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Separation of the KX–KXO_3–KXO_4 (X = Cl, Br, I) System by "Solventing-Out" Processes

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Abstract

This paper deals with the separation of a mixture of electrolytes into its separate constituents by using the effect of "solventing-out"—the precipitation of a salt from an aqueous solution by the addition of a miscible organic solvent (MOS). An analytic expression is found for the dependence of the precipitated fraction on the ratio of the volumes of the MOS/aqueous solution. Required conditions for separation of two electrolytes in either one stage or in a multistage process are stated. The system KX–KXO_3–KXO_4 (where X is Cl, Br, or I) is analyzed more extensively.

1. INTRODUCTION

Many studies were made on the "salting-out" process, i.e., on the separation of organic solvents from aqueous solution by the addition of certain electrolytes. The theoretical explanation for this process assumes that the water molecules prefer to be surrounded by electrolyte ions rather than by nonelectrolyte molecules which are removed from the aqueous solution. This indicates the possibility of the opposite process, i.e., "solventing-out," which means the separation of electrolytes from the aqueous solution by the addition of miscible organic solvents (MOS). This possibility was proven by a number of investigators. Hull and Owens (*1*) showed that KI and KIO_3 can be separated by the addition of 1,4-dioxane to the aqueous solution of the two electrolytes. Their experiments showed that the addition of 1,4-dioxane precipitates KIO_3 while KI remains in solution. A year later Alfassi and Feldman (*2*) reported on the separation of KBr and $KBrO_3$ by the addition of

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acetone to an aqueous solution of the two salts. In 1979 Alfassi (*3*) discussed the possibility of separation of electrolytes by the addition of several water miscible organic solvents to aqueous solutions of different electrolytes. Our research was done in order to study the possibility of using MOS to precipitate electrolytes from concentrated aqueous solutions and separating the electrolytes system KX-KXO_3-KXO_4 by using different precipitation properties of the various organic solvents and the electrolytes.

The importance of the separation methods for the KX–KXO_3–KXO_4 system is due to the preparation methods of KXO_3 and KXO_4 which lead to mixtures of the three electrolytes. The conventional method for preparing KXO_3 is given by the reaction(*4*)

$$3XO^- \rightarrow XO_3^- + 2X^-$$

The reaction is performed in an alkaline environment by slight warming. For the preparation of ClO_3^- the electrolysis of highly concentrated solutions of Cl^- is the more usual method. The appearance of OH^- ions and Cl_2 near the electrodes leads to the following reaction:

$$6OH^- + 3Cl_2 \rightarrow 5Cl^- + ClO_3^- + 3H_2O$$

Two methods are known for the preparation of ClO_4^-: one by electrolytic oxidation of $KClO_3$ and one by strong warming of $KClO_3$ which leads to the following reaction:

$$4KClO_3 \rightarrow 3KClO_4 + KCl$$

2. EXPERIMENTAL AND RESULTS

All the experiments were performed at room temperature (18–20°C). The precipitation of the electrolytes was done from saturated aqueous solutions. The saturation was assured by dissolution of a large amount of electrolyte in hot water and letting the hot solution be cooled to room temperature. The appearance of crystals of salt at the bottom of the vessel proved the saturation. The electrolytes were precipitated by the addition of various amounts of MOS (2–50 cc) to 10 cc of saturated solution, followed by decanting, drying, and weighing of the precipitate. The concentration of the electrolyte in the saturated solution was determined by the evaporation of 10 cc of the saturated solution to dryness and weighing. The following electrolytes were studied: KCl, $KClO_3$, $KClO_4$, KBr, $KBrO_3$, KI, and KIO_3. The organic solvents studied as precipitation solvents were acetone and acetonitrile. The results are shown in Tables 1–5.

3. ANALYTICAL EXPRESSION

Various functional correlations of the result in Tables 1–3 were studied. Figure 1 shows a nonlinear dependence between the precipitated fraction f and the added volume of MOS per unit volume of aqueous solution V and indicates an exponential dependence. The exponential dependence is proven in Figs. 2–4 in which the precipitation of KBr, $KBrO_3$, KCl, $KClO_3$ and KIO_3 from aqueous solution by acetone and acetonitrile is shown.

It can be seen that except for large values of f ($f > 0.8$–0.9), the precipitated fraction f of the electolytes can be described quite accurately by

$$f = K \ln \frac{V}{V_c}$$

TABLE 1

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

	f				
V	KCl	$KClO_3$	KBr	$KBrO_3$	KIO_3
0.1					0.390
0.15					0.482
0.2	0.244	0.189	0.102	0.408	0.561
0.3					0.652
0.4					0.736
0.5	0.407	0.321	0.276	0.575	0.802
0.7	0.518	0.362	0.339	0.659	0.868
1.0	0.578	0.414	0.383	0.738	0.915
1.5	0.707	0.480	0.480	0.816	0.951
2.0	0.765	0.541	0.534	0.850	0.965
3.0	0.847	0.603	0.655	0.917	0.967
4.0	0.894	0.671	0.707	0.949	0.968
5.0	0.911	0.718	0.763	0.954	0.976

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

	f				
V	KCl	$KClO_3$	KBr	$KBrO_3$	KIO_3
0.1		np[a]			0.305
0.15		np			0.379
0.2	0.124	np	0.042	0.117	0.418
0.3		np			0.526
0.4		np			0.577
0.5	0.252	np	0.144	0.344	0.642
0.7	0.303	np	0.183	0.445	0.708
1.0	0.360	np	0.232	0.534	0.766
1.5	0.450	0.051	0.298	0.637	0.822
2.0	0.482	0.194	0.347	0.702	0.856
3.0	0.533	0.279	0.413	0.791	0.905
4.0	0.549	0.418	0.468	0.858	0.919
5.0	0.583	0.502	0.508	0.905	0.933

[a] np means no precipitation at all.

TABLE 3
The Solubility (g electrolyte/1 cc aqueous solution) of the Various Electrolytes

Electrolyte	KCl	$KClO_3$	KBr	$KBrO_3$	KIO_3
g electrolyte/1 cc Saturated solution	0.30265	0.06337	0.54122	0.06129	0.08044

TABLE 4
The V_c and K Values for the Various Electrolytes Using Acetone as the MOS

Electrolyte	KCl	$KClO_3$	$KClO_4$	KBr	$KBrO_3$	KI	KIO_3
V_c	0.064	0.074	>5	0.140	0.0125	>5	
K	0.216	0.164	—	0.208	0.162	—	

TABLE 5
The V_c and K Values for the Various Electrolytes using Acetonitrile as the MOS

Electrolyte	KCl	$KClO_3$	$KClO_4$	KBr	$KBrO_3$	KI	KIO_3
V_c	0.087	1.4	>5	0.175	0.125	>5	
K	0.148	0.393	—	0.146	0.250	—	

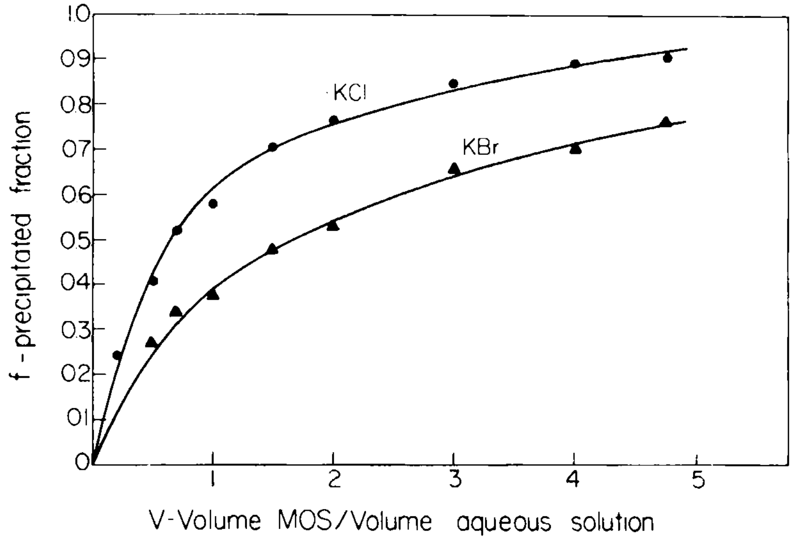

FIG. 1. The precipitated fraction f of KCl and KBr as a function of V (added volume of MOS/volume aqueous solution) using acetone as MOS.

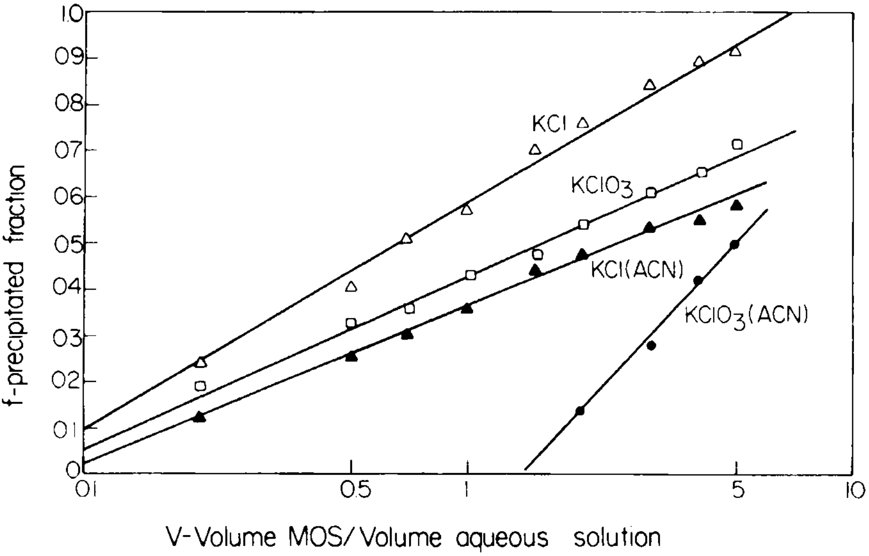

FIG. 2. The precipitated fraction f of KCl and KClO$_3$ as a function of V (added volume of MOS/volume aqueous solution) using acetone and acetonitrile as MOS.

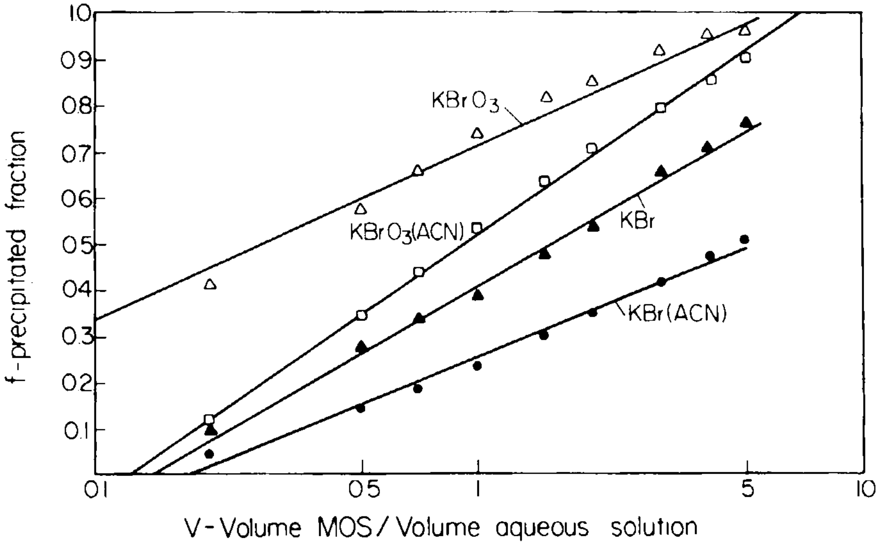

FIG. 3. The precipitated fraction *f* of KBr and $KBrO_3$ as a function of *V* (added volume of MOS/volume aqueous solution) using acetone and acetonitrile as MOS.

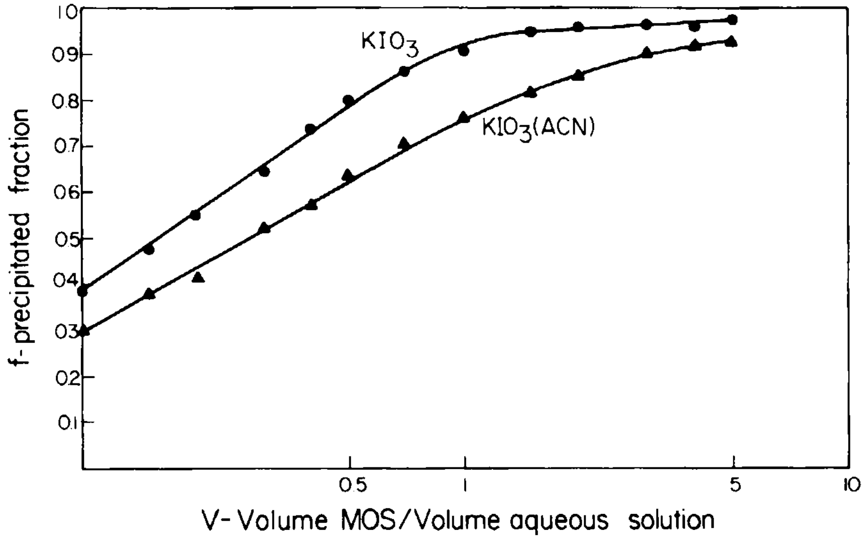

FIG. 4. The precipitated fraction *f* of KIO_3 as a function of *V* (added volume of MOS/volume aqueous solution) using acetone and acetonitrile as MOS.

V_c can be understood as the minimum value of V that is required to precipitate at all and K is a precipitation constant.

It is clear that this equation cannot hold for all values of V. This equation predicts an unlimited increase of f, for large values of V, whereas there is no physical meaning for f greater than 1. Thus the slower increase of f (above $f \sim 0.8$–0.9) requires another equation which will increase asymptotically to unity for large V. This behavior is seen clearly in the results for KIO_3 (Fig. 4) where, up to $f \sim 0.8$–0.9, f is a linear function of ln V while for larger f's, f increases only very slowly with V. It has to be mentioned that usually f will never reach unity, since the electrolyte has small solubility in a pure organic solvent.

4. CONDITIONS FOR THE SEPARATION OF A SYSTEM OF ELECTROLYTES

4.1. One-Stage Separation

If the electrolytes system A,B fulfills the requirement $V_{c_A} \gg V_{c_B}$, then the separation of the aqueous solution of electrolytes A,B can be done in one stage. In this case the amount of MOS required to precipitate electrolyte A is much larger than that needed for precipitation of B. In an ideal case in which $V_{c_A} \approx \infty$ (i.e., there is no value of V that may precipitate A), it is expected that by the addition of a large amount of MOS, A will remain in solution while B will precipitate almost completely.

4.2. Multistage Separation

4.2.1. $V_{c_A} > V_{c_B}$

If the electrolytes system A,B does not fulfill the requirement $V_{c_A} \gg V_{c_B}$ but still fulfills $V_{c_A} > V_{c_B}$, then the separation of the electrolytes A,B cannot be performed in one step but can still be done in several stages. It cannot be done in one stage since the amount of MOS required for precipitation of most of electrolyte B may at the same time precipitate too large an amount of A. In this case the precipitation must be done in several stages; each stage must include controlled precipitation of B, according to the V_{c_A} and V_{c_B} values, such that only negligible fractions of A will also be precipitated. The precipitation is then followed by evaporation of the MOS from the aqueous solution and the excess of water in order to again reach the saturation of the aqueous solution with respect to B. In the last step pure electrolyte A is precipitated. The basic requirement for that process is a considerably lower boiling point for the MOS than that of water. In the selection of an MOS for any precipitation process, the MOS with the lower boiling point will be preferable if both have the same precipitation properties, due to less energy required for separation.

4.2.2. $K_A > K_B$

If the electrolytes system A,B does not fulfill the requirement $V_{c_A} > V_{c_B}$ (i.e., $V_{c_A} \approx V_{c_B}$) but it fulfills $K_A > K_B$, then the electrolytes system A,B in aqueous solution can still be separated by the addition of MOS in several stages. In a system like this, one can easily see that there exists a value of V which will precipitate most of electrolyte A and only small amounts of B. In such a case the remaining solution will contain most of B and a very low fraction of A. This liquid phase will be heated up to remove the MOS. Further heating will remove a part of the water up to resaturation with respect to A. In the last step, a large fraction of electrolyte B will be precipitated as pure solid. The remaining aqueous solution will be returned to the mother liquid. Dissolving the solid phase that had precipitated from the original solution (containing a high fraction of A and a low fraction of B) in a small amount of water, just enough to dissolve the entire amount of B, will result in a saturated solution in A + B and will be returned to the mother liquid. Most of the electrolyte A will remain in the solid phase. Thus, by using the process described, one may get two solid phases that include the electrolytes A and B separately and a saturated aqueous solution with respect to both A and B.

This process can be understood more clearly by the following example. A V-mL saturated solution contains α moles of electrolyte A and β moles of B. Let us assume that the addition of a certain amount of MOS to a V-mL saturated solution precipitates 0.9α mol of A and 0.1β mol of B (i.e., $f_A = 0.9, f_B = 0.1$). Thus the remaining solution will contain 0.1α mol of A and 0.9β mol of B. Evaporation of MOS from the aqueous solution followed by evaporation of 90% of the water will lead to $V/10$ mL of saturated aqueous solution containing 0.1α mol of A and 0.1β mol of B and, in addition, a solid phase which consists of 0.8β moles of B. The dissolving of the original precipitate (which consists of 0.9α mol of A and 0.1β mol of B) in $V/10$ mL of water will lead to a saturated solution which contains 0.1α mol of A and 0.1β mol of B, leaving 0.8 mol of A in the solid phase. Thus, at the end of this stage we get two solid phases, one of 0.8α mol of A and one of

0.8β mol of B, and $V/5$ mL of saturated solution containing 0.2α mol of A and 0.2β mol of B which will be returned to the mother liquid.

5. SIMULTANEOUS “SALTING-OUT” AND “SOLVENTING-OUT”

The addition of acetonitrile to a concentrated solution of either KBr or KCl leads to precipitation of a large fraction of the salt together with the separation of the two solvents. This effect has the disadvantages that since the two solvents are not miscible any more, less electrolyte can be precipitated. On the other hand, less organic solvent has to be removed from the aqueous solution.

6. THE SEPARATION OF REAL SYSTEMS

6.1. The KCl–KClO$_3$–KClO$_4$ System

Addition of acetone to saturated solutions of KCl, $KClO_3$, and $KClO_4$ separately proves that acetone precipitates KCl and $KClO_3$ well, while $KClO_4$ remains in solution even after the addition of a large amount of acetone to the aqueous solution. This enables the separation of $KClO_4$ from the KCl–$KClO_3$–$KClO_4$ system by one stage as described in Section 4.1. However, acetone cannot be used to separate KCl and $KClO_3$ in one stage.

Addition of acetonitrile to saturated solutions of KCl and $KClO_3$ proves that acetonitrile precipitates KCl well, while $KClO_3$ has a high value for Vc ($V_{c_{KClO_3}} = 1.4$) which requires the addition of a very large amount of acetonitrile to the solution in order to obtain any precipitation. These conditions are suitable for separation of KCl–$KClO_3$ by several stages as described in Section 4.2.1. Figure 2 shows that the addition of 1 mL acetonitrile to 1 mL saturated solutions of KCl and $KClO_3$ will lead to f values (precipitated fraction) of 0.45 and about 0, respectively.

Summarizing, the separation of the KCl–$KClO_3$–$KClO_4$ electrolyte system can be achieved by using two MOS’s. $KClO_4$ will be separated by the addition of a large amount of acetone to the original solution containing the three electrolytes. At the end of this stage, $KClO_4$ will remain in solution while the other two will be in the precipitate. Dissolving of the precipitate in water and controlled addition of acetonitrile to the solution will lead to the separation of the other two by several stages.

6.2. The KBr–KBrO$_3$ System

The separation of the KBr–KBrO$_3$ system by use of MOS was suggested first by Alfassi and Feldman (*2*) who used acetone in order to get free radiobromine from irradiated KBrO$_3$. Tables 1 and 2 give the extent of precipitation of KBr and KBrO$_3$ as a function of the added volume of acetone and acetonitrile. These results indicate several possibilities for separation according to the different organic solvents which act as MOS's.

By using acetone as the MOS, the KBr–KBrO$_3$ system can be separated by a multistage process as described in Section 4.2.1. Figure 3 shows that the addition of 0.15 mL acetone to 1 mL aqueous saturated solutions of KBr and KBrO$_3$ (separately) yields precipitated fractions of 0 and 0.4, respectively.

By using acetonitrile as the MOS, the two electrolytes can be separated by a multistage separation process as described in Section 4.2.2. Figure 3 shows that the addition of 6 mL acetonitrile to 1 mL saturated solutions of KBr and KBrO$_3$ (separately) precipitates 0.5 and 0.95 of the solutes, respectively. It should be noted that in a KBr–KBrO$_3$ system containing high fractions of KBrO$_3$ and low fractions of KBr (a situation that occurs in radiolysis of KBrO$_3$), the separation of the two electrolytes may be performed in one step by using acetone as the MOS. In this case, as was proved by Alfassi and Feldman (*2*), the acetone precipitates most of the KBrO$_3$ while the precipitated amount of KBr is negligible.

By comparing the effectiveness of the two organic solvents as precipitating agents, it seems that there is no advantage of one organic solvent over another. However, as an MOS with a lower boiling point is preferable, it is more advantageous to use acetone than acetonitrile.

6.3. The KI–KIO$_3$ System

Hull and Owens (*1*) showed that the separation of the KI–KIO$_3$ system can be performed by the addition of a large amount of 1,4-dioxane to the aqueous solution containing the two electrolytes. In that case, 1,4-dioxane precipitates KIO$_3$ while KI remains in solution. However, the high boiling point of 1,4-dioxane (101°C), which is very near to that of water, makes the separation of 1,4-dioxane from the aqueous solution by evaporation very difficult. Our study proved that separation of the KI–KIO$_3$ system may also be done by using either acetone or acetonitrile. For the two organic solvents, the precipitate contains only KIO$_3$ while KI remains in solution. Acetone is preferable to acetonitrile since a smaller amount is required. Figure 4 shows that the addition of only 1 mL acetone to 1 mL saturated solution of KIO$_3$ is equired to precipitate 90% of the KIO$_3$. This is in addition to the advantage f a lower boiling point.

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