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Solvent Extraction From Molten Salts. VII.[1] Formation of Anionic Zinc Mixed-Halide Complexes

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In partition experiments of zinc halides between a polyphenyl eutectic mixture and molten $LiNO_3$-KNO_3 eutectic, various amounts of mixed potassium halide were added to the salt melt, in large excess over the zinc halide. The over-all distribution ratio D for zinc species was determined radiometrically. From the results, it was possible to calculate the complex formation constants

$$\alpha_{ij} = \frac{[ZnA_iB_j^{(i+j-2)-}]}{[ZnA_2][A^-]^{i-2}[B^-]^j}$$

and the "ligand mixing" constants

$$X_{ij} = \frac{[ZnA_iB_j^{(i+j-2)-}]^2}{[ZnA_{i+1}B_{j-1}^{(i+j-2)-}][ZnA_{i-1}B_{j+1}^{(i+j-2)-}]}$$

with A^- and B^- representing chloride–bromide, chloride–iodide, or bromide–iodide. No evidence was found for the existence of complexes containing more than two iodides or three bromides. The stability of mixed complexes, while relatively low at 150°, was found to increase at higher temperatures.

In previous work,[2] the formation of anionic mixed-halide complexes of mercury(II) in molten nitrate had been investigated. Following distribution studies on pure[3] and mixed zinc halides,[1] it seemed promising to use the same solvent extraction technique to investigate the formation of anionic mixed-halide complexes of zinc in molten nitrate. The polyphenyl phase in this work is not of interest for its own sake but serves merely to fix the relative chemical potentials of the various neutral zinc-containing species in the $LiNO_3$–KNO_3 eutectic.

Experimental Section

The molten nitrate was prepared as described in part V of this series,[3] however, without addition of zinc salts. Binary mixtures of potassium halides, totaling between 0.01 and 0.8 *m*, were added to the mixture. The polyphenyl phase composition was as described in the same work, and 10^{-3} *m* zinc halide solutions in the polyphenyl were similarly prepared. Since the salt melt: organic phase mass ratio was very near 3.5 in all experiments, the free halide was always in large excess over the halide bound in zinc complexes, so that the latter could be neglected. The ratio of molalities of potassium halide originally added, $R = [B^-]_{added}/[A^-]_{added}$, varied between $^1/_7$ and 7 and was taken to be equal to $[B]_{total}/[A]_{total}$ and to the ratio of molalities of free halide, $[B^-]/[A^-]$. For each mixture of halides A–B, experiments were carried out with both ZnA_2 and ZnB_2 solutions in polyphenyl as the starting material.

Phase contacting and separation, as well as radiometric determination of the over-all distribution ratio for all Zn(II) species, were carried out as previously described[3]

$$D = \frac{\text{cpm/g of polyphenyl phase}}{\text{cpm/g of salt melt phase}}$$

was obtained within ±3%.

Results

Figures 1–3 show the variation of D with the total concentration of free halide (X^-) and with the ratio R, in the systems chloride–bromide, chloride–iodide, and bromide–iodide, respectively, at 150, 180, and 200°. Since, in each system, alternating experimental results were obtained with ZnA_2 and ZnB_2, respectively, as starting materials, and these results appear to agree quite well, the assumption $[A^-]_{total} \approx [A^-]_{initial} \approx [A^-]_{free}$, etc., seems to be justified. It further appears that large concentrations of free chloride decrease the distribution ratio significantly, but such decrease does not take place when the dominant halide is Br^- or I^-. The crossing of curves relating to different values of R at 150° is due to the maximum in the plot of D *vs.* R obtained in the absence of added halide.[1]

Discussion

As in the work on anionic mercury(II) complexes,[2] the Sillén–Marcus approach[4,5] was used for treatment of the data.

The organic phase contains the neutral dihalides MA_2, MAB, and MB_2, where M represents the metal, in this case Zn. The salt melt contains tetracoordinated, binegative species,[1,3] but for the sake of clarity, the NO_3^- groups and the charges will not be shown. It is further assumed that, owing to the addition of potassium halide in excess, the dissociation of zinc halides (formation of trinitrato or tetranitrato complexes) will be negligible. The species assumed to occur in the salt melt are therefore MA_2, MAB, MB_2, MA_3, MA_2B, MAB_2, MB_3, MA_4, MA_3B, MA_2B_2, MAB_3, and MB_4, or in general MA_iB_j. Such a system will be governed by the distribution constants K_A, K_B, and K_{AB} (as defined in part VI[1]) and by the over-all formation constants for all existing complexes $\beta_{ij} = [MA_iB_j]/[M][A]^i[B]^j$. It is however more convenient to use the constants

$$\alpha_{ij} = \frac{\beta_{ij}}{\alpha_{20}} = \frac{[MA_iB_j]}{[MA_2][A]^{i-2}[B]^j}$$

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(1) Part VI: M. Zangen, *Inorg. Chem.*, **7**, 138 (1968).
(2) Part III: M. Zangen and Y. Marcus, *Israel J. Chem.*, **2**, 155 (1964).
(3) Part V: M. Zangen, *Inorg. Chem.*, **7**, 133 (1968).
(4) L. G. Sillén, *Acta Chem. Scand.*, **10**, 803 (1956).
(5) Y. Marcus, *ibid.*, **11**, 811 (1957).

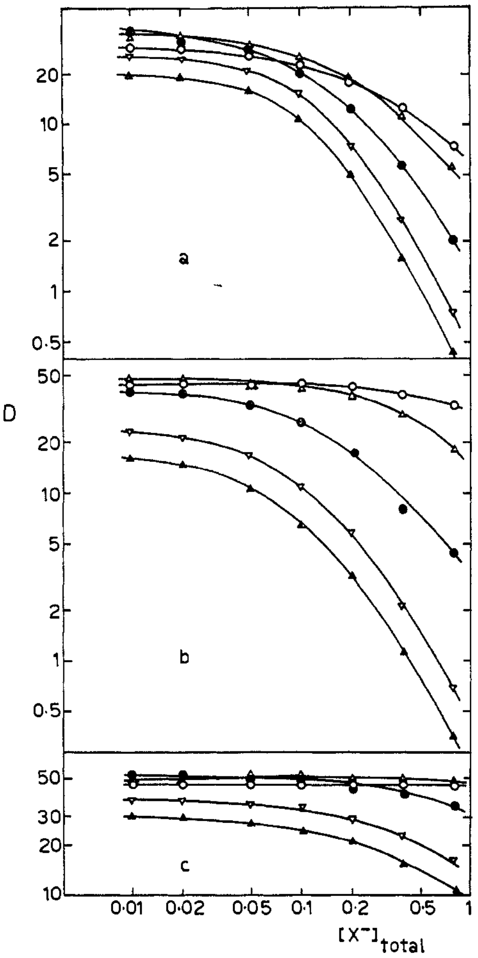

Figure 1.—Over-all distribution ratio of Zn(II) species between molten $LiNO_3$–KNO_3 and polyphenyl mixture at 150°, as a function of total halide content in the salt melt, the ratio bromide: chloride (a), iodide:chloride (b), or iodide:bromide (c) being: 7 (○), 3 (△), 1 (●), $^1/_3$ (▽), or $^1/_7$ (▲).

In this notation, the constants K_3 (as defined in part V[3]) will be written α_{30} if referring to A, α_{03}/α_{02} if referring to B, and the constant K_4 (only possible for A = chloride[3]), will be written α_{40}/α_{30}.

The over-all distribution ratio

$$D = \frac{\{[MA_2] + [MAB] + [MB_2]\}_o}{\{[MA_2] + [MAB] + [MB_2] + [MA_3] + [MAB_2] + [MB_3] + [MA_4] + [MA_3B] + [MA_2B_2] + [MAB_3]\}_s}$$

(where the subscripts o and s represent the organic and salt melt phases, respectively) can, after division throughout by $[MA_2]$ and using $[B] = R[A]$, be written

$$D([A],R) = \frac{K_A + K_{AB}\alpha_{11}R + K_B\alpha_{02}R^2}{1 + \alpha_{11}R + \alpha_{02}R^2 + [A](\alpha_{30} + \alpha_{21}R + \alpha_{12}R^2 + \alpha_{03}R^3) + [A]^2(\alpha_{40} + \alpha_{31}R + \alpha_{22}R^2 + \alpha_{13}R^3)}$$

Introducing the auxiliary constants

$$C_0(R) = \frac{K_A + K_{AB}\alpha_{11}R + K_B\alpha_{02}R^2}{1 + \alpha_{11}R + \alpha_{02}R^2} \tag{1}$$

$$C_1(R) = \frac{\alpha_{30} + \alpha_{21}R + \alpha_{12}R^2 + \alpha_{03}R^3}{1 + \alpha_{11}R + \alpha_{02}R^2} \tag{2}$$

$$C_2(R) = \frac{\alpha_{40} + \alpha_{31}R + \alpha_{22}R^2 + \alpha_{13}R^3}{1 + \alpha_{11}R + \alpha_{02}R^2} \tag{3}$$

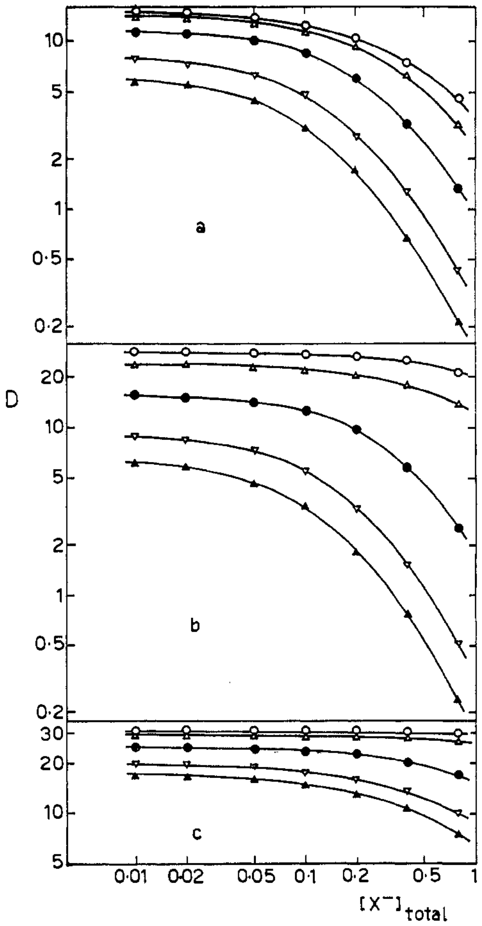

Figure 2.—Over-all distribution ratio of Zn(II) species between molten $LiNO_3$–KNO_3 and polyphenyl mixture at 180°, as a function of total halide content in the salt melt, the ratio bromide: chloride (a), iodide:chloride (b), or iodide:bromide (c) being: 7 (○), 3 (△), 1 (●), $^1/_3$ (▽), or $^1/_7$ (▲).

we have for each value of R

$$\frac{1}{D} = \frac{1 + C_1[A] + C_2[A]^2}{C_0} \tag{4}$$

By analysis of the variation of $1/D$ with [A], the values of $C_0(R)$, $C_1(R)$, and $C_2(R)$ can be deduced.

It is now possible to calculate α_{11} and α_{02} from eq 1, using the previously determined values[1] of K_A, K_B, and K_{AB}. Likewise, using the previously[3] determined values of $K_{3(A)} = \alpha_{30}$ and $K_{3(B)} = \alpha_{03}/\alpha_{02}$, eq 2 can be solved for α_{21} and α_{12}. Finally, using $\alpha_{40} = K_{3(A)}K_{4(A)}$,[3] eq 3 yields the values of α_{31}, α_{22}, and α_{13}.

Table I shows the C values thus found (accuracy ±7%), in the chloride–bromide, chloride–iodide, and bromide–iodide systems. C_2 was found to be negligible in the bromide–iodide system: D shows no inverse second-power dependence on halide concentration.

Table II shows the derived α values (obtained with an accuracy of ±20%).

The above values can be used to calculate the fraction of $[Zn]_{total}$ present in the various species and, hence, D for various values of total $[X^-]$ and R in each mixed-halide system. In most of the results, the agreement

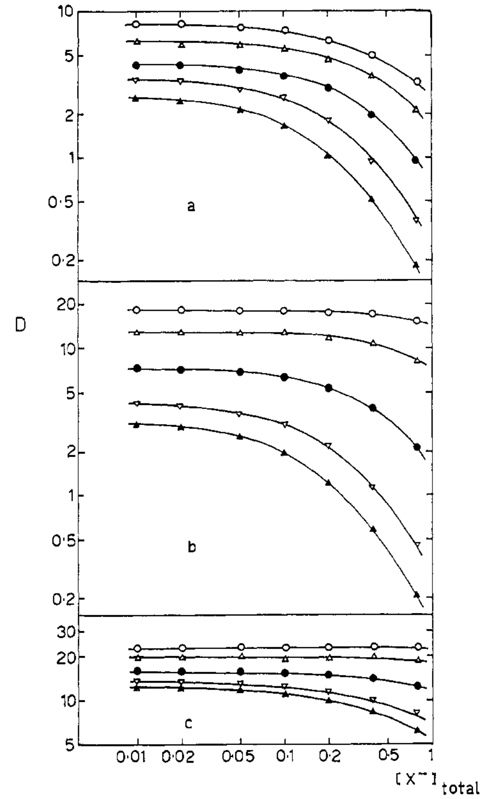

Figure 3.—Over-all distribution ratio of Zn(II) species between molten $LiNO_3$–KNO_3 and polyphenyl mixture at 200°, as a function of total halide content in the salt melt, the ratio bromide: chloride (a), iodide:chloride (b), or iodide:bromide (c) being: 7 (○), 3 (△), 1 (●), $^1/_3$ (▽), or $^1/_7$ (▲).

TABLE I

C VALUES

	150°			180°			200°		
R	C_0	C_1	C_2	C_0	C_1	C_2	C_0	C_1	C_2
				A. Chloride–Bromide System					
7	30	25	55	15.2	16.1	66	8.3	10.9	45
3	36	11.3	60	14.5	8.8	43	6.4	5.1	24
1	37	12.1	77	11.8	6.1	34	4.4	3.2	14.7
$^1/_3$	26	3.2	88	8.3	6.6	39	3.5	3.9	17.5
$^1/_7$	20	1.89	90	6.3	7.3	49	2.7	5.0	22
				B. Chloride–Iodide System					
7	45	3.1	5.7	28	2.2	6.8	18.4	1.54	5.1
3	49	4.6	18.5	24	2.6	10.3	13.1	1.61	5.8
1	42	8.5	63	15.9	4.1	22	7.4	2.4	9.7
$^1/_3$	25	10.7	83	9.2	6.1	36	4.3	3.9	17.4
$^1/_7$	17.8	11.0	88	6.6	7.1	43	3.2	5.2	23
				C. Bromide–Iodide System					
7	46	0.062		31	0.23		23	0.196	
3	51	0.30		30	0.51		20	0.37	
1	52	1.31		25	1.14		15.9	0.71	
$^1/_3$	38	2.3		19.9	1.67		13.5	1.14	
$^1/_7$	30	2.5		17.5	1.86		12.6	1.43	

TABLE II[a]

α VALUES

System	Temp, °C	α_{11}	α_{02}	α_{30}	α_{21}	α_{12}	α_{03}	α_{40}	α_{31}	α_{31}	α_{13}
Cl–Br	150	0.26	0.8	11	6	6	2.0	90	28	41	0
Cl–Br	180	1.4	0.8	8	5	5	1.5	50	20	35	4.0
Cl–Br	200	3.9	0.8	7	5	5	1.3	32	15	33	3.7
Cl–I	150	0.19	0.6	11	2.8	1.4	0	90	13	0	0
Cl–I	180	1.2	0.6	8	2.4	1.2	0	50	8	3.2	0
Cl–I	200	2.8	0.6	7	2.3	1.1	0	32	7	3.6	0
Br–I	150	0.19	0.8	2.6	0	0	0	0	0	0	0
Br–I	180	1.1	0.8	2.0	1.3	0	0	0	0	0	0
Br–I	200	2.7	0.8	1.8	1.4	0	0	0	0	0	0

[a] α_{0x} was found negligible throughout; α_{20} is unity by definition.

between D_{exptl} and D_{calcd} is within the experimental error.

It can be seen that the α_{02} values found in this work agree well with the β_{02}/β_{20} values that can be calculated from part V. The fact that these are smaller than unity may be explained by a steric effect due to the complexing NO_3^- ions.

The α_{11} values are found to be very dependent on temperature. This is in agreement with the results in part VI, where the stability of mixed zinc bihalide increased strongly with temperature. On the other hand, most α values relating to species containing more than two halide ions decrease with temperature. Since formation involves replacement of nitrate by halide,[1,3] this phenomenon should be seen as an entropy effect, whereby the inclusion of nitrate in the complex is favored at higher temperatures. As such, it is consistent with the strong increase with temperature of the ionization of zinc dihalides (*i.e.*, the replacement of halide by nitrate), as found in molten nitrate eutectic without added potassium halide.[3]

A good way to express the stability of mixed complexes is to calculate the "ligand mixing" equilibrium constants, defined as

$$X_{ij} = \frac{\alpha_{ij}^2}{\alpha_{(i+1)(j-1)}\alpha_{(i-1)(j+1)}} = \frac{[MA_iB_j]^2}{[MA_{i+1}B_{j-1}][MA_{i-1}B_{j+1}]}$$

and to compare these with the "statistical" X_{ij} values. The obtained X_{ij} values are shown in Table III. It can be seen that the values of X_{11}, which is identical with K_s(A–B) as defined in part VI, agree well with the previous results.

TABLE III

System	Temp, °C	X_{11}	X_{21}	X_{12}	X_{31}	X_{22}
Cl–Br	150	0.084	0.55	3.0	0.21	...
Cl–Br	180	2.4	0.63	3.3	0.23	15
Cl–Br	200	19	0.71	3.8	0.21	20
Cl–I	150	0.060	0.51	...	...	...
Cl–I	180	2.4	0.60	...	0.40	...
Cl–I	200	13	0.69	...	0.42	...
Br–I	150	0.045	...	...	...	...
Br–I	180	1.5	...	...	...	...
Br–I	200	9.1	...	...	...	...
Statistical		4.0	3.0	3.0	2.67	2.25

The low stability which was generally found for mixed complexes (except the 1–1 at 200° and the 2–2 in the chloride–bromide system) is in good agreement with results previously obtained for mercury chloride–iodide and bromide–iodide systems at 150°.[2] Because of the smaller size of the zinc ion, the steric effects causing destabilization of mixed complexes can be expected to be stronger in this case and to exist even in the chloride–bromide system. On the other hand, polarization effects may favor the more symmetrical complex, which may account for the higher stability of $ZnCl_2Br_2$.

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