

Minimum Reflux in Liquid–Liquid Extraction

Santanu Bandyopadhyay^a and Calin-Cristian Cormos^b

^a*Energy Systems Engineering, Indian Institute of Technology, Bombay, Powai, Mumbai 400 076, India, E-mail: santanu@me.iitb.ac.in*

^b*Department of Chemical Engineering, Faculty of Chemistry and Chemical Engineering, University "Babeş-Bolyai", Arany Janos 11, Cluj-Napoca 400028, Romania, E-mail: cormos@chem.ubbcluj.ro*

Abstract

In a simple countercurrent arrangement of different stages of liquid–liquid extraction operation, the richest extract leaving the operation is in equilibrium with the feed. However, by using reflux it is possible to enrich the extract further. A simple counter current liquid–liquid extraction operation with reflux is analogous in its essentials to distillation. In this paper, the method based on Invariant Rectifying-Stripping (IRS) curves, originally proposed to calculate minimum reflux and minimum energy requirement in distillation, has been extended to liquid–liquid extraction. The equivalent IRS curves for a ternary liquid–liquid extraction predicts the feed location in the counter current process. It also predicts the minimum reflux requirement for a given separation and minimum amount of solvent required.

Keywords: liquid extraction, IRS curves, feed location, minimum solvent.

1. Introduction

Liquid–liquid extraction is a separation process that takes advantage of the distribution of a substance between two insoluble liquids phases [1]. Feed to be separated is mixed with extracting solvent to produce a solvent-rich phase, called extract, and a solvent-lean phase, called raffinate. In a simple countercurrent arrangement of different stages of liquid–liquid extraction

operation, the richest extract leaving the operation is in equilibrium with the feed. However, by using reflux it is possible to enrich the extract further [1,2]. Advantages and applications of liquid–liquid extraction vis-à-vis other separation methods are discussed in Treybal [3]. A simple counter current liquid–liquid extraction operation with reflux is analogous in its essentials to distillation [1]. A minimum amount of extracting solvent is required to achieve desired separation. Similar to distillation, this corresponds to minimum reflux required for separation. Minimum reflux for a ternary system can be calculated on the triangular diagram [1]. Because of crowding on the triangular diagram Janecke coordinates are preferred. This is equivalent to rectangular diagram of Ponchon-Savarit method for binary distillation.

Bandyopadhyay et al. [4] introduced a novel pair of temperature–enthalpy curves, known as the Invariant Rectifying-Stripping (IRS) curves, to address thermodynamic analysis and energy conservation opportunities in distillation processes. The IRS curves are invariant to the column configuration (i.e., feed location in the column and number of stages) and depend only on sharpness of separation as well as operating pressure of the column. They are useful for setting quantitative targets such as minimum energy requirement (for condenser and reboiler duties), appropriate feed location, proper feed preconditioning, scope for side-condensers/reboilers, as well as thermo-economic optimization of a distillation column. In this paper, the concept and applicability of IRS curves have been extended to liquid extraction. The equivalent IRS curves for a ternary liquid–liquid extraction predicts the feed location in the counter current process. It also predicts the minimum reflux requirement for a given separation and minimum amount of solvent required. The proposed methodology is demonstrated through an illustrated example.

2. Countercurrent Extraction with Reflux

Schematic diagram of a countercurrent liquid–liquid extraction with reflux has been shown in Fig. 1. The feed solution (F) is separated into an extract product (P_E) and a raffinate product (P_R). Stages, right of the feed stage, enrich the extract primarily to produce E_1 . This is equivalent to rectifying section in distillation and is called extract enriching section. After removal of either all or most of the extracting solvent (S_E), the final extract product (P_E) is removed, allowing a portion of the stream to provide external reflux (R_0) to the enriching section. The solvent separator (equivalent to the condenser in distillation) is generally a distillation operation. Note that, the extract product (P_E) and also the external reflux (R_0) need not to be saturated. Similarly, stages left of the feed stage (Fig. 1), constitute the raffinate stripping section primarily to produce raffinate product ($P_R = R_n$). This is equivalent to stripping section in distillation. Extracting solvent (S) is put directly in the last stage.

The mass and component balances (in solvent free basis) for the overall system as well as the overall mass balance for the solvent can be written as:

Minimum reflux in liquid-liquid extraction

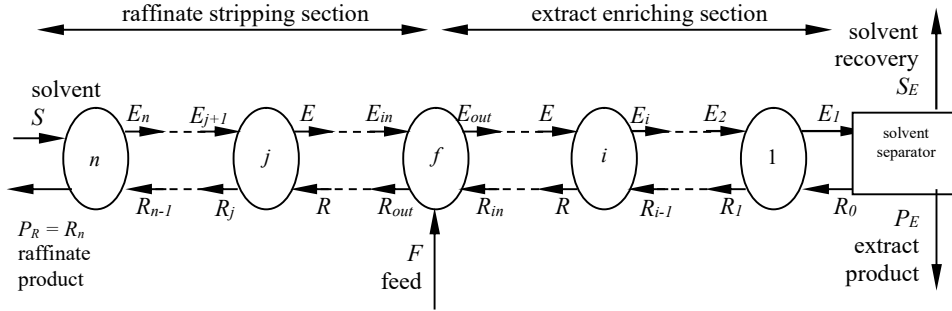


Fig. 1. Schematic diagram of a countercurrent liquid—liquid extraction process with reflux.

$$P_E + P_R = F \quad (1)$$

$$P_E x_E + P_R x_R = F z \quad (2)$$

$$P_E N_{PE} + P_R N_{PR} - F N_F = S - S_E \equiv \Delta \quad (3)$$

Where N represents solvent concentration (in solvent free basis). Last equation defines the parameter Δ which is the constant mass difference for the solvent. Solving first two equations results in the following:

$$P_E = F (z - x_R)/(x_E - x_R) \quad (4)$$

$$P_R = F (x_E - z)/(x_E - x_R) \quad (5)$$

2.1. Extract Enriching Section

For stages 1 to i in the enriching section in Fig. 1, the overall mass and component balances (solvent free basis) are:

$$E = P_E + R \quad (6)$$

$$E y = P_E x_E + R x \quad (7)$$

Whenever x and y are in equilibrium, these equations yield the minimum flows for extract (E) and raffinate (R):

$$E = P_E (x_E - x)/(y - x) \quad (8)$$

$$R = P_E (x_E - y)/(y - x) \quad (9)$$

The mass balance of the solvent is used to evaluate the solvent surplus ($M_B = S_E$).

$$M_B = E N_E - P_E N_{PE} - R N_R \quad (10)$$

$$M_B = P_E [N_E (x_E - x)/(y - x) - N_R (x_E - y)/(y - x) - N_{PE}] \quad (11)$$

The quantity M_B signifies the minimum solvent to be removed at the end of the enriching section to carry out a separation from x to x_E . This solvent surplus is then plotted as a function of composition to give an x vs. M_B curve. This is equivalent to the invariant rectifying curve in distillation [4].

2.2. Raffinate Stripping Section

Similar to the enriching section, for stages from j to n in the stripping section (Fig. 1), solution of the overall mass and component balances (solvent free basis) yield the minimum flows for extract (E) and raffinate (R) in the stripping section whenever x and y are in equilibrium. The mass balance of the solvent is used to evaluate the solvent deficit (M_S).

$$M_S = P_R [N_{PR} + N_E (x - x_R)/(y - x) - N_R (y - x_R)/(y - x)] \quad (12)$$

The quantity M_S signifies the minimum solvent to be added at the end of the stripping section to carry out a separation from x_R to x . This solvent deficit is then plotted as a function of composition to give an x vs. M_S curve. This is similar to the invariant stripping curve in distillation [4]. It may be noted that the solvent is assumed to be pure.

When these two curves are plotted on the same concentration–solvent flow axis, a novel set of curves are obtained. Physically, these curves correspond to the solvent surpluses and deficits for the enriching and stripping sections, respectively. It must be emphasized that the solvent surpluses and deficits are calculated on the basis of the minimum flows by neglecting the effect of the feed. The curves extend from x_E to x_R on the concentration scale.

A ternary two-phase system has exactly three degrees of freedom as per Gibb's phase rule. On specifying the operating pressure, temperature and the separation, the system becomes deterministic. Therefore, M_B and M_S are functions of composition only. Equations (3 – 5, 11, and 12) may be combined to determine the following relationship between M_B and M_S :

$$M_S = M_B - F [N_E (z - x)/(y - x) + N_R (y - z)/(y - x) - N_F] + \Delta \quad (13)$$

The above relation may be employed to target the feed location. For this purpose, a fundamental analysis needs to be performed at the feed stage.

2.3. Feed Stage Analysis

The overall mass (solvent free basis), component balances and mass balance for the solvent at a feed stage (stage f in Fig. 1) are as follows:

$$E_{in} + R_{in} + F = E_{out} + R_{out} \quad (14)$$

$$E_{in} y + R_{in} x + F z = E_{out} y + R_{out} x \quad (15)$$

Minimum reflux in liquid-liquid extraction

$$E_{in} N_E + R_{in} N_R + F N_F = E_{out} N_E + R_{out} N_R \quad (16)$$

Equations (15) and (16) assume the feed stage is pinched [1]. This is equivalent to a distillation column operating at the minimum thermodynamic condition [4]. Through some algebraic manipulations, it is possible to show that

$$M_S = M_B + \Delta \quad \text{at the feed stage} \quad (17)$$

These curves may be translated vertically. Depending on the sign of Δ (as defined in equation (3)), the following conventions may be adopted for translations of these curves:

- (a) If $\Delta \geq 0$, then the curve representing the enriching section is translated up by Δ , with no shift for the curve representing the stripping section.
- (b) If $\Delta < 0$, then the curve representing the stripping section is translated up by $|\Delta|$ with no shift for the curve representing the enriching section.

Mathematically, the vertical horizontal translations of these curves may be represented as:

$$M_{BT} = M_B + \Delta / 2 + |\Delta / 2| \quad (18)$$

$$M_{ST} = M_S - \Delta / 2 + |\Delta / 2| \quad (19)$$

Equations (17) – (19) may be combined to obtain

$$M_{ST} = M_{BT} \quad \text{at the feed stage} \quad (20)$$

Thus, the important conclusion is that the point of intersection of the translated curves defines the target composition for locating the feed (x_F).

2.4. Minimum Reflux

If the feed is properly located at x_F , then the absolute minimum solvent requirement and its removal (equivalent to minimum reflux) for a liquid–liquid extraction process may be established as follows. The portion of the translated curve representing the enriching section left of x_F and the portion of the translated curve representing the stripping section right of x_F may be circumscribed by a right-angled trapezium. Then, the pinch on these curves is defined as the point touching the horizontal side of the trapezium. The heights of the parallel sides of the trapezium at the right and left define the minimum solvent requirement and minimum solvent removal targets, respectively (see Fig. 2). Figure 2 illustrates the case where the intersection point of these translated curves determines the pinch ($x_{pinch} = x_F$). This is often the case. However, the above-described methodology is applicable to exceptions where a pinch may exist either in the enriching or in the stripping section. These

minimum solvent targets are related to and, in a sense, define the minimum reflux target.

2.5. Illustrative Example

This example was taken from Treybal [2]. A 1000 kg/h mixture of ethylbenzene (50%) and styrene (50%) is separated at 25°C using diethylene glycol as solvent. Products are specified to have 10% and 90% styrene. Extended IRS curves for this example are shown in Fig. 2. From these curves, it may be targeted that the feed should be located at $x_F = 0.501$ and the minimum solvent requirement is 9662 kg/h of diethylene glycol. Minimum reflux may be targeted to be 5.23 which match closely with the value of 5.7 reported by Treybal [3].

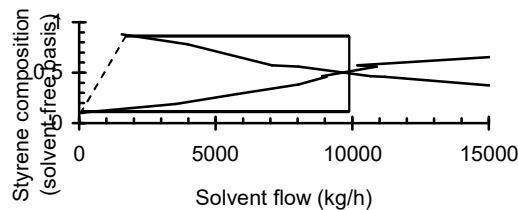


Fig. 2 Extended IRS curves for the ethylbenzene–styrene example.

3. Conclusion

In this paper, the method based on Invariant Rectifying-Stripping (IRS) curves, originally proposed to calculate minimum reflux and minimum energy requirement in distillation [4], has been extended to liquid–liquid extraction. The equivalent IRS curves for a ternary liquid–liquid extraction also predict the feed location in the counter current process.

4. References

- [1] R.E. Treybal, Liquid Extraction, McGraw-Hill, New York, 1951.
- [2] J.D. Seader and E.J. Henley, Separation Process Principles, 2nd Ed., John Wiley & Sons (Asia), 2006.
- [3] R.E. Treybal, Mass-Transfer Operations, McGraw-Hill, Singapore, 1981.
- [4] S. Bandyopadhyay, R.K. Malik, and U.V. Shenoy, Comp. Chem. Eng., 23 (1999) 1109.