

TABLE 4. DATA FROM RUN MADE IN RECTIFICATION COLUMN

Compounds	Overhead Temp., °C.	Stillpot Temp., °C		Relative Volatility	Time to Reach Equil., h
		at start	After 1.5 h		
Blank	49	53	53	1.42	0.5
DMSO	63	54	86	5.97	1
DMSO (R)	63	54	84	5.90	1
Adiponitrile	62	54	85	5.43	1
Sulfolane	62	54	84	4.52	1
Sulfolane (R)	59	55	84	4.43	1
Glycerine	49	53	69	1.67	0.5
Ethylene glycol	56	54	77	2.72	1
DMSO + Adiponitrile	62	54	87	4.89	1
DMSO (R) + Sulfolane (R)	62	54	84	4.62	1
Sulfolane (R) + Adiponitrile (R)	61	55	82	4.27	1
DMSO + Glycerine	57	56	70	2.89	1
Sulfolane + Glycerine	56	55	76	2.74	1
DMSO (R) + Sulfolane (R) + Adiponitrile (R)	61	55	83	4.06	1
DMSO (R) + Sulfolane (R) + Glycerine (R)	60	55	76	3.19	1

of pure isopropyl ether at 630 mm Hg (84 kPa); and the acetone goes to the stillpot with the extractive distillation agent. The designation R by the extractive distillation agent means that the same material was recovered and reused to show its stability in repeated operation. When the acetone-extractive distillation agent mixture taken from the stillpot is redistilled, acetone comes off in the usual way at its normal boiling point, 56°C.

The results obtained in the rectification column and presented in Table 4 show that vapor-liquid equilibrium data obtained in the Othmer still can be successfully used to demonstrate the effectiveness of extractive distillation in the separation of pure isopropyl ether from acetone.

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Solventing out of Electrolytes from their Aqueous Solution

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INTRODUCTION

It has been found that miscible organic solvents can precipitate a large fraction of some electrolytes from saturated aqueous solutions. Hull and Owens (1975) showed that KI and KIO₃ can be separated in an aqueous solution by an addition of large amount of 1,4 dioxane which precipitates KIO₃ while the KI remains in solution. A year later, Alfassi and Feldman (1976) used acetone to separate KBr and KBrO₃ to get carrier-free radiobromide. Mosseri and Alfassi (1982) studied the separation of the KX-KXO₃-KXO₄

system (when X = Cl, Br or I) by using several miscible organic solvents. Further study has been done also by Alfassi (1979).

The precipitation of salts from aqueous solution using miscible organic solvents can be named "solventing out" process by being of a similar origin as the reverse process "salting out" summarized by King (1969), where the addition of electrolytes is used to remove water from miscible organic solvents. In both cases there is a competition between the electrolytes and the organic solvents molecules on the water molecules.

This study was done to point out the possibility of using low

TABLE 1. PHYSICAL AND THERMODYNAMIC DATA FOR WATER AND LOW BOILING POINT MISCIBLE ORGANIC SOLVENT. HEAT EVAPORATION ΔH_v FROM DEAN (1979) BOILING POINTS AND DENSITY FROM WEAST (1974)

Solvent	Temp. Boiling Point (°C) at 760 mm Hg	Pres. Boiling Point (mm Hg) at 20°C*	ΔH_v kcal/mol	Density g/cm ³ at 20°C	ΔH_v kcal/L
Water	100	17.54	9.945	1.00	552.5
Acetone	56.2	184.80	6.952	0.7899	94.5
Methanol	64.96	92.68	8.240	0.7914	203.5
Propylamine	47.8	258.90		0.7173	
Isopropylamine	32.4	473.32		0.8889	

* Approximated value based on correlation from Weast (1974).

TABLE 2. FRACTION f PRECIPITATED FROM A SATURATED AQUEOUS SOLUTION OF KIO_3 BY ADDITION OF V ML MOS TO 1 ML AQUEOUS SOLUTION

V	f		
	Isopropylamine	Propylamine	Acetone
0.04	0.146	0.056	0.157
0.06	0.257	0.160	0.245
0.08	0.373	0.242	0.302
0.10	0.413	0.290	0.390
0.15	0.542	0.426	0.482
0.25	0.681	0.606	0.627
0.40	0.806	0.739	0.739
0.50	0.842	0.787	0.802
0.70	0.900	0.853	0.868
1	0.944	0.907	0.915
2	0.986	0.977	0.965
3	0.994	0.992	0.967
4	0.995	0.995	0.968
5	0.998	0.994	0.976

TABLE 3. FRACTION f PRECIPITATED FROM A SATURATED AQUEOUS SOLUTION OF K_2SO_4 BY ADDITION OF V ML MOS TO 1 ML AQUEOUS SOLUTION

V	f		
	Isopropylamine	Propylamine	Acetone
0.04	0.108	0.119	0.052
0.06	0.244	0.216	0.202
0.08	0.305	0.288	0.264
0.10	0.406	0.363	0.331
0.15	0.512	0.494	0.482
0.25	0.656	0.677	0.681
0.40	0.788	0.840	0.807
0.50	0.895	0.880	0.870
0.70	0.950	0.919	0.915
1	0.961	0.960	0.952
2	0.976	0.978	0.977
3	0.982	0.979	0.987
4	0.988	0.981	0.990
5	0.992	0.982	0.990

boiling points miscible organic solvents for the electrolytes precipitation which will enable the recovery of these electrolytes from their aqueous solution using relatively inexpensive low-temperature heat source (such as solar energy) or by applying vacuum without heating; i.e., the heat will come from the ambient environment. This is preferable to using more expensive higher-temperature heat sources for the removal of the water from the electrolytes solutions by boiling.

Various low boiling points miscible organic solvents are available for the precipitation process, such as methanol, acetone, propylamine and isopropylamine. Appropriate physical data for those solvents are given in Table 1. It was checked that none of those solvents azeotropes with water at atmospheric pressure.

TABLE 4. V_c AND K VALUES FOR K_2SO_4 AND KIO_3 USING PROPYLAMINE, ISOPROPYLAMINE AND ACETONE AS MOS

MOS	Propylamine		Isopropylamine		Acetone	
	K_2SO_4	KIO_3	K_2SO_4	KIO_3	K_2SO_4	KIO_3
K	0.304	0.301	0.304	0.293	0.326	0.261
V_c	0.029	0.036	0.029	0.024	0.035	0.023

DATA PRESENTATION AND DISCUSSION

Data for the precipitation of two electrolytes by three low boiling point miscible organic solvents (MOS) are given in Tables 2 and 3. These tables give the fraction f of KIO_3 and K_2SO_4 , respectively,

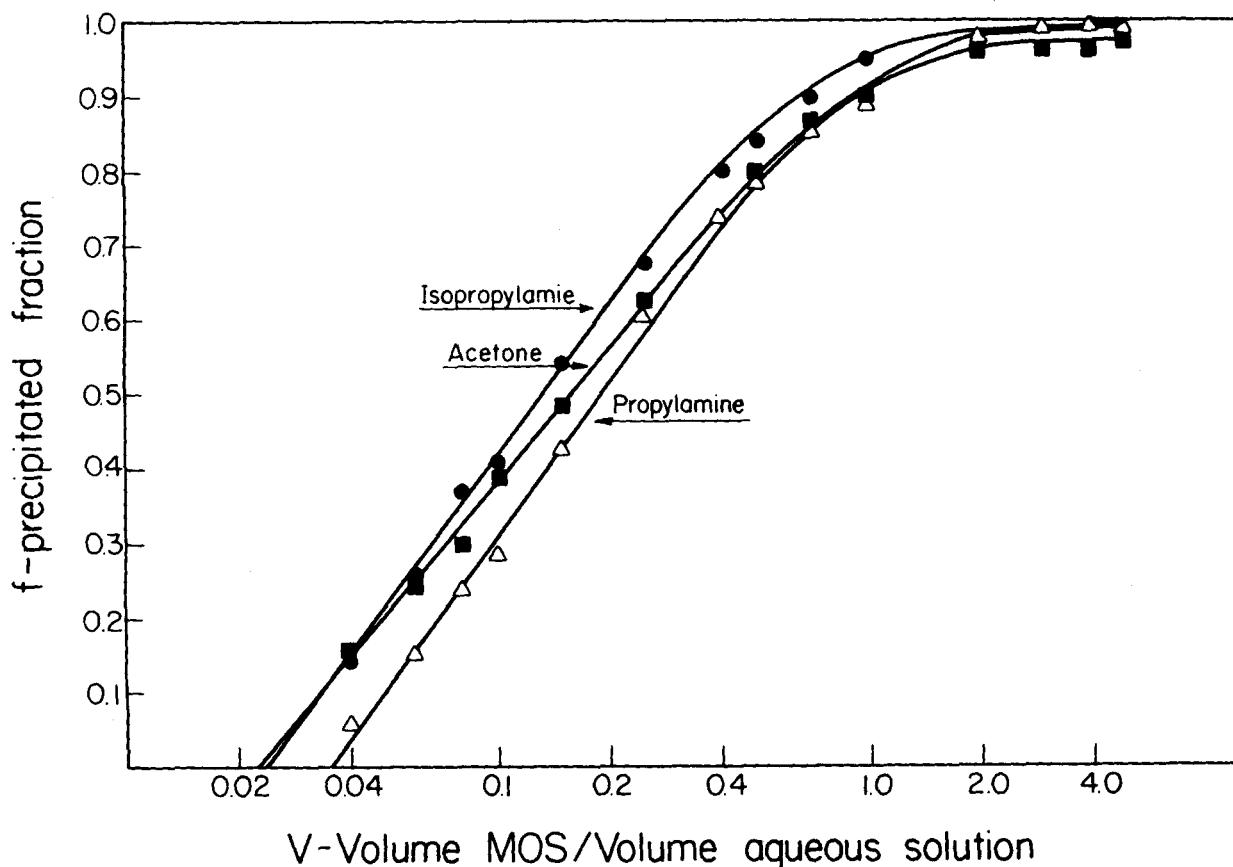


Figure 1. Dependence of the precipitated fraction of KIO_3 on the added volume of MOS.

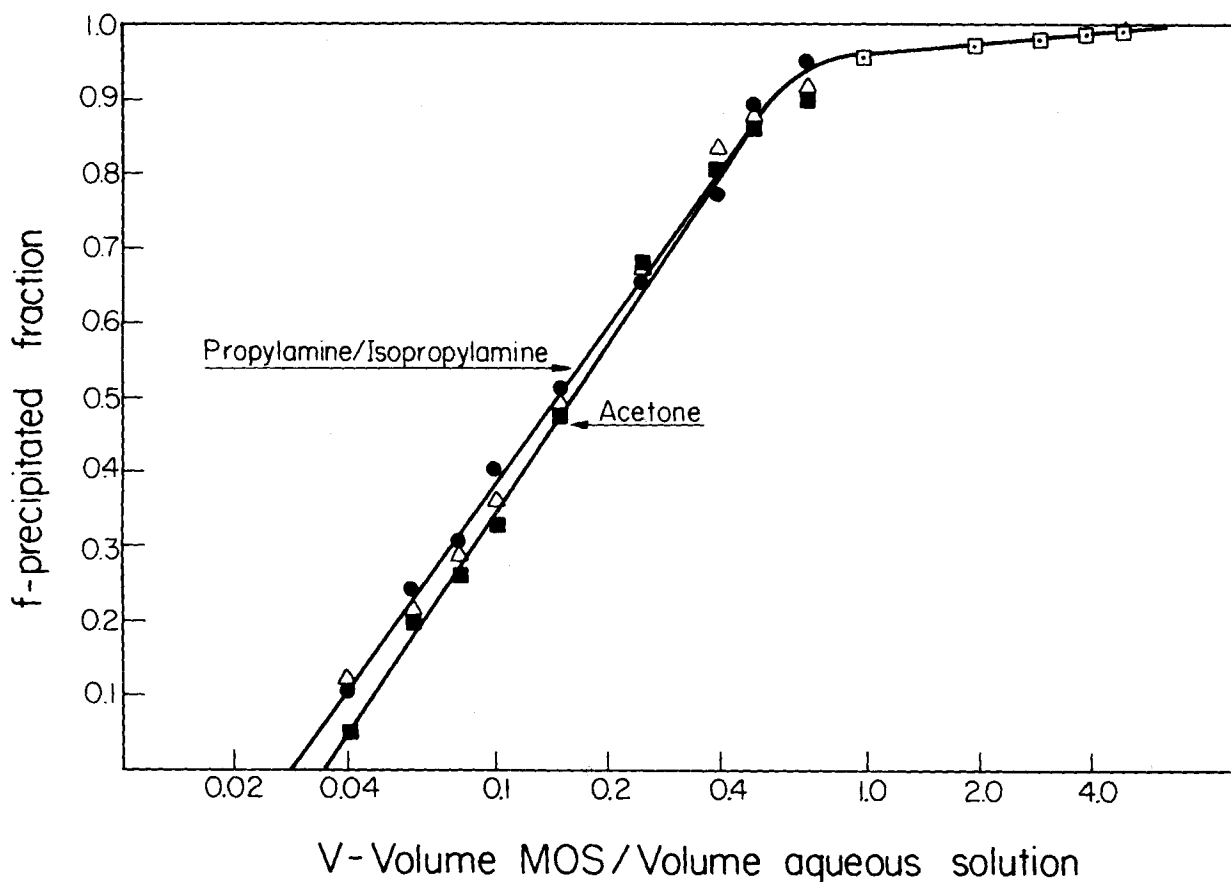


Figure 2. Dependence of the precipitated fraction of K_2SO_4 on the added volume of MOS.

which are precipitated from 1 mL saturated aqueous solution by a V mL of MOS. Figures 1 and 2 show that, for not too high values of f ($f \sim 0.8-0.9$), f can be described quite accurately by:

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

where V_c can be understood as the minimal value of V which is required to precipitate at all and k is the "solventing out" constant. For higher value of f , f increases more slowly with V . It is reasonable that for high enough V , f will start to decrease, reaching zero for very high values of V , as the electrolytes might have a small solubility also in an organic solvent. These figures and tables clearly show that, from the solvents studied, the best one regarding precipitating is isopropyl amine. It is also the best one regarding its lowest boiling point which enable its recovery very easy under reduced pressure.

To summarize, the use of isopropyl amine can reduce considerably the cost of recovery of K_2SO_4 and KIO_3 from their aqueous solutions. For example, the addition of 0.7 L of isopropyl amine to 1 L of saturated aqueous solution of K_2SO_4 precipitate 95% of the salt. To obtain 99% of the salt, 3 to 4 L of isopropyl amine are required. However, the recovery of 4 L of isopropylamine by evaporation (b.p. = $33^\circ C$) is less expensive than the removal of 1 L of water.

It should be noted that the discussed method is not a general one, although it can be used for many electrolytes. It will be applicable only for electrolytes in which a large fraction of the salt is precipitated by a relatively small volume of organic solvent.

NOTATION

- f = precipitated fraction
- k = solventing out" constant
- V = MOS's volume per 1 mL saturated aqueous solution
- V_c = minimal value of V which is required to precipitate at all

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