Problem of liquid junction potential in molten salt solutions*

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Diffusion potential measurements for molten $SnCl_2$—$SnBr_2$, $SnCl_2$—SnI_2, $PbCl_2$—$PbBr_2$, and $PbCl_2$—PbI_2 systems have been carried out by means of EMF determination of anionic concentration cells. The measured values of diffusion potentials permit to suppose that the transport numbers of anions Cl^- and Br^- or Cl^- and I^- change proportionally to the mole fractions of corresponding salts.

Диффузионные потенциалы в солевых расплавах $SnCl_2$—$SnBr_2$, $SnCl_2$—SnI_2, $PbCl_2$—$PbBr_2$ и $PbCl_2$—PbI_2 исследованы методом измерений ЭДС анионных концентрационных цепей. Измеренные диффузионные потенциалы позволяют предполагать, что числа переноса анионов Cl^- и Br^- или Cl^- и I^- меняются пропорционально мольной доли соответствующих солей.

Recently, concentration galvanic cells are repeatedly used in order to obtain proper thermodynamic data for a number of molten metal halide or nitrate systems. They are characterized by a relatively simple construction and good reproducibility of electromotive force (EMF) measurement results.

On the other hand, the ignorance of diffusion or liquid junction potential values (E_D) at the contact between two different molten salt solutions partly limits their application. However, the authors of the most so far published experimental works [1—3], as well as theoretical ones [4—6] concerning this problem, assumed that the values of diffusion potentials are very small (in the range of 1 mV) in comparison to the measured EMF values — but there is also an available number of literature data [7, 8] which prove that the diffusion potential, in dependence on temperature and on the difference of concentration at the junction boundary, may attain values up to 20 mV.

The reason for such different opinions is probably the accepted criterion of evaluation of the "experimental" diffusion potential from the difference between

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the EMF of a concentration cell with transference and EMF's of appropriate formation cells [9]. This method is not exact especially in case of small diffusion potential values. The errors could be large due to the summation of errors — for concentration and especially for formation cells.

Solely in the case of concentration cells containing molten salt solutions with a common ion, reversible against both electrodes *e.g.*

$$\mathrm{Ag}\,|\,(X_1)\ \mathrm{AgCl} + (X_2)\ \mathrm{AgBr}\,\|\,(X_1')\ \mathrm{AgCl} + (X_2')\ \mathrm{AgBr}\,|\,\mathrm{Ag} \qquad (A)$$

or

$$\mathrm{C,\ Cl_2}\,|\,(X_1)\ \mathrm{AgCl} + (X_2)\ \mathrm{KCl}\,\|\,(X_1')\ \mathrm{AgCl} + (X_2')\ \mathrm{KCl}\,|\,\mathrm{Cl_2,\ C} \qquad (B)$$

the diffusion potential is measured directly and its value is more reliable than the indirect one. Thus far, however, only a few studies [9—13] have been carried out by this method. Therefore, employing the above-mentioned method, we have measured the values of diffusion potentials in $SnCl_2$—$SnBr_2$, $SnCl_2$—SnI_2, $PbCl_2$—$PbBr_2$, and $PbCl_2$—PbI_2 systems.

Experimental

Anhydrous $SnCl_2$, $PbCl_2$, and $PbBr_2$ were obtained by passing (for 3—4 h) dry hydrogen chloride or hydrogen bromide through molten appropriate salts (anal. grade) previously dried in desiccator. Absorbed hydrogen chloride or hydrogen bromide was removed from the melt by heating for several hours and then the purified argon was passed through the molten salts. Dry stannous bromide was obtained by vacuum distillation of $SnBr_2$ (chem. pure). Anhydrous lead iodide was obtained by a very careful (due to its great decomposition ability) melting in vacuum of PbI_2 (anal. grade). The preparation of pure SnI_2 is rather difficult [14]. High purity tin was dissolved in hot, concentrated (57%) hydroiodic acid. When the bubbling of hydrogen was finished the product was quickly filtered, then dried over P_2O_5 and melted at 370°C with metallic tin under argon atmosphere to reduce the accompanying amounts of SnI_4. The heating was stopped after three days and the salt was refined by two-step vacuum distillation.

The construction of the electrolytic cell employed in this study is described elsewhere [15].

The careful preparation and desiccation of components of molten salts and formation of homogeneous solutions of these salts was a principal requirement for obtaining reliable results. Besides, it was stated that a very good reversibility and reproducibility of measured EMF values (± 0.15 mV) were obtained only when the resistance of galvanic cells was in the limits of 100—500 Ω.

Results

The EMF's of anionic concentration cells of the following type were measured

$$\underset{\text{(liquid)}}{\mathrm{Me}}\,|\,0.50\ \mathrm{MeCl_2} + 0.50\ \mathrm{MeY_2}\,\|\,(X_1)\ \mathrm{MeCl_2} + (X_2)\ \mathrm{MeY_2}\,|\,\underset{\text{(liquid)}}{\mathrm{Me}}$$

where Me = Sn^{2+}, Pb^{2+}; Y = Br^-, I^-, and the X_1 values were equal each time to 0.30, 0.40, 0.60 or 0.70.

In all cases the EMF's of cells $Me|MeY_2||MeCl_2|Me$ constructed using exclusively pure fused salts were also measured for comparison. The EMF's of investigated cells are listed in Table 1.

Table 1

Diffusion potentials ($E_D = E_{II} - E_I$ in mV) of the cells
(I) $Sn|0.50\ SnCl_2 + 0.50\ SnY_2||(X_1)\ SnCl_2 + (X_2)\ SnY_2|Sn$ (II)

Y	$X_1 = 0.30$	$X_1 = 0.40$	$X_1 = 0.60$	$X_1 = 0.70$	t, °C
Br^-	−0.48	−0.11	0.33	0.50	305
	−0.54	−0.13	0.39	0.60	355
I^-	−0.33	−0.18	0.28	0.89	305
	−0.25	−0.25	0.26	—	355

(I) $Sn|SnY_2||SnCl_2|Sn$ (II)

Y	$E_{II} - E_I$	t, °C
Br^-	1.05	305
	0.87	355
I^-	4.60	355
	5.70	400

(I) $Pb|0.50\ PbCl_2 + 0.50\ PbY_2||(X_1)\ PbCl_2 + (X_2)\ PbY_2|Pb$ (II)

Y	$X_1 = 0.30$	$X_1 = 0.40$	$X_1 = 0.60$	$X_1 = 0.70$	t, °C
Br^-	0.12	0.17	0.34	0.45	475
	0.16	0.21	0.41	0.58	525
I^-	−0.40	−0.39	0.25	0.54	475
	−0.62	−0.59	0.28	—	525

(I) $Pb|PbY_2||PbCl_2|Pb$ (II)

Y	$E_{II} - E_I$	t, °C
Br^-	1.08	525
	1.62	570
I^-	5.70	525

Due to the relatively high vapour pressure of investigated salts as well as easiness of thermal decomposition of molten SnI_2 and PbI_2 the measurements have been performed only at two different temperatures insignificantly higher than the melting temperature of pure salts or their solutions. But it was obvious that in general the measured potential was increasing with temperature (as it was stated also by other authors [6, 8]) and depending on concentration in the right half-cell.

Discussion

From considerations in the introduction it follows that the problem of diffusion potential in molten salts is not yet explicitly solved and has provoked already several controversies. Among studies [9—13] carried out by the method of direct measurements of diffusion potential values only *Stern*'s work deals with anionic concentration cells for the system AgCl—AgBr.

For such type of cells (A) the heterogenic potential at both electrodes is, according to definition, the same because the activity of common cation expressed by mole or ionic fraction is equal to unity. The measured potential consists therefore only of diffusion potential and must arise from differences in the mobilities and transport numbers of anions. So the equation [16] for the potential of such a concentration cell (assuming that $\mathrm{d} \ln a_{Ag^+} = 0$ and $\Sigma t_i = 1$) is the same as the general equation for the diffusion potential value

$$F(E_{II} - E_I)/RT = FE_D/RT = -\int_I^{II} \frac{t_i}{z_i} \mathrm{d} \ln a_i \qquad (1)$$

$$(i = j, k, \ldots)$$

If by t_1 and t_2 we denote the transport numbers of anions Cl^- and Br^- and by a_1 and a_2 the respective activities of AgCl and AgBr a following equation [16] (after introducing the Gibbs—Duhem relation) is obtained

$$-FE_D/RT = \int_I^{II} \frac{t_1X_2 - t_2X_1}{X_2} \mathrm{d} \ln a_1 \qquad (2)$$

According to the above formula the liquid junction potential is equal to zero in case when the expression in the numerator $t_1X_2 - t_2X_1 = 0$.

Stern's data indicated rather considerable differences between mobilities of both anions (the obtained values of E_D were up to 15 mV) while the very precise EMF measurements of thermoelectric cells executed by *Keuning* [17] for AgCl—AgBr and AgCl—AgI systems do not confirm previous results. Therefore we have repeated Stern's investigation and additionally the EMF's of anionic concentration cells for the system AgCl—AgI have been measured [18]. The found diffusion potentials (Table 2) are very small (usually less than 1 mV) and do not confirm the earlier results for the system AgCl—AgBr [10].

Table 2

Diffusion potentials ($E_D = E_{II} - E_I$ in mV) of the cells
(I) Ag | 0.50 AgCl + 0.50 AgY || (X_1) AgCl + (X_2) AgY | Ag (II)

Y	$X_1 = 0.30$	$X_1 = 0.40$	$X_1 = 0.60$	$X_1 = 0.70$	t, °C
Br^-	0.16	0.03	1.24	0.73	530
I^-	−0.65	−0.09	0.41	0.90	530

(I) Ag | AgY || AgCl | Ag (II)

Y	$E_{II} - E_I$	t, °C
Br^-	1.96	530
I^-	7.60	580

The diffusion potentials found in this work for tin and lead halide systems are also very small and agree very well with those for silver halide systems. Little differences between the values of respective potentials for silver, tin, and lead systems were caused by various temperatures at which they had been measured as well as by different ionization state of each salt.

According to eqn (*2*) it should be supposed that the transport numbers of Cl^- and Br^- or Cl^- and I^- anions in the investigated solutions and probably in other mixtures with a common cation change proportionally to the mole fractions of corresponding salts.

Similar conclusions, for the case of different cations of both components, have been drawn earlier by *Murgulescu* and *Marchidan* [2], who measured the EMF's of concentration cells of the systems AgCl—KCl, AgBr—LiBr, AgBr—$PbBr_2$, and $PbCl_2$—KCl and by *Laity* [1] for the system $AgNO_3$—$NaNO_3$.

On the other hand, the data of *Emons* and *Bräutigam* [12] for alkali metal chloride—alkaline earth chloride mixtures pointed out the considerable differences in mobilities of both cations.

Thus far the knowledge of the variation of diffusion potentials with temperature and composition of the electrolyte forming the liquid junction is too poor to make a general statement about the values of diffusion potentials in molten salts. But it should be supposed that they are much lower in mixtures with a common cation than in mixtures with a common anion. The mixtures with a common cation, from the thermodynamic point of view, show also much lower deviations from the ideal behaviour. Moreover, *Sternberg* and *Vasilescu* [19] investigating the ultrasonic velocity and compressibility arrived to the conclusion that the mixtures with a common cation (AgCl—AgBr, $PbCl_2$—$PbBr_2$, *etc.*) are quasi ideal, *i.e.* that the packing of ions (in liquid) does not change when the anion Br^- is replaced by Cl^-

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