

Bromine Concentration with Rise in Density of Sea Bitterns

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ABSTRACT

The bitterns available from the solar salt industry contain about 2 to 2.5 parts of bromine per thousand parts and are considered to be a good source for its recovery. It is present in the bitterns as magnesium bromide, a most soluble salt in the system. Bromine content of this salt is liberated by replacement with chlorine gas. Since bromine does not separate in solid phase and continuously concentrates with the increase in density of bitterns, studies were carried out to find the optimum density stage and yield of bromine to facilitate its processing. Although bromine is removed from the solution into the chloride crystals during progressive solar evaporation of brine, the concentration of bromine in the brine increases because only part of it enters the chlorides. The bromine distribution ratio has been worked out by dividing the percentage of bromine in the solid phase by the percentage of bromine in total solids in 100 ml. of the equilibrium liquid phase. This work indicates that up to the density range of 34.5°Be' , the bromine content increases while the volume of liquid is reduced. Between this density and 35.2°Be' the value of distribution ratio steeply rises, indicating that bromine is being taken up in solid solution in the form of KBr with its isomorphous salt KCl . This phenomenon is repeated between 37.3°Be' and 37.5°Be' when again bromine in the form of $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ enters into solid solution with its another isomorphous salt $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

INTRODUCTION

With the recent development of Petro-Chemical Industries the economic importance of bromine cannot be overstated in the industrial organic chemistry. It is present in seawater to the extent of about 0.06 to 0.07 parts per thousand parts. Recovery of bromine from seawater therefore involves handling of very large quantity of seawater. Bitterns available from the solar salt industry having a Sp.gr. 1.262 (30°Be') contain about 2.0 to 2.5 parts per thousand and is considered as a good source for its recovery. It is present in bitterns as magnesium bromide and is the most soluble salt in the system. This compound is not recoverable as such but its bromine content is liberated by replacement with chlorine gas. In attaining the density of 30.0°Be' the original volume of seawater gets reduced to about 2 percent. It is a normal practice to process bitterns for recovery of bromine at this density at which it is discharged from the salt winning plants. In regions enjoying

semiarid or arid climate it is possible to evaporate bitterns beyond this density by solar evaporation and further reduce its volume. It was therefore thought worthwhile to study the concentration and distribution of bromine over the entire solar evaporation range of bitterns from 30°Be' (Sp.gr. 1.262) to 39.5°Be' (Sp.gr. 1.377) to know how its concentration increases and to strike optimum density point at which it can be more gainfully processed.

EARLIER WORK

It is reported by Omer B. Raup (1) that as the dissolved constituents of seawater gets concentrated through evaporation, bromine increases from 65 parts per million (ppm) in normal seawater to about 500 ppm. at the beginning of halite precipitation. During the stage, when only halite precipitates prior to the separation of the first potash salts, the concentration of bromine in brine increases from 500 ppm.

to about 2,300 ppm., while the bromine content in halite increases from a minimum of 68 ppm. to 270 ppm. (2).

It has been reported by W. Scherdtner et al (4) that bromine does not separate in solid phase during evaporation of bitterns but occurs in solid solutions in the chlorides. The quantity of bromine in such chlorides bears a definite relationship to the bromine content of the brine from which the chloride crystallizes. This definite relationship is expressed by a distribution coefficient which is constant for a particular chloride at low bromine concentrations. The effect of temperature on the distribution coefficient is negligible. Different chlorides have different but definite distribution coefficients and where two or more chlorides crystallize simultaneously from a brine, the bromine enters each chloride in the same ratio as if only that one chloride was present. Therefore the bromine contents of these chlorides bears a definite relationship to each other. The significance of the distribution of bromine ions in solid phases of chlorides and the solutions from which they crystallize, and the use of bromine content as a genetic and prospecting criterion, have been long known. The distribution coefficient for all chlorides are always less than one. Consequently during the progressive evaporation of brine, although bromine is removed from the solution into the chloride crystals, the concentration of bromine in the brine progressively increases because only part of it enters the chlorides.

Earlier investigators on various salt deposits have used the bromine content of halite (Br/NaCl) to indicate the degree of concentration of evaporated ocean water (3) e.g. in a marine salt sequence the normal bromine contents rise from 0.007 wt % Br/NaCl at the bottom of 0.02 wt % at the beginning of potassium precipitation which is taken as an index for locating the potash deposits. In many salt deposits all magnesium and potassium in halite is believed to occur in three minerals viz. carnallite, sylvite and minor kieserite. Kieserite being a sulphate is not isomorphous with halite

and therefore contains no bromine. Also it does not affect the bromine determination of halite associated with it in mineral deposits.

Russian and German workers have expressed the bromine distribution coefficients for chlorides in slightly different ways and thus the constants used by them differ numerically. The Russian workers express it as the ratio of weight percent of bromine in solid chloride phase to the weight percent of bromine in the dry residue (total solids) of the equilibrium liquid phase (4) while the German workers express it as the ratio of the weight percent of bromine in solid chloride to the weight percent of bromine in the remaining liquid phase.

EXPERIMENTAL

In the present work for obtaining the Experimental data 30 liters of 30.4° Be' bitterns were subjected to solar evaporation in a tray having 1,800 cm² surface exposure. During the progressive evaporation, at close intervals of density rise, salts separating out were collected centrifuged and the mother liquid left over was subjected to further evaporation. The reduction in volume of liquid at each stage was noted. The composition of salts separated and the liquid phase in equilibrium were determined each time by following standard analytical methods.

Bromine was determined titrimetrically according to the Willard Heyn modification method for its estimation in the presence of much chloride ion given by R. Belcher and C.L. Wilson (5). The method consists in oxidizing the bromide to bromate with sodium hypochlorite solution, the excess of which is decomposed by sodium formate. The bromate is then determined by adding potassium iodide, acidifying the solution with hydrochloric acid and titrating the liberated iodine with sodium thio-sulphate using a starch indicator. Each time a blank determination was carried out. The quantitative oxidation of bromide into bromate takes

TABLE I

Percentage of Ionic Composition and Probable Compounds Present in the Liquid and Solid Phase at Equilibrium Concentrates

Density °Be'	Volume ml.	Liquid Phase						Solid Phase					
		SO ₄	Br	Mg	CL	K	Na	SO ₄	Br	Mg	CL	K	Na
30.4	30,000	6.59	0.22	5.04	19.70	1.39	5.42						
31.7	25,000	7.58	0.26	5.87	19.45	1.57	4.26	0.70	0.01	0.52	57.98	0.12	36.89
32.2	22,286	8.16	0.28	6.49	19.87	1.76	3.58	0.91	0.01	0.65	58.56	0.09	37.13
33.0	18,304	8.11	0.32	7.46	20.50	2.14	1.90	19.58	0.01	5.33	29.00	0.08	18.03
34.2	15,985	6.89	0.34	7.68	21.69	2.50	1.48	25.63	0.02	6.86	21.33	0.16	13.02
34.5	13,026	6.82	0.41	8.53	23.95	2.46	1.35	23.44	0.04	6.49	27.36	8.72	11.55
35.2	10,665	6.51	0.49	9.25	25.30	1.94	1.03	11.74	0.17	8.07	31.30	7.08	6.54
36.2	8,296	4.66	0.59	9.53	25.86	0.73	0.73	13.17	0.18	8.99	27.87	5.64	4.11
37.3	6,250	3.85	0.77	11.41	30.91	0.11	0.49	13.88	0.20	9.93	28.22	5.24	3.15
37.5	5,395	3.50	0.85	12.58	34.37	0.05	0.42	6.23	0.43	11.14	29.53	0.06	1.17
38.8	4,110	4.13	0.99	12.36	34.08	0.03	0.35	3.87	0.52	12.30	34.58	0.09	1.16
39.4	3,222	3.34	1.10	12.46	33.87	0.02	0.31	4.02	0.55	11.96	32.54	0.09	0.53

place in 5 to 10 minutes at 90°C. The reduction of the excess hypochlorite by formate solution to formic acid is done while the solution is hot. The analytical results obtained are presented in Table 1.

The bromine distribution ratio has been worked out by dividing the percentage of bromine in the solid phase by the percentage of bromine in total solids in 100 ml. of the equilibrium liquid phase and is given in Table 2. The percentage of bromine in solid phase has been estimated from a sample of solid phase from which the adhering mother liquor was removed by pressing the sample in folds of filter paper.

TABLE 2
Distribution Ratio of Bromine in Relation to
Progressive Evaporation of Sea Bitterns

Sr.No.	Density °Be'	Distribution Ratio of Bromine
1.	31.7	1.465
2.	32.2	1.348
3.	33.0	1.637
4.	34.2	3.483
5.	34.5	4.792
6.	35.2	22.822
7.	36.2	21.105
8.	37.3	20.247
9.	37.5	48.989
10.	38.8	47.639
11.	39.4	49.652

CONCLUSIONS

The values of distribution ratio indicate that during solar evaporation of bitterns up to the density range of 34.5° Be' (Sp.gr. 1.314) the liquid phase due to simultaneous reduction in volume gets enriched in its bromine content. The values beyond this density steeply increase till the density of 35.2° Be' (Sp.gr. 1.322) is reached indicating that bromine is being taken up in solid solution. In the region of separation of potassium chloride from 35.2° Be' (Sp.gr. 1.322) to 37.3° Be' (Sp.gr. 1.348) these values indicate that the distribution ratio is practically constant due to the precipitation of bromine in the form of potassium bromide going into solid solution with its isomorphous salt potassium chloride which precipitates in the mixed salt. These values again show a sharp rise between 37.3° Be' (Sp.gr. 1.348) to 37.5° Be' (Sp.gr. 1.351) and a similar phenomenon is exhibited till 39.3° Be' (Sp.gr. 1.374). Here bromine enters into solid solution as magnesium bromide with its another isomorphous salt magnesium chloride hexahydrate. The separation of bromine in solid phase in the form of potassium bromide from 35.2° Be' (Sp.gr. 1.322) to 37.3° Be' (Sp.gr. 1.348) in preference to sodium bromide is inferred from the relative solubility data of the system NaBr·2H₂O + KBr as given in Table 3. This clearly indicates that potassium bromide is

TABLE 3
Equilibrium in the System Potassium Bromide-Sodium
Bromide-Water (Vlassov and Bergman, 1943)

Gm. NaBr/100 gm sat. soln.		Gm. KBr/100 gm sat. soln.
41.5	at 0°C	4.7 NaBr·2H ₂ O
41.2		4.8 NaBr·2H ₂ O + KBr
39.4		6.1 KBr
	at 10°C	
43.0		5.0 NaBr·2H ₂ O
42.6		5.4 NaBr·2H ₂ O + KBr
42.3		5.7 KBr
	at 20°C	
45.3		3.6 NaBr·2H ₂ O
43.8		6.3 NaBr·2H ₂ O + KBr
41.6		7.5 KBr
	at 25°C	
45.6		5.2 NaBr·2H ₂ O
44.4		6.7 NaBr·2H ₂ O + KBr
41.2		8.2 KBr
	at 30°C	
47.9		2.6 NaBr·2H ₂ O
46.3		5.3 NaBr·2H ₂ O + KBr
45.0		7.1 KBr
	at 50°C	
48.15		8.18 NaBr
37.64		13.48 KBr
36.94		14.42 KBr

about nine times less soluble than sodium bromide in water and it must necessarily precipitate in preference to sodium bromide. This work thus brings out that for the recovery of bromine the optimum density of bitterns is at 34.5° Be' (Sp.gr. 1.314) up to which concentration bromine content in the liquid phase is not lost in the separating solid phase. This work has also confirmed the view that bromine enters into solid solution with potassium chloride and magnesium chloride hexahydrate as potassium bromide and magnesium bromide hexahydrate respectively.

In the recovery of bromine from bitterns by replacement with chlorine gas the quantity of liquid required to be handled at 34.5° Be' (Sp.gr. 1.314) is about 57 percent less than required to be handled at 30.0° Be' (Sp.gr. 1.262). The debromination efficiency observed at this density is about 95 percent and only 0.2 to 0.25 gm./litre of bromine is carried away with the effluent. This can be recirculated in the recovery tower for further recovery. The effect of increase in viscosity at the higher concentration of bitterns is also reduced due to higher temperatures of bitterns subjected to processing.

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