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## Electromigration and Diffusion of Cadmium and Indium in Liquid Sodium\*

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**Abstract**—Mass transport induced by an electric current (electromigration) and by a concentration gradient (diffusion) was measured as a function of temperature in liquid sodium containing small amounts of cadmium or indium. While the calculated diffusion coefficients fall within values normally found for diffusion in liquid alloys, the electromigration behavior was strikingly different from observations in liquid mercury and bismuth alloys. In sodium, cadmium and indium migrate to the anode (in mercury and bismuth, they migrate to the cathode) with mobilities 25 to 50 times larger than in mercury or bismuth. These findings are explained, at least qualitatively, by a recently proposed model which describes electromigration in terms of an electron drag. The data are in better agreement when expressed as a "coefficient of electron drag", which is dependent on the current density, than as a mobility, which is a velocity per unit field.

### Introduction

In a previous investigation,<sup>1</sup> the electromigration behavior of silver, cadmium, indium, tin and antimony was determined in liquid bismuth. The mobilities of these solutes in bismuth were found to be similar to their respective mobilities in liquid mercury.<sup>2,3</sup> From the results of these studies, a model was proposed<sup>4</sup> to explain, semi-quantitatively, electromigration in liquid alloys. The model attributes electromigration predominantly to "electron drag", which is the result of an exchange of momentum during electron-ion coupling.

Since this model was based primarily on observations of solutes migrating in heavy metal solvents, it was desirable to compare electromigration in a light metal solvent. Sodium, although presenting experimental difficulties, offers many advantages as the solvent in such a study: it has a very low atomic weight, it is monovalent and electronically

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simple, and it has a low electrical resistivity to contrast with the high resistivities of mercury and bismuth. In addition, it has sufficient solubility for the same series of solutes, Ag, Cd, In, Sn, and Sb, which had been measured in mercury and bismuth. It was desired to use these elements as the migrating species since they have similar atomic mass while having a wide range of chemical valences and electrical resistivities. Also, they all have radioisotopes, which greatly aid in the analyses.

To date, electromigration of cadmium and indium has been measured in liquid sodium, and these results are presented in this paper. Diffusion coefficients of the solutes in the same alloys have been measured for comparison with the electromigration results.

### Experimental Technique.

Electromigration in liquid sodium was measured by a capillary-reservoir technique<sup>5,6</sup> similar to that used for measurements in liquid heavy metals. However, whereas the heavy metals are often contained in a quartz apparatus and are only protected at elevated temperatures, the highly contaminable sodium alloys must be fully protected from the atmosphere at all times. A special stainless steel apparatus was designed and constructed in conjunction with a vacuum-inert gas dry box, permitting direct transfer of materials between the dry box and the apparatus in an argon atmosphere. Using this equipment, described in detail elsewhere,<sup>7</sup> the sodium alloys remain apparently pure and available for experimentation for several weeks.

To measure electromigration, several capillaries are simultaneously filled with a molten alloy of sodium containing about 1 atom per cent of radioactive solute. The capillaries are made of Pyrex or quartz, 1 mm in I.D. and 5 cm long, and have tungsten electrodes sealed in one end. A direct current is passed through two of the capillaries for a measured time interval; other capillaries sample the alloy in the reservoir. The final amount of solute in each capillary is measured by radiochemical analysis.

Assuming that the recently proposed model is valid, then the commonly used electric mobility (velocity per unit field) is not the appropriate parameter to express electromigration. Instead, one should like to relate the solute motion with the current flow. The following expression is believed to be a true representation of the exchange of solute between

capillary and reservoir :

$$J_i = P_i N_i J_e, \quad (1)$$

where  $J_i$  is the solute atom flux across the capillary orifice,  $P_i$  is a proportionality constant which is a probability of electron drag,  $N_i$  is the solute atom fraction and  $J_e$  is the electron flux. This equation is valid so long as the experiments are terminated before the critical time,  $\tau$ , which is the time it takes the concentration gradient formed in the capillary to reach the orifice. According to Klemm,<sup>8</sup>

$$\tau = \frac{L^2}{\pi D_{\text{eff}}}, \quad (2)$$

where  $L$  is the capillary length and  $D_{\text{eff}}$  is an "effective" diffusion coefficient, usually much larger than the "true" diffusion coefficient due to convective mixing produced by the current.

In a "short-time" experiment ( $t < \tau$ ) back diffusion can be ignored and from Eq. (1) one can then solve for the "coefficient of electron drag"

$$P_{\text{drag}} = \frac{n_i}{N_i n_e}, \quad (3)$$

where  $n_i$  is the number of solute atoms crossing the capillary orifice and  $n_e$  the number of electrons passing through the alloy in the same time interval.

Measurements of electromigration in liquid sodium were made at temperatures ranging from about 140 to 330°C. Except for a brief evacuation necessary for the filling of the capillaries, the system contained a positive argon pressure to minimize volatilization of the sodium.

An additional problem experienced with the sodium alloys arises from the large increase in Na density caused by the alloying addition. The effect of this density differential had been previously encountered in bismuth alloys,<sup>9</sup> but it is magnified in the sodium alloys because of the greater difference in the densities of solvent and solute. For example, an addition of 1 atom per cent Cd increases the density of sodium by more than 5%.<sup>10</sup> Thus, when cadmium or indium concentrates in the upper region of the capillary, the density differential causes a stirring action which greatly increases  $D_{\text{eff}}$  in Eq. (2), with a corresponding decrease in  $\tau$ . This situation dictated experiments of very short duration made with low current densities, restricting the amount of solute change in each capillary and limiting the experimental precision. In a majority

of the experiments the solute weight change in each capillary was less than 0.3 mg.

To measure diffusion, several capillaries sealed at one end were simultaneously filled with the alloy at a temperature between 150 and 200°C. When cool, the capillaries were taken into the dry box and cleaned. The orifice of each capillary was ground down to the contracted alloy column to insure contact with the liquid metal. Two capillaries were then mounted on the capillary holder, orifice up, and immersed in a reservoir of pure liquid sodium. Solute diffusion was made to proceed up the capillary to prevent unfavorable density conditions within the capillary. The capillaries were constantly rotated in the reservoir at 1 rpm to maintain proper boundary conditions.

After a measured time interval, the capillaries were removed from the reservoir and gamma counted to determine the remaining solute content. This was compared to the original solute content in the capillaries before undergoing diffusion, and the diffusion coefficient was found from a numerical solution to the equation

$$\frac{M_t}{M_\infty} = \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-D(2n+1)^2 \pi^2 t / 4L^2}, \quad (4)$$

where  $M_t$  is the total amount of solute leaving the capillary in time  $t$ ,  $M_\infty$  the corresponding quantity after infinite time,  $D$  the diffusion coefficient, and  $L$  the capillary length. The value of  $M_\infty$  is corrected for loss due to expansion of the alloy column in the sodium reservoir.

### Experimental Results

The results of the electromigration measurements are summarized in Table 1. In each experiment the current passed through two capillaries; the electrode in one capillary was made the cathode and the electrode in the other was the anode. The electrons flow from cathode to anode. Both cadmium and indium concentrate in the capillaries containing the anode and become depleted from the capillaries containing the cathode, indicating that cadmium and indium migrate against the electron flow in liquid sodium.

The relatively large differences between the amounts of solute entering and leaving the capillaries in each experiment is for the most part attributed to inaccuracies in determining the solute concentration in the

TABLE I Electromigration of Cadmium and Indium in Liquid Sodium

Solute	Expt.	$C_0$ atom % Solute	Temp. °C	Time Hr	Current Density amp/cm <sup>2</sup>	% Change in Solute in Cap. Containing Anode	% Change in Solute in Cap. Containing Cathode	Average $P_{\text{ass}} \times 10^3$ atom/electron
Cd	Cd-1	1.2 <sub>1</sub>	181	2	500	+41.3	-41.7	2.15
	Cd-3	1.0 <sub>4</sub>	163	1	500	+18.5	-20.7	1.44
	Cd-4	1.6 <sub>3</sub>	228	1	500	+15.8	-23.2	2.00
	Cd-5	1.1 <sub>6</sub>	292	1	250	+16.6	-9.4	2.79
	Cd-6	1.1 <sub>6</sub>	150	1.5	250	+10.5	-14.3	1.71
	Cd-7	1.2 <sub>2</sub>	218	1	500	+17.4	-15.7	1.70
	Cd-8	0.8 <sub>8</sub>	212	1	250	+13.9	-11.8	2.72
	Cd-9	0.8 <sub>7</sub>	254	1	250	+8.3	-11.6	2.20
	Cd-10	0.7 <sub>4</sub>	330	1	250	+18.3	-10.3	3.28
	In	In-1	0.7 <sub>2</sub>	205	2	250	+28.5	-29.5
In-2		0.7 <sub>6</sub>	176	1	500	+20.5	-31.2	3.01
In-4		1.1 <sub>6</sub>	225	1	250	+9.6	-16.7	3.02
In-5		0.7 <sub>6</sub>	317	1	250	+10.9	-23.4	3.97
In-8		0.4 <sub>8</sub>	146	1	250	+8.0	-14.6	2.53
In-9		0.5 <sub>6</sub>	267	1	125	+7.4	-8.7	3.58
In-10		0.5 <sub>5</sub>	300	1	125	+10.8	-8.0	4.39
In-11		0.5 <sub>2</sub>	164	1	125	+6.4	-4.2	2.40
In-12		0.5 <sub>5</sub>	216	1	125	+10.5	-6.0	3.84

reservoir. The solute change in each capillary is found from the difference between the final amount of solute in the alloy and the initial amount of solute, determined from the sample capillaries. Since the net solute change is only a few tenths of a milligram, an error in the determination of  $C_0$  is greatly magnified in the final calculation of the solute change in a capillary.

In several experiments, notably Cd-4 and In-4,  $C_0$  was markedly higher than in the previous and subsequent experiments ( $C_0$  was intentionally changed after experiments Cd-7 and In-5). This is attributed to segregation of the solute, concentrating in the lower region of the reservoir, which was perhaps insufficiently stirred prior to the filling of the capillaries. It is believed, however, that the solute distribution remained constant during the short experiment duration, and the segregation did not introduce any additional experimental errors.

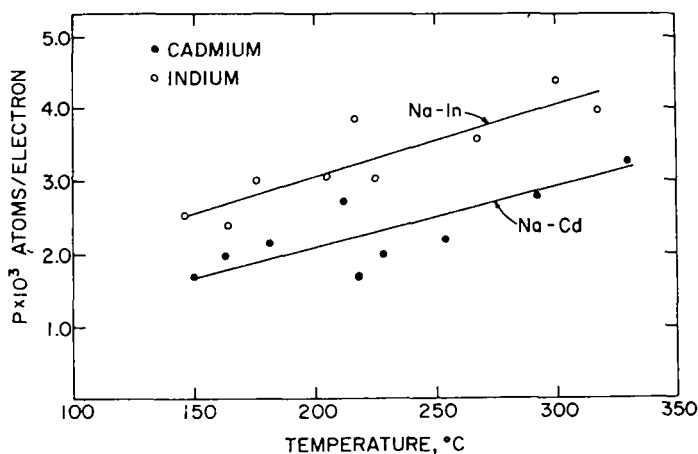


Figure 1. Temperature dependence of the coefficients of drag for Cd and In in liquid Na.

In Fig. 1, values of  $P$  are plotted as a function of temperature and an apparently linear relationship is observed. The deviations of the values of  $P$  from the least-squares straight lines are not nearly as great as are the differences in the solute changes in the two capillaries of each experiment. This is because  $P$  is calculated from the average of the amount of solute leaving one capillary and entering the other, and such averaging essentially minimizes uncertainties in the reservoir composition.

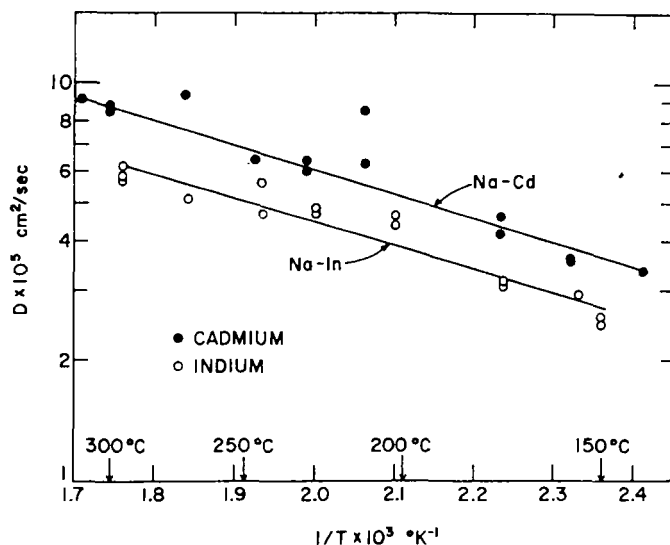


Figure 2. Temperature dependence of the diffusion coefficients for Cd and In in liquid Na.

The results of the diffusion measurements are shown in Fig. 2, in which the temperature dependence of  $D$  for less than 1 atom per cent cadmium and indium in liquid sodium is plotted in the traditional manner. Solving the Arrhenius rate equation by a least-squares program, the following relationships are found:

$$D_{Cd} = 1.13 \times 10^{-3} \exp [(-2.910)/RT] \text{ cm}^2/\text{sec} \quad (5)$$

$$D_{In} = 0.70 \times 10^{-3} \exp [(-2.720)/RT] \text{ cm}^2/\text{sec}. \quad (6)$$

### Discussion

Table 2 lists the electromigration behavior of cadmium and indium in liquid mercury, bismuth, and sodium. Although the results in mercury and bismuth are very similar, electromigration in sodium is strikingly different. Whereas in mercury and bismuth both solutes migrate to the cathode with relatively large mobilities, in sodium the solutes migrate to the anode with mobilities 25 to 50 times larger. However, diffusion of these solutes in sodium proceeds at rates quite normal for liquid alloys. Calculated values of "effective valence" (proportional to the ratio of mobility to diffusion coefficient) are  $-19.6$  for cadmium and



TABLE 2 Electromigration Behavior of Cadmium and Indium in Several Liquid Metals

Solute	Direction of Solute Migration	$U \times 10^4$ cm <sup>2</sup> /v-sec	Reference	Calc. $P_{drag} \times 10^4$ atoms/electron
Solvent: Hg at room temperature				
Cd	Cathode	9.7-10.6	2, 3	5.7-6.2
In	Cathode	8.5	3	5.0
Solvent: Bi at 500°C				
Cd	Cathode	10.6	8	6.8
In	Cathode	8.8	8	5.6
Solvent: Na at 200°C				
Cd	Anode	250		21.1
In	Anode	~400*		30.5

\* Based on estimated values for the resistivities of Na-In alloys.

—43 for indium at 200°C. Indeed, species migrating in liquid sodium have been assigned effective valences with even larger magnitudes.<sup>11</sup> If an effective valence were a valid physical property, and there were an appreciable field effect, then sodium must have an impossibly large positive valence.

These findings may be explained by the recently proposed model for electromigration in liquid alloys.<sup>4</sup> The model assumes that as the electrons flow through the alloy, they interact with the alloy ions and are scattered by them. This scattering process, which gives rise to the electrical resistivity, is not entirely elastic and momentum is transferred from the electrons to the ions. Since the ions have different scattering cross sections, and since the liquid is incompressible, the species with the larger cross section should receive a greater "push" toward the anode, displacing the other species to the cathode.

As a measure of the scattering cross section, the resistivity of the pure metal at its melting point is used; these values, taken from Cusack and Enderby,<sup>12</sup> are given for the metals of interest in Table 3. The assump-

TABLE 3 Electrical Resistivities of the Alloy Components at Their Melting Points

Element	Na	In	Cd	Hg	Bi
$\rho_L, \mu\Omega\text{-cm}$	9.6	33.1	33.7	91	130

tions are made that each species of the alloy scatters electrons as it does in its pure state and that the relevant liquid structures are the same. Thus it may be seen that Cd and In do not scatter electrons as strongly as Hg or Bi, and in this alloy the solvent is "dragged" to the anode displacing the Cd or In to the cathode. On the other hand, Cd and In have greater electrical resistivities than Na, and preferentially migrate to the anode in Na. Although Cd and In have nearly identical values of  $\rho_L$ , in Hg and in Bi above 380°C Cd has a greater mobility toward the cathode. This would indicate that in these alloys In experiences stronger electron-ion coupling than does Cd. It is thus self-consistent that, in Na, In has a greater mobility than Cd toward the anode.

To understand the very large mobilities found in liquid Na, one must realize that it is apparently the electron flow and not the applied field that is causing the electromigration. Thus, the standard "mobility", which is a velocity, per unit field, is a meaningless parameter. This has not been apparent, since most of the presently available data involve electromigration in heavy metals having similar electrical resistivities. In sodium, however, a given field will result in a current flow about 10 times that in mercury and about 14 times that in bismuth.

A parameter based on a proportionality between atom flux and electron flux tends to normalize electromigration data. This may be seen in Table 2 by comparing the values of  $U$  and  $P$  in the different solvents. A further example of this may be seen in the Bi-Sn electromigration data reported by Verhoven.<sup>13</sup> The mobility of Bi in Sn is reported to be about a factor of 3 larger than the mobility of Sn in Bi. However, calculated values of  $P$  are nearly the same over the entire composition range, which is predictable since  $\rho_L(\text{Bi}) \sim 3 \rho_L(\text{Sn})$ .

Neglecting mass differences, which are suspected to play only a minor role in influencing alloy separations,<sup>1</sup> the coefficient of drag should be approximately proportional to the difference in the electrical resistivities of the alloy components. This relationship is indeed observed for electromigration in Hg and Bi; however, at first glance the Na results are not consistent with the heavy metal results. The values of  $P$  for Cd and In in Na, which are several times larger than for these same solutes in Hg or Bi, would require resistivities of Cd and In over 300  $\mu\Omega\text{-cm}$ .

One of the assumptions made to obtain a working model for the electron drag effect was that each species of the alloy scatters electrons as it does in its pure state. There is evidence to indicate that this assumption,

which is apparently valid for the heavy metal alloys studied, may not be applicable to the sodium alloys. Freedman and Robertson<sup>14</sup> found that an addition of 1 atom per cent Cd increases the resistivity of liquid sodium by over 40%. Preliminary results of Adams<sup>15</sup> indicate that  $\Delta\rho$  is nearly linear with additions up to 9–10 atom per cent Cd. It is estimated that additions of indium increase the resistivity of sodium to an even greater extent than does cadmium. If it may be assumed that the increased resistivities result from scattering by the solute ions, then cadmium and indium have “effective” resistivities in sodium an order of magnitude greater than the values for the pure elements.

Two possible explanations for “abnormal” scattering by these solutes in sodium are offered. The first involves the presence of a compound in the liquid alloy. Sodium and cadmium form a very stable compound,  $\text{NaCd}_2$ ,<sup>16</sup> which melts at 384°C. Weeks and Davies<sup>10</sup> found volumetric and thermodynamic evidence of a strong Na–Cd interaction in dilute liquid alloys. Although the Na–In phase diagram has not been determined, the existence of a compound,  $\text{NaIn}$ , has been reported.<sup>16</sup> In mercury alloys<sup>3</sup> the existence of compounds has reportedly hampered electromigration in the liquid state. Bonding with sodium in the liquid could account for the high “effective” resistivities assigned to cadmium and indium.

Alternatively, large scattering cross sections may be attributed to a change in the electronic properties of the solute atoms when alloyed. Sodium has a structure which differs greatly from the structures of the polyvalent elements. Preliminary calculations<sup>15</sup> suggest that if cadmium and indium take the sodium structure the solute atoms will have scattering cross sections considerably larger than in their pure state. Thus, to gain a better understanding of electromigration in sodium alloys one must first determine the behavior of the solute in the sodium alloy.

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