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Precipitation of Nitrates and Nitrites by "Solventing Out" from Aqueous Solutions

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Abstract

The separation of nitrates from nitrites and the separation of various nitrates and nitrites by "solventing out" from aqueous solution by three miscible organic solvents were studied.

INTRODUCTION

Many of the processes for separation of electrolytes are based on their different solubilities in water. The use of mixtures of water with miscible organic solvents (MOS) enlarges this possibility since electrolytes which have similar solubilities in water may have very different solubilities in water–MOS systems.

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, e.g., King (*1*). This process is explained by the assumption that the water molecules prefer to be surrounded by 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 MOS, will occur. Hull and Owens (*2*) showed that KI and KIO_3 can be separated by the addition of 1,4-dioxane to an aqueous solution of the two electrolytes. 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

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general concept has been discussed by Alfassi (*4*) using data on the solubilities of several salts in a mixture of water-MOS. Mosseri and Alfassi (*5*) studied the separation of the systems $KX-KXO_3-KXO_4$ (X = Cl, Br, I) by using acetone or acetonitrite 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

$$f = K \log V/V_c \tag{1}$$

where V_c is the minimum value of V is required before any precipitation occurs and K is a precipitation constant.

This work was done in order to study the possibility of using MOS to separate nitrates and nitrites, or the nitrates or nitrites of different cations.

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 precipitate proves the saturation of the solution. The solubility was measured by taking 1 mL of the solution to dryness at 250°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 250°C and weighed. The ratio of this weight to the weight of 1 mL of dried aqueous solution is the precipitated fraction f. All experiments were done at room temperature (20–22°C).

RESULTS AND DISCUSSION

One-Step Separation

Table 1 gives the fraction precipitated by the addition of a 10-fold volume of three MOS's (acetone, acetonitrile and tetrahydrofuran) to saturated aqueous solutions of nitrates and nitrites.

TABLE 1

Precipitation Table: f = Precipitated Fraction of NO_3^- and NO_2^- Salts in Ac, AcN, and THF for $V = V_{\mathrm{MOS}}/V_{\mathrm{aqueous\ solution}} = 10^a$

Salt	Acetone	Acetonitrile	Tetrahydrofuran
$LiNO_3$	—	—	—
$NaNO_3$	0.809	0.743	0.516
KNO_3	0.685	0.613	0.698
NH_4NO_3	0.691	0.788	0.658
$Mg(NO_3)_2$	—	—	—
$Ca(NO_3)_2$	—	—	—
$Sr(NO_3)_2$	0.344	—	—
$Ba(NO_3)_2$	0.654	0.668	0.652
$Pb(NO_3)_2$	0.885	0.896	0.399
$Cr(NO_3)_3$	—	—	—
$CO(NO_3)_3$	—	—	—
$Cd(NO_3)_3$	—	—	—
$Ni(NO_3)_2$	—	—	—
$Cu(NO_3)_2$	—	—	—
$AgNO_3$	—	—	—
$UO_2(NO_3)_2$	—	—	—
$NaNO_2$	0.546	—	—
KNO_2	—	—	—

[a] A dash indicates no precipitation for $V = 10$.

A dash indicates that no precipitation occurs. Thus, Table 1 shows that KNO_3 can be separated from KNO_2 by all three solvents, while $NaNO_2$ can be separated from $NaNO_3$ only by the use of acetonitrile or tetrahydrofuran since acetone precipitated both.

KNO_2 can be separated from $NaNO_2$ only by the use of acetone. The fact that not all the precipitable electrolyte was precipitated can be overcome (i.e., to enable complete separation of the two electrolytes) either by addition of larger amounts of MOS (see Table 2) or, preferably, by a two-step process. In the latter process the addition of a MOS in the first step to a saturated aqueous solution of Electrolytes A and B precipitates only fraction f of Electrolyte A, while all of Electrolyte B remains in solution. In the second step all the MOS is evaporated, followed by evaporation of fraction f of the original water. In this step Electrolyte A remains in solution while fraction f of Electrolyte B is precipitated, leaving an aqueous solution saturated with both A and B with volume $1 - f$ of the original one. This solution is added back to the mother liquor.

TABLE 2

MOS	Salt	1	2	3	4	5	6
Acetone	$NaNO_3$	.337	.471	.578		.710	
	KNO_3	.424	.528	.592	.628	.670	
	NH_4NO_3	n.p.	.166	.262	.412	.464	.535
	$Sr(NO_3)_2$	n.p.	n.p.	n.p.	.025	.080	.132
	$Ba(NO_3)_2$	.228	.378	.496	.555	.584	.600
	$Pb(NO_3)_2$	.375	.533	.651	.711	.772	.818
Acetonitrile	$NaNO_3$	.185	.248	.323	.382	.477	.540
	KNO_3	.171	.300	.383	.446	.501	.538
	NH_4NO_3	n.p.	.070	.149	.267	.386	.451
	$Ba(NO_3)_2$	.143	.304	.419	.514	.565	.606
	$Pb(NO_3)_2$	.380	.530	.653	.712	.765	.821
Tetrahydrofuran	$NaNO_3$	.090	.158	.202	.243	.295	.367
	KNO_3	.332	.431	.510	.544	.593	.611
	NH_4NO_3	n.p.	n.p.	.119	.140	.172	.275
	$Ba(NO_3)_2$	.167	.259	.352	.434	.501	.546
	$Pb(NO_3)_2$	.042	.075	.101	.118	.149	.225

[a]n.p. = no precipitate.

Multisteps Separation

Table 1 shows only on the possibility of separation of two electrolytes when one is precipitated and the other is not. Yet, two electrolytes can be precipitated even when both are precipitated but to a different extent.

Table 2 gives the fraction precipitated f as a function of the ratio of the volumes of the MOS and the aqueous solution V. Figure 1-3 show that as found for other electrolytes, f and V are related by

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

as long as the liquids form one phase. When two liquid phases are formed, a "bend" is seen in the curve.

Table 3 gives the values of K and V_c for various systems studied. For one phase V_c can be understood as the minimal volume of MOS that has to be added to 1 mL aqueous solution to lead to any precipitation. For two phases, V_c no longer has this meaning.

Precipitation of Nitrates in Various MOS[a]

f for *V* of									
7	8	9	10	12	13	15	20	25	30
.776	.799		.809		.857		.916		
.669	.679	.680	.685			.690	.701		
.576	.629	.684	.691			.869	.898		
.166	.250	.300	.344			.552	.721		
.615	.640	.640	.654						
.858	.873	.877	.885						
.578		.590	.743	.796		.892			
.544	.564	.610	.613			.640	.693		
.553	.634		.788						
.661	.664	.666	.668						
.866	.877	.885	.896						
.414	.437	.485	.516	.651		.732	.811		.850
.635	.654	.694	.698		.723	.724	.725	.730	.731
.384		.570	.658						
.610	.628	.645	.652						
.278	.316	.350	.399						

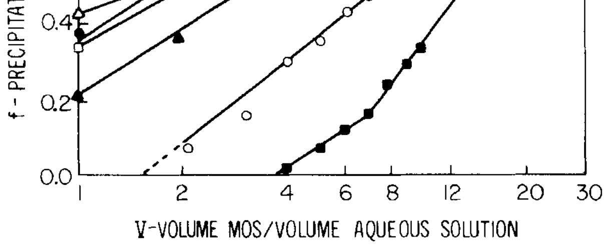

FIG. 1. The precipitated fraction, *f*, of nitrates as a function of *V* (added volume MOS/volume aqueous solution) for acetone: (□) $NaNO_3$, (△) KNO_3, (○) NH_4NO_3, (■) $Sr(NO_3)_2$, (▲) $Ba(NO_3)_2$, (●) $Pb(NO_3)_2$.

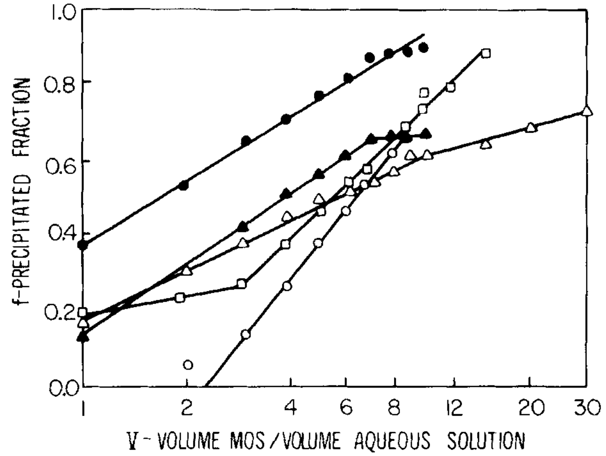

FIG. 2. The precipitated fraction, f, of nitrates as a function of V (added volume MOS/volume aqueous solution) for acetonitrile. The symbols are defined in the Fig. 1 legend.

Optimal Separation

These values of K and V_c give also details on the most economical process for the separation of Electrolytes A and B. Assume that to 1 mL saturated aqueous solution containing S_A and S_B grams of A and B, we add V mL of MOS which leads to precipitation of the fractions f_A of Electrolyte A and f_B of Electrolyte B, where $f_A > f_B$. The precipitate and the solution will be treated according to the following scheme:

Precipitate

The precipitate will be dissolved in f_B mL water, leading to an aqueous solution saturated in both Electrolytes A and B and leaving a precipitate which is pure Electrolyte A. Its amount is $(f_A - f_B)S_A$. The solution formed is transferred to the mother liquor.

Solution

Evaporation of all the MOS followed by evaporation of f_A mL water will lead to precipitation of $(f_A - f_B)S_B$ of pure Electrolyte B, leaving

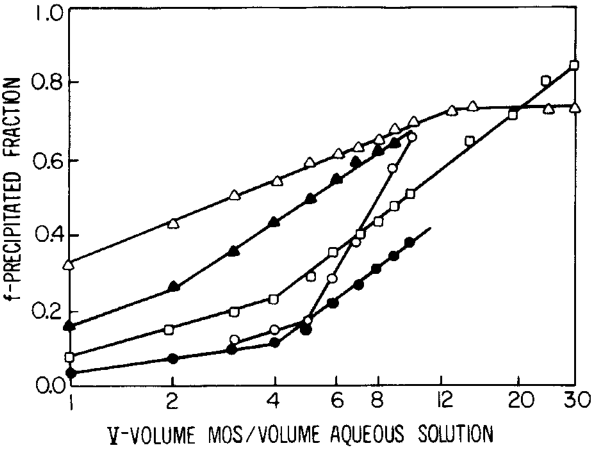

FIG. 3. The precipitated fraction, f, of nitrates as a function of V (added volume MOS/volume aqueous solution) for tetrahydrofuran. The symbols are defined in the Fig. 1 legend.

$(1 - f_A)$ mL aqueous solution saturated with both A and B. This remaining solution is added to the mother liquor.

These processes lead to the separation of fraction $f_A - f_B$ of each of the electrolytes. In these processes, for 1 mL saturated aqueous solution we use and evaporate V mL MOS and evaporate f_A mL water and were left with $1 - (f_A - f_B)$ mL of the original solution. Thus, for complete separation of the electrolytes in 1 mL saturated aqueous solution, the total amount of MOS required is

$$V_{\mathrm{MOS}} = \sum_{n=0}^{\infty} V[1 - (f_A - f_B)]^n = \frac{V}{f_A - f_B} \tag{2}$$

and the amount of water evaporated is

$$V_{\mathrm{H_2O}} = \sum_{n=0}^{\infty} f_A[1 - (f_A - f_B)]^n = \frac{f_A}{f_A - f_B} = 1/(1 - f_B/f_A) \tag{3}$$

Substituting $f_A = K_A \ln (V/V_{cA})$ and $f_B = K_B \ln (V/V_{cB})$ leads to:

$$V_{\mathrm{MOS}} = \frac{V}{(K_A - K_B) \ln V + \ln (V_{cB}^{K_B}/V_{cA}^{K_A})} \tag{4}$$

TABLE 3
The V_c and K Values for NO_3^- Salts in Few MOS

Salt	Number of phases	Acetone		Acetonitrile		Tetrahydrofuran	
		V_c	K	V_c	K	V_c	K
$NaNO_3$	1	0.238	0.527	0.230	0.280	0.449	0.250
	2	0.294	0.016	1.453	0.856	2.010	0.776
KNO_3	1	0.060	0.348	0.417	0.451	0.124	0.364
	2	1.71×10^{-12}	0.053	0.044	0.258	8.991	0.023
NH_4NO_3	1	1.243	0.773	2.009	1.037	0.961	0.235
	2	—	—	—	—	4.029	1.585
$Sr(NO_3)_2$	1	3.628	0.588	—	—	—	—
	2	5.051	1.191	—	—	—	—
$Ba(NO_3)_2$	1	0.393	0.551	0.608	0.616	0.326	0.329
	2	0.022	0.247	1.135×10^{-14}	0.045	0.742	0.599
$Pb(NO_3)_2$	1	0.227	0.576	0.195	0.541	0.575	0.535
	2	4.631×10^{-5}	0.166	—	—	3.192	0.797

$$V_{H_2O} = \frac{K_A \ln V - K_A \ln V_{cA}}{(K_A - K_B)\ln V - (K_A \ln V_{cA} - K_B \ln V_{cB})} \tag{5}$$

Differentiating Eq. (4) with respect to V (the ratio of volumes of MOS and water in each step) and equating it to zero gives the value of V which will lead to the minimal value of $V_{MOS} - V_{MIN}$:

$$V_{MIN} = \exp\left[1 - \ln(V_{cB}^{K_B}/V_{cA}^{K_A})/(K_A - K_B)\right] \tag{6}$$

and the minimal value of V_{MOS} is

$$V_{MIN}/(K_A - K_B)$$

Substituting $K_B = 0$ for the case where only A is precipitated leads to the previously found requirement (*6*)

$$V_{MIN} = eV_{cA} \tag{7}$$

The derivative of V_{H_2O} with respect to V is

$$\frac{dV_{H_2O}}{dV} = \frac{K_A K_B \ln(V_{cB}/V_{cA})}{V[(K_A - K_B)\ln V + K_B \ln V_{cB} - K_A \ln V_{cA}]^2} \tag{8}$$

The sign of these derivatives depends on either $V_{cB} > V_{cA}$ or $V_{cA} > V_{cB}$. Since we choose $f_A > f_B$, this usually means $V_{cB} > V_{cA}$, which means that V_{H_2O} is an increasing function of V and there is no minimal value. For the case where $V_{cA} = V_{cB}$ and $f_A > f_B$ is due to $K_A > K_B$, Eq. (8) shows that V_{H_2O} is constant, independent of V. From Eq. (5) it is seen that in this case:

$$V_{H_2O} = \frac{K_A}{K_A - K_B}$$

SYMBOLS

f	precipitated fraction
f_A, f_B	precipitated fraction of Electrolytes A and B
K	"solventing out" constant
K_A, K_B	"solventing out" constants of Electrolytes A and B
S_A, S_B	weight of A and B (g) in 1 mL saturated aqueous solution

V	MOS's volume per 1 mL saturated aqueous solution
V_c	minimal value of V required to precipitate all
V_{cA}, V_{cB}	minimal value of V mL Electrolytes A and B to precipitate all
V_{MIN}	minimal value of V

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