Polymer Purification Through Solvent Addition: Physical Implications and Modeling of Separation Units

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Synopsis

   Addition of solvents may ease removal of small amounts of volatile residues from polymeric materials. Enhanced separation thus obtained is due to the influence of the solvent on the vapor–polymer–liquid equilibria and to its influence on the increase of the diffusion rate of the impurities. The problem has been examined through a mathematical model describing the behavior of the units employed in the purification. Examples of applications are illustrated in which prediction of the behavior of purification units are performed from small-scale apparatus experiments.

INTRODUCTION

   The removal of small amounts of volatile residues from polymeric materials represents an important step in many polymer processing plants. Such purification processes have raised crucial problems connected with the necessity of meeting environmental, health, and safety regulations. The impurities are monomers, solvents, and condensation by-products. These are usually removed by vacuum or steam stripping of polymer melts or polymer particles. In some cases the residues are tightly bound to the polymeric materials, and this makes the preceding treatments difficult or requiring very long operating times. In these cases, if the polymer is brought into contact with one of its volatile solvents which is easily separable, the elimination of the impurities is facilitated.

   It could be convenient to perform the purification process in two steps. In the first, the polymeric material is brought into contact with a stream of a mixture of an inert gas and an appropriate solvent. A schematic of this extractive purification process is shown in Figure 1. The rational design of the described purification units represents a difficult problem in which both interphase equilibria and mass transfer phenomena must be taken into account. The recent developments of molecular thermodynamics and of molecular theories of transport phenomena offer a valuable contribution for modeling the mentioned units. This approach in fact decreases the number of empirical parameters present in the models, and therefore it decreases the amount of experimental information needed for the description of the phenomena under examination.

   Our analysis will be focused on a system of particles of an amorphous monodisperse polymer to which a local equilibrium liquid structure can be attributed. In such a situation, the local relaxation in the system is fast compared with the diffusion process, and a Fickian approach can be employed to describe the mass

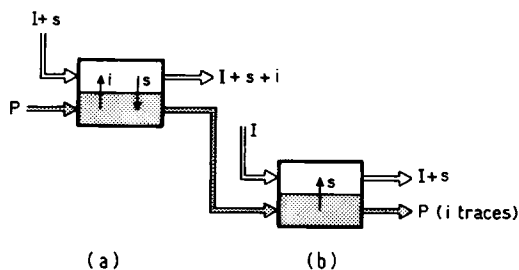* Present address: Caffaro S.p.A., Brescia, Italy.

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Fig. 1. Scheme of the purification units: I, inert gas; P, polymer; i, impurity; s, solvent; (a) unit for removing i; (b) unit for removing s.

transfer processes. The preceding assumption is reliable if the material under examination is at a temperature higher than the glass transition temperature.

On the basis of the previous assumptions, some models of purification units will be developed. These will be applied to some cases in order to emphasize the role of physical factors in the purification processes.

THERMODYNAMICAL ASPECTS

Let us assume that equilibrium exists at the polymer–gas interphase, while concentration gradients are present inside the two phases. In process design, the required phase equilibrium information is usually expressed by K factors:

$$K_i(T,P,\mathbf{x}_i,\mathbf{y}_i) = \frac{y_i}{x_i} = \frac{\gamma_i^p f_i^0}{\varphi_i P} \tag{1}$$

where γ_i^p is the activity coefficient of the ith component in the polymeric phase, f_i^0 is the standard-state fugacity, and φ_i is the vapor-phase fugacity coefficient. For condensable components, as considered here, f_i^0 is the fugacity of the pure liquid at the system temperature and pressure, it is calculated from

$$f_i^0 = p_i^0 \varphi_i^0 \exp \int_{p_i^0}^{P} \frac{\tilde{V}_i}{RT} dP \tag{2}$$

where p_i^0 is the vapor pressure and φ_i^0 is the saturation fugacity coefficient of pure component i at the system temperature. φ_i^0 and φ_i are readily calculated using for example the virial equation of state.[1]

Since $\Sigma_j K_j x_j$ must be equal to 1, it follows that

$$y_i = \frac{K_i x_i}{\sum_j K_j x_j} \simeq \frac{K_i x_i}{\sum_{j \neq p} K_j x_j} = \frac{x_i}{\sum_{j \neq p} \alpha_{ij} x_j} \tag{3}$$

where p indicates the polymer. In deriving the last equation, the low volatility of the polymer with respect to the other components ($K_p \simeq 0$) has been taken into account. Besides, $\alpha_{ij} = K_j/K_i$. In the presence of an inert gaseous component with negligible solubility, the previous equation must be modified as follows:

$$y_i = \frac{K_i x_i (1 - y_I)}{\sum_{j \neq p} K_j x_j} = \frac{x_i (1 - y_I)}{\sum_{j \neq p} \alpha_{ij} x_j} \tag{4}$$

The determination of the K factors implies experimental measurements essentially devoted to the evaluation of the activity coefficients γ_i^p. Molecular ther-

modynamics allows the prediction of the values of liquid phase activity coefficients by treating the system as a mixture of functional groups. These, when added, make up the molecular species present.[2]

Between the different proposed group contribution methods, particular relevance must be given to the Unifac method, which has also been successfully extended to polymer solutions in a recent article.[3] Since our analysis will be limited to amorphous polymer solutions, with liquidlike structure, the procedure indicated will be employed for the evaluation of γ_i^p coefficients which appear in eq. (1).

The Gibbs free energy of the mixture is assumed to be the sum of the following three contributions:

C (*combinatorial*): associated with the difference in molecular size and shape.

R (*residual*): associated with the energy interactions between the groups.

FV (*free volume*): associated with the change of volume in the mixing process, since the polymer molecules are more tightly packed than the solvent molecules.

As a consequence of the preceding assumptions, the logarithm of the activity coefficient may be written as

$$\ln \gamma_i^P = \ln \gamma_i^c + \ln \gamma_i^R + \ln \gamma_i^{FV} \tag{5}$$

The different contributions present in this equation are evaluated from molecular properties, particularly from the volumes, surfaces, and interaction energies of the molecular groups. Specifically, the following parameters are employed: van der Waals or hard-core molecular volume per unit mass:

$$b_i = \frac{1}{M_i} \sum_k \nu_k^{(i)} \tilde{b}_k \tag{6}$$

van der Waals surface per unit mass:

$$q_i = \frac{1}{M_i} \sum_k \nu_k^{(i)} \tilde{q}_k \tag{7}$$

Interaction parameter:

$$\psi_{kl} = \exp[-(U_{kl} - U_{ll})/RT] = \exp[-a_{kl}/T] \tag{8}$$

U_{kl} being the mean potential energy of interaction between the groups k and l.

The combinatorial term depends only on the volume and surface properties of the molecules through their weight fractions w_i:

$$\ln \gamma_i^c = f \left[\left(\frac{w_i q_i}{\sum_j w_j q_j} \right), \left(\frac{w_i b_i}{\sum_j w_j b_j} \right) \right] \tag{9}$$

The residual contribution is expressed as follows:

$$\ln \gamma_i^R = \sum_k \nu_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \tag{10}$$

where Γ_k is the group activity coefficient and $\Gamma_k^{(i)}$ is the group activity coefficient of group k in a reference solution containing only molecules of type i. The form of eq. (10) guarantees the attainment of the normalization condition:

$$\lim_{w_i \to 1} \gamma_i^R = 1 \tag{11}$$

The coefficients Γ are evaluated from the values of the interaction parameters ψ_{kl} and from the weight concentrations of the groups in the mixture:

$$\chi_k = \frac{\sum_i \nu_k^{(i)} w_i}{\sum_i \sum_l \nu_l^{(i)} w_i} \tag{12}$$

It follows that

$$\left.\begin{array}{c} \Gamma_k \\ \Gamma_k^{(i)} \end{array}\right\} = \Gamma(\chi_k, T) \tag{13}$$

The form of the functions (9) and (13) and the details of their application are described in the previously mentioned article.

Finally, the FV contribution can be evaluated by means of the equation of state proposed by Flory,[4] which gives the following equation:

$$\ln \gamma_i^{FV} = 3c_i \ln \left[\frac{(\tilde{v}_i^{1/3} - 1)}{(\tilde{v}_M^{1/3} - 1)}\right] - c_i \left[\frac{(\tilde{v}_i/\tilde{v}_M) - 1}{1 - (1/\tilde{v}_i^{1/3})}\right] \tag{14}$$

$\tilde{v}_{i,M}$ being a reduced volume given by the ratio between the volume per unit mass of i, or of the mixture M, and the hard-core molecular volume given by eq. (7); $3c_i$ is the number of external degrees of freedom per solvent molecule.

Diffusion in Polymer

At present, there exists no general theory capable of describing the complete range of the diffusional behavior exhibited by polymer–solvent systems. The subject has been recently reviewed by Vrentas and Duda.[5]

For the problem under examination, let us limit our analysis to the case of concentrated polymer mixtures. In such a situation it is reasonable to represent the mixture as an ensemble of pseudobinary systems of the kind i–p. It is advisable to approach the problem from a thermodynamic point of view. At the interphase, the chemical potentials of component i are equal, while inside the phases the driving forces for the mass transfer processes are given by their gradients.

According to the hydrodynamic theory of diffusion, such gradients must be balanced by the diffusion resistance associated to the transfer of momentum between the molecules[6]:

$$\nabla \mu_i = \left(\frac{\partial \mu_i}{\partial c_i}\right)\left(\frac{\partial c_i}{\partial z}\right) = -c_p \xi_{ip}(\mathbf{u}_i - \mathbf{u}_p) \tag{15}$$

where $\xi_{ip} = \xi_{pi}$ are the friction coefficients. The mass diffusion flux of the ith component relative to the velocity of p is given by

$$\mathbf{J}_i^p = \rho_i(\mathbf{u}_i - \mathbf{u}_p) \tag{16}$$

From the last two equations we have

$$\mathbf{J}_i^p = -\frac{\rho_i \bar{V}_p}{\xi_{ip}}\left(\frac{\partial \mu_i}{\partial c_i}\right)_{T,P} \frac{\partial c_i}{\partial z} = -D_{ip}\frac{\partial c_i}{\partial z} \tag{17}$$

where D_{ip} is the Fickian diffusion coefficient of i in the polymer. When chemical potential gradients disappear, the process of mutual diffusion ceases, but not the molecular motions. Therefore, it is still possible to define the self-diffusion coefficients D_i and D_p.

According to Bearman,[6] a relation between ξ_{ip}, D_i, and D_p can be obtained. From it, the following equation is derived:

$$D_{ip} = \frac{D_i x_p + D_p x_i}{RT} \left(\frac{\partial \mu i}{\partial \ln x_i}\right)_{T,P} \simeq D_i x_p \left(\frac{\partial \ln a_i}{\partial \ln x_i}\right)_{T,P} \tag{18}$$

where $a_i = \gamma_i^p x_i$ is the activity of component i in the polymer–solvent system. In deriving eq. (18), it has been taken into account that the ratio D_p/D_i^0 is negligible at low solvent concentrations.

Although the theoretical justification for the use of eq. (18) is weak, recent experimental research indicates that the approximation presented in eq. (18) is reasonably good for concentrated polymer solutions.[7] The only theory which has been sufficiently developed at the present time to describe the complex diffusional processes in concentrated polymer mixtures is the free-volume theory.[1] It assumes that the normal statistical fluctuations in the local density open up voids of molecular sizes into which a diffusing molecule may jump. The process does not require activation energy, and the frequency of the diffusion jumps depends on the probability of the occurrence of a local void greater than some minimum or critical volume V^*. The theory has also been applied to polymer–solvent systems giving the following expression for the self diffusion coefficient:

$$D_i = D_i^0 \exp\left[-\gamma \left(\frac{w_i V_i^* + w_p \xi V_p^*}{V_f}\right)\right] \tag{19}$$

where γ is a factor $(0.5 \leq \gamma \leq 1)$ introduced because the same free volume V_f is available to more than one molecule. V_i^* is the specific critical volume of component i, while V_p^* is the specific critical volume for the displacement of a jumping unit of polymer. The parameter ξ is defined by $\xi = V_i^* M_i/V_p^* M_j$, where M_j is the molecular weight of a jumping unit of the polymer.[8] It is basic to point out that eq. (19) was derived for a binary system of one solvent and a polymer. Its use in ternary systems implies an approximation which can be removed according to the procedure proposed by Ferguson and Von Meerwall.[9]

It is reasonable to expect that the value of V_i^* should be approximately equal to the molecular volume b_i, previously defined by eq. (6).

The specific free volume V_f has been evaluated as the difference between the specific volume of the mixture and the hard core molecular volume, given by eq. (6):

$$V_f = V_M - b = V_M - \sum_i w_i b_i \tag{20}$$

Admittedly we take this as a fairly uncouth position, since not all the free volume in a system is available for molecular migration. In fact, only that free volume which is redistributed without significant activation energy requirements should be considered in eq. (20).

From this it may be constructed that the free volume, in free volume formulation of molecular transport, cannot be deduced from the first principles. For the above reasons, eqs. (19) and (20) have been pragmatically employed by leading the uncertainty involved in the previous assumption on the value of D_i^0. It will shortly be shown that its reliability, and that of the entire model, will be tested in reference to its ability to describe experimental data.

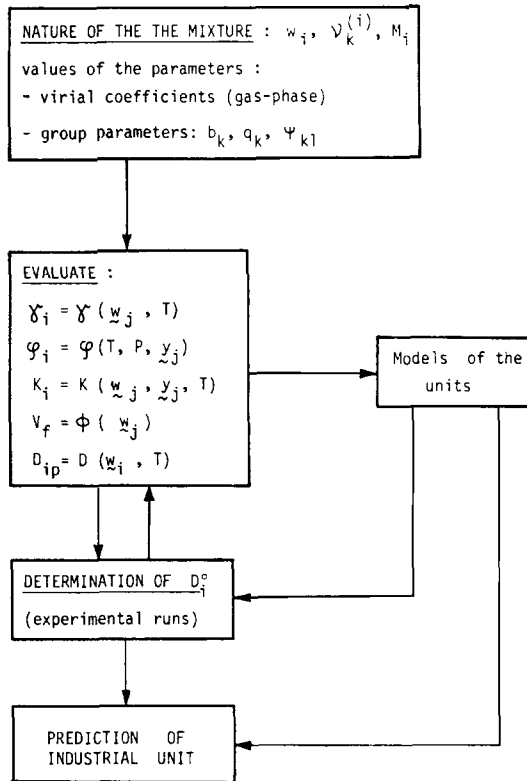Summarizing the procedure, on the basis of the available information on the

Fig. 2. Block diagram of the operating procedure.

molecular groups, it is possible to obtain a self-consistent set of physicochemical data and build the model for a purification unit. Only the values of D_i^0 are assumed to be adjustable parameters of the models.

TABLE I
Characteristic of the Materials and Parameters Employed in the Calculations

Chlorinated rubber
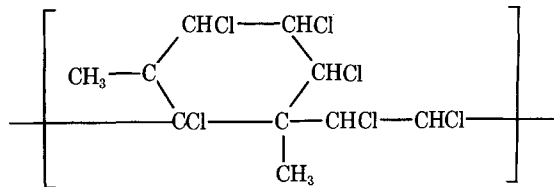
Specific weight 1.63

Carbon tetrachloride
Specific weight 1.595
Antoine constants: $A = 7.02447$; $B = 1161.00$; $C = 224$
Acetone
Specific weight 0.792
Antoine constants: $A = 6.9339$; B = 1242.43; C = 230
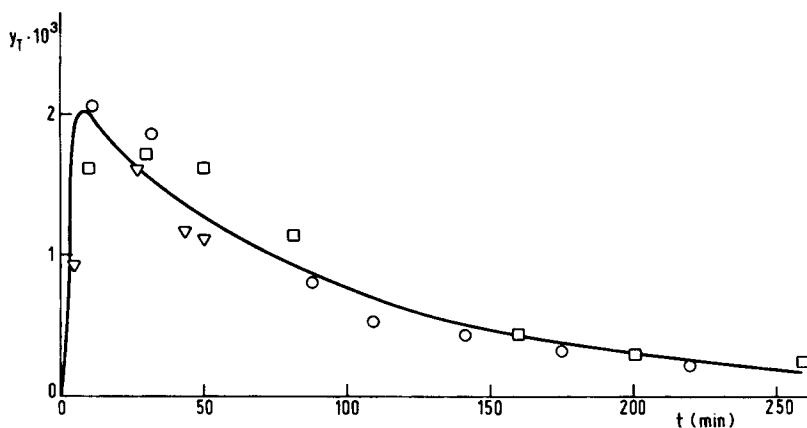The Unifac parameters were taken from refs. 3 and 11.

Fig. 3. Experimental data obtained for the system: chlorinated rubber with CCl$_4$, treated with acetone. Gas flow rate, 0.088 mole/min; mole fraction of acetone in feed, 0.17; temperature, 40°C; (△, □) runs performed by passing the gaseous stream through the particle bed; (○) runs performed by licking the bed of particles. Continuous curve: calculated.

Models for the Purification Units

The fundamental equations describing the purification units are obtained by using mass balances, over the entire or differential volume, for both the gas stream and the polymeric phase. These equations are linked together by the mass transfer rate expressions obtained by considering transport at the gas–particle interphase and intraparticle diffusion.

Mathematical solution to the spherical intraparticle diffusion problem has been obtained by several investigators, and the results were reviewed by Glueckauf,[10] who proposed the following approximate analytic solution:

$$r_i = \frac{\partial \overline{C}_i}{\partial t} = \frac{60 D_{ip}(\overline{C}_i, T)}{d_p^2} (C_i^{\text{i}} - \overline{C}_i) \tag{21}$$

TABLE II
Values of the Parameters Used in the Model Fit Shown in Figure 3

$d_p = 0.01$ cm	$M_A = 58.08$
$V = 38.6$ cm^3	$M_T = 153.8$
$\epsilon = 0.82$	$M_P = 379.25$
polymer holdup = 1 g	
$X_A^0 = 0$	$V_A^* = 0.673$ cm^3/g
$X_T^0 = 2.28 \times 10^{-4}$ mole/g	$V_T^* = 0.334$ cm^3/g
$T = 60°$C	$V_P^* = 0.409$ cm^3/g
$F = 0.204 \ 10^{-4}$ mole/sec	$\gamma = 1$
$y_A^0 = 0.168$	$M_j = M_i$
$y_T^0 = 0.$	$\dfrac{\partial \ln a_A}{\partial \ln X_A} = 1 - 470.46 X_A$ [a]
$y_I^0 = 0.832$	
$\rho_A = 0.792$ g/cm^3	$\dfrac{\partial \ln a_T}{\partial \ln X_T} = 1 - 617.38 X_T$ [a]
$\rho_T = 1.595$ g/cm^3	
$\rho_P = 0.300$ g/cm^3	$K_A = -2.5821 \times 10^5 X_A + 757.7$ [a]
$\tilde{\rho}_g = 3.66 \times 10^{-5}$ mole/cm^3	$K_T = -6.829 \times 10^5 X_T + 1315.2$ [a]

[a] Empirical correlations derived by fitting the Unifac method[3,11] results.
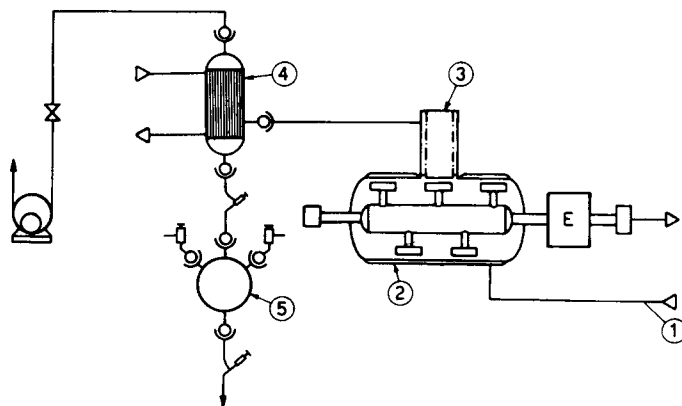
Fig. 4. Scheme of pilot purification unit: 1, input of the superheated vapor solvent; 2, solid mixing unit; 3, bag filter; 4, solvent condenser; 5, storage of the condensed solvent.

where the index i indicates the interphase, r_i is the rate of the mass transfer process (in moles of i/time volume), and $\overline{C}_i$ is the mean concentration in the particle. It can be expressed also as a function of the gas-phase concentrations, and the two expressions for r_i can be equated. The following equation is obtained:

$$\frac{60D_{ip}(\overline{C}_i, T)}{d_p^2}(C_i^i - \overline{C}_i) = ak_{gi}P(y_i - y_i^i) \tag{22}$$

TABLE III
Comparison between the Experimental Output Data of the Pilot Unit and the Results of the Model

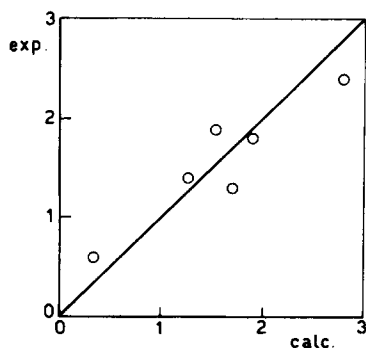| Run No. | Time, sec | Gas feed, mole/sec | Weight in the solid, % | | | |
| | | | Experimental | | Calculated | |
			A	T	A	T
1	7200	1.326×10^{-3}	3.7	.6	4.26	.33
2	1800	6.063×10^{-3}	2.7	1.3	2.96	1.70
3	2700	1.594×10^{-3}	2.8	1.9	3.11	1.54
4	1800	2.835×10^{-3}	2.7	1.8	2.76	1.91
5	900	5.747×10^{-3}	3.0	2.4	1.93	2.78
6	2700	2.729×10^{-3}	3.3	1.4	2.27	1.27

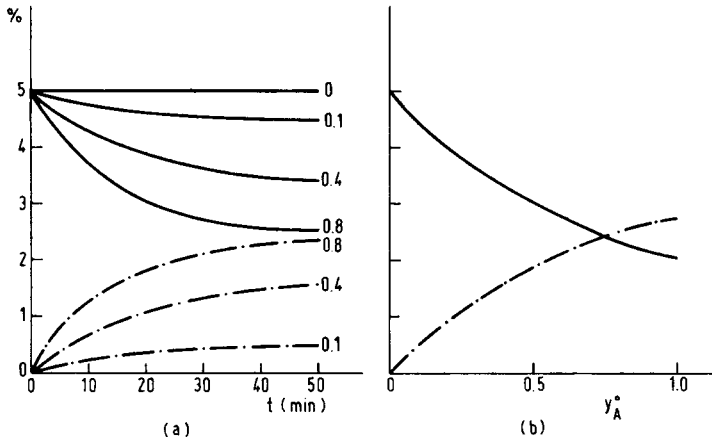Fig. 5. Experimental vs. calculated amount of CCl_4 in the solid (wt %).

Fig. 6. Simulation of a PM unit. Flow rate of polymer, 125 g/min; flow rate of gas, 0.56 mole/min; mass of the solid in the unit, 3710 g. (a) Percentages of T (continuous lines) and of A (dotted lines) in the solid as function of time. Different lines correspond to different amounts of acetone in the gas stream. (b) Percentages of T (continuous line) and of A (dotted line) at the exit after 65 min, as function of mole fraction of acetone in the feed.

where y_i^i and C_i^i are the values of the concentrations at the interface linked by the equilibrium eq. (1), and k_{gi} is the mass transfer coefficient of component i in the gaseous phase, and it depends on the operating conditions.

Two types of purification units have been considered: with perfect mixing (PM) and with a plug flow (PF) of the two streams. In the former case (PM), the following equations, which give the dynamic mass balance of volatile components, can be derived:

Gaseous phase

$$\tilde{\rho}_g V \epsilon \frac{dy_i}{dt} = -(1 - \epsilon)Vr_i + F\left(\frac{y_i^0}{1 - \sum_{j \neq I} y_j^0} - \frac{y_i}{1 - \sum_{j \neq I} y_j}\right) \tag{23}$$

Condensed phase

$$\rho_p(dX_i/dt) = W/V(X_i^0 - X_i) + r_i(1 - \epsilon) \tag{24}$$

For the gaseous phase, the following equation expresses the overall balance:

$$F\left(\frac{1}{y_I^0} - \frac{1}{y_I}\right) - (1 - \epsilon)V\sum_i r_i = 0 \tag{25}$$

The initial condition are given by the values of the concentrations of the different species at the beginning of the operation.

In the second case (PF), the concentration gradients of the different species are present along the axis. If we consider a differential section dz of the unit, the following balance equation can be derived:

Gaseous phase

$$\partial G_i/\partial z + \epsilon\tilde{\rho}_g(\partial y_i/\partial t) = -(1 - \epsilon)r_i \tag{26}$$

Condensed phase

$$W/A(\partial X_i/\partial z) + \rho_p(\partial X_i/\partial t) = (1 - \epsilon)r_i \tag{27}$$

Assuming now the plug flow unit operating in a steady-state condition, the mass balance on the gaseous phase reduces to

$$\partial G_i/\partial z = -(1 - \epsilon)r_i \tag{28}$$

while the concentration on the condensed phase may be obtained by an overall material balance between the entrance section ($z = 0$) and the generic section z:

$$(G_i - G_i^0) \pm W/A(X_i - X_i^0) = 0 \tag{29}$$

where the plus sign holds for a cocurrent unit and the minus sign for a counter-current unit. Then the mathematical model reduces to a system of normal differential equations of first order, where the initial conditions are given by the flow rate of all components in the gaseous phase in the entrance section ($z = 0$) of the unit.
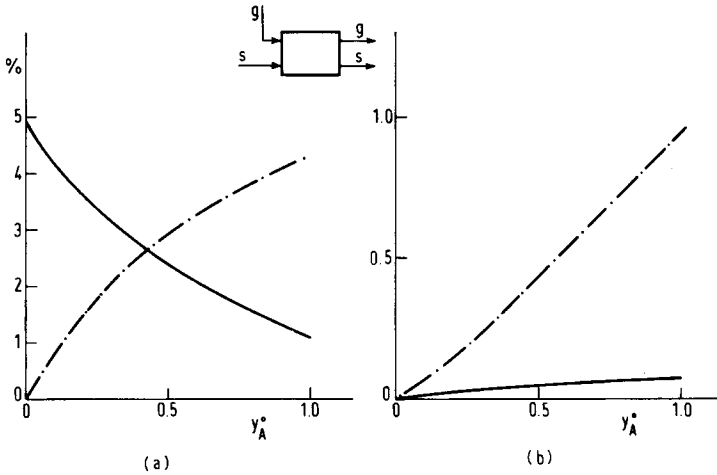

Fig. 7. Simulation of a PF unit. Flow rates as in Fig. 4. (a) Percentages in the solid at the exit, under stationary conditions, as function of mole fraction of acetone in the feed. (b) Mole fractions of A and T in the gas phase as a function of mole fraction of acetone in the feed. Continuous lines, T; dotted lines, A.
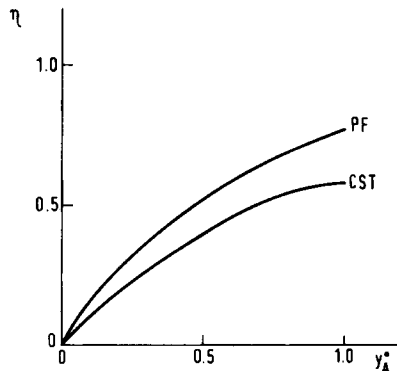

Fig. 8. Comparison between the effectiveness of PF and PM units as a function of the amount of acetone in the feed.

The system of eqs. (23) and (24) as well as the system of eqs. (28) and (29), for the PM and the PF unit, respectively, together with eqs. (1), (21), and (22) describing the mass transfer between the two phases, can be numerically integrated with a marching procedure (for example, the Runge–Kutta method).

It is worthwhile to point out that in the countercurrent unit case the conditions of the streams of the two phases are given on the opposite sides of the unit; therefore, at the entrance section one of the two streams is unknown and the marching procedure cannot be applied. This difficulty has been overcome by using the following trial and error procedure:

(1) Choose a value for the unknown stream conditions at the entrance section.

(2) Evaluate the profile along the unit by integrating the system of eqs. (28) and (29) with a marching procedure.

(3) Check the stream conditions at the exit section and iterate the procedure with new values at the entrance section.

In both cases, PM and PF, the change in the equilibrium and transfer properties, from one integration step to the next because of the change in the phase composition, has been taken into account. A block diagram of the operating procedure is shown in Figure 2.

Example Applications

Let us now consider the application of the described procedure to a specific problem. Particularly we want to consider the purification of chlorinated rubber. This contains as impurity carbon tetrachloride, which is employed as a solvent in the chlorination process.

In Table I, the characteristics of the material are summarized. Simple vacuum or steam treatments are unable to lower the amount of CCl_4 beyond 5% (by weight). On the contrary, if the material is treated with acetone, the impurity is removed in a reasonable time. The acetone dissolved from the material is readily removed by vacuum.

In order to apply the described calculation procedure, it was necessary to determine the coefficients D_A^0 and D_T^0 which are the only adjustable parameters in the model. This experimental determination was done under dynamic conditions.

A stream of air containing acetone was passed through a bed (diameter 1 cm, height 2 cm) of particles. The concentration of carbonium tetrachloride at the exit flow was measured by gas chromatography. Runs were also performed by licking the bed of particles.

The same curve fits the experimental data reported in Figure 3 for the two cases. This indicates that under our operating conditions the resistance to mass transfer was essentially localized inside the particles. The experimental data were simulated with the PM model with $W = 0$. A good interpretation of the experimental data was obtained by attributing to the parameters D_i^0 the following values (A = acetone, T = tetrachloride):

$$D_A^0 = 8.20 \times 10^{-9} \; (cm^2/sec), D_T^0 = 1.07 \times 10^{-9} \; (cm^2/sec)$$

These results emphasize that acetone has a higher intrinsic tendency to diffuse in the polymer than tetrachloride.

All the parameters employed in the model are summarized in Table II. On the basis of such values and by applying the described models, it is possible to predict the behavior of some industrial purification units. We have specifically considered the output data of a standard pilot unit of Buss Company. It is a semibatch equipment with a polymer holdup of 2.6 kg. All the experimental runs have been performed at a fixed temperature of 80°C, and the amount of CCl_4 in the polymer was 4.8% in weight.

A scheme of the employed equipment is illustrated in Figure 4. The experimental runs reported in Table III have been obtained through different values of the feed rate, constituted of pure acetone. Each run is characterized by a time value at which it was interrupted and the polymer analyzed. Both amounts of acetone and carbon tetrachloride were determined. The results are summarized in Table III together with calculated values.

Figure 5 shows a graphic comparison between the experimental and calculated amounts of CCl_4; it reveals that the points are uniformly scattered around the diagonal. On the whole it appears that despite the mentioned approximation, particularly the one involved in eq. (20), the prediction is satisfactory and therefore justifies the application of the model according to the scheme illustrated in Figure 2.

It also seems to be of interest to analyze the influence of the operating conditions on the separation effectiveness. Let us consider a PM unit which works under the conditions indicated in the legend of Figure 6(a). The integration of eqs. (23) and (24) allows us to obtain the transient concentrations of T and A at the exit of the unit.

It was found that, at the selected operating conditions, more than 50 min are required to achieve steady state. The influence of acetone on the purification process is significant. Increasing its percentage in the feeding also increases the amount of T removed from the polymer significantly. This is illustrated by the curves given in Figure 6(b), where the percentages of T and A in the solid, under stationary conditions, are shown as a function of the amount of acetone in the feed.

In Figures 7(a) and (b), the results of a series of calculations performed on a PF unit are reported. The figures give the compositions in the condensed (a) and gaseous (b) phases at the exit of the unit, as a function of the amount of acetone in the feed. These results qualitatively confirm the ones reported in Figure 6. It can be seen that the PF unit has advantages over the PM unit. In fact, if we define separation effectiveness as

$$\eta_{CCl_4} = \frac{(p\%_{CCl_4})_{in} - (p\%_{CCl_4})_{out}}{(p\%_{CCl_4})_{in}}$$

the behavior illustrated in Figure 8 is obtained. This clearly emphasizes the need to limit backmixing effects, especially at high solvent percentages.

NOMENCLATURE

a	outer particles surface are (area/volume)
a_i	activity of component i
A	section area of the unit
$\hat{b}_k$	van der Waals volume of group k, per mole
C_i	molar concentration of i in the polymer

$\overline{C}_i$	mean molar concentration of i in the polymer
d_p	diameter of particles
D_i, D_p	self diffusion coefficients
D_{ip}	diffusion coefficient of component i in the polymer
D_i^0	coefficient of eq. (19)
f_i	fugacity of component i
F	flow rate of inert gas (mole/time)
G_i	flow rate of component i (mole/time $\cdot$ section)
k_{gi}	gas phase mass transfer coefficient of component i (mole/area$\cdot$time$\cdot$pressure)
K_i	interphase equilibrium factor of component i
$p\%_{CCl_4}$	wt % of CCl_4 in the rubber
P	pressure
$\tilde{q}_k$	van der Waals surface of group k, per mole
r_i	rate of mass transfer of component i (moles/volume of solid $\cdot$ time)
T	temperature
$\mathbf{u}_i$	diffusion velocity of component i
v	volumetric flow rate of gas
$\tilde{v}_i$	reduced volume of component i
V	volume of the unit
V_f	free volume of the polymer per unit mass
V_i^*	critical diffusion volume of component i for unit mass
$\tilde{V}_i$	molar volume of component i
w_i	weight fraction of component i in the condensed phase
W	mass flow rate of the polymer, solvent free
x_i	molar fraction of component i in the polymer
X_i	moles of i per unit mass of pure polymer
y_i	molar fraction of component i in the gas phase
z	axial coordinate
γ_i	activity coefficient of component i
ϵ	bed particles void fraction
η	effectiveness of the unit
μ_i	chemical potential of component i
ξ_{ip}	fraction coefficient
ρ_i	density of component i (mass/volume)
ρ_p	bulk density of polymer (mass/total volume)
$\tilde{\rho}_g$	molar density of gaseous phase
$\nu_k^{(j)}$	number of k groups in j molecules
φ_i	fugacity coefficient of component i
χ_k	weight fraction of group k in the mixture
ψ_{kl}	interaction parameter

Subscripts

i, j, m	volatile components
k	molecular group
p	polymer
I	inert component
A	acetone
T	carbon tetrachloride

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