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The Separation of Electrolytes in Aqueous Solution by Miscible Organic Solvents

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Abstract

The feasibility of using a miscible organic solvent to precipitate electrolytes from aqueous solutions was studied. Two electrolytes in an aqueous solution can be separated if their precipitating constants λ's fulfill the requirements $\lambda_2 > \lambda_1$, $\lambda_1 < 2.5$, $\lambda_2 > 2.0$.

INTRODUCTION

Electrolytes have been used to remove organic compounds from water for many years—ever since the Middle Ages—in a process called "salting out." A layer rich in ethanol may be "salted out" from ethanol–water mixtures by the addition of potassium carbonate. The discovery of this fact is usually attributed (*1*) to the wandering alchemist and missionary Raymond Lully (ca. 1232–1315) who described a method of preparing almost pure ethanol from wine. In biochemistry, "salting out" is used quite frequently to isolate purified enzymes, mainly by addition of ammonium sulfate (*2*). A common explanation for this effect is that the water molecules which surround the ions are not available for the solution of the molecules of the nonelectrolytes.

This explanation also indicates the existence of the opposite process. The addition of polar organic molecules to aqueous solutions will lead to capture of part of the water molecules and subsequently reduces the solubility of electrolytes. Until recently not much work had been done

on this reverse process, i.e., the precipitation of salts from aqueous solution by the addition of *miscible* organic solvents (MOS), which can be called "solventing out." Hull and Owens (*3*) showed that KI and KIO_3 can be separated quite efficiently in an aqueous solution by the addition of large amounts of 1,4-dioxane which precipitated the KIO_3 while the KI remained in solution. Alfassi and Feldman (*4*) used acetone to separate KBr and $KBrO_3$ in order to get carrier-free radiobromine. This paper discusses the possibility of using the MOS to precipitate and separate various electrolytes.

PRECIPITATION OF A SINGLE ELECTROLYTE

Alfassi and Weiss (*5*) have found that the solubility of an electrolyte in a homogeneous mixture of water and MOS (with S in milligrams per milliliter) can be described by

$$S = S^w \exp(-\lambda f) \tag{1}$$

where S^w is the solubility in pure water, f is the volume fraction (neglecting the volume of mixing), and λ is a constant characteristic of the salt and the solvent termed "the precipitating constant." Table 1 gives the experimental results (*5*) of S^w and λ, obtained by least squares regression of

$$\ln S = \ln S^w - \lambda f$$

Most of these results were calculated from the solubilities of 0 to 80% (volume) of MOS, except a few cases where "salting out" of the two solvents (phase separation) already occurs at 60%. Above 80% MOS, the solubility is usually quite small and the measurements are not accurate enough to be useful.

Neglecting the change of volume with mixing, the amount of salt precipitated by the addition of V ml of MOS to 1 ml of saturated aqueous solution is given by

$$P = S^w(1 - [V + 1]\exp[-\lambda V/(V + 1)]) \tag{2}$$

Equation (2) is a maximum type function. Increasing the volume of the added MOS, V, always leads to a smaller solubility per unit volume, but a larger volume of solution. By differentiating Eq. (2) and equating to zero, it can be seen that P has a maximum for

$$V = \lambda - 1 \tag{3}$$

TABLE 1

Least Squares Parameters of Eq. (1) for Several Parameters

Salt	Solvent	ln S^w	λ
K_2SO_4	Acetone	6.87 ± 0.12	4.49 ± 0.18
	Tetrahydrofuran	6.87 ± 0.24	4.95 ± 0.35
	Methanol	6.75 ± 0.19	3.28 ± 0.28
Na_2SO_4	Dioxane	7.96 ± 0.27	7.60 ± 0.38
	Acetonitrile	7.60 ± 0.15	3.14 ± 0.22
	Acetone	7.79 ± 0.18	5.73 ± 0.27
	Methanol	7.82 ± 0.17	4.41 ± 0.24
Na_2S	Methanol	8.15 ± 0.04	0.300 ± 0.079
Na_2SO_3	Acetone	8.23 ± 0.17	6.60 ± 0.24
	Methanol	8.07 ± 0.06	5.14 ± 0.12
$NaClO_3$	Acetonitrile	8.82 ± 0.01	0.836 ± 0.062
	Dioxane	8.88 ± 0.06	1.45 ± 0.09
NaCl	Dioxane	8.04 ± 0.02	1.67 ± 0.07
KBr	Acetonitrile	8.58 ± 0.02	0.821 ± 0.087
$KBrO_3$	Acetonitrile	6.70 ± 0.08	2.63 ± 0.11
	Dioxane	6.58 ± 0.13	4.22 ± 0.18
$NaNO_2$	Dioxane	8.69 ± 0.04	1.13 ± 0.13
KI	Acetonitrile	9.21 ± 0.05	0.590 ± 0.103
	Dioxane	9.20 ± 0.03	0.989 ± 0.061
KIO_4	Acetonitrile	5.17 ● 0.02	0.639 ± 0.024
	Dioxane	5.15 ± 0.03	1.05 ± 0.05
$MgSO_4$	Methanol	8.16 ± 0.04	0.902 ± 0.137

The maximum fraction of salt that can be precipitated is given by

$$P_{max} = 1 - \lambda \exp(1 - \lambda) \tag{4}$$

One important conclusion of Eqs. (3) and (4) is that if λ is smaller or equal to unity for a system salt–MOS, no precipitation occurs when the MOS is added to the saturated aqueous solution. In other words, for $\lambda \leq 1$, every positive V will lead to negative value of P in Eq. (2).

Table 2 gives the maximum fractions of electrolyte that can be precipitated for various precipitating constants λ.

TABLE 2

Maximum Fraction of Electrolyte That Can Be Precipitated ($V = \lambda - 1$)

Precipitating constant, λ	Maximum fraction, P_{max}
1.0	0
1.2	0.018
1.5	0.090
1.8	0.191
2.0	0.268
2.5	0.442
3.0	0.594
3.5	0.713
4	0.801
5	0.908
6	0.960
7	0.983
8	0.993
9	0.997
10	0.999

SEPARATION OF TWO ELECTROLYTES

Two salts in aqueous solutions might be separated by the addition of MOS if the two electrolytes have different precipitating constants for this MOS, $\lambda_2 > \lambda_1$. The best situation is when one of the electrolytes—the one with the lower precipitating constant—is not precipitated at all. This happens either if λ_1 is smaller than 1 or for $\lambda_1 > 1$ if the volume of MOS is large enough, since P in Eq. (2) becomes negative for large enough V. Assuming that the solubility of one salt is not influenced much by the presence of the other salt, Table 3 gives the minimum volume of MOS, V, required so that the addition of 1 ml of saturated aqueous solution will not lead to precipitation. In this case of $\lambda > 1$, it is preferable to add the aqueous solution to the MOS to assure no precipitation of the electrolyte instead of adding the MOS to the aqueous solution which would first cause precipitation and then redissolution. As can be seen from Table 3, it might be practical to separate the two salts only if the smaller precipitating constant is less than about 2.5, since otherwise a too large volume of MOS is required. The condition for the larger λ is that it has to be larger than 2.0 because, if it is less than 1, none of the salts will be precipitated, and for $1.0 < \lambda_2 < 2.0$, less than 25% of the second electrolyte will be precipitated.

TABLE 3

Minimum Value of V to Obtain $P < 0$ in Eq. (2) for Various Precipitating Constants

Precipitating constant, λ	Volume, V (ml)
1.1	0.2
1.2	0.46
1.3	0.74
1.4	1.05
1.5	1.40
1.6	1.80
1.7	2.24
1.8	2.74
1.9	3.30
2.0	3.93
2.2	5.40
2.4	7.24
2.6	9.52
2.8	13
3	16
3.2	21
3.4	26
4.0	50

In the case of two salts with λ_1 and λ_2, $\lambda_2 > \lambda_1$ and $\lambda_1, \lambda_2 > 3$, both salts will be precipitated unless we use an unreasonably large volume of MOS. The precipitate will be enriched in the salt of λ_2, whereas the solution will be enriched in the salt with precipitating constant λ_1. The enrichment factor of the precipitate is given by

$$E_p = \frac{1 - (V + 1) \exp [-\lambda_2 V/(V + 1)]}{1 - (V + 1) \exp [-\lambda_1 V/(V + 1)]} \tag{5}$$

and the enrichment factor of the solution is given by

$$E_S = \exp [(\lambda_2 - \lambda_1)V/(V + 1)] \tag{6}$$

The enrichment of the solution is an increasing monotonous function of V whereas E_P is a function with minimum for $V = \lambda_1 - 1$.

For very small V, so that $V/(V + 1) \ll 1/\lambda_2$,

$$E_p = \frac{\lambda_2 - 1}{\lambda_1 - 1} \tag{7}$$

whereas the minimum value for E_P ($V = \lambda_1 - 1$) is

$$E_p = \frac{1 - \lambda_1 \exp(\lambda_2/\lambda_1 - \lambda_2)}{1 - \lambda_1 \exp(1 - \lambda_1)} \quad (8)$$

Quite high enrichment can be obtained for small V if $\lambda_2 \gg \lambda_1$, but only a small fraction of the electrolyte is precipitated. Table 4 gives an example of the fractions precipitated for $\lambda_2 = 8$ and $\lambda_1 = 4$, and the enrichment obtained in the precipitate.

It is quite clear that it is preferable when one of the electrolytes is not precipitated at all, i.e., $\lambda_1 < 2.5$. As can be seen from Table 1, the value of λ varies with the organic solvent; usually less polar solvents (lower dielectric constants) have higher λ's. Thus, if λ_1 is too large for one MOS, it is better to find another MOS with a higher dielectric constant.

The preceding treatment was done for homogeneous mixtures. Highly charged ions have high "salting out" coefficients (*1*, *6*) and, as a consequence, it is impossible to obtain homogeneous solutions of MOS–

TABLE 4

Fractions of Electrolytes Precipitated by Addition of V ml of MOS to 1 ml of Saturated Aqueous Solution of Two Electrolytes with $\lambda_2 = 8$ and $\lambda_1 = 4$, Respectively

V (ml)	Precipitated fraction of electrolyte with $\lambda_2 = 8$	Precipitated fraction of electrolyte with $\lambda_1 = 4$	Enrichment in the precipitate
0.01	.0669	.0292	2.29
0.02	.128	.0569	2.25
0.03	.184	.0833	2.21
0.04	.235	.108	2.17
0.05	.283	.132	2.14
0.08	.403	.176	2.05
0.1	.468	.235	1.99
0.2	.684	.384	1.78
0.4	.858	.553	1.55
0.6	.920	.643	1.43
1.0	.937	.673	1.39
5.0	.982	.786	1.26 (minimum)
10.0	.992	.710	1.40
15.0	.991	.624	1.59
25.0	.988	.444	2.22
35.0	.985	.263	3.74
45.0	.982	.081	12.13
50.0	.980	Not precipitated	

water–triple charged cations (with high concentrations of MOS). This treatment is especially appropriate for singly charged cations.

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