MASS TRANSFER IN EXTRACTIVE DISTILLATION OF ETHANOL/WATER BY PACKED COLUMNS

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Introduction

Extractive distillation has already proved to be an economically and technically feasible alternative in the separation of close boiling compounds or azeotropic mixtures. The kind of solvent generally used in extractive distillation has low volatility in order to prevent its vaporization with the overhead product and to maintain a high concentration in the liquid phase. Furthermore, the solvent is often comparatively viscous. These factors might be responsible for a decrease in the efficiency of mass transfer during the operation.

Mass transfer in extractive distillation is a rather untreated subject except for the research efforts of Weiss and Arlt⁽⁷⁾ on acetone-methanol separation in plate columns. The present paper reports the effect of solvent concentration on mass transfer coefficients in extractive distillation. It also compares some of the existing empirical correlations used for estimating mass transfer coefficients in packed columns. Finally, a new specific correlation for liquid film mass transfer in extractive distillation is presented.

1. Experimental

The data used in this analysis were obtained in a glass column of the following dimensions: 4.0 cm inside diameter and 45.0 cm height in the enriching section; 4.5 cm inside diameter and 45.0 cm height in the stripping section. The column was packed with 0.5 cm glass Raschig rings. The distillation experiments were carried out using the azeotropic mixture ethanol-water with ethylene glycol as solvent. This system was selected because of reported advantages of extractive distillation in ethanol dehydration when compared to the traditional azeotropic distillation⁽³⁾.

At the end of each experimental run liquid samples were taken from each inlet and outlet stream as well as from the bottom of the stripping section. Their water content was determined by Karl-Fischer titration. The total composition of each sample was also analysed by gas chromatography. This analysis has shown that the distillate does not contain

any ethylene glycol which confirms prior experimental and simulation results^(3, 4). The simulation of this process, on plate columns, has shown that the ethylene glycol concentration in the distillate is lower than 0.05 mole%⁽⁴⁾. For these reasons, the distillate was able to be completely determined by knowing only its water content. The bottom product, a ternary mixture, was determined by a material balance and the result was checked by the gas chromatography. The ranges of experimental conditions are shown in **Table 1**.

The phase equilibrium of the ternary mixture ethanol-water-ethylene glycol was calculated using an NRTL-equation with temperature-dependent parameters⁽³⁾. The relative volatilities of both ethanol and water are very large when compared to ethylene glycol. Due to its very low volatility, the solvent occurs almost exclusively in the liquid phase along the entire packed bed. This keeps its mole fraction constant in the enriching section. In the stripping section its mole fraction is also constant, but at a lower level due to the dilution effect of the ethanol-water feed.

The temperature profile shows a similar behaviour. In the enriching section the temperature remains constant at a greater value due to the higher solvent concentration in this part of the column. Temperature decreases in the region of the ethanol-water feed and it is also approximately constant for the most part of the stripping section. Only near the bottom does it increase abruptly due to the high solvent concentration in the reboiler⁽³⁾.

The negligible amount of ethylene glycol in the vapor phase along the entire packed bed and its approximately constant concentration in the liquid phase over each section of the column suggest that the solvent could be treated as a non-transferring component. This assumption makes it possible to reduce the ternary system into a pseudobinary one. Such an approach was suggested by Van Winkle⁽⁶⁾ for extractive distillation with very low volatile solvents. Lynn and Hanson⁽²⁾ have used the same approach to investigate the energy requirement of the ethanol-water extractive distillation with ethylene glycol as a solvent. In the pseudobinary method the compositions are computed on a solvent-free basis. **Figure 1** shows the operating

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Table 1. Experimental conditions

3.2×10^2	$\leq$	G_L (kg/hr·m ²)	$\leq$	2.2×10^3
2.3×10^2	$\leq$	G_G (kg/hr·m ²)	$\leq$	1.2×10^3
1.40	$\leq$	r	$\leq$	2.10
0.47	$\leq$	S/F	$\leq$	3.10
0.180	$\leq$	x_S	$\leq$	0.680
0.590	$\leq$	x_{IF}	$\leq$	0.860
0.003	$\leq$	x_{2S}	$\leq$	0.009

Fig. 1 Operating diagram for the extractive distillation of ethanol and water in solvent-free basis

diagram for a typical experimental run together with the corresponding pseudobinary equilibrium curve. Since the molar latent heats of ethanol and water are approximately equal and since the solvent is a non-transferring component, one can assume that equimolar counter-transfer occurs. In this case, the average volumetric mass transfer coefficients could be determined, with the help of the corresponding pseudobinary equilibrium curves, by the transfer unit approach applied to each section of the column:

$$K_{OL}a = \left(\frac{L-S}{A z} \right) \int_0^z \frac{dX_1}{(X_1 - X_1^*)} \quad (1)$$

2. Results and Discussion

After the experimental volumetric mass transfer coefficients were obtained, attempts were made to compare them with the results of some reported empirical correlations proposed to describe mass transfer in packed columns (Onda *et al.*⁵) and Bolles and Fair¹).

Figure 2 shows the comparison between experimental and estimated values for the volumetric mass transfer coefficient vs. the liquid phase Reynolds number. It is clear that the experimental values are significantly lower than those estimated by the Onda and Bolles and Fair correlations. Although glycol vaporization could be neglected, the solvent affects the mass transfer process through its effect on the vapor-liquid equilibrium and its influence on the physical properties of the liquid-phase, particularly on its viscosity. Due to the high glycol concentrations, the liquid-phase viscosities become considerably different from those occurring in the systems commonly

Fig. 2 Experimental and estimated overall volumetric mass transfer coefficients

Fig. 3 Effect of solvent mole fraction on the overall volumetric mass transfer coefficients

tested in distillation mass transfer experiments. This can justify why the existing correlations are not able to estimate adequately the mass transfer coefficients of the extractive distillation. In addition, it was found that for each experimental run the volumetric coefficient in the enriching section is lower than the corresponding one in the stripping section (Fig. 2). This behaviour can be attributed to the higher solvent concentration in the enriching section and to the lower liquid phase Reynolds number in this part of the column when compared to the corresponding ones at the stripping section in each experimental run. This effect is further illustrated in **Fig. 3**, which shows that an increase in solvent mole fraction causes a reduction of the volumetric mass transfer coefficients. As is already well known, the greater the viscosity, the lower the diffusivity and the mass transfer efficiency will be.

Nevertheless, only the liquid phase is affected by the solvent. The vapor phase, due to the low volatility of ethylene glycol, is a binary mixture (ethanol/water) over almost the entire column. Its characteristics are basically the same as those of most systems commonly used in mass transfer experiments. This fact presents the possibility to calculate the vapor film mass transfer coefficients using an

Fig. 4 Overall, liquid film and vapor film volumetric mass transfer coefficients

existing correlation. Then it is possible to estimate the volumetric liquid film mass transfer coefficient for each experiment, starting from the experimental mass transfer coefficients, $K_{OL}a$, and the concept of additivity of resistances given by Eq. (2):

$$\frac{1}{K_{OL}a} = \frac{1}{m k_G a} + \frac{1}{k_L a} \quad (2)$$

The results presented in Fig. 3 were obtained using Onda's model for estimating k_G and a , and determining the slope of the equilibrium line, m , for each section of the packed bed as given by Eq. (3), reported by Yoshida *et al.*⁽⁸⁾:

$$m = \frac{K_{OL}a}{K_{OG}a} \quad (3)$$

The m values obtained range from 0.27 to 1.06 but since the equilibrium curve is not a straight line, this approach with an average slope would provide only an estimation of the liquid film coefficient. Nevertheless, it is at least sufficiently accurate for engineering purposes and can provide a good evaluation of the relative size of the mass transfer resistances in each phase.

In Fig. 4, one can see that the rate of mass transfer is undoubtedly liquid phase controlled. Since the vapor film coefficients are several times higher than the liquid film coefficients, the vapor phase resistance can be neglected in Eq. (2) and the volumetric liquid film coefficient becomes equal to the average volumetric coefficient obtained experimentally. These results make extractive distillation in packed columns a special case when compared to ordinary distillation. The mass transfer in packed columns must normally account for resistance in both vapor and liquid phases. Through the analysis of an extensive data bank, Bolles and Fair⁽¹⁾ have concluded that in most of the systems studied, the liquid-phase resistance to mass transfer was relatively low. On the other hand, in extractive distillation, the reverse occurs: due to the specific characteristics imposed by the solvent, mass transfer appears to be largely liquid film controlled.

The experimental volumetric coefficients were

Fig. 5 Comparison of the experimental results and those estimated by Eq. (4). The line represents the estimated values

employed in order to obtain an empirical correlation for extractive distillation. The $k_L a$ could be expressed in terms of Reynolds, Schmidt and a ratio between Weber and Froude Numbers:

$$\left(\frac{(k_L a) M_L}{\rho_L D_L a_t^2} \right) = 0.0029 \left(\frac{G_L}{a_t \mu_L} \right)^{0.69} \left(\frac{\mu_L}{\rho_L D_L} \right)^{0.75} \left(\frac{\rho_L g}{\sigma_L a_t^2} \right)^{-1.37} \quad (4)$$

The mean error is about 20% (Fig. 5). The correlation incorporates the effect of the liquid phase properties and hydrodynamic regime on the liquid film and also on the effective interfacial area. Without specific experimental measures, it is impossible to identify the exact influence of the solvent on both separately. Regardless, the results indicate that liquid film coefficients and the effective interfacial area are strongly affected by solvent in extractive distillation.

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Nomenclature

a	= specific effective interfacial area	[m ⁻¹]
a_t	= specific surface of dry packing	[m ⁻¹]
A	= column cross section area	[m ²]
D_L	= more volatile component (ethanol) diffusivity in liquid phase	[m ² ·hr ⁻¹]
g	= acceleration of gravity	[m·s ⁻²]
G_G	= vapor superficial mass velocity	[kg·hr ⁻¹ ·m ⁻²]
G_L	= liquid superficial mass velocity	[kg·hr ⁻¹ ·m ⁻²]
F	= feed rate of ethanol/water	[kmol·hr ⁻¹]
k_G	= vapor film mass transfer coefficient	[kmol·hr ⁻¹ ·m ⁻² ·Δy ⁻¹]
k_L	= liquid film mass transfer coefficient	[kmol·hr ⁻¹ ·m ⁻² ·Δx ⁻¹]
K_{OG}	= overall mass transfer coefficient based on vapor composition	[kmol·hr ⁻¹ ·m ⁻² ·Δy ⁻¹]
K_{OL}	= overall mass transfer coefficient based on liquid composition	[kmol·hr ⁻¹ ·m ⁻² ·Δx ⁻¹]
L	= total molar liquid rate in enriching or in stripping section	[kmol·hr ⁻¹]
m	= average slope of equilibrium curve	[-]
M_L	= average liquid molecular weight	[kg·kmol ⁻¹]

r	= reflux rate	[-]
S	= solvent feed rate	[kmol·hr ⁻¹]
S/F	= solvent to feed ratio	[-]
x_{IF}	= mole fraction of ethanol in ethanol-water feed	[-]
x_S	= liquid-phase mole fraction of the solvent in enriching or in stripping section	[-]
x_{2S}	= mole fraction of water in solvent feed	[-]
X_I	= liquid-phase mole fraction of ethanol in solvent free basis	[-]
X_I^*	= mole fraction of ethanol in solvent free basis, in equilibrium with vapor of composition Y_I	[-]
X_{IB}	= mole fraction of ethanol in bottom product, in solvent free basis	[-]
X_{ID}	= mole fraction of ethanol in distillate, in solvent free basis	[-]
X_{IE}	= liquid-phase mole fraction of ethanol at the bottom of the stripping section, in solvent free basis	[-]
Y_I	= vapor-phase mole fraction of ethanol in solvent free basis	[-]

z	= packing height	[m]
μ_L	= liquid phase viscosity	[kg·m ⁻¹ ·hr ⁻¹]
ρ_L	= liquid phase density	[kg·m ⁻³]
σ_L	= liquid phase surface tension	[kg·s ⁻²]

Literature Cited

- 1) Bolles, W. L. and J.R. Fair: *Chem. Eng.*, **12** (7), 109-116 (1982)
- 2) Lynn, S. and D.N. Hanson: *Ind. Eng. Chem. Process Des. Dev.*, **25**, 936-941 (1988)
- 3) Meirelles, A., S. Weiss and H. Herfurth: *J. Chem. Tech. Biotechnol.*, **53**, 181-188 (1992)
- 4) Meirelles, A.: PhD Thesis, TH Merseburg, Germany (1987)
- 5) Onda, K., H. Takeuchi and Y. Okumoto: *J. Chem. Eng. Japan*, **1** (1), 56-62 (1968)
- 6) Van Winkle, M.: "Distillation", McGraw-Hill, New York (1967)
- 7) Weiss, S. and R. Arlt: *Chem. Eng. Process.*, **21**, 107-113 (1987)
- 8) Yoshida, F., T. Koyanagi and T. Katayama: *Ind. Eng. Chem.*, **46** (9), 1756-1762 (1954)