Journal of Chemistry
Vol. 18A, July 1979, pp. 13-15

Surface Diffusion of Chloride & Iodide Ions on Silver

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Received 19 *September* 1978; *accepted* 22 *January* 1979

A frontal-type surface diffusion of labelled Cl^- and I^- ions adsorbed on silver has been investigated employing radiotracer technique. The migration of the labelled front takes place (i) along a clean surface of the metal (surface diffusion) or (ii) along an adjoining adsorbed layer of identical thickness of ions of the same kind (surface self-diffusion) or (iii) of different kind (surface inter-diffusion). Diffusion coefficients are measured for 1, 10 and 25 layer-thicknesses at different temperatures. Mutual repulsion of dipoles, which are predominant in the adsorbed phase, is more effective at low layer-thicknesses and is enhanced at high temperatures.

We had reported earlier[1] our results on the study of surface self-diffusion of I^- ions adsorbed in mono and multilayers on copper and aluminium using radiotracer technique. In this paper we present results on the surface diffusion, including self- and inter-diffusion, of Cl^- and I^- ions on silver substrate. Recently the radiotracer technique has been used in the study of surface diffusion of Pu on UO_2 (ref. 2 and 3) and surface self-diffusion of Cu, Ag and Au[4,5].

Materials and Methods

A sheet of silver (99.9% pure) annealed at 600° for 1 hr was cut to give rectangular strips of the size 6×1 cm^2. The silver strips were subjected to mechanical polishing using emery paper nos (0), 2(0) and 3(0) in sequence, and chemical polishing, using 2:1 HNO_3 bath, as previously described[6].

On the basis of our earlier data[6,7] on the rate of uptake of halide ions on silver it was possible to grow adsorbed films of these ions to any desired layer-thickness approximately. During the adsorption of halide ions from aqueous solution by silver, electroneutrality around the surface region was maintained by the generation of an equivalent amount of OH^- ions[8]. The silver in contact with the adsorbate got oxidised to Ag^+ to hold the I^- in the adsorbed layer[8]. The electron released reacted[9] (i) with the dissolved oxygen to form OH^- (ie. $2e^- + O + H_2O \longrightarrow 2\,OH^-$) or (ii) with the H_3O^+ to form H_2 ($H_3O^+ + 2e^- \longrightarrow H_2 + OH^-$). The number of layers represents the number of ions adsorbed per metal atom assuming 1:1 adsorption. The surface population on [100] plane of silver was computed as 1.2×10^{15} atoms/cm^2 on the basis of X-ray data[10].

The diffusing source consisted of labelled Cl^- or I^- ions adsorbed over half the surface area (3×1 cm^2) of the silver strip. The other half was (i) left bare in the case of surface diffusion study, (ii) coated with the unlabelled ions of the same kind and to a thickness identical with that of the active layer in the former half for surface-self diffusion study, and (iii) coated with the unlabelled ions of a different kind but of the same thickness as the active layer for inter-diffusion study.

The specimen strips were kept in an electric muffle at a constant temperature (±0.5°) in the range of 325° — 440° for a definite length of time (upto 8 hr.). The strips were autoradiographed before and after the heat treatment. Each specimen strip was then cut into smaller strips of 2 mm width on both sides of the boundary between the two halves and the radioactivity on each measured with a thin end-window GM tube under conditions of constant geometry.

Boundary conditions — For the initial distribution of the labelled species occupying a finite region of the surface, the state is described by the following boundary conditions : (i) at time $t = 0$, $C = C_0$ for $x \leqslant 0$ and $C = 0$ for $x \geqslant 0$, where the distance $x = 0$ at the boundary; (ii) at time $t > 0$, $C = C_0$ for $x = -a$; and $C = 0$ for $x = +a$, where a is half the length of the strip and C the surface concentration expressed in terms of activity (in counts per min) per cm^2. A mathematical solution to this problem was given by Crank[11] employing Fick's second law in the case of diffusion of a line source

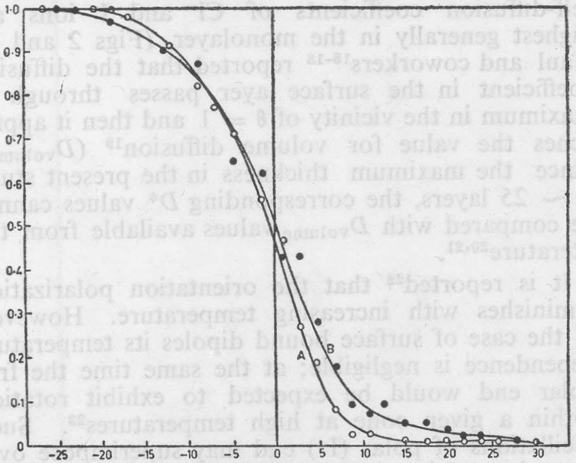

Fig.1-Gaussian distribution curve for the surface self-diffusion of I^- ions through (A) I^- ions at 350°C and surface inter-diffusion of I^- ions through (B) Cl^- ions at 375°C on silver.

into an infinite solid and then considering the extended distribution to be composed of infinite number of line sources. Under the present conditions the surface migration of labelled ions should follow a typical Gaussian distribution. This has been found to be so as is evident from the curves in Fig. 1. The solution[12] for diffusion of a finite source crossing the boundary ($x = 0$) is given by Eq. (1).

$$D^* = \frac{S^2\pi}{b^2 C_0^2 t} \quad \ldots(1)$$

where D^* is the diffusion coefficient of the tracer ion, C_0 is the initial activity per cm^2 of the source and S is the total activity crossing the boundary of width $b(=1$ cm in the present case) in time t. The equation is applicable to a medium of finite length as long as the concentration changes near the two ends of the medium are negligible, as required by the boundary conditions.

Results and Discussion

Adsorption of a halide ion, X^-, from its aqueous solution on silver leads to the formation of Ag^+X^- as a product of chemisorption[6]. This complex may further develop into an insoluble halide complex as $(AgX_2)^-$ with the progressive increase in adsorption with time.

Surface diffusion and surface self-diffusion — The earliest work[13] on surface mobility of films of electropositive elements over a tungsten filament took into account the spreading force due to the repelling dipoles; the latter being formed between each adatom and its 'electrical image' at the substrate metal. The spreading force increasing with the increase in coverage (θ) reaches a maximum value at $\theta = 1$. A parallel orientation of dipoles perpendicular to the metal surface envisaged for $\theta \leq 1$ may not continue beyond a monolayer but it would gradually disappear with further increase in adsorbed amount. The overall structure of the multilayer phase would tend to approach more to that of the bulk silver halide (neglecting the presence of silver halide complexes for the sake of simplicity). Under these conditions the spreading force due to mutually repelling dipoles would be less effective in the case of multilayers[14]. Both surface diffusion and surface self-diffusion coefficients of Cl^- and I^- ions are highest generally in the monolayer, (Figs 2 and 3). Haul and coworkers[15-18] reported that the diffusion coefficient in the surface layer passes through a maximum in the vicinity of $\theta = 1$ and then it approaches the value for volume diffusion[19] (D_{volume}). Since the maximum thickness in the present study is $\sim$ 25 layers, the corresponding D^* values cannot be compared with D_{volume} values available from the literature[20,21].

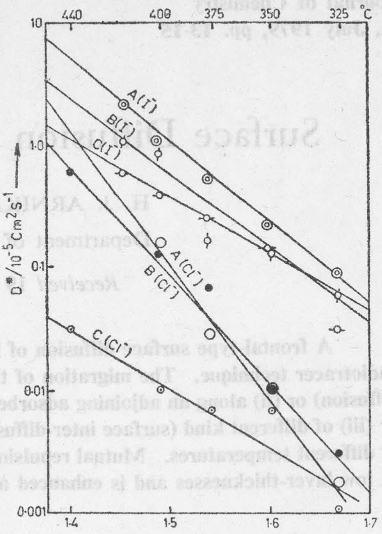

Fig. 2 — Arrhenius plot for surface self-diffusion of Cl^- and I^- ions on silver at various thicknesses [(A) monolayer (B) 10 layers and (C) 25 layers]

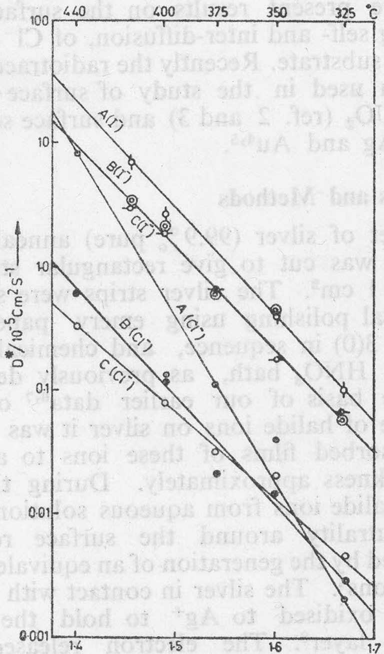

Fig. 3 — Arrhenius plot for surface diffusion of Cl^- and I^- ions on silver at various thicknesses [(A) monolayer (B) 10 layers and (C) 25 layers].

It is reported[22] that the orientation polarization diminishes with increasing temperature. However, in the case of surface bound dipoles its temperature dependence is negligible; at the same time the free polar end would be expected to exhibit rotation within a given cone at high temperatures[23]. Such oscillations of polar (I^-) end may superimpose over mutual repulsion of I^- adions. The two effects act simultaneously and reinforce each other at elevated temperatures, resulting in enhanced diffusion coefficients in the case of monolayers. On the contrary, in a multilayer phase disorientation of dipoles increase with increasing thickness away from the surface; thereby reducing the contribution due to (i) free end vibrations of dipoles at elevated temperature and (ii) mutual repulsion of dipoles to the resultant spreading force. For diffusion in multilayers , therefore a situation arises where the diffusion coefficients are low (Figs 2 and 3) while at the same time their temperature dependence is also low (Table 1).

D^* values for surface diffusion are higher than those

TABLE 1 — ACTIVATION ENERGIES OF SURFACE AND SURFACE SELF-DIFFUSION OF TRACER Cl^- and I^- IONS ADSORBED ON SILVER TO DIFFERENT THICKNESSES

Layer thickness	E_a/(kJ mol^{-1})			
	Surface diffusion		Surface self-diffusion	
	Cl^-	I^-	Cl^-	I^-
1	258.7	169.3	209.4	133.8
10	169.3	154.7	179.3	117.5
25	134.6	154.7	93.2	90.3

TABLE 2 — COEFFICIENTS OF SURFACE INTER-DIFFUSION OF TRACER Cl^- IONS THROUGH Br^- AND I^- IONS AND OF TRACER I^- IONS THROUGH Cl^- AND Br^- IONS ADSORBED ON SILVER TO DIFFERENT THICKNESSES

Medium of diffusion	$D^*/10^{-5}$ cm^2 sec^{-1} at 375°		
	1 layer-thickness	10 layer-thickness	25 layer-thickness
	Inter-diffusion of tracer Cl^-		
I^-	0.01	0.001	0.001
Br^-	0.02	0.004	0.001
Cl^-	0.03	0.075	0.007
	Inter-diffusion of tracer I^-		
Br^-	0.41	2.55	5.62
Cl-	0.36	0.78	1.01
I^-	0.54	0.15	0.26

for surface self-diffusion for both Cl^- and I^- ions adsorbed to 25 layer-thickness. This also holds good for 1 and 10 layer-thicknesses of I^- adions. This observation is explained on the basis that during surface diffusion the multilayer front collapses[24] over a bare surface to a monolayer and this process continues until the whole of the available surface gets uniformly covered. The movement of this monolayer would correspond to both higher D^* and E values.

Generally, $D^*_{I^-} > D^*_{Cl^-}$ for both the diffusion processes (Figs. 1 and 2). Correspondingly, $E_{I^-} < E_{Cl^-}$ (Table 1). This result is also consistent with the fact that $D^*_{I^-} > D^*_{Cl^-}$ for volume diffusion of Cl^- in AgCl (ref. 20) and of I^- in AgI (ref. 21)

Surface inter-diffusion — Data on inter-diffusion at 375° of Cl^- through Br^- and I^- and of I^- through Cl^- and Br^- at 1, 10 and 25 layer-thicknesses are presented in Table 2. The results reveal that the diffusion of I^- ions through Cl^- ions is faster than that of Cl^- ions through I^- ions. It had been earlier established from our work on desorption[6] in aqueous solutions of Cl^- and I^- ions preadsorbed on silver that Cl^- ions are readily replaced by I^- ions while the reverse is more difficult. This was attributed to the lower oxidation potential of Ag, AgCl (s), Cl^- electrode. The inter-diffusion of I^- ions occurs by the replacement of Cl^- ions. The movement of Cl^- ions is sluggish in comparison to that of I^- ions as noted from the data on surface diffusion and surface self-diffusion studies so that the frequency of occupying I^- sites by Cl^- via exchange will always be less than the frequency of Cl^- replacement by I^-. Thus when I^- ions of the unlabelled side migrate after crossing the boundary into the labelled Cl^- film their flow rate will be greater than that of the Cl^- ions moving simultaneously in the reverse direction. The coefficient of inter-diffusion of I^- ions through Cl^- (and Br^-) ions is thus higher than that of Cl^- ions through I^- (and Br^-) ions.

The present findings in respect of the relative orders of inter-diffusion coefficients, viz. $D^*_{I^-}$ (Br^-) > $D^*_{I^-}$ (Cl^-) and $D^*_{Cl^-}$ (Br^-) > $D^*_{Cl^-}$ (I^-), where the bracketed Cl^-, Br^- and I^- represent the medium of diffusion, are consistent with our earlier results[6,25] on the relative rates of displacement, viz. (i) that of preadsorbed (Br^-) by I^- > (Cl^-) by I^-, (ii) that of preadsorbed (Br^-) by Cl^- > (I^-) by Cl^- and (iii) that of preadsorbed (Cl^-) by I^- > (I^-) by Cl^-. The increase in $D^*_{I^-}$ (Br^-) and $D^*_{I^-}$ (Cl^-) with increase in layer-thickness suggests the dominant role of diffusion of I^- via displacement of Br^- or Cl^- ions in multilayers as against in monolayers.

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