Application of an Empirical Internal Mobility Equation to the Molten Binary Bromide System (Li,K)Br Studied by Chemla's Group

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Dedicated to the late Professor Marius Chemla at the semicentennial of the Chemla effect

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The empirical equation previously presented for the internal mobilities of molten salts is found to be valid for the data obtained by Chemla's group on the binary system (Li,K)Br containing a trace amount of Na^+ [Chemla et al., Electrochim. Acta **14**, 505 (1969)]. The value of $u_M(V_m - V_{0M})$ (u_M denotes the internal mobility of Li^+, Na^+ and K^+, and V_{0M} is the correction of V_m) is constant independently of the molar volume V_m in the whole investigated concentration range at given temperatures 823 K, 923 K, and 1023 K, except for K^+ in pure LiBr at 1023 K, which may be attributed to the agitation effect by Li^+ ions. The values of V_{0M} are evaluated and their physical meaning is discussed.

Key words: Empirical Equation; Internal Mobility; Molten (Li,K)Br; Molar Volume Dependence.

We have previously found an empirical equation for the internal mobility u_M of several ions M^+, in molten mixture systems in the case that perturbations such as the free space effect, the agitation effect and the tranquilization effect are negligible [1, 2]:

$$u_M = [A_M/(V_m - V_{0M})] \exp(-E_M/RT), \qquad (1)$$

where V_m is the molar volume, T the temperature, E_M the activation energy, R the gas constant, and A_M and V_{0M} are constants characteristic of the respective cations M^+. Equation (1) holds, for example, for nitrate and chloride mixtures [2]. In general, however, (1) is not valid for the full composition range, presumably owing to perturbations. To our knowledge, for alkali bromide systems only the data on the external mobilities presented by Chemla's group [3 – 5] are available. The temperature and the concentration data (given in digital form [3]) are shown on the phase diagram of (Li,K)Br [6] in Figure 1. In some cases a trace amount of radioactive Na^+ was present. This mixture system is the one where the Chemla effect [7] was discovered by countercurrent electromigration, i. e., the Klemm method. The

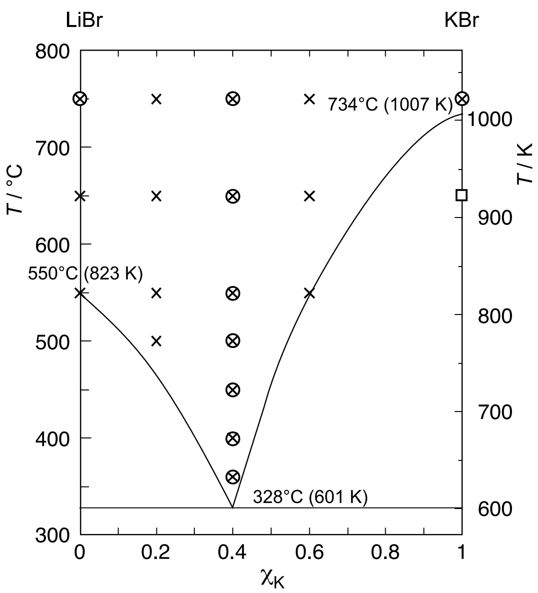
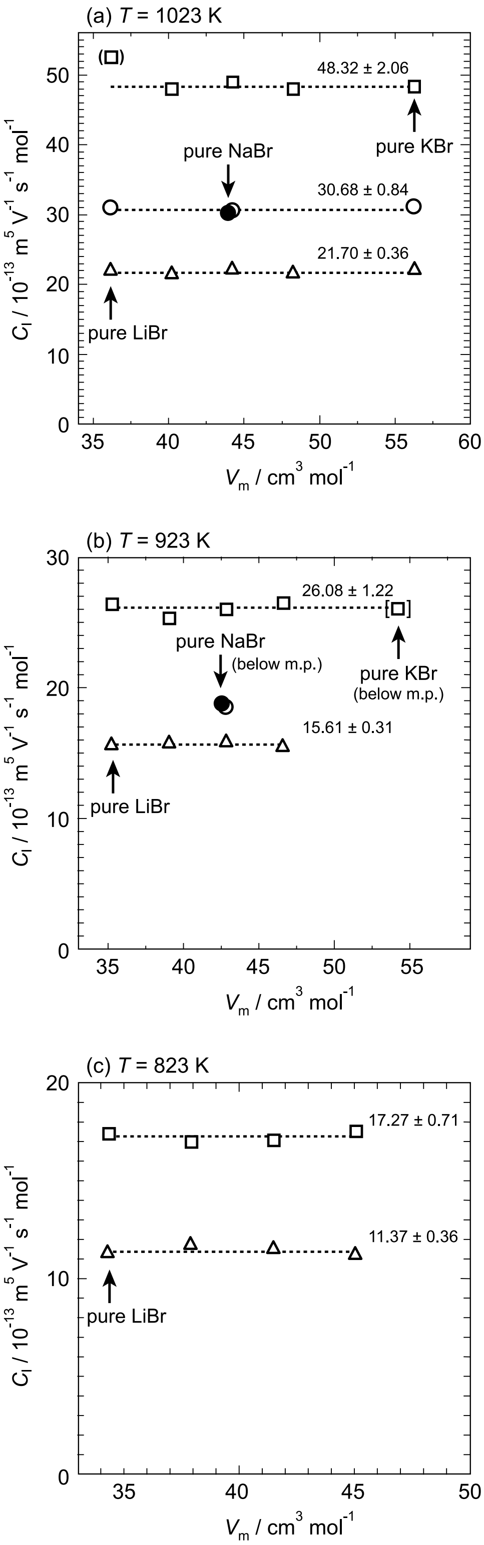


Fig. 1. The mole fractions and temperatures plotted on the phase diagram of (Li,K)Br [6], where the original data on the external mobilities, u^e, have been given [3]. ×, u^e have been obtained for Li^+, K^+ and Br^-; ◯, in addition, Na^+ is contained; □, at $x_K = 1$ and 923 K, u_K is estimated by extrapolation with respect to the temperature.



⟵ Fig. 2. The C_{IM} $[= u_M(V_m - V_{0M})]$ plotted against the molar volume, V_m. (a) 1023 K; (b) 923 K; and (c) 823 K. The C_{IM} values are given in the figure. In (a), in the least square fit, for K^+ the value for $V_m = 36.20$ cm^3 mol^{-1} ($x_K = 0$) is not counted, while for Na^+ the value for $V_m = 43.99$ cm^3 mol^{-1} (pure NaBr) is counted; in (b), for K^+ the value for $V_m = 54.18$ cm^3 mol^{-1} ($x_K = 1$) is counted.

mobility isotherms of Li^+ and K^+ have a crossing point.

The internal mobility u_M of a cation M^+ is easily obtained from the external mobilities $u_M{}^e$ of the cation and $u_{Br}{}^e$ of the anion by $u_M = u_M{}^e + |u_{Br}{}^e|$. We will show in the following that the data fit (1) in the whole investigated range except for one point (u_K in pure LiBr at 1023 K). From (1) it follows

$$u_M(V_m - V_{0M}) = A_M \exp(-E_M/RT). \tag{2}$$

The left-hand and right-hand sides of (2) are denoted as C_{IM} and C_{IIM}, respectively. Then

$$C_{IM} = C_{IIM}, \tag{3}$$

where

$$C_{IM} = u_M(V_m - V_{0M}), \tag{4}$$

$$C_{IIM} = A_M \exp(-E_M/RT). \tag{5}$$

As the values of u_M and V_m in (4) are available at 823 K, 923 K, and 1023 K at more than two concentrations, C_{IM} and V_{0M} can be calculated by a least square fit. Thus, the C_{IM} (M = Li^+ and K^+) values at 1023 K, 923 K, and 823 K are plotted against the molar volume in Figs. 2a – c at these temperatures. Figures 2a – c reveal that these C_{IM} (M = Li^+ and K^+) values are constant independently of the molar volume in the whole investigated concentration ranges except for C_{IK} in pure LiBr at 1023 K. This upward deviation may be ascribed to the agitation effect [2] on u_K by the vigorous motion of the abundant light and small Li^+ ions. As the agitation effect is expected at higher temperatures, one expects that this effect is not seen at lower temperatures such as 923 K and 823 K.

For Na^+, which was contained in a trace amount, the external mobilities at 1023 K have been measured at three concentrations, as shown in Figure 1. The internal mobility of pure NaBr can be estimated by $u_{Na} = \kappa V_m/F$, where κ is the conductivity and F the Faraday constant. Thus u_{Na} in pure NaBr is calculated to be $2.045 \cdot 10^{-8}$ m^2 V^{-1} s^{-1} at 1023 K from the available data on the conductivity and the density [8]; the

Table 1. Estimated values of V_{0M} in cm^3 mol^{-1}.

M	1023 K	923 K	823 K	773 K	723 K	673 K	633 K
Li^+	26.1 ± 0.3	27.2 ± 0.2	27.6 ± 0.3	27.7	27.8	28.0	28.1
Na^+	21.0 ± 0.6	23.0	24.6	25.1	25.6	26.2	26.4
K^+	6.5 ± 1.7	18.5 ± 1.1	21.4 ± 0.7	22.2	23.2	24.2	24.6

The values with the sign $\pm$ are calculated from the experimental data by a least square fit; the other values are estimated ones. The values differ slightly from those in [9].

melting point of NaBr is 1023 K [6]. Under the assumption that V_{0Na} in pure NaBr is equal to that at the three concentrations of (Li,K)Br, the values of C_{INa} and V_{0Na} are also calculated by a least square fit. As Fig. 2a shows, the C_{INa} value of pure NaBr is practically equal to those in the system (Li,K)Br. At 923 K (lower than melting point by about 100 K), the u_{Na} value is evaluated as $1.129 \cdot 10^{-8}$ m^2 V^{-1} s^{-1} by extrapolation with respect to the temperature. The value of C_{INa} in pure NaBr ($18.86 \cdot 10^{-13}$ m^5 V^{-1} s^{-1} mol^{-1}) is also practically equal to that of Na^+ ($18.43 \cdot 10^{-13}$ m^5 V^{-1} s^{-1} mol^{-1}) at $x_K = 0.4$ ($V_m = 42.82$ cm^3 mol^{-1}) in (Li,K)Br, as seen also in Figure 2b.

Under the assumption that E_M and A_M are independent of temperature at temperatures below 923 K, these values can be calculated from C_{IIM} (= C_{IM}) at 823 K and 923 K for Li^+ and K^+. From these E_M and A_M, the values of C_{II} at lower temperatures can be determined; C_{II} for Na^+ is interpolated from the values for Li^+ and K^+ [9]. The V_{0M} values at lower temperatures are calculated from u_M at $x_K = 0.4$ according to

$$V_{0M} = V_m - C_{IIM}/u_M. \qquad (6)$$

These V_{0M} values are given in Table 1. They are reasonable in that they converge with decreasing temperature.

Since the average number density of the common anion ρ is equal to N_A/V_m, where N_A is the Avogadro number, we assume that $1/(V_m - V_{0M})$ should be proportional to the local number density of the counter anions around M^+ on a molecular level. V_{0M} may be regarded as a correction of V_m due to the deviation of the local structure from the uniformly distributed one. The finding that V_{0Na} is practically equal in pure NaBr and in the system (Li,K)Br also supports this assumption. Since the cation attracts the anion, it is reasonable that V_{0M} is positive and in the order $V_{0Li} > V_{0Na} > V_{0K}$, because the coulombic interaction is stronger in the order Li^+-Br^- $>$ Na^+-Br^- $>$ K^+-Br^-. It is also understandable that the increase of the V_{0M} values with decreasing temperature has the order of the rate of increase of $Li^+ < Na^+ < K^+$. V_{0Li} is nearly constant below, say 800 K.

The fact that the internal mobilities of the M^+ at given temperature is proportional to the local number density of the anions around M^+ is consistent with the dynamic dissociation model [10], where the internal mobility must be strongly related with the separation motion of the cation from a reference anion toward a neighbouring anion.

In contrast to other mixtures studied so far, such as chlorides and nitrates, the value of C_I is constant in the broad investigated concentration range at a given temperature in the present system. This is presumably because the V_{0M} value is constant owing to the constant local structure around the cations, which may be due to the large anion size of Br^- in comparison to the cations. Further, a slow change in the local structure in the course of time may also be caused by the large mass of the Br^- anion.

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