THE INFLUENCE OF MARANGONI EFFECT BY RECTIFICATION OF MIXTURES
CHLOROFORM – BENZENE AND METHANOL - WATER

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Abstract

Rectification is a basic industrial method for separation of liquid homogeneous multicomponent mixtures to obtain individual components of high purity. Surface tension is hydrodynamic phenomenon with complex effect on the kinetics of mass transfer process. Studying the phenomenon by rectification, it has been established that positive mixtures form stable interphase boundary and show higher efficiencies. To describe the disturbances at the interphase boundary induced by the gradient of the surface tension, a number of experiments were carried out aiming to find explanation of the mass transfer processes taking place under the effect of Marangoni.

The aim of the present work is to obtain experimental data on the influence of Marangoni effect on the efficiency of separation of two model mixtures (chloroform-benzene and methanol - water) in a glass rectification column with one sieve tray.

Key words: rectification, surface tension, effect of Marangoni

1. INTRODUCTION

The effect of Marangoni is a hydrodynamic phenomenon induced by the gradient of surface tension at phase boundary. It is well known that the Marangoni effect can stir up small scale disturbances at this boundary (Okhotsimskii 1998) which have significant influence on the mass transfer through the phase boundary by distillation of components with big difference between their surface tensions. Many researchers have studied the Marangoni effect in rectification columns of various types. First Zuiderweg and Harmens (Zuiderweg 1958) studied the effect of the changes of the surface tension on the formation of the phase boundary and carried out experiments with packed column, tray column and thin layer column. Comprehensive studies have been published (Lu 1996, Lu 1997, Sha 2010, Wu 2001, Wu 2010) on Marangoni effect induced by adding normal alcohols and surfactants.

Despite the numerous studies, the role of Marangoni effect in real mass transfer processes is is still not fully elucidated because it is hard to distinguish between the Marangoni effect and the various other influences under conditions of turbulent gas-liquid two-phase flow.

In the present work, the method of Zuiderweg (Zuiderweg 1983) was used. For the estimation of the effect of the surface tension on the local efficiency (E Og), the stabilization index was selected, also known as M-index. It is the product of process driving force in the liquid phase and the gradient of the liquid phase surface tension (Zuiderweg 1983):

\[ M = \left( x - x^* \right) \frac{\Delta \sigma}{\Delta x} \]

The aim of the present work is to obtain experimental data on the influence of the Marangoni effect of the efficiency of separation by rectification of two model mixtures (chloroform-benzene and methanol-water) in a glass rectification column with one sieve tray.

2. EXPERIMENTAL

The experiments were carried out in a glass pilot installation (Biddulph 1990). The column has outer weirs for elimination of the wall effect on the forming gas-liquid layer. The small tray diameter (32
mm) makes the assumption of full mixing of the liquid correct and allows for direct experimental determination of the local efficiency.

The first stage of the experiment included the search for suitable method for determination of the compositions of inlet and outlet flows. As accurate enough and at the same time easily applicable method, the method of refractometric determination of the compositions was selected. For this purpose, the dependence of the coefficient of refraction on the compositions of the mixtures studied (chloroform-benzene and methanol-water) at 20°C were plotted according to literary data (Abramova 1964). Samples were taken for analysis from the vapor flows at the inlet and the outlet of the tray, as well as the outlet liquid. The temperature was measured by local mercury thermometers in the cube and at column top. The visual observations of the two-phase layer showed the formation of hydrodynamically stable layer. Foam height was measured visually.

3. RESULTS AND DISCUSSION

The change of the M-index depending on the composition of the mixture chloroform-benzene is shown in Fig.1. The M-index values varied within the interval 0,02 - 0,12 mN/m, with the plot M=f(x) changing only slightly.

![Fig. 1 Dependence of M-index on the composition of the mixture chloroform-benzene](image1)

For the mixture methanol-water, the change of M-index is presented in Fig.2. The values varied in the interval 1,7 - 19,7 mN/m, with the plot showing a maximum in the range 0,5 -0,7 mol/mol.

![Fig. 2 Dependence of M-index on the composition of the mixture methanol-water](image2)
The values of the M-index for the composition methanol-water are 400 to 600 times higher than these for chloroform-benzene. It can be easily explained by comparing the phase diagrams for the two mixtures (Figs. 3 and 4) and the change of the surface tension of both mixtures on the composition (Fig. 5).

Fig. 3 Phase diagram y-x at p=const for the mixture chloroform-benzene

Fig. 4 Phase diagram y-x at p=const for the mixture methanol-water

Based on the results obtained, it can be concluded that the mixture chloroform-benzene belongs to the neutral mixtures for which \( \frac{d\sigma}{dx} \approx 0 \) while the mixture methanol-water belongs to the positive mixtures for which \( \frac{d\sigma}{dx} < 0 \), i.e., the surface tension decreases with the increase of the more volatile component.
It was attempted to make a quantitative estimation of the influence of the surface tension on the local efficiency (\( E_{\text{OG}} \)). For this purpose, the dependence of \( E_{\text{OG}} \) on the M-index was determined using the experimental data on \( E_{\text{OG}} \) and reading the M-index values for each mixture at the experimental values of \( x \) for the corresponding \( E_{\text{OG}} \). The results obtained are shown in Fig.6 for the mixture methanol-water and Fig.7 for chloroform-benzene. For methanol-water (Fig.6), the change of M-index affects \( E_{\text{OG}} \) which varied in the interval from 87% to 98.3%, i.e. the surface tension exerted certain effect on the degree of separation by rectification of the positive mixture methanol-water.

Fig. 6 Dependence of the local efficiency on the M-index for the mixture methanol-water

Fig.7 shows the results obtained for the mixture chloroform-benzene. It can be seen from the figure that the change of M-index did not have effect on the \( E_{\text{OG}} \), i.e. the surface tension had no effect on the degree of separation by rectification of the neutral mixture studied.
4. CONCLUSIONS

1. Experimental studies on the efficiency of separation by rectification of 2 model two-component mixtures: chloroform-benzene and methanol-water were carried out using laboratory rectification with one sieve tray.

2. The change of the stabilizing M-index with the change of the compositions of the mixtures chloroform-benzene and methanol-water was analyzed.

3. A growing dependence of the local efficiency on the M-index was found for the positive mixture methanol-water.

4. It was found that the M-index does not affect the degree of separation of the neutral mixture chloroform-benzene.

5. The separation efficiency for the positive mixture methanol-water was found to be by about 25% higher than that for the neutral mixture chloroform-benzene.

5. REFERENCES


