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Abstract

In the EVA copolymers process (ethylene and vinyl acetate copolymers), the stream recycle ethylene contains vinyl acetate and acetic acid as impurities. It is necessary to remove the acetic acid to increase the quality of the final product. The removal of acetic acid by absorption with differents solvents has been investigated. Mass transfer coefficients needed for absorber simulation and design were obtained. The experimental data indicate that the resistance of a liquid film to mass transfer is practically negligible when using water and vinyl acetate as solvents. The absorber was simulated by using a nonequilibrium model which reproduced the experimental results to deviations of less than 20%

Key Words: Removal; Absorption; Nonequilibrium model

INTRODUCTION

The ethylene and vinyl acetate copolymers (EVA copolymers) form a group of products characterized by their high versatility. Among the properties of these copolymers are their thermal stability, resistance to thermal distortion, resistance to the aging, and chemical resistance (*1*, *2*). These properties enable EVA copolymers to be used in such applications as the production of plastics for packing food, materials for medical use, adhesives, etc. The EVA copolymers were initially developed by DuPont (*3*, *4*), and at present over 10^5 metric tons are produced each year. In Spain these copolymers are produced by Repsol Quimica S.A. Its plant is located in Puertollano and has a production of 25,000 metric tons/year (*5*).

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EVA copolymers are produced industrially by the reaction of ethylene with vinyl acetate at high pressures (≃ 2000 atm) and high temperatures (150–200°C), using organic peroxides as catalysts (*6*). The stream produced is expanded, forming a liquid stream containing the copolymer and a gas stream mixture of ethylene, vinyl acetate, the catalyst solvent, and acetic acid. This acetic acid is produced by the degradation of the copolymer in the expansion step, and its removal is necessary to improve the quality of the final product.

The main ways of removing acidic impurities of gases are absorption (either physical absorption or absorption into a solution of a chemical base), adsorption (on zeolites, activated carbon, etc.), or chemical conversion to other compounds (*7*). In our study we used absorption as the method to remove acetic acid (*8*, *9*).

The development of an industrial separation method to remove acetic acid from the ethylene stream implies the previous selection of a specific solvent which is compatible with the rest of the process step. The absorber simulation and design need the determination or estimation of mass transfer coefficients and equilibrium data.

In the present work, the removal of acetic acid by absorption was studied in order to select the best solvent for separation and to determine the individual and overall mass transfer coefficients. A nonequilibrium model (*10–12*), like the one used by us in other investigations (*13*), was developed to simulate the absorption process.

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EXPERIMENTAL

The laboratory absorption column is a Pyrex column of 2.15 cm i.d. and 82 cm in length, packed with graphite spheres and cylinders. This type of laboratory absorber has been widely used in basic mass transfer studies (*14*, *15*). A schematic diagram of the equipment is given in Fig. 1. The absorbing liquid was fed to the top of the column from a 10-L reservoir by using a peristaltic pump. The liquid flow was regulated and measured with a valve and a rotameter, respectively. A countercurrent stream of gas, regulated and measured with a needle valve and a diaphragm (0.1–2.0 m^3/h) or with a mass flow controller (<0.1 Nm^3/h), was introduced to the bottom of the column.

In some experiments the gas stream was initially saturated by passing it through a saturator containing the solvent.

In order to achieve the low concentration of acetic acid required for this study, gas mixtures of air–acetic acid and ethylene–acetic acid were produced by evaporating acetic acid in a mixer in the gas stream and using a syringe pump to inject it.

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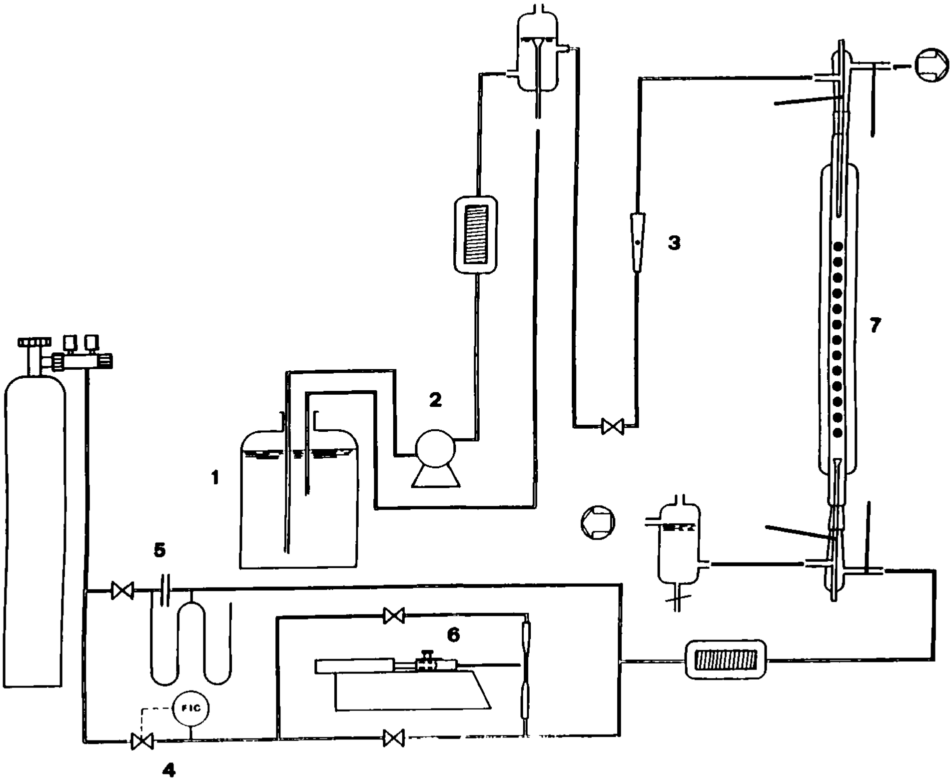

FIG. 1. Diagram of experimental equipment: (1) Reservoir, (2) peristaltic pump, (3) rotameter, (4) mass flow controller, (5) diaphragm, (6) syringe pump, (7) absorber.

The liquid and gas samples were analyzed by gas chromatography by using a chromatograph equipped with a thermal conductivity detector and an automatic valve. The column employed was a 3-m long, 1/4 in. o.d. glass column, packed with Porapak-QS (80–100 mesh).

RESULTS AND DISCUSSION

Solvent Preselection

Semicontinuous absorption experiments were performed by bubbling a mixture of air and acetic acid through a fixed volume of solvent. The solvents used were water, the compounds of the process (vinyl acetate and *n*-decane), and the basic solutions (NaOH and $CaCO_3$). The inlet and

TABLE 1
Solvent Preselection

Operation method	Gas stream: Mixture	Gas stream: Flow (g/h)	Gas stream: Acetic acid (ppm)	Liquid stream: Solvent	Liquid stream: Flow (L/h)	Acetic acid retained (%)
Semicontinuous	Air and acetic acid	94.2	16,000	Water	—	95
				Vinyl acetate	—	88
				n-Decane	—	92
				NaOH (1 *N*)	—	99
				NaOH (0.5 *N*)	—	99
				$CaCO_3$ (1 *N*)	—	98
Continuous	Air and acetic acid	98.6	8,000	Water	3.25	98
				Water	11.00	99
				Vinyl acetate	3.25	89
				Vinyl acetate	11.00	97
				n-Decane	3.50	80
				NaOH (1 *N*)	3.25	99
				NaOH (0.5 *N*)	3.25	98
	Ethylene and acetic acid	99.0	8,000	Water	3.5	>99
				Vinyl acetate	3.5	97
				n-Decane	3.5	89

outlet gas streams were analyzed by gas chromatography to obtain the acetic acid retained. The experimental results are given in Table 1. They show: (1) all the solvents investigated have high retention capacities (>85%), and (2) the retention capacities of the basic solutions employed are very similar.

Continuous absorption experiments with water, vinyl acetate, *n*-decane, and basic solutions of NaOH as the solvent were made. The gas stream (air–acetic acid or ethylene-acetic acid) was fed to the bottom of the absorber in countercurrent with the solvent. As in the discontinuous experiments, the inlet and outlet streams were analyzed by gas chromatography. The experimental results are summarized in Table 1.

The results obtained with gas mixtures of air–acetic acid indicate (1) that the use of soda solutions doesn't substantially improve the results obtained with water as solvent, and (2) the organic compounds of the process used as solvents (vinyl acetate and *n*-decane) can be employed to remove the acetic acid as shown by their high retention capacities.

The results obtained with ethylene–acetic acid mixtures confirmed the validity of using water, vinyl acetate, and *n*-decane as solvents to remove acetic acid from the mixtures.

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Mass Transfer Coefficients

Individual Mass Transfer Coefficients in the Gas Phase

Evaporation experiments of pure liquids (water, vinyl acetate, *n*-decane, and acetic acid) in an ethylene stream were made by varying the gas flow rate (690–1600 g/h) and the temperature (290–300 K) with a constant liquid flow (9.8 L/h).

Individual mass transfer coefficients in the gas phase were calculated from the experimental data by using the following expression (*16*, *17*):

$$k_g = K_G = \frac{Q_G p_o}{\Delta p_{\mathrm{ml}} R T a} \qquad (1)$$

In Fig. 2 the experimental and calculated values of k_g are compared. They were used in the following semiempirical equations obtained in our laboratory (*16*, *18*):

$$\mathrm{Sh}_G = 0.19\mathrm{Re}_G^{-1/3}\mathrm{Sc}_G^{-1/2}\mathrm{Im}_G^{3} \qquad (2)$$

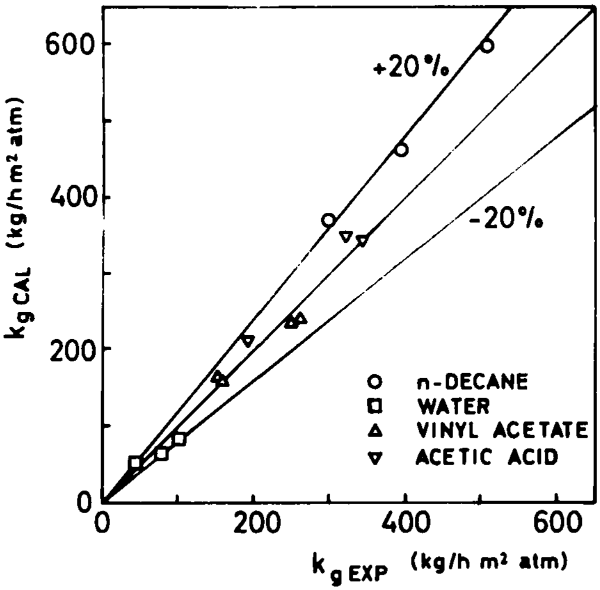

FIG. 2. Comparison of experimental values of k_g and the estimated values found by using Eqs. (2) and (3).

for the acetic acid–ethylene and *n*-decane–ethylene systems and

$$\mathrm{Sh}_G = 0.23\mathrm{Re}_G^{-0.38}\mathrm{Sc}_G^{-0.56}\mathrm{Im}_G^0 \tag{3}$$

for the water–ethylene and vinyl acetate–ethylene systems.

As can be observed, the equations employed reproduce the experimental results with deviations of less than 20%, confirming the validity of the equations selected to estimate the individual coefficients of these compounds.

Overall Mass Transfer Coefficients on a Gas-Phase Basis

Absorption experiments of ethylene–acetic acid mixtures with water, vinyl acetate, and *n*-decane as solvents were made, varying the liquid flow (8.5–11.5 L/h), the composition of the gas stream (2000–4000 ppm of acetic acid), and the temperature (290–300 K).

The overall acetic acid mass transfer coefficients on a gas-phase basis were calculated from the experimental data by using the following equation (18):

$$K_G = \frac{Q_L c_o}{(t\Delta p_{\mathrm{ml}}} \tag{4}$$

In Fig. 3 the experimental values of K_G and the individual coefficients k_g estimated by Eq. (2) are compared. Both coefficients practically coincide in the ethylene–acetic acid–water and ethylene–acetic acid–vinyl acetate systems. It is therefore deduced that when these solvents are used, the resistance of the liquid film is practically negligible. This does not occur in the ethylene–acetic acid–*n*-decane system, probably due to the different polarities of acetic acid (a very polar compound) and *n*-decane (a nonpolar compound).

Because the removal of acetic acid with *n*-decane as solvent is not as extensive as with water and vinyl acetate, and that the use of water as solvent requires its later removal, vinyl acetate was chosen as the most adequate solvent to remove acetic acid.

Absorber Simulation

Nonequilibrium Stage Model

A nonequilibrium stage model was developed for simulation of countercurrent multicomponent separation (*10–12*). The model has been used to simulate absorption experiments with good success (*19*, *20*). In this

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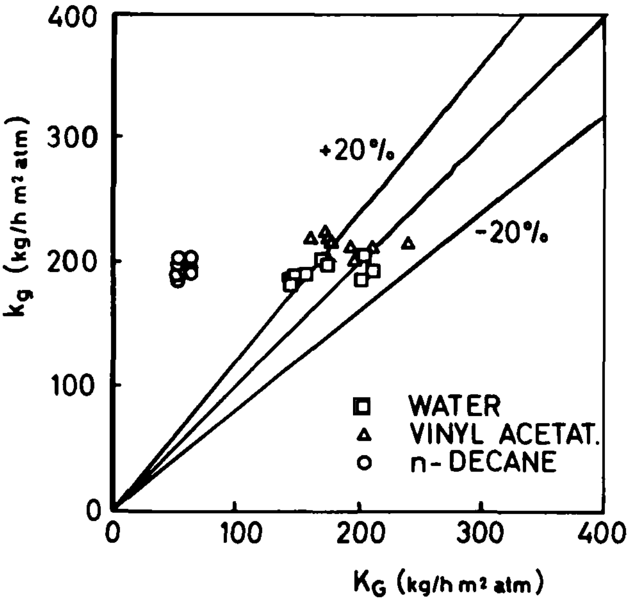

FIG. 3. Comparison of experimental values of K_G and k_g and the estimated values found by using Eq. (2).

model, the absorber consists of a sequence of nonequilibrium stages; each stage represents a real tray in the case of a multistage unit or a section of a continuous contacting device such as a packed column. In these stages the component's mass and energy balances were defined for each phase as were the mass and energy transfer rate equations and the interface equilibrium relations. A key feature of the model is that all the equations are solved simultaneously.

In our study the absorber simulation was made assuming the following simplifications:

Only one nonequilibrium stage (Fig. 4).
Absorption was an isothermal process.
Solubility of ethylene in solvent was negligible.
Mass transfer resistance of the solvent in the liquid phase was practically negligible.

Taking into account these simplifications, the mathematical model was constituted by the equations summarized in Table 2. Simultaneous resolution of these equations made possible the absorber simulation.

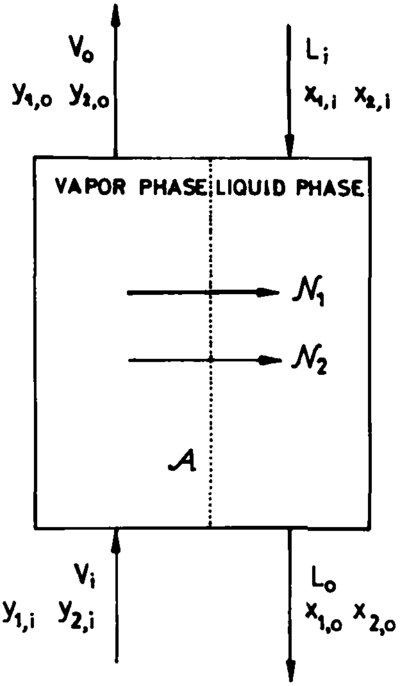

FIG. 4. Schematic representation of a nonequilibrium stage.

TABLE 2
Nonequilibrium Stage Model Equations

Component mass balances:	
Vapor phase:	
Acetic acid:	$v_1 - y_{1,i}V + N_1 = 0$
Vinyl acetate:	$v_2 - y_{2,i}V + N_2 = 0$
Liquid phase:	
Acetic acid:	$l_1 - x_{1,i}L - N_1 = 0$
Vinyl acetate:	$l_2 - x_{2,i}L - N_2 = 0$
Rate equations:	
Vapor phase:	
Acetic acid:	$N_1 - k_{g,1\text{eff}}\mathcal{A}\Psi_{1,\text{eff}}p_T(\bar{y}_1 - y_1^I) + \bar{y}_1 N_T = 0$
Vinyl acetate:	$N_1 - k_{g,2\text{eff}}\mathcal{A}\Psi_{2,\text{eff}}p_T(\bar{y}_2 - y_2^I) + \bar{y}_2 N_T = 0$
Liquid phase:	
Acetic acid:	$N_1 - k_{1,1}\mathcal{A}c_T(x_1^I - \bar{x}_1) + \bar{x}_1 N_T = 0$
Interphase equilibrium relations:	
Acetic acid:	$\mathcal{K}_1 x_1^I - y_1^I = 0$
Vinyl acetate:	$\mathcal{K}_2 x_2^I - y_2^I = 0$

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Results

Absorption experiments of ethylene–acetic acid mixtures with vinyl acetate as the solvent were made, varying the liquid flow (8.5–11.5 L/h), the composition of the gas stream (2000–4000 ppm of acetic acid), and the temperature (290–300 K).

The absorber simulation was carried out by simultaneously solving the set of nine nonlinear, algebraic equations (Table 2) by using a computer program based on the Marquardt algorithm (*21*). For this, it was necessary to estimate the equilibrium data and mass transfer parameters and coefficients.

Mass Transfer Rate Equations in the Gas Phase. The equations employed to describe the mass transfer are based in "effective diffusivities" in which the interaction between the different components is negligible. The mass transfer fluxes through the gas phase were calculated as follow (*19*):

$$N_j = k_{g,j\mathrm{eff}}\mathfrak{a}\Psi_{j,\mathrm{eff}}p_T(\bar{y}_j - y_j^I) + \bar{y}_jN_T, \qquad j = 1, 2 \tag{5}$$

In this equation, $k_{g,j\mathrm{eff}}$ is the "effective" mass transfer coefficient calculated from

$$k_{g,j\mathrm{eff}} = \frac{1 - \bar{y}_j}{\sum_{k=1}^{c} \frac{\bar{y}_k}{k_{g,kk}}}, \qquad j = 1, 2 \tag{6}$$

and $\Psi_{j,\mathrm{eff}}$ is a corrector factor that accounts for the influence of the mass transfer rates on the mass transfer coefficients:

$$\Psi_{j,\mathrm{eff}} = \frac{\phi_j}{\exp \phi_j - 1}, \qquad j = 1, 2 \tag{7}$$

where ϕ_j are calculated from

$$\phi_j = \frac{k_{g,j\mathrm{eff}}\mathfrak{a}}{N_T}, \qquad j = 1, 2 \tag{8}$$

The individual mass transfer coefficients k_g were calculated from Eqs. (2) and (3). The interfacial area $\mathfrak{a}$ was calculated from the experimental data by using a method described elsewhere (*16*).

TABLE 3
Parameters of Equation (12)

Compound	a_{1j}	$a_{2j} \times 10$	$a_{3j} \times 10^4$	$a_{4j} \times 10^7$
Acetic acid	25.503	−2.506	8.184	−8.866
Vinyl acetate	−14.755	1.664	−6.210	7.710

Mass Transfer Rate Equations in the Liquid Phase. The mass transfer rate of acetic acid through the liquid phase was calculated as follows (*10*):

$$N_1 = k_{l,1} a c_T (x_1^i - \bar{x}_1) \tag{9}$$

where $k_{l,1}$ is the mass transfer coefficient through the liquid phase calculated from the following equation (*15*):

$$\mathrm{Sh}_L = 2.79\mathrm{Re}_L^{2/3}\mathrm{Sc}_L^{1/3}\mathrm{Ga}^{0.38}\mathrm{Ts}^{0.42} \tag{10}$$

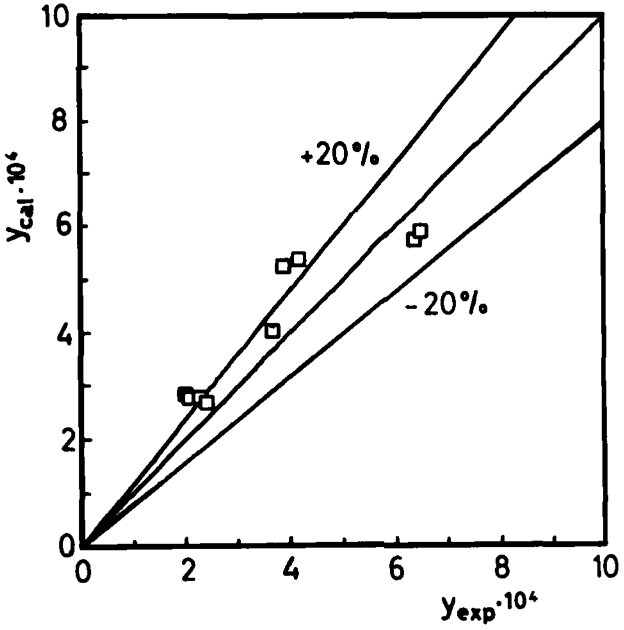

FIG. 5. Comparison of experimental and predicted molar fractions of acetic acid in the outlet gas stream.

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Estimation of Equilibrium Data. The equilibrium ratios were calculated from

$$\mathcal{K}_j = \frac{y_j}{x_j} = \frac{\gamma_j f_j^{oL}}{\Phi_j p_T} \tag{11}$$

where the activity and fugacity coefficients and the fugacities for the different compounds were calculated by using the method described by Prausnitz et al. (*22*) with the parameters given in the same work. Taking into account that in all the experiments the pressure remained constant (0.95–0.97 bar), the estimated equilibrium constants were correlated with temperature by

$$(\mathcal{K}_j/T)^{1/3} = a_{1j} + a_{2j}T + a_{3j}T^2 + a_{4j}T^3 \tag{12}$$

These parameters are summarized in Table 3.

In Figs. 5 and 6 the experimental values of the outlet gas-phase composition and the calculated values with the nonequilibrium stage model are compared. As can be observed, the model reproduced with good agreement the experimental results, showing deviations of less than 20%.

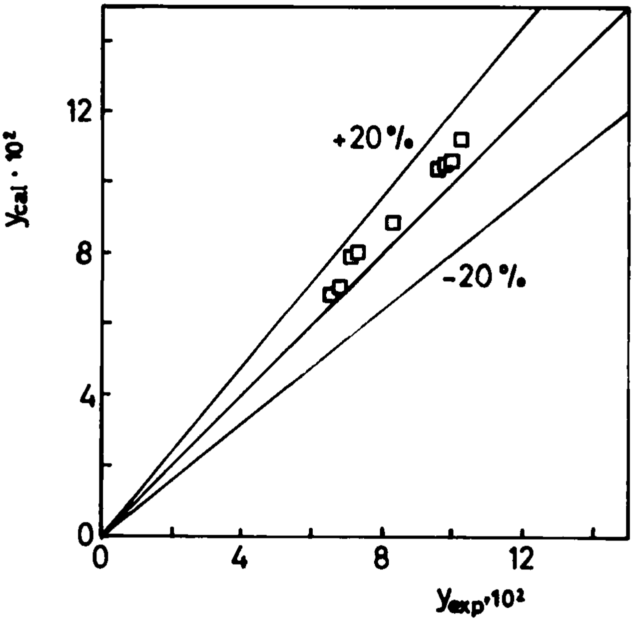

FIG. 6. Comparison of experimental and predicted molar fractions of vinyl acetate in the outlet gas stream.

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SYMBOLS

a	interfacial area of the column (m^2)
c	liquid-phase composition, mol/m^3
f^{oL}	standard-state fugacity
Ga	Galileo number
Im	drift factor
k	mass transfer coefficient (mol/h·m^2·atm or m/h)
K_G	overall mass transfer coefficient on gas-phase basis (mol/h·m^2)
$\mathcal{K}$	equilibrium constant
l	liquid component flow rate (mol/h)
L	liquid flow rate (mol/h)
N	mass transfer rate (mol/h)
p	pressure (atm)
Δp_{ml}	logarithmic-mean driving force (atm)
Q	volumetric flow rate (m^3/h)
R	universal gas constant (atm·m^3/mol·K)
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
T	temperature (K)
Ts	surface tension number
v	gas component flow rate (mol/h)
V	gas flow rate (mol/h)
x	liquid-phase composition
y	gas-phase composition

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Greek Letters

γ	activity coefficient
Ψ	flux correction factor
Φ	fugacity coefficient

Subscripts

eff	effective value of property
G, g	pertains to gas phase
i	inlet value
j	component number
L, l	pertains to liquid phase
o	outlet value
T	total
1	relative to acetic acid
2	relative to vinyl acetate

Superscripts

I pertains to interface
$-$ averaged bulk value

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