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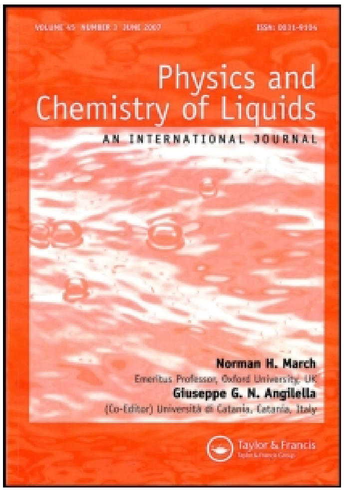

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C. Roxbergh[a]; T. Persson[a]; A. Lodding[a]
[a] Physics Department Chalmers, University of Technology, Gothenburg, Sweden

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Electrotransport of Sodium in Liquid Potassium Metal

C. ROXBERGH, T. PERSSON and A. LODDING

Physics Department
Chalmers University of Technology
Gothenburg, Sweden

Abstract—The electromigration of ^{22}Na has been studied in liquid Na–K of two compositions, about 1% and 11% Na. For the low Na alloy the effective charge number Z^*_{exp} (of tracer motion relative to container) ranges from about -12 at the m.p. to -5.5 at 300 °C, and for 11% Na from -3.5 at the m.p. to -2.5 at 150 °C. The migration velocity, obtained by a method free from convective disturbances, is found to be by an order of magnitude higher than that quoted in one earlier investigation, and by some 50% higher than another set of data. Theoretical arguments, connecting Z^*_{exp} with the resistivity increment per impurity atom, are well borne out by the present results, and also predict the change of sign observed at higher Na concentrations.

Since the 1920s, numerous investigations have been made of electrolytic de-mixing effects in binary metallic liquids.(1–4) Many of the data are rather inaccurate, mainly due to convection effects(5,6) and to difficulties in chemical analysis.

To gain as quantitative information as possible about the parameters in electrotransport, a phenomenon in which electronic and atomic mobilities are closely linked, one is well advised to choose a relatively simple binary system in which both the electron structure and the diffusive effects have already been studied. Such a system is Na–K.(7–13) Three earlier electrotransport investigations of liquid Na–K of different compositions have been reported. Drakin and Maltsev(14) in 1954 found that at low Na contents sodium migrates towards the anode, at high Na concentrations towards the cathode. Fifteen years later Jousset and Huntington(15) confirmed that the migration velocity changes sign at about 60% Na, and showed that this is theoretically plausible. Subsequently Epstein and Dickey(16) made measurements on both dilute and concentrated alloys, confirming the cross-over point of Ref. 15, but finding much higher mobilities than Ref. 14. The present study was initiated in order to check the discrepancies of earlier data and to provide accurate results especially in the low Na range. It was also hoped that theory might be given a test and discussion, in terms of measurable parameters, in regard to the temperature and concentration dependence of electrotransport.

1. Experimental Arrangement

The technique was in principle the same as that applied by Lodding(2) to electrolytic isotope separation in liquid metals (Haeffner effect). Essentially the same type of capillary cell and procedure has also been utilized by more recent workers.(15,16) The electrotransport occurs by the passage of direct current along a column of the melt inside a glass capillary sealed at one end and connected at the other with an " infinite " reservoir. The main features are shown schematically in Fig. 1.

The precision bore capillary, 0.8 mm in diameter, about 11 cm

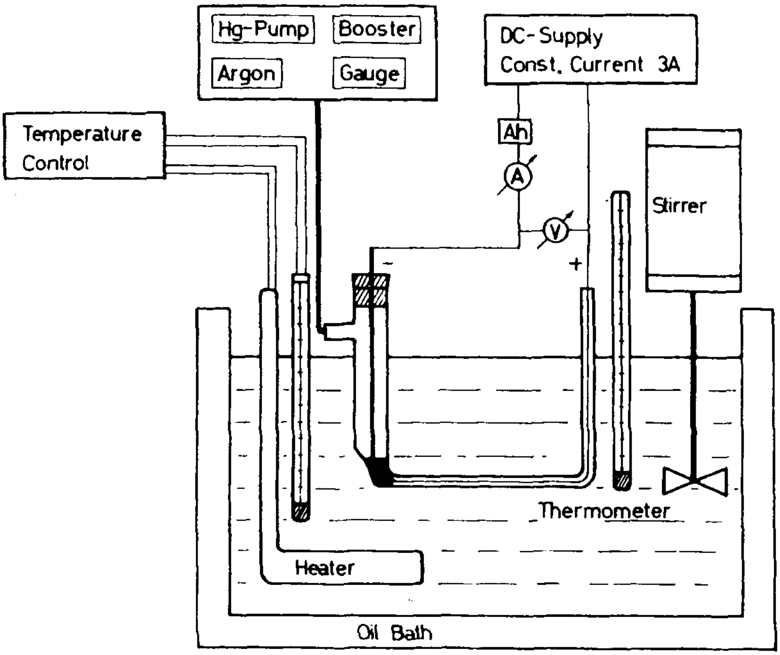

Figure 1. Schematic drawing of the experimental arrangement.

long, was made from Pyrex glass (Veridia). This limited the operating temperature for K-rich alloys to about 330 °C, above which the liquid began to react with the glass.

The metal was introduced into the capillaries by a vacuum method described in several earlier publications. For the details, including also the maintenance and corrections of temperature, the current control and monitoring, one may refer to Ref. 2. As a particularly important point it should be mentioned that this is a non-steady-state method. The duration of each experiment must be kept short enough so that no composition change arises near the open end of the capillary. The critical time for this to occur in a capillary of length l is⁽²⁾

$$t_c = l^2/\pi D_{\mathrm{eff}}, \tag{1}$$

where D_{eff} is the effective back-diffusion coefficient, containing both the molecular diffusion D and convection effects. Taking $D \approx 10^{-4}$ cm^2/sec in the present arrangement, one finds t_c to be of the order of 4 days. The main sources of systematic convection were calculated (according to Ref. 5) to be effectively suppressed by using relatively small electrolysis currents (3 A, corresponding to about 600 A/cm^2) and keeping the horizontal capillaries in a bath where the temperature fluctuations were only about ± 0.2°. However, to safeguard against occasional disturbances, such as vibrations or current fall-out, the duration of experiment was in all cases kept below one-third of the critical time corresponding to $D_{\mathrm{eff}} = D$.

After concluded electrolysis the metal in the cell was allowed to solidify, after which the capillary was sectioned into about 1 cm long portions for the determination of the current induced concentration profile.

The main experimental innovation was the use of radioactive tracer, which allowed the concentration determination with an accuracy of a couple of percent, a substantial improvement as compared with atomic absorption analysis⁽¹⁵,¹⁶⁾ or resistance measurements.⁽¹⁴⁾ The ^{22}Na isotope was introduced by mixing about 1 mC of active NaCl (Amersham) with several cm^3 of the filtered liquid metal under protective atmosphere, and homogenizing for about a week with the mixture in a temperature bath. As no long-lived K isotope could be procured, the method was best applicable to small Na concentrations. Two compositions were chosen, containing (according to ion microprobe analysis at Cameca, Courbevoie) 0.8 ± 0.1%, resp. 11.3 ± 0.5% Na. For the Na-poor alloy the tracer was mixed with 99% pure K metal (Koch–Light), while the other composition was produced by adding 99.9% pure Na (Merck).

The tungsten electrode fused into the closed end of the column had a diameter of 0.45 mm and reached about 5 mm into the capillary. The DC supply (Oltronix) stabilized the current within better than 0.5% of the nominal value, thus allowing a good time integration. The total current was independently registered by calibrated coulometers with an accuracy of ½%. The temperature bath (Lauda) was thyristor controlled within 0.2 °C, and the temperature inside the column could be computed (from current and heat conductivity)(2) to about ± 1.25 °C.

The ^{22}Na activity of each capillary section was determined by means of a hollow crystal scintillation spectrometer.

2. Evaluation of Primary Results

A typical concentration profile is shown in Fig. 2. Sodium is seen to enrich considerably at the anode. It can be noticed that the

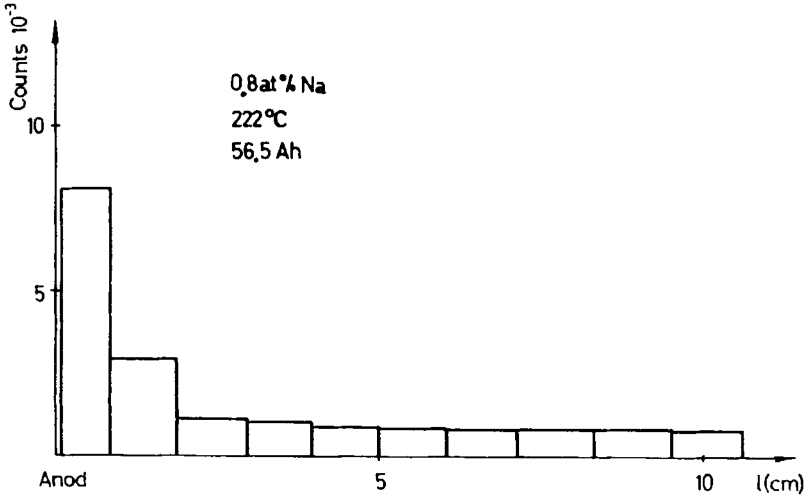

Figure 2. Typical concentration profile of ^{22}Na in capillary after passage of direct current, showing original composition, temperature and integrated current.

requirement that no enrichment occur near the open end is amply fulfilled. The non-steady-state method integrates all composition changes on one side of a section arbitrarily chosen at a point P where the change is known to be zero. The computed entity is the migration velocity (relative to the bulk of metal) v_{exp} *at* this section, i.e. unaffected by the considerable changes at the closed end. Another advantage, as compared to steady-state methods, is that the effective back-diffusion D_{eff} does not enter the evaluation of v_{exp}. If the summed total activity on the closed capillary side of the chosen point P, column length l, is $A_0 = I_0 l$ before electrolysis (I_0 being the original activity per cm) and $A = A_0 + \Delta A$ after electrolysis, then $\Delta A = I_0 v_{\text{exp}} t$ (t being electrolysis time), and the migration velocity P is given by

$$v_{\text{exp}} = (\Delta A/A)(l/t). \tag{2}$$

The results are conveniently expressed by the effective charge number, Z^*_{exp}, defined by

$$v_{\text{exp}} = (D_i/kT) Z^*_{\text{exp}} Ee, \tag{3}$$

where D is the interdiffusion coefficient, E the field and e the electronic charge. If the integrated current is L, the specific resistivity $\bar{\rho}$ and the capillary area S, Eqs. (2) and (3) can be easily combined to

$$Z^*_{\text{exp}} = \frac{kT}{D_i} \frac{lS}{Le\rho} \frac{\Delta A}{A}. \tag{4}$$

To substitute into Eq. (4) D^* for Na in K was taken from Refs. 8 and 9 (for the 11.3% Na composition the Darken relation $D_i = D^*_{\text{Na}}(1 - c_{\text{Na}}) + D^*_{\text{K}} c_{\text{Na}}$ was used, where D^*_{Na} is the Na tracer diffusion in pure K and D^*_{K} that for K in Na). The resistivity of pure K was obtained from Liquid Metals Handbook⁽¹²⁾ and the increment due to alloying from the curve combined from different sources in Ref. 15. To obtain l (the effective length of the analyzed metal corresponding to the operating temperature) from the totalled length of the capillary sections, a density correction is made, of the order of 10%, at the highest T.

TABLE 1 Effective charge numbers of ^{22}Na electrotransport (relative to container) in liquid K–Na.

Composition %Na	Temperature °C	$-Z^*_{exp}$
0.8 ± 0.1	74.1	10.51 ± 0.74
	80.9	12.61 ± 0.95
	99.6	10.55 ± 0.83
	100.7	10.68 ± 0.80
	139.8	8.85 ± 0.89
	167.6	8.45 ± 0.63
	180.0	6.76 ± 0.51
	222.0	7.40 ± 0.56
	222.1	7.55 ± 0.57
	262.0	6.49 ± 0.45
	287.3	6.43 ± 0.38
	305.5	5.06 ± 0.30
11.3 ± 0.5	80.6	3.30 ± 0.23
	99.5	3.48 ± 0.21
	153.2	2.73 ± 0.20

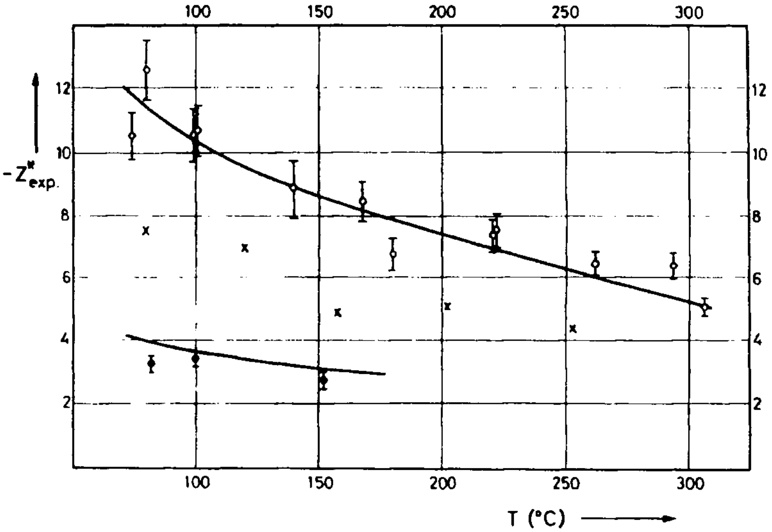

Figure 3. Experimental charge numbers Z^*_{exp} plotted versus temperature. Open circles: 0.8% Na. Filled circles: 11.3% Na. Crosses: from Ref. 16, quoted 1.4% Na. Curves: Z^* calculated from Eq. (13a) with $D_e = D$ and $\rho^*_{e\Omega} = 1.6$, resp. 1.3 $\mu\Omega$ cm/%.

Table 2 Comparison of results at low Na concentrations, obtained from different investigations. Method A: steady-state, 20 cm long tube, abt 2.5 mm diam, 2 Amps, abt 330 hours.(14) Method B: non-steady-state, 5 cm, 1 mm, 4 Amps, 4 hrs.(16) Method C: non-steady-state, 11 cm, 0.8 mm, 3 Amps, 16 hrs (this work; see also Ref. 25).

Method	Composition %Na	$-Z^*_{\mathrm{Na-K}}(100\,^\circ\mathrm{C})$	$-Z^*_{\mathrm{Na-K}}(250\,^\circ\mathrm{C})$
C	0.8	10.1	6.6
B	1.4	7.2	4.7
A	3.3	0.47	—
C	11.3	3.4	—
A	14.0	0.14	—

The computed experimental charge numbers are listed in Table 1 and plotted in Fig. 3. Also shown in Fig. 3 are the results of the investigation by Epstein and Dickey,(16) at a quoted composition of 1.4% Na. Table 2 lists all data hitherto obtained at low Na compositions, at two temperatures. The present values are seen to be somewhat higher than, but in qualitative agreement with, those of Ref. 16. On the other hand, the Z^* values from the earliest investigation, Ref. 14, fall short by at least a power of ten. As pointed out in Refs. 20 and 10, the passage of electric current through a molten metal in a cylindrical tube gives rise to several types of electro-convection. Mixing also results from any variations in temperature and density during experiment.(5) All this contributes to the effective diffusion coefficient D_{eff}. In the evaluation of short-time experiments, as in the present work (via Eq. (1)) and in Ref. 16, the effective diffusion coefficient does not enter, but if D_{eff} is too great, the critical time t_c may be exceeded, in which case composition changes reach the reservoir, and the obtained Z^* values become too small. As said above, for this to happen in the present study, D_{eff} would have to be more than twice the molecular D-value. According to quoted conditions, the same order of safety against overstepping t_c was maintained in Ref. 16. It should, however, be closer looked into, whether the main electroconvective mechanisms, electro-osmosis and magnetohydrodynamic stirring,(20) could not in spite of the precautions reach such proportions as to " lose " tracer-enriched material. The electro-osmotic part, D_{eo}, has been calculated for the present conditions (according to Ref. 5); it was found that it should amount to less than 20% of D. This contribution at any given temperature depends⁽⁵⁾ only on the square of the current density, and as this entity was roughly the same in Ref. 16 as here, the discrepancy cannot be explained by D_{eo}. The second main contribution, D_{mhd}, is, at each temperature, proportional to $j^4r^4\vartheta^2$, where j is the current density, r the radius and ϑ the "effective conicity" of the near-cylindrical tube. D_{mhd} has been calculated for the present set-up with precision-bore 0.8 mm Veridia capillaries to be only about $0.05D$. However, in Ref. 16 relatively short, 1 mm, quartz capillaries were used, where the factor ϑ could possibly be by a factor 4 or more greater than in our Veridia cells. This would give a D_{mhd} equal to or greater than D. Further, the times of heating or cooling were in Ref. 16 comparatively long in relation to anneal time, which would, as shown in Ref. 5, introduce another sizable convective term. It therefore appears plausible that between the two sets of non-steady-state results, some 30% of our Z^*_{exp}-values, may be explicable by convective losses in the earlier study.

As regards the results quoted by Drakin and Maltsev,⁽¹⁴⁾ they were obtained using a steady-state design with a wide (2.5 mm approx.), long and repeatedly bent glass tube, with both ends open. The current densities were very moderate, only about a thirtieth of those in the short-time studies, and the temperature changes (using a thermostat with boiling water) small and slow. The convection effects are therefore likely to have been insignificant. Substituting the diffusion coefficient at 100 °C into Eq. (1) one finds that the critical time t_c at which composition should begin to change in the middle of the separation tube is as high as about a month. However, the duration of the experiments in Ref. 14 was only about two weeks, which means that the conditions of steady state, on which the evaluation was based, had not even begun to realize. The enrichment profile was therefore much too low. Thus in this case the discrepancy appears caused by insufficient duration of electrolysis in the older study.

3. Discussion

Electrotransport is considered⁽²⁻⁴,¹⁷⁻¹⁹⁾ to be caused mainly by transfer of momentum from conduction electrons to "disordered" atoms. Such atoms are not only impurities but also, e.g., atoms changing place with vacancies, or, in liquids, atoms diffusing at large density fluctuations. It is thus to be expected in a dilute alloy that not only the solute atoms, but also those of the solvent, are affected by electrotransport forces.

During electrolysis the column geometry is given by the shape of the cell; the reference mark is a point P on the capillary. The entity of particular interest is, however, the velocity of transport relative to the bulk of the alloy. As both Na and K are transported to the closed end of the capillary (anode), a back-flow must take place to compensate the requirement of constant volume. The observed velocity is, accordingly,

$$v_{\mathrm{exp}} = v_{\mathrm{Na}} - v_0, \tag{5}$$

where v_0 is the back-flow velocity. If the volume associated with a solute atom is V_{Na} its concentration (atom fraction) is c_{Na}, and an analogous notation is used for solvent atoms, then

$$v_0(c_{\mathrm{Na}} V_{\mathrm{Na}} + c_{\mathrm{K}} V_{\mathrm{K}}) = v_{\mathrm{Na}} c_{\mathrm{Na}} V_{\mathrm{Na}} + v_{\mathrm{K}} c_{\mathrm{K}} V_{\mathrm{K}}. \tag{6}$$

Combining (5) and (6), one obtains

$$v_{\mathrm{exp}} = (v_{\mathrm{Na}} - v_{\mathrm{K}}) \frac{c_{\mathrm{K}} V_{\mathrm{K}}}{c_{\mathrm{K}} V_{\mathrm{K}} + c_{\mathrm{Na}} V_{\mathrm{Na}}} \tag{7}$$

and by the definition of Z^*, introducing also the charge numbers Z^*_{Na} and Z^*_{K} relative to the bulk (not, like Z^*_{exp}, relative to container),

$$\left(\frac{D_i}{D^*_{\mathrm{Na}}}\right) Z^*_{\mathrm{exp}} = \left(1 + \frac{c_{\mathrm{Na}} V_{\mathrm{Na}}}{c_{\mathrm{K}} V_{\mathrm{K}}}\right)^{-1} \left(Z^*_{\mathrm{Na}} - \frac{D^*_{\mathrm{K}}}{D^*_{\mathrm{Na}}} Z^*_{\mathrm{K}}\right). \tag{8a}$$

If V_{Na} and V_{K} are taken to be the respective atomic volumes, then the first bracket on RHS is less than one per cent from unity for the 0.8% Na alloy, and 0.93 for the 11.3% alloy. The ratio $D^*_{\mathrm{K}}/D^*_{\mathrm{Na}}$ is(8,9) 0.92 ± 0.03 throughout the investigated temperature and concentration range.

At this stage it should be pointed out that the entity measured in the two earlier investigations is not the effective tracer velocity, but the relative migration velocity of the two species, $v_{\mathrm{Na}} - v_{\mathrm{K}}$. The corresponding Z^* values should here be distinguished by a special subscript, such as " Na–K " and from Eq. (6) follows

$$Z^*_{\text{Na-K}} = \left(1+\frac{c_{\text{Na}}V_{\text{Na}}}{c_{\text{K}}V_{\text{K}}}\right)Z^*_{\text{exp}}\,. \tag{8b}$$

An expression satisfying several theories$^{(4,17,19,10)}$ gives the effective charge number as

$$Z^* = \bar{Z}\left(A-\frac{\sigma^*}{\sigma}\right)\left(\frac{D_e}{D}\right), \tag{9}$$

where $\bar{Z}$ is the number of conduction electrons per atom, A expresses the ratio of the degrees of ionization of the diffusing atom and an average atom, σ^* is the scattering cross-section of a diffusing atom and σ that of an average atom. D_e/D takes into account the possibility$^{(10)}$ of departure from the Nernst–Einstein relation (i.e. of different mechanism of diffusion on one hand, electrotransport on the other). In an alkali alloy it may be with fair certainty assumed$^{(21)}$ that $\bar{Z}$ and A are near to unity. The scattering cross-sections are proportional to the respective resistivity contributions, and so Eq. (9) may be simplified to

$$Z^*\left(\frac{D}{D_e}\right) = 1-\frac{\rho^*}{\bar{\rho}}, \tag{10}$$

where $c\rho^*$ is the resistivity increment due to the molar fraction c of the migrating species, and $\bar{\rho}$ the resistivity of the alloy.

The scattering which causes electrotransport can be considered to be due to two kinds of " disorder ". One is the " chemical " difference between solvent and solute, of the type investigated resistometrically by Linde.$^{(23)}$ The other is the scattering during a diffusion jump (thought responsible for self-transport). If the first mechanism corresponds to ρ^*_C, and the scattering at the half-way point of a diffusive step to ρ^*_D, one may write

$$\rho^* = \tfrac{1}{2}\rho^*_D+\rho^*_C, \tag{11}$$

the factor $\frac{1}{2}$ accounting for a near-sinusoidal shape of the saddle-point barrier. In a liquid it seems conceivable that $\rho_D{}^*$ is relatively small; however, the experimental fact of self-transport (Haeffner-effect) suggests that non-negligible scattering takes place at relatively large voids in a range of diffusion-furthering void sizes.

The observed transport of Na may accordingly be described by

Eq. (8b) together with

$$Z^*_{\mathrm{Na-K}}\left(\frac{D}{D_{\mathrm{e}}}\right) = 1 - \frac{(\frac{1}{2}\rho^*_D + \rho^*_C)_{\mathrm{Na}}}{\bar{\rho}} - \left(\frac{D^*_{\mathrm{K}}}{D^*_{\mathrm{Na}}}\right)\left[1 - \frac{(\frac{1}{2}\rho^*_D + \rho^*_C)_{\mathrm{K}}}{\bar{\rho}}\right]. \qquad (12)$$

At these low concentrations of Na it is fairly justified to make the approximation $D^*_{\mathrm{K}} \simeq D^*_{\mathrm{Na}}$ (introducing only some 8% error in the last term on RHS, which in itself is at most 20% of the total). One may then write

$$Z^*_{\mathrm{exp}} = -\left(\frac{D_{\mathrm{e}}}{D}\right)\left(1 + \frac{c_{\mathrm{Na}}\,V_{\mathrm{Na}}}{c_{\mathrm{K}}\,V_{\mathrm{K}}}\right)^{-1}\left(\frac{\rho^*_{\mathrm{eff}}}{\bar{\rho}}\right), \qquad (13a)$$

with

$$\rho^*_{\mathrm{eff}} = \tfrac{1}{2}\Delta\rho^*_D + \Delta\rho^*_C, \qquad (13b)$$

the Δ denoting differences between Na and K in the corresponding entities.

In Fig. 3, the measured Z^*_{exp} values are plotted together with curves representing Eq. (12a) with $D_{\mathrm{e}} = D$, arbitrarily (at this stage) adopting ρ^*_{eff} values of 1.6, resp. 1.3, for the two concentrations. In both cases the experimental temperature behaviour is seen to be very well represented. This prompts the conclusion that D/D_{e} is in fact practically unity, i.e. that the transport mechanisms are identical (questioned in Ref. 15). The essential correctness of the arguments leading to Eqs. (13) is also reasonably supported. The next step should be to discuss the magnitudes of the parameters contained in ρ^*_{eff}.

From measurements of the Haeffner-effect in potassium(2,10) the effective " defect resistivity " $\frac{1}{2}\rho^*_{\mathrm{D}}$ can be assessed to lie between 0.2 and 1.0 $\mu\Omega$ cm/% of diffusing species. This is to be understood as a mean value, averaging the scattering at atoms diffusing by steps ranging from zero to about nearest-neighbour-distances. The distribution of adjustment lengths (" voids ") is likely to be rather unaffected by the presence of a homovalent impurity; a reasonable guess for the difference between Na and K is therefore $\frac{1}{2}\Delta\rho^*_D \simeq (0 \pm 0.4)$.

The dependence of resistivity on the composition in liquid Na–K alloys has been plotted, on the basis of various investigations, in Ref. 15. Approximate resistivity values at 100 °C are (in $\mu\Omega$ cm) 15.5 in pure K and 9.6 in pure Na.(12) The plot of $\bar{\rho}$ vs. c_{Na} is nearly parabolic, with its maximum about 48 $\mu\Omega$ cm, situated at 44% Na.

For a binary of perfectly miscible homovalent components A and B, the excess resistivity due to mixing is theoretically expected(24) to be

$$\begin{aligned} c_A(\rho_C^*)_A + c_B(\rho_C^*)_B &= \text{const.}\,[c_A(1-c_A)^2 + c_B(1-c_B)^2] \\ &= \rho_0^*\, c_A(1-c_A). \end{aligned} \tag{14}$$

One computes from the value of the maximum,(11,12,15) about 33 $\mu\Omega$ cm above the mean of the pure metal resistivities, an admixture contribution $\rho_0^* \simeq 1.35\ \mu\Omega\ \text{cm}/\%$, with only slight temperature dependence.

In the expression for Z^*_{exp}, via Eq. (12b), enters the difference

$$\Delta\rho_C^* = \rho_0^*[(1-c_{\text{Na}})^2 - c_{\text{Na}}{}^2] = \rho_0^*(1-2c_{\text{Na}})\,. \tag{15}$$

Substitution of $\rho_0^* = 1.35$ yields $\Delta\rho_C^* = 1.35$, resp. 1.07 for the two concentrations. If this is combined with $\frac{1}{2}\Delta\rho_D{}^* \simeq 0.25$, which lies well within the above-mentioned plausibility range, very good agreement is obtained with the experimentally found ρ^*_{eff} values (Fig. 3), viz. 1.6 resp. 1.3. The experimental data are thus well represented, at both concentrations, by

$$Z^*_{\text{exp}} = -\left(1+\frac{c_{\text{Na}}V_{\text{Na}}}{c_{\text{K}}V_{\text{K}}}\right)^{-1}\bar{\rho}^{-1}[\rho_0^*(1-2c_{\text{Na}}) + \tfrac{1}{2}\Delta\rho_D^*]\left(\frac{D^*_{\text{Na}}}{D_i}\right), \tag{16}$$

with $\rho_0^* \simeq 1.35\ \mu\Omega\ \text{cm}/\%$ and $\frac{1}{2}\Delta\rho_D^* \simeq 0.25\ \mu\Omega\ \text{cm}/\%$.

Expressing this in terms of the relative motion of the two species, and using the more rigorous Eq. (12) instead of (13), one may apply this reasoning also to higher Na concentrations, where the departure of $D_{\text{K}}^*/D_{\text{Na}}^*$ from unity becomes more appreciable. The expression becomes

$$\begin{aligned} Z^*_{\text{Na-K}} = -(\bar{\rho})^{-1}[\rho_0^*(1-2c_{\text{Na}}) &+ \tfrac{1}{2}\Delta\rho_D^* \\ &- (1-D_{\text{K}}^*/D_{\text{Na}}^*)(\bar{\rho} - \tfrac{1}{2}\rho^*_{D\text{K}} - c^2_{\text{Na}}\rho_0^*)] \end{aligned} \tag{17}$$

This does in fact predict(25) a change of sign at about 60% Na, as found in earlier experiments,(14–16) if the above parameters are used along with(10) $\frac{1}{2}\rho^*_{D\text{K}} \simeq 0.6$.

It can be concluded that this model, connecting electrotransport mobility with " defect resistivities ", well predicts the magnitude as well as the temperature dependence of the effective charge number, and also provides a semi-quantitative prediction of the change of sign at higher Na concentrations.

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