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Electromigration in Liquid Na-K Alloys*

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The direction of electromigration in liquid Na-K alloys reverses with composition. Coefficients of electron drag have been measured in dilute alloys, where the separation is greatest, and in an alloy of composition approximating the null point. Theoretical calculations of the electron-ion interactions in these alloys, have been used to refine the Epstein-Paskin model for electromigration in liquid alloys, and to explain the observed reversal.

INTRODUCTION

Atom motion in liquid alloys in the presence of an electric field has been attributed to the action of the electron stream on the metal ions.[1] Based on studies of solute migration in liquid mercury,[2,3] bismuth,[4,5] lead,[6] tin,[7] and antimony,[6] a very definite relationship was found[6] between the direction of solute migration and the relative resistivities of the solute and the solvent: In every alloy the species with the greater resistivity migrated to the anode. (No electromigration was observed in Hg-Tl and Hg-Pb alloys, but values of ρ for Hg, Tl, and Pb are similar.) Furthermore, a semiquantitative correlation was found for values of the coefficient of electron drag, P, used to express solute migration, and the solute-solvent resistivity difference. This correlation is quite good for electromigration of polyvalent solutes in the polyvalent solvents studied, but deviations were seen for electromigration of monovalent Ag and Cu in liquid Bi. Greater deviations from this correlation were found in a recent study of electromigration of polyvalent solutes Cd and In in monovalent Na.[8] The solutes migrated to the anode, as expected, but the values of P were found to be much greater than predicted by the resistivity difference.

A logical extension of these studies is an investigation of electromigration in an alloy of two monovalent species. Since the electronic structures of alkali metals are simple and understood in contrast to the noble metals, Na and K were chosen for this study. Theoretical calculations of the electrical properties of Na and K have been successfully performed; thus reliable estimates of the electron-ion coupling in these metals are available. Earlier experimental work of Drakin and Maltsev[9] had yielded the surprising result that the direction of migration of the Na (and hence that of the K) reverses as the alloy compositions are varied from pure Na to pure K. However, the electromigration parameters obtained by the steady-state technique used by these authors cannot be directly converted to values of P. Reliable measurements of the drag coefficient were needed in order to refine the simple model relating P with the resistivity difference. Substituting theoretical calculations of the electron-ion coupling leads to a possible explanation for the interesting reversal in electromigration direction found in Na-K alloys.

EXPERIMENTAL

The alloy compositions selected for study were Na–1-at.% K, Na–10-at.% K, Na–34-at.%K, and K–1-at.% Na. High-purity, recently gettered Na and K obtained from Mine Safety Appliances Research Corp. were used to prepare the alloys. The experimental technique used in this study is similar to that previously used to measure electromigration of Cd and In in liquid Na.[8] All handling and experimentation were performed in a specially designed vacuum-inert gas dry box and attached apparatus,[10] in which the alloys showed no sign of oxidation for several weeks.

Weighed amounts of Na and K were charged into a stainless steel crucible, heated in an argon atmosphere, and sufficiently stirred to form a homogeneous alloy. Four quartz capillaries, 1 mm in i.d., 5 cm long, and containing tungsten electrodes sealed at one end, were simultaneously filled in the alloy reservoir. A direct current was passed through two of the capillaries for a measured time interval; the other two capillaries served to determine the original composition of the alloy, C_0. The contained alloy in each capillary was analyzed for solute concentration by atomic absorption. (In the case of the concentrated alloy, analysis was made for both Na and K contents.)

Unlike the experiments of Drakin and Maltsev,[9] which were run for very long times to reach steady-state distributions, the experiments in this study are "short-

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TABLE I. Electromigration in dilute liquid Na-K alloys.

Expt. No.	Solute	C_0 at.% solute	Temp. (°C)	Duration (h)	Current density (A/cm²)	% change in solute in capillary containing Anode	Cathode	Average P (10^{-4} atom/electron)
1A	K	1.1_5	172	2	250	+3.5	−1.9	2.8_7
2A		1.1_3	108	4	250	+5.0	−4.8	2.6_1
3A		1.1_3	136	1	500	+2.5	−2.5	2.8_7
1B		1.2_3	172	4	500	+10.5	−13.9	3.2_0
2B		1.2_2	117	4	500	+9.9	−13.1	2.9_3
3B		1.2_4	256	4	500	+12.6	−18.2	3.8_9
4B		1.2_7	304	3	500	+9.2	−10.4	3.5_5
5B		1.1_9	281	3	500	+11.0	−12.5	3.9_8
7B		1.3_0	216	4	500	+12.8	−7.8	2.8_2
6A	K	9.8	95	6	500	+13.7	−9.5	1.9_6
7A		10.2	176	6	500	+13.5	−12.1	2.1_5
8A		9.9	213	4	500	+13.2	−7.7	2.5_8
1C	Na	1.4_2	165	4	500	+24.8	−32.2	4.3_8
2C		1.4_2	122	4	500	+29.7	−31.0	4.3_5
3C		1.4_6	76	4	500	+22.2	−23.7	3.2_6
4C		1.4_6	205	4	500	+39.9	−36.9	5.4_2
5C		1.4_3	258	4	500	+37.8	−37.8	6.1_3

time"; the atom exchange between capillary and orifice can be attributed solely to electromigration. Under these conditions, the coefficient of electron drag, P_i, is calculated from the equation

$$P_i = n_i / N_i n_e, \tag{1}$$

where n_i is the number of i ions crossing the capillary orifice, N_i is the atom fraction of i, and n_e is the number of electrons passing through the alloy. A positive value of P_i indicates preferential migration of that species with the electrons to the anode, a negative value indicates displacement to the cathode.

Experiments were performed at temperatures ranging to 300°C; above this temperature the quartz is severely attacked by the molten alloy. The experimental data for the dilute alloys are given in Table I and for the concentrated alloy are given in Table II. The alloys were prepared in the following manner. A small amount of K was added to slightly over 100 g of Na to form alloy *A*, containing about 1 at.% K. After several experiments, further K additions were made, increasing the concentration first to ~10 and then to ~34 at.% K. Alloy *B* was prepared from 2 g K and 100 g Na, and alloy *C* from 1 g Na and 150 g K.

In each experiment current flowed through two capillaries; the electrode in one capillary was made the cathode and the electrode in the other served as anode. In the dilute alloys the solute content increased in the capillary containing the anode and decreased in the capillary containing the cathode, indicating a migration of the solute atoms from cathode to anode with the electron stream. In the concentrated alloy no electromigration was observed at temperatures below 200°C, with only a very slight separation of the components noticeable at higher temperatures. These calculated values of the drag coefficient are plotted versus temperature in

TABLE II. Electromigration in the concentrated Na-K alloy.

Expt. No.	Temp. (°C)	Duration (h)	Current density (A/cm²)	Species	C_0[a] (at.%)	% change in C_0 in capillary containing Anode	Cathode	Average P (10^5/atom/electron)
9A	159	6	500	K	$33._8$	0	0	0
				Na	$63._4$	0	0	0
10A	104	8	500	K	$34._9$	0	0	0
				Na	$63._5$	0	0	0
11A	207	6	500	K	$34._2$	−1.5	+1.1	~1.0[a]
				Na	$63._0$	+1.4	−1.0	~1.0[b]
12A	51	10	500	K	$34._3$	0	0	0
				Na	$63._3$	0	0	0
13A	110	24	1000	K	$35._5$	0	0	0
				Na	$67._2$	0	0	0
14A	201	24	1000	K	$35._3$	−4.3	+6.0	−0.9
				Na	$66._9$	+1.8	−6.0	0.6
15A	290	24	1000	K	$32._8$	−4.6	−3.9	−0.7
				Na	$63._8$	+4.1	0	0.4
16A	250	24	1000	K	$34._3$	−3.8	+10.0	−1.3
				Na	$66._8$	+2.5	−5.0	+0.7

[a] Values of C_0 reflect the uncertainty in the chemical analysis, amounting to about 3%.
[b] Insufficient change in concentration for meaningful calculation of P.

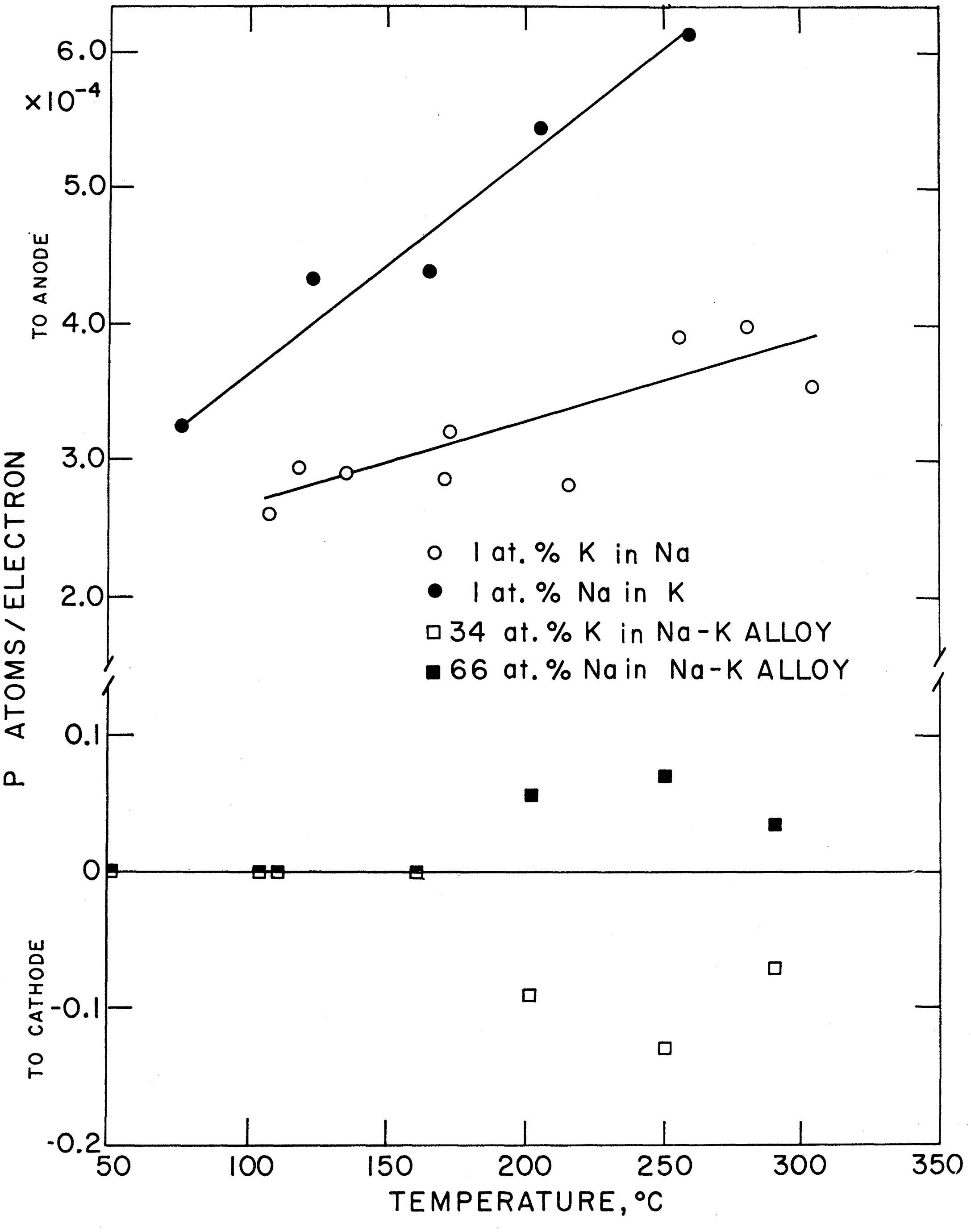

FIG. 1. Coefficient of electron drag, *P*, for liquid Na-K alloys as a function of temperatures. The straight lines were fitted to the experimental data.

Fig. 1 for the very dilute and the concentrated alloys; the results from experiment numbers 6A, 7A, and 8A are not plotted.

The absence of electromigration in the concentrated alloy at low temperatures is in agreement with the work of Drakin and Maltsev, who reported the null point occurring in an alloy containing slightly more than 60 at.% Na. The separation occurring at temperatures above 200°C, although very slight (note the expanded scale for this alloy in Fig. 1), is real. A similar temperature phenomenon has also been recently reported by Jousset and Huntington,[11] who have recently examined

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the electromigration in two Na-K alloys with compositions on either side of the null point.

DISCUSSION

Electromigration in liquid alloys may be attributed to the interaction of the electron stream and the metal ions.[1] As the electrons scatter from the metal ions, momentum is transferred to the ions. The amount of momentum each ion species receives depends primarily on its electron-ion scattering cross section, and, since electromigration in liquids is inherently a competitive phenomenon, the rate of separation in the alloy should depend on the difference in the scattering cross sections. As a first approximation, the electrical resistivities of each species at its melting point has been taken as the measure of its scattering cross section in the alloy. In a metal, an ion is screened by the conduction electrons and an electron interacts with the screened ion. The screening depends on the density of the electrons and so the interaction between an electron and an ion will depend on the density of the conduction electrons. In a dilute alloy, the resistivity of the pure solvent is a good measure of the solvent's cross section, whereas the solute's cross section may differ from that in its pure form, if the electron density in the alloy differs appreciably from that of the pure solute. The resistance of the pure solute taken as a first approximation of the scattering cross section worked quite well for the systems in which both elements were polyvalent; in these systems the electron densities of both elements are similar. This simple correlation breaks down in a number of instances involving monovalent ions and a better measure of the electron-ion coupling in an alloy is required.

Considerable progress has been made in recent years towards an understanding of the electrical properties of liquid metals. Ziman has formulated a theory of the resistance and thermopower of pure metals[12] and also of liquid alloys.[13] Like electromigration, the resistance of a metal requires a calculation of the electron-ion interaction. Several models have been proposed for this interaction and one of the most useful is that of Meyer *et al.*,[14] who have calculated the phase shifts of an electron at the Fermi level for the alkali metals, over a range of densities. The probability of deflection of an electron through an angle θ can be found from the scattering amplitude $f(\theta)$,[15]

$$f(\theta)=\frac{1}{2ik}\sum_l (2l+1)(e^{2i\eta_l}-1)P_l(\cos\theta)\,, \qquad (2)$$

where η_l is the lth partial-wave phase shift and k is the momentum. The model of Meyer *et al.*[14] has given results for both the resistance and the thermopower of the alkali metals,[16,17] and their alloys,[18,19] that are in good agreement with experimental data. Thus, we shall here use their phase shifts to estimate the scattering power of the ions. When an electron is scattered by an ion, the momentum lost by the electron is transferred to the ion. The component of momentum parallel to the electric field causes the net displacement of the ion which results in electromigration. This effect is largest when the direc-

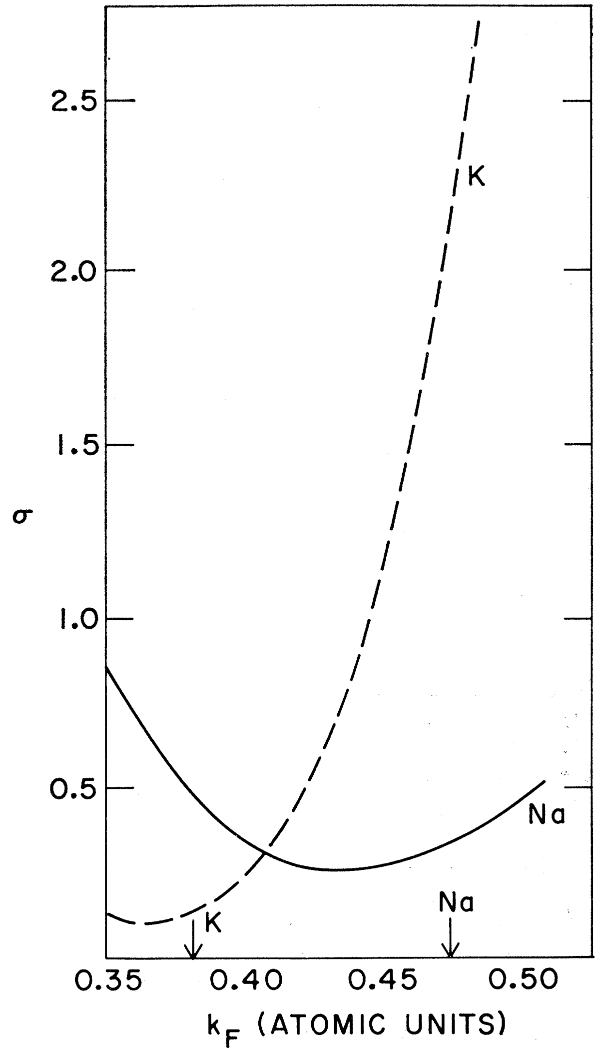

FIG. 2. Back-scattering cross section, σ in arbitrary units, of Na and K ions immersed in an electron gas with Fermi momentum k_F. The two arrows show the values of k_F appropriate to the pure liquids Na and K at the respective melting points.

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tion of motion of the electron is reversed, so we will take the probability of back-scattering of an electron as an appropriate measure of the liability of an ion to migrate with the electron stream. Putting $\theta=\pi$ in Eq. (2) and omitting factors which are the same for both ion species, we can write in a dimensionless form the appropriate cross section σ for scattering by a given ion, as

$$\sigma=(x^2+y^2)\,, \tag{3}$$

where

$$x=\sum_l (-)^l(2l+1)\sin 2\eta_l\,,$$
$$y=\sum_l (-)^l(2l+1)(1-\cos 2\eta_l)\,. \tag{4}$$

The phase shifts used in Eq. (3) must be evaluated for an electron at the Fermi level of the alloy. For Na-K alloys in which the conduction band contains one electron per atom, the Fermi momentum k_F is given by

$$k_F=(3\pi^2 n)^{1/3}\,, \tag{5}$$

where n is the number of atoms per unit volume. Values of k_F are 0.474 a.u. for pure Na, and 0.382 a.u. for pure K, at the respective melting points. In an alloy, k_F will have some intermediate value and can be calculated from the density of the alloy.

Scattering cross sections have been calculated over an appropriate range of k_F using Eq. (3); the phase shifts were interpolated from the table given by Meyer *et al.*[14] Our theory is based on the assumption that the separation of the components in electromigration is governed by the difference in cross sections. We show how the experimental results can be predicted and explained using this assumption. Figure 2 shows the scattering cross sections for Na and K versus k_F. The most striking feature is that these two curves cross, predicting that the direction of migration of the two components reverses at some composition, as in fact is observed experimentally. Examining Fig. 2 more closely, the following predictions can be made and compared with the experimental data shown in Fig. 1:

(1) For a dilute solution of K in Na, $k_F=0.474$, $\sigma_K>\sigma_{Na}$, and K should migrate to the anode. Conversely for a dilute solution of Na in K, $k_F=0.382$ and $\sigma_{Na}>\sigma_K$, so that Na should migrate to the anode.

(2) The two cross sections are equal for $k_F=0.407$, and no separation should be expected. Close to this value, however, secondary effects may upset the delicate balance, and displace the null point.

(3) If the temperature of an alloy is raised, the density decreases. This implies that the value of k_F for an alloy of fixed composition shifts to the left in Fig. 2, so that the difference between the cross sections changes. Although this is not the only effect of raising the temperature (for example, the ease of motion of the ions also will change with temperature), in Fig. 2 we can see how the change in cross sections with temperature affects electromigration. Firstly, for a dilute solution of Na in K, raising the temperature increases $|\sigma_{Na}-\sigma_K|$, so that the separation should increase. For the dilute solution of K in Na, raising the temperature reduces $|\sigma_{Na}-\sigma_K|$. In Fig. 1, it is seen that P increases rapidly with temperature for Na in K, but more slowly for K in Na. Presumably, in the latter case the other effects of temperature are competing against the decreasing difference in cross sections; in all previous studies the magnitude of P has been observed to increase with temperature. A further interesting feature occurs at the null composition. Following the above argument, as the temperature is increased, k_F decreases and σ_{Na} becomes slightly greater than σ_K. We would expect a slight separation to occur with Na preferentially migrating to the anode, as is observed.

CONCLUSION

Through the introduction of available calculations of electron-ion coupling in Na-K alloys, the empirical model for electromigration has been extended. This refinement makes possible an explanation for the observed reversal in direction of electromigration in Na-K alloys and increases confidence that the basic mechanism of electromigration is understood. This work represents a further step towards the development of a quantitative theory of electromigration in liquid alloys.