Marcus' data. There exists also the posssibility of a solvent interaction, similar to that suggested previously[18] for the uncharged mixed mercuric halides, since the binary HgX_4^{-2} ions, being tetrahedral,[19] have a symmetric charge distribution, while the distribution of charge on the ternary complexes should be asymmetric.

Acknowledgments.—The authors are indebted to the American Cyanamid Company for the grant of a predoctoral fellowship to T. G. Spiro (1959–1960) and to the United States Atomic Energy Commission for partial support of the work under Contract AT-(30-1)-905.

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Association Constants of Lead and Bromide Ions in Molten Sodium Nitrate–Potassium Nitrate Mixtures and their Comparison with the Quasi-Lattice Theory

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Received September 19, 1962

The association constants K_1 and K_2 for the formation of $PbBr^+$ and $PbBr_2$ were evaluated from electromotive force measurements in molten mixtures of $NaNO_3$ and KNO_3. The constants K_1 and K_2 in mole fraction units are, respectively, 250, 125 at 240°, 190, 85 at 280°, and 170, 70 at 300° when the solvent is equimolar $NaNO_3$ and KNO_3. A variation in the composition of the solvent changes the value of the association constants so as to give stronger binding as the proportion of KNO_3 increases. The temperature dependence of the association constants, within the experimental error, is predictable from calculations based on the quasi-lattice model.

Introduction

In this paper, the association constants for the formation of the species $PbBr^+$ and $PbBr_2$ in molten $NaNO_3$–KNO_3 mixtures are evaluated from electromotive force measurements. The values are compared with the equations

$$K_1 = Z(\beta_1 - 1) \qquad (1)$$

$$K_1K_2 = \frac{Z(Z-1)}{2}(\beta_1\beta_2 - 2\beta_1 + 1) \qquad (2)$$

which have been derived from the quasi-lattice model,[3-5] where K_1 and K_2 are the association constants for the formation of $PbBr^+$ and $PbBr_2$, respectively, Z is a coördination number, $\beta_i = \exp(-\Delta A_i/RT)$, and ΔA_i is the specific free energy of bond formation. In previous papers,[6] it was shown that for the association of monovalent ions, ΔA_i is independent of temperature for any given association in any system. Recently, it was demonstrated[7] that the equations also hold for the association of a divalent ion (cadmium) with Br^- and I^-. Since the quasi-lattice theory applies to monovalent ions only, this indicates that calculations based on the model, *i.e.*, eq. 1 and 2, are more general than is implied by the model.

The comparison of experimental measurements with eq. 1 and 2 in this paper was made to further test the applicability of these equations for predicting the temperature coefficient for associations involving a divalent ion. The influence of the solvent cation on the association constants also was measured by varying the composition of the $NaNO_3$–KNO_3 melt.

Experimental

Reagent grade NaBr was dried at 300° and stored in a desiccator. Reagent grade $Pb(NO_3)_2$ was dried in a vacuum oven at 150° and likewise stored in a desiccator. Otherwise the procedure, apparatus, and methods of calculation were essentially the same as described previously.[6,7]

Results and Discussion

It was demonstrated[7] that silver–solid silver halide electrodes are reversible to halide ions in molten nitrates and that the activity coefficient of the alkali halide, $\gamma_{(Na,K)X}$, may be evaluated from e.m.f. measurements of the cell

$$\text{Ag} \;\Big|\; \begin{matrix}\text{NaBr}\\ \text{AgBr(s)}\\ \text{(Na,K)NO}_3\end{matrix} \;\Big\|\; \begin{matrix}\text{Pb(NO}_3)_2\\ \text{NaBr}\\ \text{AgBr(s)}\\ \text{(Na,K)NO}_3\end{matrix} \;\Big|\; \text{Ag}$$

and the equation

$$\Delta E = \frac{-RT}{F} \ln \gamma_{(Na,K)X} \qquad (3)$$

From the change in e.m.f. (ΔE) occurring with the addi-

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TABLE I

E.M.F. CHANGES OF THE CELL IN MILLIVOLTS ON ADDITION OF $Pb(NO_3)_2$

Temperature 240°

Solvent: 50 mole % $NaNO_3$; 50 mole % KNO_3

$R_{NaBr} = 8.47 \times 10^{-4}$		$R_{NaBr} = 2.08 \times 10^{-3}$	
$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.	$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.
0.189	2.3	0.198	2.5
0.348	4.0	0.669	6.5
0.770	7.6	1.53	12.5
1.33	12.0	2.37	18.2
1.99	16.9		
3.10	24.2		

Temperature 280°

Solvent: 25 mole % $NaNO_3$; 75 mole % KNO_3

$R_{NaBr} = 1.01 \times 10^{-3}$		$R_{NaBr} = 1.98 \times 10^{-3}$	
$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.	$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.
0.166	2.3	0.164	2.7
0.330	3.9	0.473	5.3
0.621	5.8	0.724	7.0
1.04	9.0	1.12	9.6
1.74	14.0	1.81	13.8
2.65	19.7	2.68	18.7
3.94	26.9	4.26	27.2
5.42	33.9	5.21	35.8
$R_{NaBr} = 2.37 \times 10^{-3}$		$R_{NaBr} = 3.54 \times 10^{-3}$	
$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.	$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.
0.132	1.2	0.132	0.8
0.274	2.5	0.265	1.8
0.586	5.4	0.622	4.6
1.08	8.9	1.13	8.0
2.08	14.8	1.74	12.3
3.43	22.4	2.75	18.8
4.67	31.0	4.14	26.1
		5.51	33.0
$R_{NaBr} = 5.10 \times 10^{-3}$			
$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.	$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.
0.304	2.4	3.31	19.8
0.512	4.0	4.21	24.7
0.942	6.3	5.14	29.6
1.50	9.7	5.64	32.3
2.30	14.0		

Solvent: 50 mole % $NaNO_3$; 50 mole % KNO_3

$R_{NaBr} = 1.02 \times 10^{-3}$		$R_{NaBr} = 1.98 \times 10^{-3}$	
$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.	$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.
0.163	1.6	0.131	1.3
0.346	3.3	0.293	2.7
0.655	5.8	0.556	4.6
1.30	10.4	0.879	6.4
2.39	17.7	1.24	9.1
4.02	26.5	1.84	12.6
5.31	33.1	2.66	17.4
		3.73	23.6
		4.86	28.9
$R_{NaBr} = 3.51 \times 10^{-3}$		$R_{NaBr} = 4.70 \times 10^{-3}$	
$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.	$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.
0.126	1.2	0.104	1.0
0.284	2.4	0.305	2.6
0.623	5.2	0.526	4.7
0.978	8.0	0.805	5.9
1.53	11.6	1.08	10.2
2.54	17.5	1.43	11.3
3.66	23.1	2.00	14.4
4.90	29.6	2.84	18.5
		4.03	24.3
		5.25	30.4

Temperature 280°

Solvent: 75 mole % $NaNO_3$; 25 mole % KNO_3

$R_{NaBr} = 1.02 \times 10^{-3}$		$R_{NaBr} = 1.99 \times 10^{-3}$	
$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.	$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.
0.124	0.8	0.127	1.0
0.339	2.4	0.333	2.2
0.635	4.6	0.638	4.5
1.01	7.7	1.12	8.0
1.81	13.6	2.01	13.5
2.66	19.0	3.17	19.8
3.80	24.5	4.61	26.8
4.78	30.4	5.80	32.6
5.37	33.3		
$R_{NaBr} = 2.60 \times 10^{-3}$		$R_{NaBr} = 4.36 \times 10^{-3}$	
$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.	$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.
0.152	1.4	0.153	1.1
0.378	3.2	0.278	3.0
0.686	5.0	0.538	4.9
1.01	7.5	0.887	6.8
1.78	12.8	1.46	9.5
2.80	18.4	2.60	15.1
4.26	26.4	4.00	22.1
5.04	30.0	5.68	29.2

Temperature 300°

Solvent: 25 mole % $NaNO_3$; 75 mole % KNO_3

$R_{NaBr} \times 1.17 \times 10^{-3}$		$R_{NaBr} = 1.84 \times 10^{-3}$	
$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.	$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.
0.165	2.1	0.157	2.0
0.513	5.2	0.305	3.5
0.865	7.6	0.534	5.1
1.43	11.4	0.845	6.9
2.11	15.2	1.49	10.6
2.83	19.0	2.09	13.7
3.95	24.2	3.26	19.9
5.40	30.6	4.54	26.1
5.80	32.8	5.82	31.8
$R_{NaBr} = 2.20 \times 10^{-3}$		$R_{NaBr} = 3.59 \times 10^{-3}$	
$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.	$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.
0.213	2.7	0.257	2.0
0.445	4.4	0.584	4.1
0.925	7.5	1.06	7.0
1.37	10.2	1.59	10.4
2.25	15.0	2.35	15.8
3.48	21.6	3.45	22.2
4.88	28.2	5.12	30.0
5.93	33.7	6.02	34.6
$R_{NaBr} = 3.70 \times 10^{-3}$			
$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.	$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.
0.217	1.4	1.28	12.8
0.542	3.5	3.28	18.0
0.930	5.7	4.74	25.3
1.51	8.6	5.92	31.9

Solvent: 50 mole % $NaNO_3$; 50 mole % KNO_3

$R_{NaBr} = 0.655 \times 10^{-3}$		$R_{NaBr} = 1.18 \times 10^{-3}$	
$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.	$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.
0.059	0.9	0.117	1.3
0.248	2.7	0.329	3.0
0.653	4.5	0.581	4.5
0.970	6.7	1.03	7.4
1.34	9.5	1.54	11.2
1.74	12.1	2.57	16.8
2.33	15.5	3.82	22.7
3.20	21.5	5.51	29.5

TABLE I (*Continued*)

Temperature 300°

Solvent: 50 mole % $NaNO_3$; 50 mole % KNO_3

$R_{NaBr} = 1.85 \times 10^{-3}$		$R_{NaBr} = 2.30 \times 10^{-3}$	
$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.	$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.
0.151	1.2	0.213	1.8
0.396	3.5	0.483	3.7
0.720	7.7	0.825	5.5
1.33	11.5	1.23	7.8
2.10	16.3	1.94	11.6
2.80	20.7	3.03	17.2
3.54	24.1	4.44	25.0
4.56	28.9	6.00	33.0
$R_{NaBr} = 3.16 \times 10^{-3}$			
$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.	$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.
0.157	1.3	2.15	13.6
0.384	3.1	3.44	19.8
0.735	5.9	5.43	28.8
1.24	9.1	6.34	34.6

Solvent: 75 mole % $NaNO_3$; 25 mole % KNO_3

$R_{NaBr} = 1.23 \times 10^{-3}$		$R_{NaBr} = 2.43 \times 10^{-3}$	
$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.	$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.
0.220	2.1	0.178	1.6
0.550	4.1	0.592	4.4
0.882	6.1	1.08	7.7
1.02	7.5	1.74	11.7
1.46	10.4	2.88	17.5
2.22	14.8	4.02	22.7
3.67	22.1	4.96	26.7
4.62	26.5	5.76	30.0
5.41	30.1		
$R_{NaBr} = 5.03 \times 10^{-3}$			
$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.	$R_{Pb(NO_3)_2} \times 10^3$	ΔE, m.v.
0.206	1.7	2.65	15.7
0.584	4.4	3.64	19.6
1.08	8.0	4.90	25.0
1 88	11.4	5.64	28.2

tions of $Pb(NO_3)_2$ to the right hand half-cell, values of $1/\gamma_{(Na,K)Br}$ were calculated at several fixed concentrations of alkali bromide. Values of ΔE obtained in 75–25, 50–50, and 25–75 mole % mixtures of $NaNO_3$ and KNO_3 at different temperatures and at several fixed concentrations of NaBr are given in Table I.

The association constants for the formation of associated lead halide species PbX^+, PbX_2, Pb_2X^{3+}, etc., are defined as

$$K_1 = \frac{R_{PbX^+}}{R_{Pb^{++}} R_{X^-}}$$

$$K_1K_2 = \frac{R_{PbX_2}}{R_{Pb^{++}} R^2_{X^-}}$$

$$K_1K_{1,2} = \frac{R_{Pb_2X^{+3}}}{R^2_{Pb^{++}} R_{X^-}}$$

etc., in which the R are mole ratios of the species indicated and in dilute solutions are essentially the same as mole fractions. The stoichiometric activity coefficient of (Na,K)X may be expressed as[7]

$$1/\gamma_{(Na,K)X} = 1 + K_1 R_{Pb(NO_3)_2} + K_1K_{1,2} R^2_{Pb(NO_3)_2} + (2K_1K_2 - K_1^2) R_{Pb(NO_3)_2} R_{(Na,K)X} + \ldots \quad (4)$$

in the range of concentrations in which the associated species follows Henry's law. Plots of $1/\gamma_{(Na,K)X}$ *vs.* the mole ratio of $Pb(NO_3)_2$ at low concentrations of alkali halide and of $Pb(NO_3)_2$ were linear. This indicates that the formation constants of polynuclear species are comparatively small relative to the first association constant. The first association constants were evaluated graphically as the limiting slopes

$$K_1 = \lim_{\substack{R_{Pb(NO_3)_2} \to 0 \\ R_{(Na,K)X} \to 0}} \left(\frac{\partial 1/\gamma_{(Na,K)X}}{\partial R_{Pb(NO_3)_2}} \right)_{R_{(Na,K)X}} \quad (5)$$

Large scale plots of $1/\gamma_{(Na,K)X}$ *vs.* the mole ratio of $Pb(NO_3)_2$ were made and the limiting slopes at $R_{Pb(NO_3)_2} = 0$ were estimated for each fixed stoichiometric mole ratio of (Na,K)X. These slopes then were plotted *vs.* the mole ratio of alkali halide ($R_{(Na,K)X}$) and extrapolated to $R_{(Na,K)X} = 0$. The intercept is equal to K_1 and from the limiting slope of this plot K_2 may be evaluated from the relationship

$$\lim_{\substack{R_{Pb(NO_3)_2} \to 0 \\ R_{(Na,K)X} \to 0}} \left(\frac{\partial^2 1/\gamma_{(Na,K)X}}{\partial R_{(Na,K)X} \partial R_{Pb(NO_3)_2}} \right) = K_1(2K_2 - K_1) \quad (6)$$

Values of K_1 and K_2 calculated from the data in Table I are given in Table II. The estimated errors are about 6% in K_1 and 12% in K_2.

TABLE II

ASSOCIATION CONSTANTS AND DERIVED PARAMETERS FOR $Pb^{++} + Br^-$ IN MOLTEN $NaNO_3$–KNO_3 MIXTURES

Composition, mole % $NaNO_3$–KNO_3	Temp., °C.	K_1	$-\Delta A_1$, kcal./mole Z = 4	Z = 5	Z = 6	K_2	$-\Delta A_2$, kcal./mole Z = 4	Z = 5	Z = 6
75–25	280	180	4.21	3.97	3.77	78	4.4	4.1	3.8
	300	160	4.23	3.98	3.78	70	4.4	4.0	3.8
50–50	240	250	4.23	4.01	3.83	125	4.5	4.2	4.0
	280	190	4.27	4.03	3.83	85	4.5	4.1	3.9
	300	170	4.30	4.05	3.84	70	4.4	4.1	3.8
25–75	280	200	4.32	4.08	3.89	82	4.4	4.1	3.9
	300	175	4.33	4.08	3.88	67	4.4	4.1	3.8

Values of ΔA_1 and ΔA_2 were calculated from eq. 1 and 2 for Z = 4, 5, and 6, which should include all reasonable values of Z. For any given solvent and any one value of Z, values of ΔA_1 are constant at all the temperatures investigated. This is further confirmation that the quasi-lattice theory is useful for predicting the temperature coefficient of K_1 for associations involving divalent ions. Within the experimental error, ΔA_2 also appears constant and independent of temperature, and does not differ greatly from ΔA_1. However, the precision of K_2 was not good enough for a precise evaluation of the temperature coefficient of K_2.

The solvent influences the value of K_1 so as to lead to stronger binding in molten $NaNO_3$–KNO_3 mixtures having a higher proportion of KNO_3. This is similar to the influence of the solvent on associations of Ag^+ and Cd^{++} with halide ions. This solvent effect has been rationalized in terms of coulomb interactions for the association of Ag^+ with Cl^- and Br^-.[6f] The picture is not as simple for polyvalent cations such as Pb^{++} and Cd^{++} although one might speculate that the Na^+ ion, which is smaller than the K^+ ion, would tend to "polarize" electrons which are involved in binding Pb^{++} and Br^- away from the bond, thus weakening the bond.