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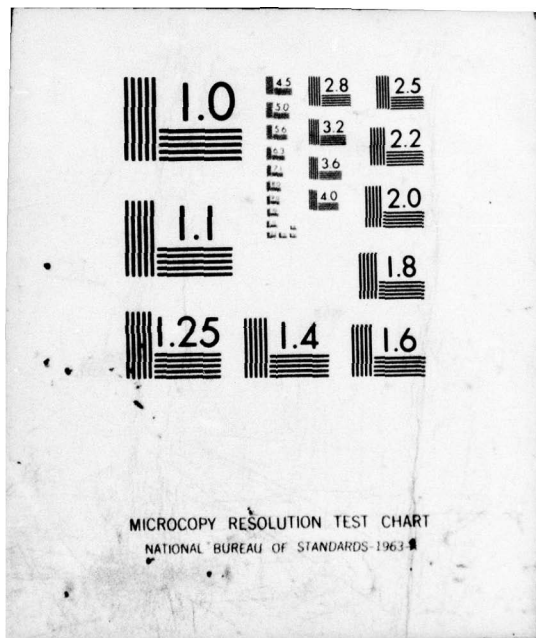
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EXAMINATION OF THE PROBLEM OF RECUPERATIVE TREATMENT OF WASTE WATER IN THE CHEMICAL INDUSTRY

[Article by I. V. Robu, Revista de Chimie (Bucharest), 17(10), 1966, pp. 627-635]

As a result of the diversity of technological processes and the ever growing volume of products, the organic chemical industry is one of the major producers of waste water polluted by organic substances harmful to river flora and fauna.

In order to solve the problem of waste water in time, before the rivers serving large population centers are endangered, it is necessary to begin construction of the waste water treatment system in the technological process, simultaneously with construction of industrial installations. Integration of the water treatment system into production installations as a whole will cause both the investments and operating expenses for treatment plants to be reflected in the cost price of products, this avoiding later additional expenses which often are difficult to justify.

This entails the necessity of elaborating the technological process for waste water treatment simultaneously with elaboration of the technologic process for production, the same importance being assigned to both processes.

An important aspect of rational solution of the waste water problem is represented by the possibility of intervention in the manufacturing technology in order to reduce the volume of waste water by recirculation, and also by separation of the channels of conventionally clean water from those of heavily polluted water. The latter can often be purified advantageously to a pollutant content permitted by biological treatment through physicochemical recuperative processes such as fractionation, extraction, adsorption, ion exchange, etc.

If one or another of the processes referred to is not effective, two processes may be combined, the waste water being passed through the respective plants in succession. The example may be given of the case of organic substances having an extremely low vapor pressure (dinitrobenzene, etc). Liquid-liquid extraction may be applied in this case, by using a solvent of relatively high volatility which may then be recovered from the water by azeotropic fractionation.

In connection with the problem of the cost effectiveness of recuperative treatment it is to be pointed out that it cannot be considered separately, but rather must be treated as part of the whole treatment system, in which the last element is usually represented by biological treatment.

Even if recuperative treatment of itself should not be cost effective in some cases, a positive economic effect can be achieved for the treatment system as a whole, with substantial reduction of the total

expenses, by recovering products and introducing them into the economic system again and by reducing the dimensions of the biological treatment plant.

Chemical processes often result in waste water more or less saturated with hazardous organic substances such as nitro derivatives, amines, ester, ethers, aromatic hydrocarbons, etc.

It is especially important to be able to establish -- on the basis of the physical properties of the respective pollutants -- the extent to which recuperative treatment is of economic value of itself or as part of and in comparison to destructive treatment (biological reduction), since biological treatment is known to require installations characterized by dimensions and consumption of utilities which are the greater, the higher is the pollutant content.

→ In what follows the simplest technology -- a fractionating column having only a stripping section and heated by direct steam -- will be used to derive the general relationship among the main variables of the process of separation by fractionation and recovery of an organic substance dissolved in water.

If the degree of recovery (percentage recovered from the column supply) is fixed, there is a univocal relationship for a given fractionation between the heat consumption (direct steam) and the number of equilibria (column height). The economic limits of the process will thus be a function of the variables represented by operating expenses and investment amortization.

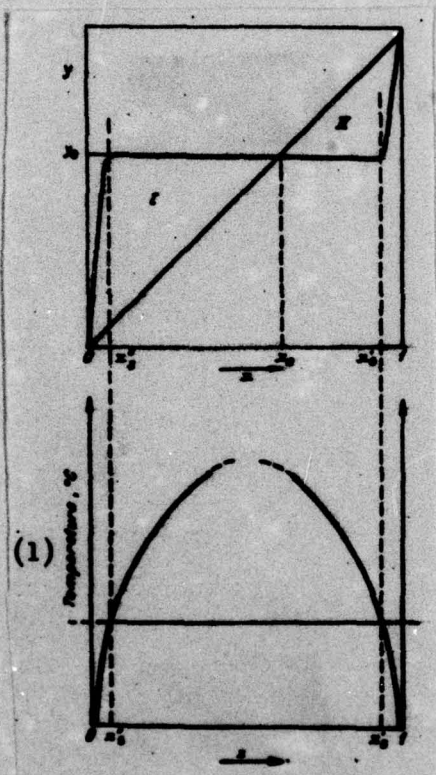
As is known, the basic element in solution of the fractionation problem is represented by the liquid-vapor equilibrium relationships. Deriving these relationships experimentally requires a large volume of work and special equipment, the respective substance being applied from case to case. On the other hand, calculating them from the mutual solubilities [1] is rather cumbersome. As regards determination of the number of equilibria on the basis of the known relations, the operation is rendered cumbersome since the number of equilibria necessary as a function of the other variable values must be calculated for each alternative resulting from judicious combination of the three parameters.

→ An analytical relation among these variables is established in what follows on the basis of the law obeyed by dilute solutions of organic substances (the solute) which are difficultly soluble in water (the solvent).

Derivation of Equilibrium Relations

As is known, these systems form azeotropes with a minimum boiling point, and the $x - y$ equilibrium curves are of the form shown in Figure 1. It is also a known fact that in the miscibility region the solute (low-concentration substance) obeys the Henry law, while the solvent (high-concentration substance) obeys the Raoult law. (The accuracy with

which this rule may be applied is the higher, the lower are the mutual solubilities.)



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Figure 1. Equilibrium and solubility curve of a partially miscible binary system of low solubility. 1. Temperature, °C.

With x'' and x' denoting the molar fractions of the more volatile component (components 1) in the two layers in equilibrium (Figure 1), the rule in question indicates that in the region in which $0 < x < x''$ the partial pressure of the solute (such as benzene in water) is $p_1 = H_1 x$, and the partial pressure of the solvent $p_2 = P_2(1 - x)$. Similarly, in the region $x' < x < 1$ the partial pressure of the solute (such as nitrobenzene in water) will be $p_2 = H_2(1 - x)$, and that of the solvent $p_1 = P_1 x$. (In these relations P_1, P_2 are the vapor pressures, H_1, H_2 the Henry constants, of components 1 and 2.) Application of these relations to limit concentrations x'' and x' yields well-known equations (1c 2), which express the Henry constants as a function of the vapor pressures and mutual solubilities at a given temperature:

$$H_2 = P_2 \cdot \frac{1 - x''}{1 - \frac{x''}{x_s''}} \quad (1)$$

$$H_1 = P_1 \cdot \frac{x'}{1 - \frac{x'}{x_s'}} \quad (2)$$

The water-nitrobenzene system is considered (Figure 1); in this case, x , y represent the molar fractions of water. If the branch of the equilibrium curve to the right of the azeotropic point ($x_a = y_a$) is considered, with P denoting the pressure of the system, the following expressions yielding the partial pressures of the water (more volatile component 1) and the nitrobenzene (more volatile component 2) may be written, in accordance with the rule for dilute solutions:

$$p_1 = P \cdot y = P_1 \cdot x \text{ and } p_2 = P(1 - y) = H_2(1 - x).$$

Division yields

$$\frac{y}{1 - y} = \frac{P_1}{H_2} \cdot \frac{x}{1 - x}$$

and accordingly

$$y = \frac{\frac{P_1}{H_2} x}{1 + x \left(\frac{P_1}{H_2} - 1 \right)}, \quad (3)$$

that is, the equilibrium curve for the branch to the right of the azeotropic point.

By proceeding in similar fashion for the branch of the equilibrium curve to the left of the azeotropic point and considering the solute to be the more volatile component, we obtain the following as the expression for the equilibrium curve:

$$\frac{y}{1 - y} = \frac{H_1}{P_2} \cdot \frac{x}{1 - x}; \quad y = \frac{\frac{H_1}{P_2} \cdot x}{1 + x \left(\frac{H_1}{P_2} - 1 \right)}. \quad (4)$$

Conversion of Coordinates [2]

In the case of azeotropic systems with a minimum boiling point, up to $x = x_a$ the convexity of the equilibrium is directed upward (Figure 1, branch I), and with $x > x_a$ the convexity of the curve is directed downward (branch II). Erection of a vertical through point x_a, y_a divides the curve into two branches having the abscissas between $0 - x_a$ and $x_a - 1$, respectively, and the ordinates between $0 - y_a$ and $y_a - 1$, respectively (Figure 2).

The practical import of and the necessity for this division are shown by the following: assume that a mixture made up of components 1 and 2 is to be fractionated and that the feed composition is $x_f < x_a$. In this case, parameters x_p, x_b and the reflux ratio being assigned (with, of course, $x_p < x_a$), the simple graphic method could be used to plot the number of plates and the problem is easy to solve. The composition of the product at the top of the column (distillate) will be near the azeotropic composition, while the less volatile component of the initial components will be obtained at the base of the column. However, if $x_f > x_a$, ordinary graphic construction may no longer be used.

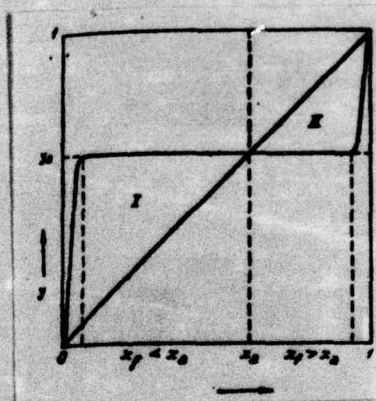


Figure 2. Conversion of coordinates.

The method proposed of dividing the equilibrium curve by vertical x_a into two branches, each branch being considered to be an independent equilibrium curve, easily solves the problem of plotting the plates by the known graphic method.

- * p refers to the product at the top of the column;
- b refers to the product at the base of the column;
- f refers to the feed.

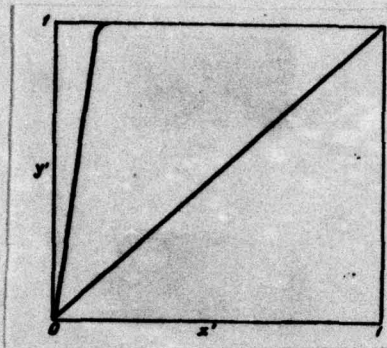


Figure 2a. Branch I of Figure 2 in coordinate system x', y' .

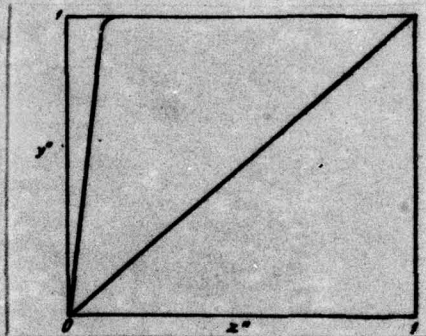


Figure 2b. Branch II of Figure 2 in coordinate system x'', y'' .

Since the equilibrium curves are usually represented in the x, y system, with their values ranging from 0 to 1, it is necessary to make a corresponding change of coordinates in order to represent each branch in such a system. If the branch is assumed to be included between 0 and x_a , it is to be seen from the Figure that any mixture having a composition falling within these limits may be taken to be a mixture in which the more volatile component is the azeotrope, while the less volatile component is component 2 of the initial mixture. Let x be the composition of a mixture falling within the limits $x = 0$ and $x = x_a$ and let x' be the composition of the same mixture in which x' is the molar fraction of the azeotrope. If the azeotropic composition is x_a , a mole of azeotrope will contain x_a moles of component 1, and $x_a - x'$ moles of azeotrope will correspond to x moles of component 1.

Analogous reasoning shows that to y molar fraction of component 1 there corresponds: $y:y_a = y:x_a = y'$ molar fraction of azeotrope in the vapor phase. Consequently, branch I of the equilibrium curve can be transposed into the system x' and y' with the limits 0 - 1, the values of x' and y' being calculated from the expressions:

$$x' = \frac{x}{x_a} \text{ and } y' = \frac{y}{y_a} \quad (5)$$

When this conversion is made, branch I of Figure 2 becomes Figure 2a.

Establishment of the relations for conversion of the coordinates for branch II is based on the following reasoning.

Let x be the composition of a mixture within the limits $x = x_a$ and $x = 1$ and let x'' be the composition of the same mixture, in which x'' represents the molar fraction of the azeotrope. One mole of azeotrope containing x_a moles of component 1 will contain $1 - x_a$ moles of component 2; consequently, to $1 - x$ moles of component 2 there will correspond $1 - x : 1 - x_a = x''$ moles of azeotrope. In a similar manner it is found that with y moles of component 1 in the vapor phase ($y > y_a$) there are associated $1 - y : 1 - y_a = 1 - y : 1 - x_a = y''$ moles of azeotrope. Hence to transpose branch II of the initial equilibrium curve to system x'', y'' with the limits 0 - 1 use may be made of the relations:

$$x'' = \frac{1 - x}{1 - x_a} \text{ and } y'' = \frac{1 - y}{1 - y_a} \quad (6)$$

Branch II of Figure 2 becomes Figure 2b as a result of the conversions.

As a result of division relations (5), (6) yield the following expressions for the slopes of the azeotrope-component 1 and azeotrope-component 2 equilibrium curves:

$$\frac{y''}{x''} = \frac{1 - y}{1 - x} \quad (7)$$

and

$$\frac{y'}{x'} = \frac{y}{x} \quad (8)$$

Combining these relations with equations (3), (4) yields:

$$\frac{y''}{x''} = \frac{1}{1-x} \cdot 1 - \frac{\frac{P_1}{H_2} \cdot x}{1 + x\left(\frac{P_1}{H_2} - 1\right)} =$$

$$= \frac{1}{1 + x\left(\frac{P_1}{H_2} - 1\right)} \quad (9)$$

$$\frac{y'}{x'} = \frac{1}{\frac{P_2}{H_1} + x\left(1 - \frac{P_2}{H_1}\right)} \quad (10)$$

These relations represent the azeotrope-component 1 and azeotrope-component 2 equilibrium curves, respectively, and may be approximated by straight lines, as is shown by the following:

For substances of very low solubility the minimum value of x in expression (9) is x'_s ; hence $x > x'_s$, and $x' \approx 1$. In this case expression (9) assumes the form

$$y'' = \frac{H_2}{P_1} \cdot x'' \quad (11)$$

Similarly, in view of the fact that $\frac{P_2}{H_1}$ in expression (10) is very small*, and at the solubility limit $x = x''_s$, equation (10) becomes

$$y' = \frac{1}{x''_s} \cdot x' \quad (12)$$

Another method of establishing the slopes of the equilibrium curves is indicated by the following: the geometry of Figure 2 yields for branch II the slope

$$\frac{1 - y''_s}{1 - x''_s} = \frac{1 - x''_s}{1 - x''_s} \quad (13)$$

*For the ethyl ether-water system, at 60 °C ratio $\frac{P_2}{H_1} = 149.4/179,500 = 0.00083$, and thus is negligible in comparison to $x''_s \approx 0.01$.

and for branch I the slope

$$\frac{y_a}{x_s''} = \frac{x_a}{x_s'} \quad (14)$$

On the other hand, allowance for $x = x_s'$ in expression (3) yields

$$y = y_a = x_a = \frac{\frac{P_1}{H_2} \cdot x_s'}{1 + x_s' \left(\frac{P_1}{H_2} - 1 \right)}$$

Substitution of the value of equation (1) for H_2 in this expression gives

$$x_a = \left(1 - \frac{P_2}{P_1} \cdot \frac{1 - x_s''}{x_s'} \right)^{-1} \quad (15)*$$

Combining this expression with equations (13), (14) and (7), (8) yields the relations

$$\frac{y''}{x''} = \frac{1}{1 + x_s' \left(\frac{P_1}{P_2} \cdot \frac{1 - x_s'}{1 - x_s''} - 1 \right)} \quad (16)$$

and

$$\frac{y'}{x'} = \frac{1}{x_s'' \left(1 + \frac{P_2}{P_1} \cdot \frac{1 - x_s''}{x_s'} \right)} \quad (17)$$

In view of the fact that $x_s' \approx 1$, equation 16 becomes

$$\frac{y''}{x''} = \frac{P_2}{P_1} \cdot \frac{1 - x_s''}{1 - x_s'} = \frac{H_2}{P_1}, \quad (18)$$

since, according to expression (1):

*This relation was applied in calculation of the composition of the azeotropes benzene-water, nitrobenzene-water, aniline-water, butyl acetate-water, ethyl ether-water, etc., compositions very near the actual ones being obtained in all cases.

$$H_2 = P_2 \frac{1 - x_s''}{1 - x_s'}$$

Similarly, since $x_s'' \approx 0$, and $x_s' \approx 1$, equation (17) becomes

$$\frac{y'}{x'} = \frac{P_1}{P_1 + P_2} \cdot \frac{1}{x_s''} \quad (19)$$

These relations show that if the solute is the component of lower volatility than the solvent, the slope of the equilibrium curve is the steeper, the higher is vapor pressure P_2 of the solute and the lower is the solubility of the solute (large x_s' value). If the solute is the component of higher volatility, the slope of the equilibrium curve increases with vapor pressure P_1 of the solute and with decrease in its solubility (small x_s'').

The general conclusion to be drawn is that separation of these systems by fractionation is the more advantageous (equilibrium curve with steep slope), the higher is the volatility of the solute in comparison to that of the solvent and the lower is the solubility of the solute.

As regards the variation of the equilibrium curve slope (equations 18 and 19) with the temperature, Figure 1 demonstrates that the slopes become steeper with lowering of the temperature, since both x_s'' and $(1 - x_s')$ become smaller at lower temperatures.

Since in both cases the product at the base of the fractionating column will in effect be only water, the temperature at the base of the column will even be the boiling point of water at the operating pressure of the column. If the product at the top of the column should be that corresponding to the azeotrope, the temperature at the top will be that of the boiling point of the azeotrope. But since, for economic reasons, the aim pursued is not to obtain the azeotropic composition with the product at the top, but rather to obtain merely a composition which separates into two layers on condensation, the temperature at the top of the column will usually be only a few degrees below the temperature at the base of the column.*.

* With many systems in which water is the more volatile component (water-nitrobenzene, water-aniline, water-butyl acetate, etc), the boiling point of the azeotrope differs by only a few degrees from the boiling point of water.

It should be noted that, when there is an appreciable difference between the boiling point of component 2 and that of the azeotrope, the temperature gradient of the fractionating column will also be appreciable, and ratio P_2/H_1 consequently may not be assumed to be constant. However, the column may be divided into several sections and ratio P_2/H_1 calculated for the temperature of each section, or the average temperature between the top and base of the column may be estimated.

Correlation of the parameters: percentage recovered, number of equilibria, steam consumption.

The simplest system for fractionation of these mixtures consists of a column with reflux supply (Figure 3).

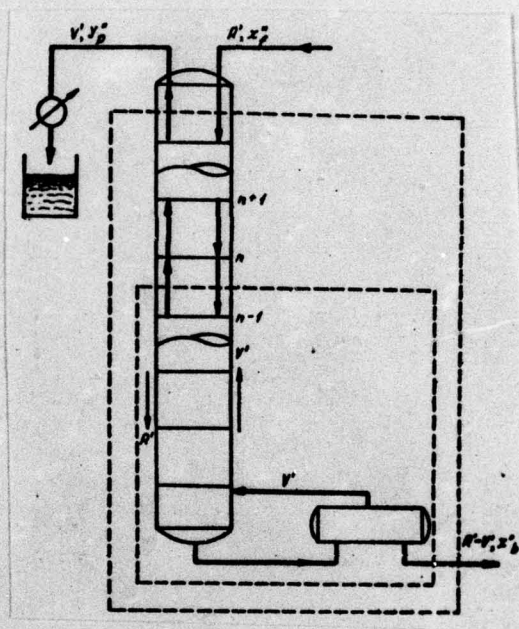


Figure 3. Azeotropic fractionating column.

With y''_{n-1} denoting the molar fraction of the azeotrope in vapor V'' which leave equilibrium $n - 1$, y''_n the molar fraction of azeotrope in liquid flux R'' leaving equilibrium n , and x''_b the molar fraction of azeotrope in the residue of the column, the balance of material (azeotrope) supplies

$$R''x''_n = V''y''_{n-1} + (R'' - V'')x''_b.$$

Omission of the subscripts and solution for y yield

$$y'' = \frac{R''}{V''} x'' - \frac{R'' - V''}{V''} x''_b.$$

This equation represents the line of operation and for the ends of the column assumes the form

$$y_b'' = \frac{R'}{V'} x_f'' - \frac{R' - V'}{V'} x_b'',$$

in which y_p'' and x_f'' are the molar fractions of azeotrope in vapor at the top of the column (distillate) and in the supply.

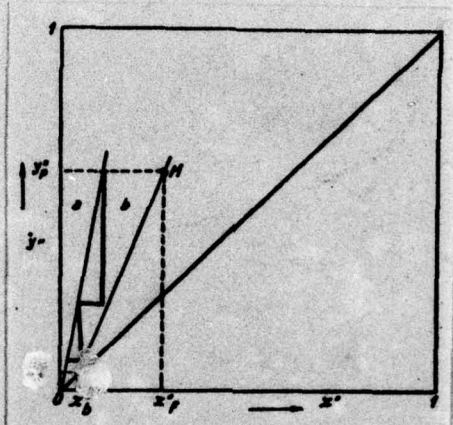


Figure 4. Determination of number of equilibria:

a. line of operation with slope $= \frac{R'}{V'}$; b. equilib-

rium line with slope $\frac{P_2}{P_1} \cdot \frac{1 - x_s''}{1 - x_s''}$ or $\frac{P_1}{P_1 + P_2} \cdot \frac{1}{x_s''}$.

Figure 4 shows the equilibrium curve and line of operation in the system x'', y'' . If vertical line $x'' = x_f''$ is drawn, the line of operation in the x'', y'' system drawn through point (x_b'', y_b'') and having slope $R':V'$ intersects at point M with coordinates $x_f'', x_b'' + \frac{R'}{V'}(x_f'' - y_b'')$. The problem of determining the number of equilibria as a function of $x_f'', x_b'', R'/V'$, and H_2/P_1 amounts to determination of the number of horizontal and vertical lines drawn between the line of operation and the equilibrium curve, from point M to point (x_b'', y_b'') . It can easily be demonstrated analytically that the number n of these horizontal lines is given by the expression

$$n = \frac{\lg \left[x_f'' \cdot x_b'' \left(\frac{R'}{V'} - 1 \right) / \left(\frac{H_2}{P_1} - \frac{R'}{V'} \right) \right] - \lg \left[x_b'' \left(\frac{H_2}{P_1} - 1 \right) / \left(\frac{H_2}{P_1} - \frac{R'}{V'} \right) \right]}{\lg \left(\frac{H_2}{P_1} \cdot \frac{V'}{R'} \right)} \quad (20)$$

It is convenient to take $R' = 1$ as the base in performing calculations for the column. In this case relation (11) becomes

$$n = \frac{\lg\left[\frac{x_f''}{x_b''} \left(\frac{H_2}{P_1} - \frac{1}{V'}\right) + \left(\frac{1}{V'} - 1\right)\right] - \lg\left(\frac{H_2}{P_1} - 1\right)}{\lg\left(\frac{H_2}{P_1} V'\right)} \quad (21)$$

If r denotes the percentage of azeotrope recovered (referred to the supply), from a material balance in terms of azeotrope there is obtained

$$r = 100\left(1 - \frac{R' - V'}{R'} \cdot \frac{x_b''}{x_f''}\right) \text{ and } \frac{x_f''}{x_b''} = \frac{1 - V'}{1 - 0.01 r}, \text{ respectively} \quad (22)$$

Substitution in equation (21) finally yields

$$n = \frac{\lg\left[\frac{1 - V'}{1 - 0.01 r} \left(\frac{H_2}{P_1} - \frac{1}{V'}\right) + \frac{1}{V'} - 1\right] - \lg\left(\frac{H_2}{P_1} - 1\right)}{\lg\left(\frac{H_2}{P_1} V'\right)} \quad (23)$$

This relation permits direct calculation of the number of equilibria (theoretical plates) for a given recover as a function of H_2 , P_1 , and V' , that is, the Henry constant of the solute (component 2), the vapor pressure of the solvent (component 1), and the degree of vaporization of the supply (steam consumption).

When the solute is more volatile than the solvent (the solute being component 1), the slope of the $H_2:P_1$ equilibrium curve in equation (23) is replaced by $\frac{1}{x_s''}$, or more accurately by $\frac{P_1}{P_1 + P_2}$, as follows from equation (12) and equation (19), respectively.

Example. We will consider the case of recovery of nitrobenzene from an aqueous solution containing 0.2% nitrobenzene by weight.

Calculation of equilibrium curve

The mutual solubilities at 100 °C are as follows:

0.8% by wt. $C_6H_5NO_2$ in H_2O

1.4% by wt. H_2O in $C_6H_5NO_2$

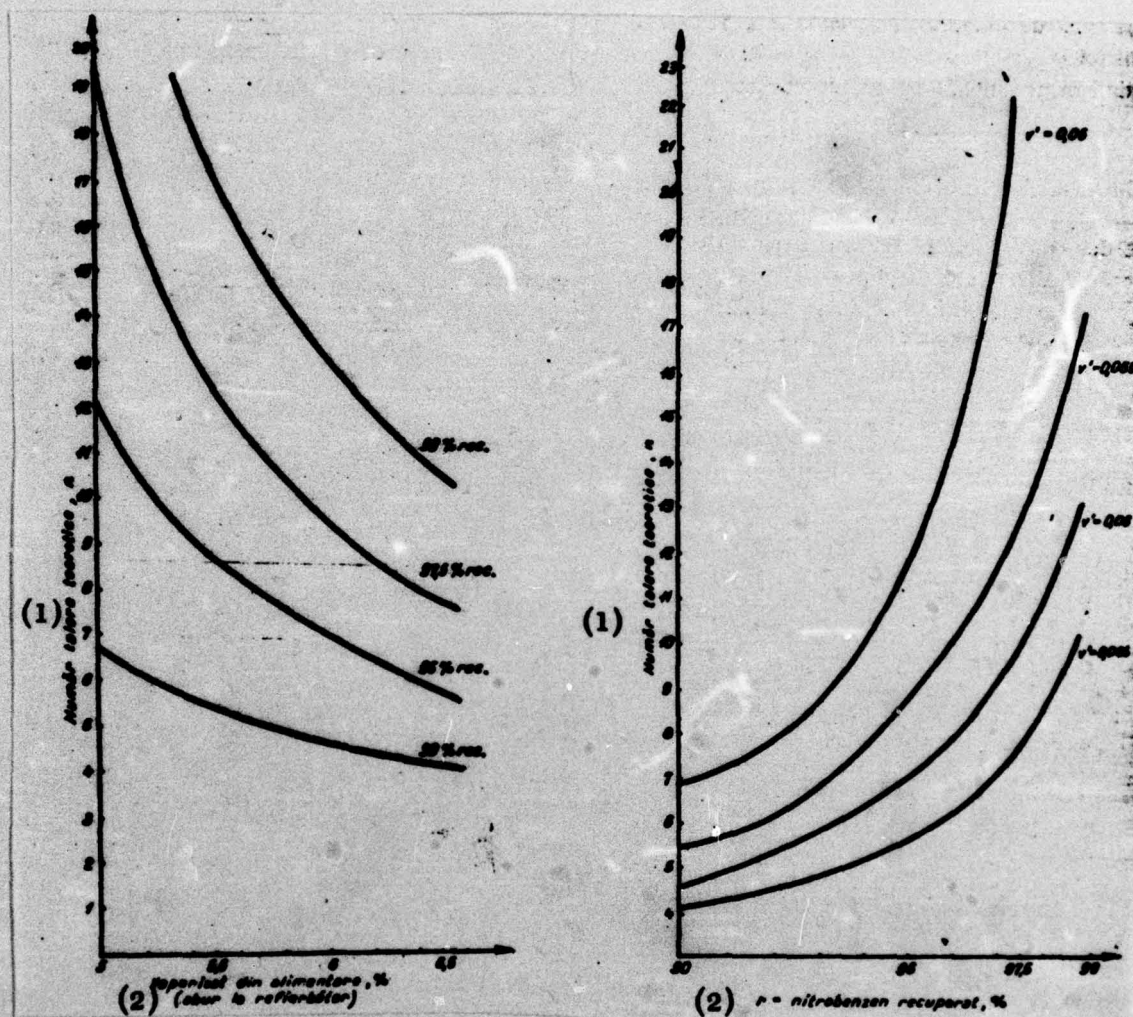


Figure 5. $n = f(r, V')$ for separation of nitrobenzene at atmospheric pressure ($t = 100^\circ\text{C}$).
 (1) Number of theoretical plates, n . (2) Vaporized from supply (steam at reboiler).

Figure 6. $n = f(r, V')$ for separation of nitrobenzene at atmospheric pressure ($t = 100^\circ\text{C}$).
 (1) Number of theoretical plates, n . (2) $r =$ nitrobenzene recovered, %.

The vapor pressures at 100°C are as follows:

$$P_1 = P_{\text{H}_2\text{O}} = 760 \text{ mm Hg}; P_2 = P_{\text{C}_6\text{H}_5\text{NO}_2} = 21 \text{ mm Hg}.$$

Conversion to molar fractions yields the following values for x'_0 and x''_0 :

$$x'_s = 0.998825; x''_s = 0.0950.$$

From relation (1) we find

$$H_2 = P_2 \frac{1 - x''_s}{1 - x'_s} = 21 \cdot \frac{0.905}{0.001175} = 16,200.$$

The equilibrium curve is obtained from relation (7):

$$y'' = \frac{H_2}{P_1} x'' = \frac{16,200}{760} x'';$$

$$y'' = 21.2 x''.$$

Calculation of number of equilibria

It follows from equation (14) that the minimum value of V' (minimum vaporization) is given by the condition

$$\frac{H_2}{P_1} V' = 1, \text{ when } n = \infty.$$

(This relation is valid for very small values of x''_b .)

For a finite number of plates

$$\frac{H_2}{P_1} V' > 1;$$

hence

$$V' > \frac{P_1}{H_2};$$

that is,

$$V' > \frac{1}{21.2}.$$

Let $V' = 0.05$ and the recovery (of azeotrope and thus of nitrobenzene) be 90%.

From relation (23) we obtain

$$r = \frac{\lg\left[\frac{1 - 0.05}{1 - 0.01 \times 90} (21.2 - \frac{1}{0.05} - 1) + (\frac{1}{0.05} - 1)\right] - \lg(21.2 - 1)}{\lg(21.2 \times 0.05)} = 6.7$$

The function $n = f(r, V')$ calculated as indicated in the foregoing is illustrated in Figures 5 and 6 for $r = 90, 95, 97.5, 99\%$ and $V' = 0.05, 0.055, 0.06, 0.065$. On the basis of these curves one can establish the optimum design conditions for the installation as a function of the heat consumption V'' , investment (column height and diameter), and degree of nitrobenzene recovery).

Experimental Part

(a) Since it was surprising to find that, according to the theoretical calculations, highly advanced recovery of nitrobenzene can be accomplished under conditions so advantageous from the technical and economic viewpoint, as is shown by Figure 5 or Figure 6 (small number of theoretical plates and low heat consumption), an attempt was made to verify the relations derived with a suitable laboratory column.

Use was made for this purpose of a column having a filling equivalent to eight theoretical plates and operating according to the system shown in Figure 3. The column was supplied continuously (by pump) with a solution of 0.2% nitrobenzene in water and the level was kept constant in the column still by means of an evacuation siphon. To avoid losses of heat through the walls and thus the formation of internal reflux, the column was introduced into a tube of greater diameter and a temperature of 100 °C was maintained in the annular air space by means of adjustable resistances. The solution of nitrobenzene in water was preheated to 98-99 °C and introduced into the top of the column at this temperature. During operation the temperature in the top and the still of the column was practically constant, being 99.5-99.8 °C and 101-101.5 °C respectively. The product of distillation in the top of the column was separated into two phases, the aqueous phase saturated with nitrobenzene and representing 5.3% of the supply amount, and the oily phase representing 94% of the nitrobenzene contained in the supply.

According to Figure 5, with around 8 t and a steam consumption of around 5.3% the recovery is approximately 94%. It follows that the relations derived are satisfactorily verified.

(b) As follows from equations (1 and 11) and Figure 1, fractionation at lower temperatures is more advantageous, owing to the fact that the mutual solubilities decrease with lowering of the temperature (Figure 1), while the volatility ratio ($P_2:P_1$) generally undergoes very little variation. The slope of the equilibrium curve (equation 11) will consequently have a higher value at lower temperatures. Figure 7 illustrates the function $n = f(r, V')$ for the water-p-nitrotoluene system at an average column temperature of 43 °C (and thus at a column operating pressure of around 55 mm Hg).

With use made of the same fractionation system as that described in the foregoing, but in operation at a pressure of 55 mm Hg, from water containing 0.1% p-nitrotoluene there was achieved a recovery of approximately 99% nitro derivative with a steam consumption of 4% referred to the amount of solution supplied. This experiment as well confirmed the theoretical calculations, as follows from Figure 7.

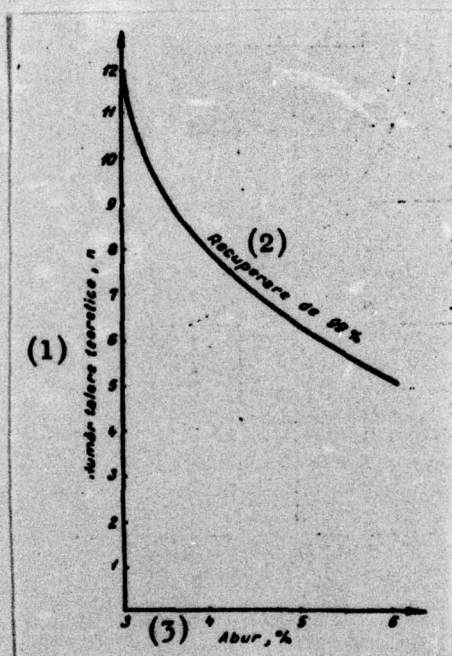


Figure 7. $n = f(r, V')$ for separation of p-mono-nitrotoluene at a pressure of 55 mm Hg; average column temperature 43 °C. (1) Number of theoretical plates, n. (2) 99% recovery.

Graphic Representation of General Relation (Equation 23)

Figure 8 illustrates the function $n = f(k, V', r)$, in which k is the slope of the equilibrium curve of the azeotrope-water system and V' and r have the meanings already defined.

Depending on whether the solute is more volatile or less volatile than water, the slope of the equilibrium curve is calculated from the expression:

$$K = \frac{P_1}{P_1 + P_2} \cdot \frac{1}{x_2^n}$$

or

$$K = \frac{P_2}{P_1} \cdot \frac{1 - x_2^n}{1 - x_2}$$

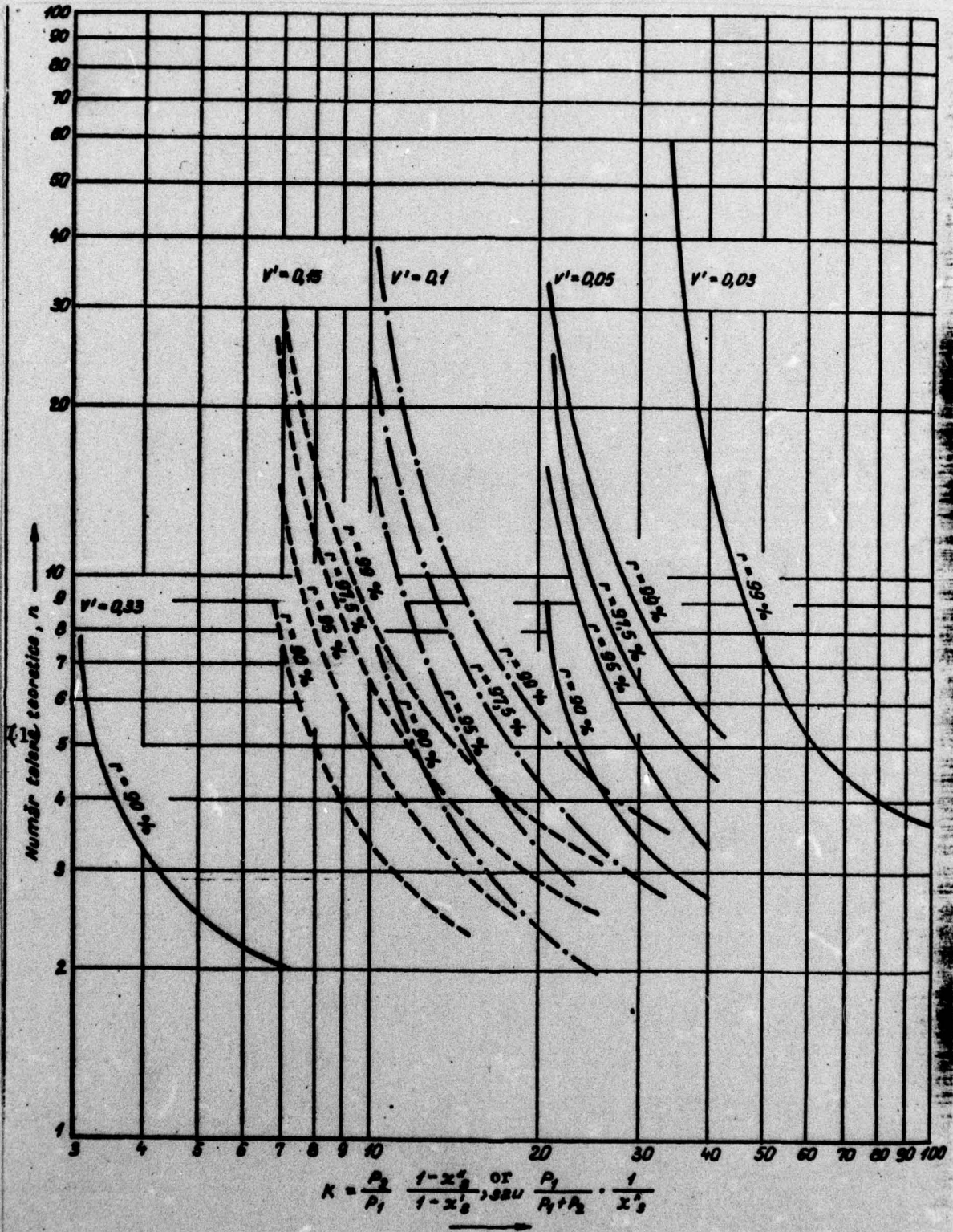


Figure 8. General relation $n = f(K, V', r)$ (equation 23). (1) Number of theoretical plates, n .

It is to be seen from equation 23 that the value of $n \rightarrow \infty$ when $\lg(KV') \rightarrow 0$, that is, vertical line $K = 1/V'$ represents an asymptote and as such may be used in evaluation of V'_{\min} for any value of K .

With K assumed to be variable and V' , r parameters, the function $n = f(K, V', r)$ is plotted in Figure 8 on the basis of equation (23); this function may be used to evaluate the theoretical equilibria of the fractionating column required as a function of the steam consumption and recovery desired. Figure 8 may also be applied to determine whether azeotropic fractionation can be employed in recovery of a given substance from waste water or whether it is advisable to apply another separation process, as is shown by the following example:

m-dinitrobenzene has a normal boiling point of 300 °C, and its solubility in water at 100 °C is 0.3 g/100 g water. At 100 °C the vapor pressure of *m*-dinitrobenzene is approximately 0.35 mm Hg. Since the solubility of water in *m*-dinitrobenzene is of the same order as that of *m*-dinitrobenzene in water, the slope of the equilibrium curve is calculated from equation (18), in which

$$P_2 = 0.35 \text{ mm Hg}$$

$$x'_s = \frac{\frac{0.3}{168}}{\frac{0.3}{168} + \frac{99.7}{18}} = 0.000324$$

$$P_1 = 760 \text{ mm Hg.}$$

Assuming $1 - x''_s = x'_s = 0.999676$, we obtain the slope

$$\begin{aligned} \frac{P_2}{P_1} &= \frac{1 - x''_s}{1 - x'_s} \\ &= \frac{0.35}{760} \cdot \frac{0.999676}{0.000324} = 1.4. \end{aligned}$$

As follows from Figure 8, at a slope value such as this the steam consumption would far exceed 33% of the supply ($V'_{\min} = 1/1.4 = 0.71$).

Similar situations are encountered with other nitro derivatives, such as *o*-nitroaniline, dinitrochlorobenzene, dinitrotoluene, etc, and with many other organic substances having high boiling points and low solubility in water. In view of the fact the operations of manufacturing these substances entail considerable waste water production, azeotropic fractionation would involve overly high specific consumptions. In such situations one can resort to extraction of the organic substance with a suitable solvent (benzene, trichloroethylene, chlorobenzene, etc) determined by

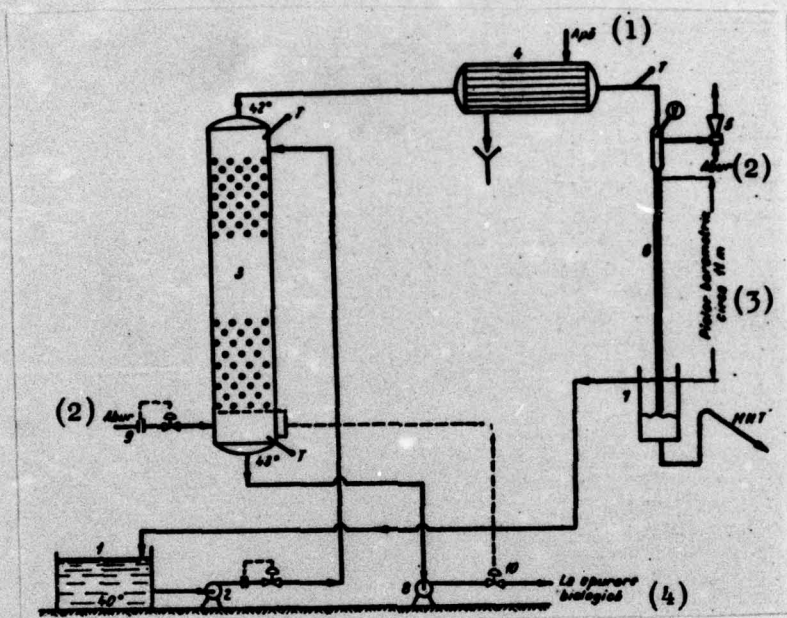


Figure 10. Recovery of mononitrotoluene (MNT) by azeotropic fractionation under vacuum: 1. decanter. 2. pump. 3. fractionating column. 4. condenser. 5. ejector. 6. barometric leg. 7. phase separator. 8. evacuating pump. 9. steam. 10. level regulator. (1) Water. (2) Steam. (3) Barometric leg, approximately 11 m. (4) To biological treatment.

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