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Separation of the System NaCl–NaBr–NaI by "Solventing Out" from Aqueous Solution

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Abstract

The precipitation of NaX ($X = Cl, Br, I$) from their saturated aqueous solution by three miscible organic solvents (MOS)—acetone, acetonitrile and isopropylamine—was studied for various MOS–aqueous solution volumes ratios. It was found that the fraction precipitated f is given by

$$f = K \log V/V_c$$

where V is the volume ratio and K and V_c are constants. For the case of NaCl this plot was found to be a broken line composed of two straight lines intersecting at the point of "salting out." A scheme is suggested to separate the three electrolytes using isopropylamine to precipitate NaCl and acetone to precipitate NaBr.

INTRODUCTION

The phenomenon of "salting out," i.e., the separation of organic solvents from aqueous solution by the addition of electrolytes, has been known for a long time (*1*). This process is explained by the assumption that the water molecules prefer to be surrounded by the electrolyte ions rather than by nonelectrolyte molecules which are removed from the aqueous solution. The same explanation predicts that for some cases "solventing out," i.e., the removal of electrolytes from aqueous solutions by a miscible organic solvent, will occur. Hull and Owens (*2*) showed that KI and KIO_3 can be separated by the addition of 1,4-dioxane to the aqueous solution of the two electrolytes.

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Alfassi and Feldman (*3*) used this method for the preparation of carrier-free ^{82}Br by the separation of KBr and $KBrO_3$ in aqueous solution via the addition of acetone. The general concept has been discussed by Alfassi (*4*) using data on the solubilities of several salts in a mixture of water–miscible organic solvent (MOS). Mosseri and Alfassi (5) studied the separation of the systems KX–KXO_3–KXO_4 (X = Cl, Br, I) by using acetone or acetonitrile as the MOS. It was found that for a ratio of volumes

$$V = V_{\text{MOS}}/V_{\text{aqueous solution}}$$

the fraction precipitated from a saturated aqueous solution, f, can be described quite accurately (except for large values of f such as $f > 0.9$) by

$$f = \mathrm{K} \log V/V_c \qquad (1)$$

where V_c can be understood as the minimum value of V which is required before any precipitation occurs and K is a precipitation constant.

Our study was done in order to study the possibility of using MOS to separate NaCl–NaBr–NaI from their saturated aqueous solution. This system is frequently found in seawater and is an important process for the separation of salts from Dead-Sea water. This system can be separated as I_2, Br_2, and NaCl by fractional oxidation with Cl_2 and extraction to CCl_4. However, when the salts NaX are needed, this method involves consumption of too much energy for the preparation of Cl_2. Our study was looking for a method of separation which would not involve any chemical reaction. In order to save energy for the removal of the MOS after separation, it is important to use low boiling point organic solvents.

EXPERIMENTAL

Saturated aqueous solutions were prepared by dissolving an excess of salt in hot distilled water and decanting the solution into a bottle which was then cooled to room temperature. The appearance of a precipitate proves the saturation of the solution. The solubility was measured by taking 1 mL of the solution to dryness at 300°C and weighing the precipitate. Varying amounts of MOS were added to 1 mL of the saturated aqueous solution, and after centrifugation the supernatant liquid was decanted and the precipitate was dried at 300°C and weighed. The ratio of this weight to the weight of 1 mL of dried aqueous solution is the precipitated fraction. All experiments were done at room temperature (20–22°C).

TABLE 1
The Precipitated Fraction *f* as a Function of *V* (added volume MOS/volume aqueous solution) for Acetone

	f	
V	NaCl	NaBr[a]
0.1	0.088	n.p.
0.2	0.150	n.p.
0.5	0.245	n.p.
1.0	0.314	n.p.
1.5	0.381	n.p.
2.0	0.409	0.088
2.5	0.497	
3.0	0.561	0.242
3.5	0.612	
4.0	0.700	0.336
4.5	0.750	
5.0	0.767	0.431
5.5	0.805	
6.0	0.853	0.520
6.5	0.892	
7.0	0.915	0.587
7.5	0.927	
8.0		0.665
8.5	0.954	
9.0		0.725
10.0	0.956	0.745
15.0	0.978	0.906

[a] n.p. = no precipitate.

Precipitation with Acetone

NaI was not precipitated for $V_{\text{acetone}}/V_{\text{aqueous solution}} = 15{:}1$. The results for the precipitated fraction *f* of NaCl and NaBr are given in Table 1 and are plotted in Fig. 1 as a function of the ratio of the solvents, $V = V_{\text{acetone}}/V_{\text{aqueous solution}}$. It can be seen in Fig. 1 that the analytical expression found previously (*5*, *6*) for some potassium salts, namely $f = k \log V/V_c$, also hold true in this case. However, for NaCl the curve is broken into two straight lines and the point of deflection is where "salting out" and "solventing out" occur simultaneously. At this point the acetone and the aqueous phases are separated along with part of the precipitated NaCl. This separation of the two liquid phases continue up to $V_{\text{acetone}}/V_{\text{aqueous solution}} \sim 10$.

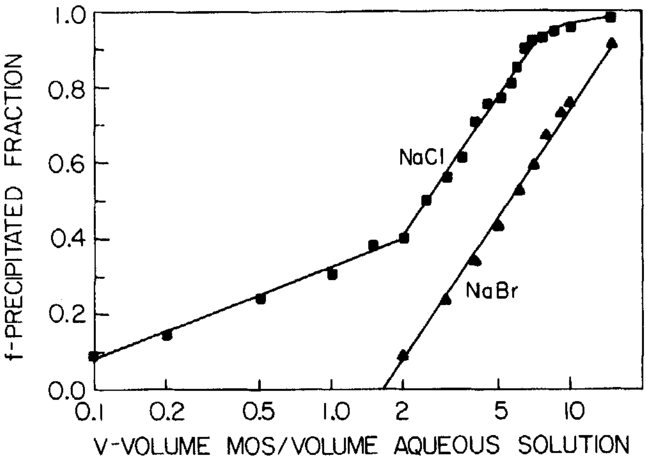

FIG. 1. The precipitated fraction f of NaCl and NaBr as a function of V (added volume MOS/volume aqueous solution) for acetone.

Two processes for the separation of NaBr and NaCl can be envisaged from this result, as previously described (5). The first process leads to precipitation of NaCl alone. Thus, by adding to V mL aqueous saturated solution of both NaCl and NaBr and $1.5V$ mL of acetone, 37% of the NaCl will be precipitated while all of the NaBr will remain in the solution. Evaporation of the acetone followed by evaporation of $0.37V$ of the water will lead to precipitation of 37% of the NaBr alone, and formation of a saturated solution in both NaCl and NaBr, which can be returned to the mother liquor.

The second process is based on precipitating both salts simultaneously, but in a different proportion than in the original solution, followed by separation by dissolving in water. This process can be understood more clearly by the following example. To V mL of the aqueous saturated solution, $7V$ mL of acetone is added. This leads to the precipitation of 90% of the NaCl together with 58% of the NaBr.

Dissolving the precipitate in $0.58V$ mL of water will dissolve all the NaBr but only a fraction of the NaCl, leaving 32% of the original NaCl alone in the precipitate. This $0.58V$ mL saturated aqueous solution can be returned to the mother liquor. The remaining water–acetone mixture contains 10% NaCl and 42% NaBr. It will evaporate up to $0.1V$ mL of water, which will lead to $0.1V$ mL of saturated solution, to be returned to the mother liquor, and 32% of the original NaBr in the precipitate. It is easily seen that quite a bit less acetone is required in the first process where, for the complete precipitation and separation from V mL of a saturated aqueous solution, the required amount of acetone is given by a geometric series

$$1.5V + 1.5(1 - 0.37)V + 1.5(1 - 0.37)^2V + \cdots = 1.5V/0.37 = 4.05V$$

Precipitation with Acetonitrile

Similarly as in the case of acetone, NaI is not precipitated at all, even for a volume ratio of 15:1. The precipitated fractions f of NaCl and NaBr for various volume ratios are given in Table 2 and plotted in Fig. 2. The analytical expressions are the same as in the case of the acetone, including a deflection point where separation of the two liquid phases occurs. At $V = 2.4$, where NaBr started to be precipitated, only 25% of the NaCl precipitated and thus acetonitrile is worse than acetone (precipitation of 37% of the NaCl) from the point of view of both the number of steps required for completion of the separation and the amounts of solvent required (2.4V compared to 1.5V for acetone). This, together with the lower boiling point of acetone, makes acetone the better choice.

TABLE 2
The Precipitated Fraction f as a Function of V (added volume MOS/volume aqueous solution) for Acetonitrile

	f	
V	NaCl	NaBr[a]
0.1	0.076	n.p.
0.2	0.098	n.p.
0.3	0.131	n.p.
0.5	0.160	n.p.
1.5	0.218	n.p.
2.0	0.243	n.p.
2.5	0.252	n.p.
3.0	0.351	0.121
4.0	0.442	0.226
5.0	0.526	0.328
6.0	0.581	0.431
7.0	0.691	0.513
8.0	0.731	0.575
9.0	0.778	0.631
10.0	0.827	0.692
12.0		0.755
15.0	0.959	0.887

[a] n.p. = no precipitate.

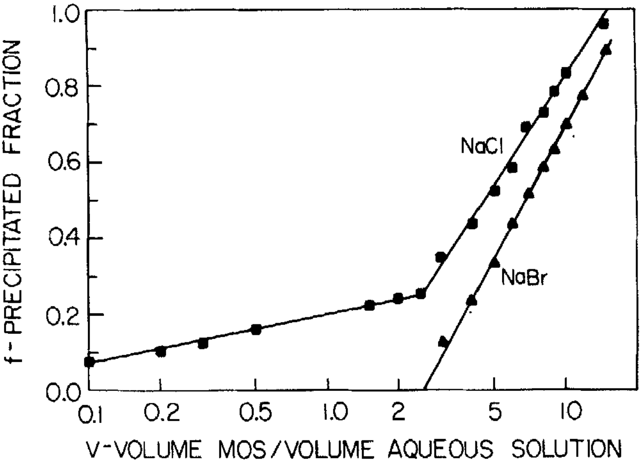

FIG. 2. The precipitated fraction *f* of NaCl and NaBr as a function of *V* (added volume MOS/volume aqueous solution) for acetonitrile.

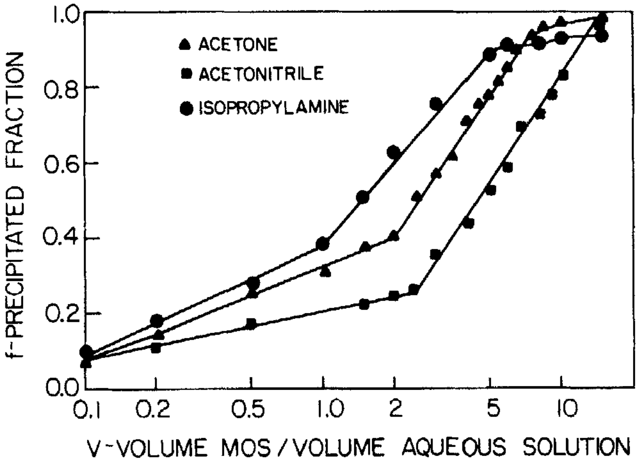

FIG. 3. The precipitated fraction *f* of NaCl as a function of *V* (added volume aqueous solution) using acetone, acetonitrile, and isopropylamine as MOS.

TABLE 3
The Precipitated Fraction f as a Function of V (added volume MOS/volume aqueous solution) for Isopropylamine

V	f_{NaCl}
0.1	0.091
0.2	0.173
0.5	0.282
1.0	0.382
1.5	0.501
2.0	0.622
3.0	0.755
5.0	0.891
6.0	0.907
8.0	0.917
10.0	0.933
15.0	0.935

Precipitation with Isopropylamine

Isopropylamine was found to be the best precipitating solvent for KIO_3 and K_2SO_4 due to both its high precipitating constant and its low boiling point (*6*). However, some caution has to be taken in its use due to the possibility of precipitation of isopropylammonium salts, as was found when precipitating $(NH_4)_2SO_4$ from aqueous solution.

Surprisingly, isopropylamine was found to be a better precipitating solvent for NaCl compared to acetone or acetonitrile (Fig. 3) while it does not precipitate NaBr (and also NaI) at all!

Data for the fraction of NaCl precipitated by isopropylamine are given in Table 3.

Table 4 gives the least squares values of V_c and K describing the data in Tables 1–3 according to Eq. (1). Thus isopropylamine can be used to separate NaCl from both NaBr and NaI. The separation of NaBr and NaI remaining in the aqueous solution after evaporation of the isopropylamine can be done by using acetone to precipitate NaBr.

The question is: What amount of acetone should be used? We can use $25V$ mL acetone on each V mL of aqueous solution, and precipitate about 98% of the NaBr, or use only $10V$ mL and precipitate 75% of the NaBr. In the latter case, after the precipitation we will evaporate all the acetone and $0.75V$ of the aqueous solution, leaving $0.25V$ mL of saturated solution which will be returned to the mother liquor of NaBr + NaI. Thus, in the last procedure we

TABLE 4
The V_c and K values (Eq. 1) for NaCl and NaBr using Acetone, Acetonitrile, or Isopropylamine.

MOS	No. of phases	NaCl V_c	NaCl K	NaBr V_c	NaBr K
Acetone	1	0.051	0.252	1.649	0.954
	2	0.775	0.956		
Acetonitrile	1	0.025	0.129	2.533	1.157
	2	1.366	0.964		
Isopropylamine	1	0.048	0.289	—	—
	2	0.302	0.731		

will use only 10/0.75 mL = 13.3V mL of acetone to recover all the NaBr, compared to 25 mL in the first process. Assuming that the addition of V mL of MOS to 1 mL of aqueous solution precipitates fraction f of the electrolyte, then the amount of MOS required to precipitate all the electrolyte is given by V/f. According to Eq. (1), V/f is given by

$$V/f = (V_c/f)\ \exp(f/K) \qquad (2)$$

Differentiation of V/f with respect to f and equating to zero leads to

$$f = K$$

which means that for each step, $v = eV_c$. Thus, for precipitating NaBr with acetone, $V_c = 1.6$ mL (for 1 mL of aqueous solution), and the most economical process will be to add 4.4 mL in each step, precipitating 40% of the NaBr in each step.

CONCLUSION

With a saturated aqueous solution of volume V containing NaCl, NaBr, and NaI, the addition of enough isopropylamine (15 mL) will lead to precipitation of more than 94% of the NaCl in a pure form. After evaporation of all the isopropylamine (bp = 33°C), acetone is added in a volume of 4.4V which will precipitate 40% of the NaBr. Evaporating the acetone and then 0.4V of the aqueous solution leads to the formation of crystals of NaI amounting to 40% of the total amount and an aqueous saturated solution in NaBr + NaI. To this solution, acetone is added again.

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