

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 from 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 dis-

tillation 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.

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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 miscible organic solvent (MOS) to a saturated aqueous solution was used to discuss the required conditions for separation of two electrolytes.

Z. B. ALFASSI

Department of Nuclear Engineering  
 Ben-Gurion University of the Negev  
 Beer Sheva, Israel

### 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

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

$V_c$  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  $V_{cA} \gg V_{cB}$  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  $V_{cA}$  will be sufficient in this case to precipitate practically all  $B$ . The ideal case will be when  $V_{cA} = \infty$ , 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

isopropylamine for each milliliter of aqueous solution, while for precipitating 90% of  $\text{KIO}_3$  only 0.7 ml of isopropylamine is required (Mosseri and Alfassi, 1983). Thus, the following multistage process will be more economical.

Let us assume that we will add  $V$  ml of MOS to 1 ml of the aqueous solution. The precipitated fraction,  $f$ , of the precipitable electrolyte  $B$  is given by Eq. 1 as  $f = k \ln V/V_c$ . The next step will be distillation of MOS followed by evaporation of  $f$  ml of the aqueous solution, which will lead to precipitation of fraction  $f$  of the other electrolyte,  $A$ , leaving  $(1 - f)$  ml of solution similar to the mother liquor, which can be treated again or returned to the original solution. The total volume of MOS required to precipitate all  $B$ ,  $V_{\text{total}}$ , is given by

$$V_{\text{total}} = V + (1 - f) \cdot V + (1 - f)^2 V + \dots = V/f \quad (2)$$

Substituting Eq. 1 for  $f$  gives

$$V_{\text{total}} = V/(k \ln V/V_c) \quad (3)$$

Differentiating  $V_{\text{total}}$  with respect to  $V$  and equating to zero lead to  $\ln V/V_c = 1$ , or

$$V_{\text{min}} = eV_c \quad (4)$$

where  $e$  is the base of the natural logarithm and  $V_{\text{min}}$  is the amount added in each step per 1 ml of aqueous solution in order to assure minimum use of MOS; the amount precipitated in each step is  $k$ . Thus, for precipitation of  $\text{KIO}_3$  with isopropylamine where  $V_c = 0.028$  and  $k = 0.251$ , it will be most economical to add in each step 0.076 ml of isopropylamine per 1 ml of aqueous solution, which will lead to precipitation of 25% of the  $\text{KIO}_3$ .

In the case  $V_{cA} \gg V_{cB}$  we saw that the one-step process is feasible, although less economical than a multistep process. However, if the system fulfills only  $V_{cA} > V_{cB}$  such that 99% precipitation of  $B$  already involves some precipitation of  $A$ , then only multistep separation is possible. Any  $V$  that fulfills  $V_{cA} > V_{cB}$  may be used in each step. If  $V_{cA} > e \cdot V_{cB}$ , it goes back to the situation described in the previous section where the same multistep process was suggested also for  $V_{cA} \gg V_{cB}$ . A characteristic case can be the separation of  $\text{NaCl}$  and  $\text{NaBr}$  by the addition of acetone, since  $V_c$ ,

$\text{NaCl} = 0.051$  and  $V_{c,\text{NaBr}} = 1.649$  (Alfassi and Ata, 1983).

In the case

$$V_{cA} \simeq V_{cB} \quad \text{but} \quad k_B > k_A$$

the separation can be done in a multistep process, since the precipitation with MOS will lead to precipitated fraction enriched with respect to  $B$ , while the fraction remaining in solution is enriched with respect to  $A$ .

## NOTATION

- $f$  = fraction of the electrolyte precipitated by MOS
- $k$  = solvating-out constant
- $V$  = MOS's volume per 1 ml aqueous solution
- $V_c$  = minimal value of  $V$  that brings to precipitation all of the electrolyte
- $V_{\text{total}}$  = total volume of MOS required to precipitate all the electrolyte in 1 ml aqueous solution in a multistep process
- $V_{\text{min}}$  = minimal value of  $V_{\text{total}}$ .

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# Direct Contact Heat Transfer with Change of Phase: Theoretical Model Incorporating Sloshing Effects

G. K. RAINA and

P. D. GROVER

Department of Chemical Engineering  
Regional Engineering College  
Hazratbal, Srinagar  
Kashmir, India

Heat transfer to dispersed liquid drops vaporizing in a continuous immiscible and low volatile liquid medium has extensive applicability in a number of engineering fields. One of the pressing problems in recent years is the application to power generation utilizing geothermal energy (Boehm et al., 1974) by means of binary cycles of refrigerants. Another representative application is the saline and wastewater treatments in which such solutions are separated into pure ice crystals and residual enriched liquids.

The objective of the present work is to extend the authors' (1982) previous theoretical analysis by considering the effect of sloshing. This effect is nonexistent for the case of small drops (less than 2 mm dia.), evaporating through high-viscosity continuous liquid phase. For the case of small drops, the rigid drop model is suitable, and the equation for the heat transfer coefficient is given by the authors (1982) as

$$h_c = 0.314 \frac{K_c}{R} \left[ \frac{UR}{\alpha_c} \right]^{1/3} \left[ (\beta - \gamma) - \frac{1}{2} (\sin 2\beta - \sin 2\gamma) \right]^{2/3} \quad (1)$$

Correspondence concerning this paper should be addressed to G. K. Raina. P. D. Grover is currently at the Department of Chemical Engineering, IIT, New Delhi, India.