THE CHEMLA EFFECT IN THE MOBILITIES
IN THE MOLten BINARY SYSTEM NaOH-KOH

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ABSTRACT

Internal mobility ratios of two cations in the molten binary system (Na, K)OH have been measured with the Klemm method. From these and available data on the densities and conductivities, the internal mobilities of Na⁺ and K⁺ ions (b_{Na} and b_{K}, respectively) have been calculated. The Chemla effect occurs except at high concentration of Na⁺ ions. b_{Na} and b_{K} decrease with decreasing concentrations of NaOH and KOH, respectively; b_{Na} is well expressed, except at a region of small molar volume, by

\[ b_{Na} = \frac{A}{(V-V_0)} \exp(-E/RT), \]

where A, V_0 and E are constant independent of temperature T and molar volume of the mixture V. Negative deviation of b_{Na} from this equation at low x_{Na} region is attributed to the free space effect traceable to the small free space. The decrease of b_{K} with an increase of NaOH concentration may be interpreted qualitatively by assuming that the OH⁻ ions become less mobile owing to the strong interaction with the Na⁺ ions.

INTRODUCTION

Molten alkali hydroxides are ionic liquids and therefore good ionic conductors. However, fundamental properties of the melts such as the structure and the mechanism of the ionic conduction have not been much as investigated as other typical ionic melts probably because of the technical difficulties due to the high chemical aggressiveness of these melts.

The order of the molar conductivities, and therefore of the internal cation mobilities b, of the following alkali hydroxides is opposed to that of other usual melts:
Thus, it is interesting to elucidate the mechanism of the ionic conduction of the molten alkali hydroxides. For this purpose, it is more informative to measure mobilities in binary mixtures than in neat melts. The binary system (Na,K)OH has been chosen for the present study, since data on the densities and the conductivities (1)(2) are available. For the measurement of ratios of the internal mobilities of the two cations, the Klemm method, i.e., a countercurrent electromigration method was employed. This method is one of the most reliable and is insensitive to a small amount of impurities such as water and carbonate ions. This advantage is particularly important for the present case.

EXPERIMENTAL

The electromigration cell shown in Fig. 1 was similar to the one used for molten carbonates (3). The furnace was a transparent one made by Trans. Temp. Co., U. S. A.

A mixture LiOH-NaOH-KOH of the eutectic composition (9.5-49-41.5 mol %) (4) was used as the catholyte in the large vessel, which also played the role of a heat bath for the separation tube. These chemicals were made by Kanto Chemical Co. Japan (LiOH H2O: min. 95 % containing max. 0.5 % Li2CO3, NaOH: min. 97 % containing max. 0.8 % Na2CO3, and KOH: min. 86 % containing max. 0.8 % K2CO3). Water contained in these chemicals was mostly evaporated when they were heated.

A mixture melt (NaOH-KOH) of a chosen concentration was stored in another small vessel of alumina, and bubbled at 723 K with dry N2 gas, which had passed through conc. sulfuric acid and molecular sieve 4A, at least for 12 hr for dehydration (5). The chemicals NaOH and KOH used in this vessel were the ones made by Merck Co. Ltd. (NaOH: min. 99 % containing max. 1% Na2CO3 and KOH: min. 85 % containing max. 1% K2CO3). Water content of the melt was measured with Karl Fischer's method (e.g., for a 50-50 mol % mixture less than 1.7%).

Two alumina tubes with different diameters (outer dia.: 6 mm and 16 mm; inner dia.: 4 mm and 10 mm, respectively, d-alumina SSA-S made by Nihon Kagaku Toygo Co. Ltd.) were connected with alumina cement (Aron Ceramic D made by Toagosei Chemical, Japan) and employed as a
separation tube. The separation tube was packed over 150 mm long with alumina powder of 150-180 μm. Both the top and the bottom of the diaphragm part of the powder were installed with alumina wool for settling the powder.

The separation tube was put into the small vessel, and after the diaphragm part was filled with the melt, the tube was transferred into the electromigration cell containing the catholyte of the ternary mixture. The separation tube was set so that the connected part of the two tubes was 2-3 cm above the level of the catholyte; by this, a possible short circuit between inside and outside was avoided. Then, electromigration was started with constant electric current of about 150 mA. Platinum wires of 1 mm Ø were used as electrodes. A mixed gas of O₂ and hot water vapor was bubbled around the cathode. Conversion of the electrodeposited metal into the original hydroxide was expected to occur.

During electromigration, dry N₂ gas was passed also through the catholyte melt to remove the excess water.

After electromigration, of 2.5-3.0 hr, the separation tube was taken out, cleaned on the outside wall and cut into pieces of ca. 10 mm long. The salt in each fraction was dissolved into distilled water, and the content of the cations was determined by flame spectrophotometry.

RESULTS

The relative difference in the internal mobilities of the two cations is defined as

$$\epsilon = \frac{(b_{Na} - b_K)}{b}$$  \hspace{1cm} (1)

where \( b = x_{Na}b_{Na} + x_{K}b_K \) \((x_{Na} \) and \( x_K \) are mole fractions of NaOH and KOH, respectively). The \( \epsilon \) value can be calculated from the distribution of the cationic species in the separation tube and the transported charge according to a formula given in Ref. (6).

Main experimental conditions and the results are given in Table 1. As the absolute values of \( \epsilon \) are large at most concentrations, relatively small transported charges in these experiments compared with those for alkali nitrates may have been enough.

Internal mobilities of the two cations are calculated from \( \epsilon \) and available data on the density and conductivity (1)(2) by using
\[ b_{\text{Na}} = \left( x \frac{V}{F} \right) (1 + x_K \epsilon) \quad , \quad (2a) \]
\[ b_K = \left( x \frac{V}{F} \right) (1 - x_{\text{Na}} \epsilon) \quad , \quad (2b) \]

where \( V \) is the molar volume of the mixture and \( F \) the Faraday constant.

**DISCUSSION**

The isotherms of \( b_{\text{Na}} \) and \( b_K \) are shown in Fig. 2. The \( b_{\text{Na}} \) and \( b_K \) decrease with decreasing \( x_{\text{Na}} \) and \( x_K \), respectively. In a certain range of concentration the Chemla effect \((7,8)\) occurs, that is, the internal mobility of the smaller cation \( \text{Na}^+ \) is smaller than that of the larger one \( \text{K}^+ \). The Chemla crossing point shifts toward higher concentration of the smaller cation, as temperature increases; this is observed also in other binary systems.

We have found that, in other mixture melts with a common anion such as alkali nitrates where Coulombic interaction between cations and anions is the predominant factor influencing the mobilities, the cation internal mobilities are well expressed by

\[ b = \left[ \frac{A}{(V-V_0)} \right] \exp\left( -\frac{E}{RT} \right) \quad , \quad (3) \]

where \( A, E, V_0 \) are the parameters characteristic of the cation of interest and almost independent of the co-cations and temperature \((9)\).

In order to see explicitly whether such an equation holds, we have plotted the reciprocal values of \( b_{\text{Na}} \) and \( b_K \) against \( V \) and found that \( b_{\text{Na}} \) is well expressed with such an equation except at low molar volume (as for \( b_{\text{Na}}^{-1} \), see Fig. 3). The solid lines are drawn with the parameters \( A = 0.494 \times 10^{-11} \text{m}^5 \text{V}^{-1} \text{s}^{-1}, E = 11.34 \text{kJ mol}^{-1} \) and \( V_0 = 11.51 \times 10^{-6} \text{m}^3 \text{mol}^{-1} \). The negative deviation of \( b_{\text{Na}} \) from Eq. \((3)\) with the parameters given above is attributable to the small effective free space. (In Fig.3 the negative deviation appears as a positive one since the reciprocal of \( b_{\text{Na}} \) is taken.)

Our interpretation why \( b_{\text{Na}} \) decreases with decreasing \( x_{\text{Na}} \) is quite similar to that often stated for other systems such as binary alkali nitrates \((10)\).

It is rather surprising that the profile of the isotherms of \( b_K \) is quite different from that of \( b_{\text{Na}} \), whereas the ionic sizes of these cations are not so different. The profile for \( \text{K}^+ \) ions in the present system

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is quite different from that in the binary system (Na, K)NO\textsubscript{3}, and rather similar to that of self-diffusion coefficients in glasses exhibiting the "mixed alkali effect" (11).

It is also surprising that the molar conductivity of neat KOH is greater than that of neat NaOH. The external cation transport numbers in NaOH and KOH have been reported by Shvedov and Ivanov (10) to be 0.10 ± 0.03 and 0.03 ± 0.03, respectively. These suggest that the mechanisms of ionic conduction may be considerably different in these melts.

It is known that in alkali chloride melts internal mobilities are strongly related with a separating motion of neighboring cations defined as the self-exchange velocity (SEV) (11). Thus, the internal mobilities also in the present system may be explained in terms of the SEV. At high x\textsubscript{K} region, the motion of OH\textsuperscript{-} ions may be great and the contribution of this motion to the SEV in K\textsuperscript{+}-OH\textsuperscript{-} pairs is much greater than that of the K\textsuperscript{+} ions. As x\textsubscript{K} decreases, that is, x\textsubscript{Na} increases, separating motion of OH\textsuperscript{-} ions from K\textsuperscript{+} ions will become less vigorous owing to the stronger interaction between Na\textsuperscript{+} and OH\textsuperscript{-} ions. Therefore, with decreasing x\textsubscript{K}, b\textsubscript{K} considerably decreases. This decrease of b\textsubscript{K} could not be attributed to the smaller free space in the present case. If this were due to the free space effect, the rate of decrease of b\textsubscript{K} would become more sharp with decreasing x\textsubscript{K}. If it is assumed that, in mixture melts, Na\textsuperscript{+}, K\textsuperscript{+} and OH\textsuperscript{-} ions move mainly in the Na\textsuperscript{+}-OH\textsuperscript{-} and K\textsuperscript{+}-OH\textsuperscript{-} pairs, respectively, the rather strange isotherm of b\textsubscript{K} can qualitatively be interpreted.

According to a study of infrared spectrometry on molten NaOH, the spectral data are interpreted in terms of hydrogen bonding or polymer formation (12). This is not inconsistent with the data on b\textsubscript{Na} in the present mixture. It needs to be studied further in connection with the ionic mobilities and the difference in the structure between NaOH and KOH melts.

In conclusion, the profile of the isotherms of b\textsubscript{Na} and b\textsubscript{K} is quite different, and the Chemla effect clearly occurs except at high concentration of NaOH. The profile of b\textsubscript{Na} is similar to that found in other ionic melts such as alkali nitrates, but that of b\textsubscript{K} is rather different from those so far found. This is interpreted by assuming that the external transport number of OH\textsuperscript{-} ions in the neat KOH is considerably great and decreases with increasing concentration of NaOH.
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Table 1. Experimental conditions and relative difference in internal cation mobility.

| $X_{Na}$ | T/K | Q/C | t/hr | $\epsilon$         |
|---------|-----|-----|------|--------------------|
| 0.249 ± 0.001 | 620 | 1370 | 2.7  | 0.1169 ± 0.0081    |
| 0.249 ± 0.001 | 640 | 1191 | 2.6  | 0.1225 ± 0.0123    |
| 0.249 ± 0.001 | 673 | 1532 | 2.7  | 0.0620 ± 0.0013    |
| 0.249 ± 0.001 | 699 | 1442 | 2.3  | 0.0076 ± 0.0015    |
| 0.249 ± 0.001 | 745 | 1430 | 2.3  | -0.0265 ± 0.0153   |
| 0.487 ± 0.003 | 470 | 1448 | 2.7  | -0.0454 ± 0.0065   |
| 0.487 ± 0.003 | 480 | 1423 | 2.8  | -0.0481 ± 0.0066   |
| 0.487 ± 0.003 | 500 | 1462 | 2.7  | -0.0918 ± 0.0120   |
| 0.487 ± 0.003 | 518 | 1478 | 3.0  | -0.1102 ± 0.0071   |
| 0.487 ± 0.003 | 593 | 1436 | 4.0  | -0.1174 ± 0.0170   |
| 0.487 ± 0.003 | 645 | 1034 | 2.7  | -0.1343 ± 0.0180   |
| 0.487 ± 0.003 | 699 | 1465 | 2.7  | -0.1208 ± 0.0120   |
| 0.487 ± 0.003 | 723 | 1320 | 2.7  | -0.1607 ± 0.0096   |
| 0.698 ± 0.001 | 697 | 1276 | 2.4  | -0.3781 ± 0.0084   |
| 0.698 ± 0.001 | 735 | 1168 | 2.3  | -0.3887 ± 0.0088   |
| 0.698 ± 0.001 | 783 | 1651 | 2.4  | -0.4160 ± 0.0043   |
| 0.807 ± 0.003 | 723 | 1297 | 2.3  | -0.4612 ± 0.0031   |
| 0.807 ± 0.003 | 753 | 1513 | 3.0  | -0.4802 ± 0.0180   |
| 0.807 ± 0.003 | 790 | 1326 | 2.3  | -0.5463 ± 0.0220   |

Q is the transported charge and t the duration.
1: gas inlet (O₂ + H₂O), 2: gas inlet (N₂), 3: Pt electrode, 4: Silicone stopper, 5: graphite cover, 6: separation tube made of alumina, 7: electric furnace, 8: alumina wool, 9: alumina powder, 10: alumina vessel, 11: nichrome heater, 12: alumina tube, 13: alumel-chromel thermocouple, 14: catholyte melt of the eutectic composition of (Li, Na, K)OH, 15: gas outlet (N₂ or H₂O).
Fig. 2. Isotherms of internal mobilities of Na\(^+\) and K\(^+\) ions.

\(b_K\) for neat KOH at 623 K, which is estimated from the extrapolated conductivity data.
Fig. 3. The reciprocal of $b_{Na}$ plotted vs. molar volume.

The lines are drawn according to Eq.(3) with the given parameters. The values corresponding to the Chemla crossing point are marked.