The Unusual Behavior of Extractive Distillation—Reversing the Volatility of the Acetone–Isopropyl Ether System

Extractive distillation can not only negate azeotropes to produce pure compounds by rectification but in some cases will reverse the volatility and bring out the less volatile component before the more volatile component. As an example, isopropyl ether, b.p. = 68.5°C, was distilled off as the overhead from mixtures with acetone, b.p. = 56.2°C, leaving the acetone in the stillpot and column until all the isopropyl ether was removed. This reversal phenomenon does not occur in the isopropyl ether-methyl ethyl ketone system, although the azeotrope is negated.

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INTRODUCTION

Many years ago Buell and Boatright (1947) noted that, when used as an extractive distillation agent, furfural would reverse the volatility of cis-butene-2 and trans-butene-2 relative to 1,3-butadiene. More recently, during the investigation of mixtures of organic compounds as extractive distillation agents, we noted that certain mixtures containing entirely different classes of compounds exhibited this phenomenon (Berg, 1982). We found that when using azeotrope, we brought out the less volatile component, isopropyl ether, as overhead product, leaving the more volatile component, acetone, in the stillpot with the extractive agent, Table 1. We have also found that some extractive distillation agents will bring out overhead methanol (b.p. 64.5°C) from methyl acetate (b.p. 56.3°C) and methanol from acetone (b.p. 56.1°C) from their binary azeotropes. When operated as a continuous rectification, the isopropyl ether comes off as pure overhead product at 63.4°C at 630 mm Hg. The acetone, in spite of its 56°C normal boiling point, stays with the extractive agent, although the temperature in the stillpot is 115–170°C.

DISCUSSION

In order to understand better this strange phenomenon of bringing the less volatile compound off as overhead from the more volatile compound, we made a series of runs in the manner of a batch distillation. Extractive distillation is invariably applied to continuous rectification, and so probably for this reason very little research has been done on the effect of extractive distillation on batch distillations. As the following data show, it appears to be a good way to learn what is going on in an extractive distillation.

Table 2 and Figure 1 show the data obtained when the acetone-isopropyl ether azeotrope is subjected to a batch-extractive distillation with dimethylsulfoxide (DMSO) as the extractive agent.

TABLE 1. PROPERTIES OF ISOPROPYL ETHER WITH ACETONE AND METHYL ETHYL KETONE

	b.p., °C	Azeotrope Composition
Isopropyl ether	68.5	
Acetone	56.2	
Methyl ethyl ketone	79.6	
Isopropyl ether-acetone azeotrope	54.2	39% IPE
Isopropyl ether-methyl ethyl ketone azeotrope	60.0	88% IPE

All data were obtained in a glass perforated plate column that calibrated 4.5 theoretical plates with ethylbenzene-*m*-xylene as the test mixture. When a mixture containing 71.4% isopropyl ether is rectified in the usual manner, the distillate comes as shown by mixture 1 in Figure 1 and Table 2. The azeotrope comes off until the acetone is exhausted and then the temperature rises as the

TABLE 2. THE COMPOSITIONS AND TEMPERATURES VERSUS TIME FOR THE MIXTURES OF ISOPROPYL ETHER AND ACETONE

Time (min)	Temp. Overhead	(°C) Bottoms	Composition (wt. %) Isopropyl Ether	In Overhead Acetone
Mixture 1: Isopropyl Ether (225 g) + Acetone (90 g) Solvent: None				
40	48.4	51.8	45.4	54.6
160	49.2	58.6	46.9	53.1
180	50.0	61.0	49.9	50.1
190	52.0	63.2	65.9	34.1
205	58.2	64.6	76.1	23.9
210	60.0	64.8	88.8	11.2
220	62.2	65.2	97.4	2.6
240	62.6	65.4	98.9	1.1
305	63.0	70.8	100.0	0.0
Mixture 2: Isopropyl Ether (30 g) + Acetone (70 g) Solvent: DMSO				
13	63.4	115.2	99.7	0.3
20	63.2	121.8	99.5	0.5
24	63.0	128.2	98.9	1.1
37	60.0	140.2	91.8	8.2
43	56.2	145.6	21.5	78.5
45	58.0	147.6	8.9	91.1
47	58.6	151.2	3.9	96.1
50	59.2	157.4	0.8	99.2
95	59.4	184.4	0.0	100.0
Mixture 3: Isopropyl Ether (70 g) + Acetone (30 g) Solvent: DMSO				
35	63.6	141.6	99.4	0.6
65	63.0	169.8	97.1	2.9
70	60.0	172.6	89.9	10.1
77	57.6	176.0	27.5	72.5
83	60.0	179.2	3.7	96.3
95	60.2	182.4	0.1	99.9
100	60.4	185.4	0.0	100.0

The solvent was added at 52 ± 2°C and at the rate of 20 ml/min.
The reflux ratio was 2.5:1.
The first drop of distillate was taken at time zero.

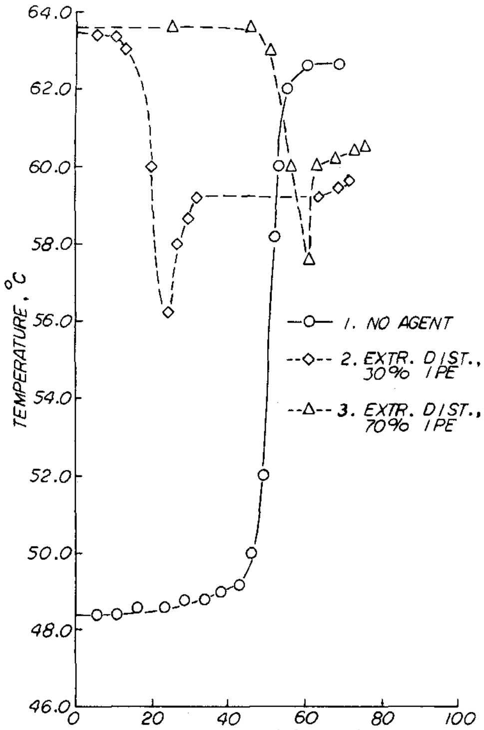

Figure 1. Weight percent of distillate versus temperature at 630 mm Hg for isopropyl ether-acetone using DMSO.

overhead composition changes to isopropyl ether. Just a standard distillation curve.

Next we rectified a mixture containing 30% isopropyl ether as a batch distillation with DMSO as the extractive agent. The DMSO at 60°C is pumped into the top of the column just below the Corad head at a rate approximately equal to the total boilup rate. Since 30% is less isopropyl ether than required by the binary azeotrope, the isopropyl ether should exhaust first. How to explain the strange behavior exhibited by this distillation curve? This seems to show that isopropyl ether comes off as long as there is any isopropyl ether in the stillpot. The separation taking place appears to be between isopropyl ether and the azeotrope. When the isopropyl ether disappears from the stillpot, the separation becomes between the azeotrope and acetone and the overhead temperature and composition drop to that of the azeotrope. However, since the isopropyl ether has been exhausted in the stillpot, the azeotrope cannot be replenished and is pushed out by the acetone. The temperature and composition indicate that acetone then comes off until it is exhausted and some extractive distillation agent begins to appear in the overhead.

In mixture 3, we have a similar run, except that here the isopropyl ether is 70%, greater than its quantity in the azeotrope. This time isopropyl ether comes off until the isopropyl ether in the stillpot exhausts. The separation appears to be between the isopropyl ether and the azeotrope. However, isopropyl ether exhausts first in the stillpot, and since we are separating isopropyl ether from the azeotrope, the azeotrope fails to form when there is no more isopropyl ether in the stillpot. The acetone pushes out the last traces of the isopropyl ether, and the analysis in Table 2 shows the pure acetone coming off at the end of the distillation. We believe that this is the first time that distillation curves such as mixtures 2 and 3 have ever been produced.

Isopropyl ether forms an azeotrope with another ketone, methyl ethyl ketone. In this case, however, isopropyl ether is normally the more volatile component. Table 3 and Figure 2 show what happens when these two are rectified in a batch column by extractive distillation. The column and the extractive agent are the same as

TABLE 3. THE COMPOSITIONS AND TEMPERATURES VERSUS TIME FOR THE MIXTURES OF ISOPROPYL ETHER AND METHYL ETHYL KETONE

Time (min)	Temp. Overhead	(°C) Bottoms	Composition (wt. %) Isopropyl Ether	In Overhead MEK
	Mixture 4: Isopropyl ether (90 g) + MEK (225 g) Solvent: None			
30	62.2	69.0	71.1	28.9
66	62.4	70.6	69.9	30.1
78	62.6	71.0	68.1	31.9
95	63.0	71.8	65.0	35.0
116	65.0	72.8	52.8	47.2
127	67.2	73.2	41.4	58.6
140	69.0	73.6	30.2	69.8
150	70.8	73.8	19.1	80.9
160	71.8	74.0	12.8	87.2
175	72.6	74.4	5.4	94.6
200	73.2	74.6	1.9	98.1
225	73.2	74.6	0.3	99.7
	Mixture 5: Isopropyl Ether (30 g) + MEK (70 g) Solvent: DMSO			
12	63.8	144.0	100.0	0.0
27	64.6	157.6	88.9	11.1
29	67.6	158.2	76.0	24.0
32	73.0	161.0	44.1	55.9
44	82.2	166.6	2.0	98.0
58	83.2	169.6	0.5	99.5
68	83.8	174.6	0.0	100.0
	Mixture 6: Isopropyl Ether (70 g) + MEK (30 g) Solvent: DMSO			
55	63.8	174.2	100.0	0.0
60	64.8	176.2	94.9	5.1
62	72.2	178.2	55.9	44.1
65	80.8	180.2	9.3	90.7
70	83.2	182.8	1.1	98.9
73	83.6	183.6	0.7	99.3
78	84.2	185.0	0.0	100.0

The solvent was added at 58 ± 2°C and at the rate of 20 ml/min.
The reflux ratio was 25:1.
The first drop of distillate was taken at time zero.

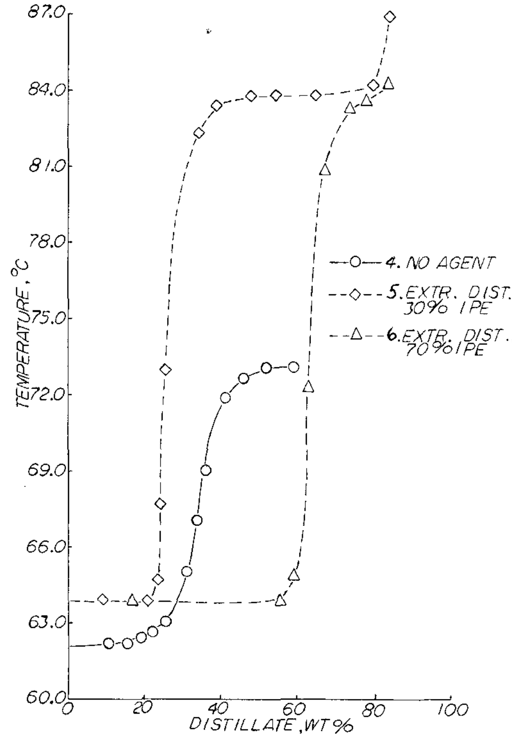

Figure 2. Weight percent of distillate versus temperature at 630 mm Hg for isopropyl ether-methyl ethyl ketone using DMSO.

employed in the acetone-isopropyl ether system. When no extractive agent is employed, mixture 4, the isopropyl ether-methyl ethyl ketone azeotrope comes off until the isopropyl ether exhausts and then the remaining methyl ethyl ketone comes off at its normal boiling point. In mixtures 5 and 6, the isopropyl ether-methyl ethyl ketone azeotrope appears to be negated by the extractive distillation agent (DMSO) and the more volatile isopropyl ether comes off until it exhausts in the stillpot. The temperature rises and the methyl ethyl ketone is produced in about 100% purity. Why is the distillation curve for mixture 4 so poor when compared with those for mixtures 5 and 6? Because the column contains only 4.5 theoretical plates and the separation of the azeotrope frm methyl ethyl ketone is fairly difficult with so few plates. With extractive distillation, the efficacy is greatly improved, which these curves show dramatically.

We have shown that sometimes, but not always, extractive distillation can reverse the volatility of two compounds and bring out overhead what is normally the less volatile compound. The more volatile compound remains in the column and stillpot at a temperature much above its normal boiling point.

LITERATURE CITED

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The Separation of Electrolytes by a "Solventing-Out" Process

The analytic expression found before for the precipitated function of an electrolyte as a function of the added volume of a miscle organic solvent (MOS) to a saturated aqueous solution was used to discuss the required conditions for separation of two electrolytes.

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INTRODUCTION

The "salting-out" process—i.e., the separation of organic solvents from solution by the addition of certain electrolytes—is a novel process that appears in classical textbooks (e.g., King, 1969). The use of the reverse process that is due to the same phenomenon, the "solventing-out" process, in which the addition of a miscible organic solvent (MOS) to aqueous solution of an electrolyte leads to the precipitation of an electrolyte, is less known. Both processes are consequences of the competition between the electrolyte and the organic solvent on the water molecules.

This paper deals with the exploitation of this phenomenon for separating a system of two water-soluble electrolytes. The addition of MOS to saturated aqueous solution of two electrolytes might lead to the precipitation of only one electrolyte, or at least separation of the original mixture into two functions, each enriched with another electrolyte.

PRECIPITATION FROM SOLUTION OF ONE ELECTROLYTE

Alfassi and Mosseri (1984) and Mosseri and Alfassi (1983) found that when V ml of MOS was added to 1 ml of saturated aqueous solution of an electrolyte the fraction of the electrolyte that was precipitated, f, obeyed the relation

$$f = k\ln(V/V_c) \qquad (1)$$

V_c can be defined as the minimum value of V required to cause any precipitation, and k is the precipitation constant.

Equation 1 will be obeyed only for a certain range of V, for the following reasons: (1) Eq. 1 has no meaning for $V < V_c$ since negative f values have no physical meaning; (2) Eq. 1 describes f as a monotonous increasing function V without any limitation, whereas physically f cannot be larger than 1, since $f = 1$ already means the precipitation of all the solute. *It was found that Eq. 1* holds for f up to 0.8–0.9. Above this value there is a slower increase. In many cases f will not reach unity, since the electrolyte also has a small solubility in the pure organic solvent. Moreover, it is reasonable to anticipate that for larger V, there will be a decrease of f with increasing V due to the larger volumes of the solvent available for dissolution, as discussed by Alfassi (1979).

If there is a system consisting of an aqueous solution saturated with two electrolytes A and B, the two electrolytes can be separated in one step if the condition $V_{c_A} \gg V_{c_B}$ is fulfilled. In this case the amount of MOS required to precipitate electrolyte A is much larger than that needed for precipitation of B. Less than V_{c_A} will be sufficient in this case to precipitate practically all B. The ideal case will be when $V_{c_A} = \infty$, i.e., where no precipitation of A occurs regardless of how large V is. Almost all B will be precipitated while A remains in the solution. A system like this is the system of KI and KIO_3. It was found that none of the solvents studied (acetone, acetonitrile, propylamine, and isopropylamine) was able to precipitate KI from aqueous solution, while more than 99.5% of the KIO_3 can be precipitated with isopropylamine or propylamine (Mosseri and Alfassi, 1983).

MULTISTAGE PROCESS FOR SEPARATION OF ELECTROLYTES

Although we describe in the previous section how separation can be done in one step, this procedure wastes both the organic solvent and the energy to remove the MOS for recovery of the electrolyte. Great savings in MOS and energy can be obtained by multistep separation. In order to precipitate 99.5% of KIO_3 we need 4 ml of