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APPENDICES

Appendix A Principle of Stripping in Co-current Operation (Cussler, 1994)

The analysis of gas desorption in a packed tower, in many cases the design engineers ordinarily want to use the analysis to estimate the tower height. In other cases, they want to use their analysis to organize experimental results as mass transfer coefficients. In any case, analysis will build on the fluid mechanics, a description that allows estimating the tower's cross section.

A.1 Stripping of a Diluted Liquid Solution

To simplify the analysis, the designers will begin with the case of a dilute solute desorbed from a liquid into a gas. This focus on the dilute limit makes the physical significance clearest. Because the liquid is diluted, the molar gas flux 'V' and the molar liquid flux 'L' are both constants everywhere within the tower. With this simplification, three key equations are needed:

(1) a solute mole balance on both gas and liquid.

(2) a solute equilibrium between gas and liquid.

(3) a solute mole balance on either gas or liquid.

These three ways are traditionally called an operating line, an equilibrium line, and a rate equation, respectively.

The designers will begin with a mole balance on the solute in both gas and liquid. This balance will make on a small tower volume $A\Delta Z$ located at position Z in the tower
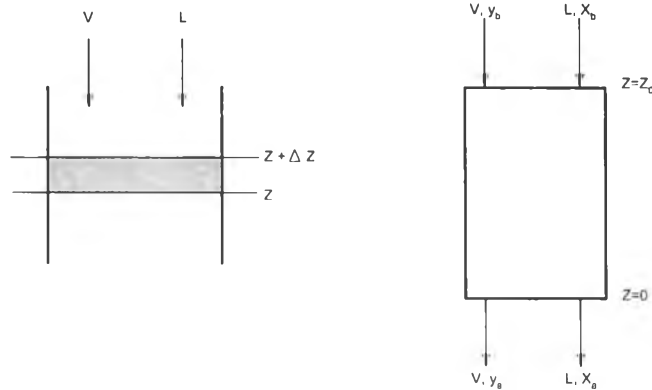
$$
\begin{bmatrix} \text{solute entering} \\ \text{minus leaving} \\ \text{in gas} \end{bmatrix} = \begin{bmatrix} \text{solute entering} \\ \text{minus leaving} \\ \text{in liquid} \end{bmatrix}
$$

$$
VA\left(y_{z+\Delta z}-y_z\right) = -LA\left(x_{z+\Delta z}-x_z\right)
$$

where y and x are the mole fractions in the gas and liquid, respectively and A is the cross section area. When this equation is divided by the volume, $A\Delta Z$

$$
V\frac{dy}{dz} = -L\frac{dx}{dz}
$$

$$
\frac{dx}{dy} = -\frac{V}{L}
$$

subject to (at $Z = 0$),

$$
y = y_a \qquad x = x_a
$$

where the subscript 'a' indicates the streams at the bottom of the tower. Remember that the gas and liquid are leaving at this position. Integrating,

$$
x = x_a - \frac{V}{L}\left(y-y_a\right) \tag{A.1}
$$

the first key equation, which is nothing more than a mole balance, is called the "operating line".

The second key equation for analyzing absorption is an equilibrium relation for the solute in the gas and in the liquid. Because the solute is dilute, this has the form

$$
y^* = mx \tag{A.2}
$$

where

    m   is closely related to a Henry's law constant.

    x   is the actual liquid mole fraction.

    y^* is the gas mole fraction which would be in equilibrium with that liquid.

This second key equation is called the "equilibrium line".

The third key relation, the rate equation, is found by another solute mole balance on the differential volume $A\Delta Z$ but on the liquid only:

$$\begin{bmatrix} \text{Solute} \\ \text{accumulate} \end{bmatrix} = \begin{bmatrix} \text{Solute flow} \\ \text{in minus out} \end{bmatrix} - \begin{bmatrix} \text{Solute lost} \\ \text{by desorption} \end{bmatrix}$$

In symbolic terms, this can be written as

$$0 = LA(x_{z+\Delta z} - x_z) - K_x a(A\Delta Z)(x - x^*)$$

Where K_x is overall liquid phase mass transfer coefficient and a is the specific area of gas-liquid interface.

Boundary condition

$$Z = Z_0 \qquad x = x_b$$
$$Z = 0 \qquad x = x_a$$

Integrating,

$$Z_0 = \frac{L}{K_x a} \int_{x_a}^{x_b} \frac{1}{x-x^*} dx \qquad (A.3)$$

However, especially in the older literature, a relation like Eq.2.3 is sometimes rearranged as

$$Z_0 = HTU.NTU \qquad (A.4)$$

where

HTU is a height of a transfer unit defined as

$$HTU = \frac{L}{K_x a}$$

and NTU is a number of transfer units given by

$$NTU = \int_{x_a}^{x_b} \frac{1}{x-x^*} dx$$

The use of HTUs and NTUs does have a sound physical interpretation. The NTUs are a measure of the difficulty of the separation, of the distance the final streams will be from equilibrium. The HTUs, on the other hand, give an idea of the efficiency of the equipment. A small HTU is a sign of a good tower, implying, for example, a large surface area per volume.

A.2 Stripping of a Concentrated Liquid Solution

To extend this analysis to desorption in concentrated solutions, the designer will begin with a mole balance on both gas and liquid.

$$0 = \frac{d}{dZ}(Vy) + \frac{d}{dZ}(Lx) \qquad (A.5)$$

Before, the flux of gas G and that of liquid L are nearly constant because the desorbing species are always dilute. Now, however, with expectance that

$$V = V_0 \frac{1}{1-y} \qquad (A.6)$$

where G_0 is the flux of the nondesorbing gas. Similarly,

$$L = L_0\left(\frac{1}{1-x}\right) \qquad (A.7)$$

where L_0 is the flux of the nonvolatile liquid. When combining these equations and integrate with boundary condition,

$$\text{at} \qquad Z = Z_0 \qquad x = x_b \qquad y = y_t$$

this find that

$$y = \frac{\left(\dfrac{y_b}{1-y_b}\right) + \dfrac{L_0}{V_0}\left(\dfrac{x_b}{1-x_b} - \dfrac{x}{1-x}\right)}{1 + \left(\dfrac{y_b}{1-y_b}\right) + \dfrac{L_0}{V_0}\left(\dfrac{x_b}{1-x_b} - \dfrac{x}{1-x}\right)} \qquad (A.8)$$

This mole balance is the operating line for a concentrated liquid.

The next step is the specification of a new equilibrium relation analogous to Equation A.2:

$$y^* = y^*(x) \qquad (A.9)$$

This relation is often not written in an analytical form, but simply presented as table or graph of experimental results. The important point is that y^* and x are no longer directly proportional, related by a single, constant coefficient. Instead, they vary nonlinearly.

The final step is a mole balance on the liquid in a differential tower volume:

$$0 = -\frac{d}{dz}(Lx)+K_xa(x-x^*) \qquad (A.10)$$

When combining this result with Eq.2.7 and rearranging,

$$Z_0 = \frac{L_0}{K_xa}\int_{x_a}^{x_b}\frac{1}{(x-x^*)(1-x)^2}\,dx = HTU.NTU \quad (A.11)$$

Where K_x is the overall coefficient based on a mole fraction driving force.

Appendix B Toluene properties

Toluene was discovered by Pelletier and Walther (1836), who obtained it by dry-distilling pine needles. Its name derived from Tolu balsam from which it was also isolated by distillation.

Toluene is a clear, colorless liquid with a distinctive smell. Toluene occurs naturally in crude oil and in the tolu tree. It is also produced in the process of making gasoline and other fuels from crude oil and making coke from coal.

This compound is used to manufacture benzoic acid, benzaldehyde, benzene, phenol, caprolactam, linoleum, toluenediisocyanates (polyurethane resins), toluene sulfonates (detergents), artificial leather and fabric and paper coating. It is also used as an intermediate in the industrial preparation of trinitrotoluene.

Preparation
1. From the light oil fraction from coal-tar distillation.
2. From the C_7-fraction of catalytically cracked oil or from mineral oil by aromatization at about 500°C (775 K) under pressure (catalytic reforming process).

Properties

Identifiers

CAS Number: 108-88-3

Chemical formula: C_7H_8

Structural formula: C_6H_5-CH_3

Synonyms: Toluol; Phenyl Methane; Methylbenzol; Metyl-
                              Benzene; Monomethyl Benzene; Methacide;
                              Tolu-sol; Antisla; Tol; Toluene.

Physical and chemical data

Molecular weight: 92.1402

Specific gravity: 0.8669

Density: 0.867 g/ml

Melting point: -93°C

Boiling point: 110.6°C

Solubilities:	Water (< 1 mg/ml at 18°C)
	Methanol (≥ 100 mg/ml at 18°C)
Vapor pressure:	40 mmHg at 31.8°C
Refractive index:	1.4968 at 20°C
Vapor density:	3.14
Flash point:	4.4°C.

Appendix C Experimental Data

Table C1 Apparent henry's law constant data: initial $[OP(EO)_7]$ = 300 mM, initial [toluene] = 150-1000 ppm, temperature 30°C

Initial [toluene] (ppm)	Equilibrium data	
	Vapor phase	Liquid phase
	Partial pressure of toluene (atm)	Total [toluene] (ppm)
149.82	0.00035567	134.45
299.98	0.00069291	255.83
398.82	0.00085915	327.04
499.39	0.00101046	385.76
693.60	0.00142527	541.48
867.00	0.00183737	711.78
998.78	0.00198588	769.80

Table C2 Solubilized and unsolubilized toluene concentration in liquid phase at equilibrium condition: initial $[OP(EO)_7]$ = 300 mM, initial [toluene] = 150-1000 ppm, temperature 30°C.

From $\quad \dfrac{H_m}{H_{Tr}} = \dfrac{x^*_{unsolubilize\ toluene}}{x^*_{total\ toluene}} = 0.038082384$

Initial [toluene] (ppm)	Equilibrium data		
	Total [toluene] (mM)	Unsolubilized [toluene] (mM)	Solubilized [toluene] (mM)
149.82	1.459	0.057	1.402
299.98	2.777	0.111	2.665
398.82	3.549	0.138	3.412
499.39	4.187	0.162	4.025
693.60	5.877	0.229	5.648
867.00	7.725	0.295	7.430
998.78	8.355	0.318	8.036

Table C4 Partition coefficient of toluene: initial $[OP(EO)_7]$ = 300 mM, initial [toluene] = 150-1000 ppm, temperature 30°C.

Initial [toluene] (ppm)	Equilibrium data	
	Mole fraction of toluene in liquid phase	Mole fraction of toluene in vapor phase
149.82	3.058×10^{-5}	0.00842
299.98	5.819×10^{-5}	0.01628
398.82	7.440×10^{-5}	0.02011
499.39	8.776×10^{-5}	0.02356
693.60	1.232×10^{-4}	0.03292
867.00	1.620×10^{-4}	0.04203
998.78	1.752×10^{-4}	0.04528

Table C3 Solubility constant (Ks): initial $[OP(EO)_7]$ = 300 mM, initial [toluene] = 150-1000 ppm, temperature 30°C.

From $\quad Ks = \dfrac{C_{sol}}{C_u\left(C_m + C_{sol}\right)}$

$C_m = C_{Total\ surfactant} - CMC$

CMC for $OP(EO)_7 \sim 0.28$ mM

$C_{Total\ surfactant} = 300$ mM

$\therefore C_m \sim C_{Total\ surfactant} \sim 300$ mM

Initial [tolene] (ppm)	Equilibrium data	
	Mole fraction of toluene in micellar phase	Solubility constant (1/mM)
149.82	2.938×10^{-5}	0.0816
299.98	5.586×10^{-5}	0.0793
398.82	7.151×10^{-5}	0.0816
499.39	8.346×10^{-5}	0.0817
693.60	1.184×10^{-4}	0.0809
867.00	1.558×10^{-4}	0.0820
998.78	1.685×10^{-4}	0.0819

Table C5 Partition coefficient of water: initial $[OP(EO)_7]$ = 300 mM, initial [toluene] = 150-1000 ppm, temperature 30°C.

Initial [toluene] (ppm)	Equilibrium data	
	Mole fraction of water in liquid phase	Mole fraction of water in vapor phase
149.82	0.99368	0.99158
299.98	0.99365	0.98372
398.82	0.99364	0.97989
499.39	0.99362	0.97644
693.60	0.99359	0.96708
867.00	0.99355	0.95797
998.78	0.99353	0.95472

Table C6 Effect of liquid flow rate on overall liquid phase mass transfer coefficient of toluene in surfactant solution: initial [OP(EO)7] = 300 mM, initial [toluene] = 300 ppm, temperature 30°C.

Flow rate (ml/min)	Pressure (torr)	Initial [toluene] (ppm)	Final [toluene] (ppm)	Final [OP(EO)$_7$] (mM)	% removal of toluene	NTU	HTU (cm)	$K_x a$ (mol/cm^3.sec)
8.2	55	300	163.787	309.348	45.404	0.6054	41.9580	0.0001995
13	55	300	233.643	312.978	22.119	0.2501	101.5738	0.0001236
17	55	300	232.909	303.572	22.364	0.2532	100.3112	0.0001669
20	55	300	239.558	303.115	20.147	0.2251	112.8616	0.0001854
30	55	300	235.699	298.242	21.434	0.2413	105.2630	0.0002982

Table C7 Effect of pressure on overall liquid phase mass transfer coefficient of toluene in surfactant solution: initial [OP(EO)7] = 300 mM, initial [toluene] = 300 ppm, temperature 30°C.

Pressure (torr)	Flow rate (ml/min)	Initial [toluene] (ppm)	Final [toluene] (ppm)	Final [OP(EO)$_7$] (mM)	% removal of toluene	NTU	HTU (cm)	$K_x a$ (mol/cm^3.sec)
130	8.2	300	263.749	295.352	12.084	0.1288	197.1672	4.35×10^{-5}
100	8.2	300	264.238	300.800	11.921	0.1270	200.0453	4.29×10^{-5}
77.5	8.2	300	234.396	299.967	21.868	0.2468	102.8985	8.34×10^{-5}
55	8.2	300	163.787	309.348	45.404	0.6054	41.9580	2.04×10^{-4}
43	8.2	300	149.055	307.246	50.315	0.6996	36.3047	2.36×10^{-4}

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