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Effect of Inert Gas Pressure on the Molecular Distillation Process

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ABSTRACT

A one-dimensional model of a short-path (molecular) distillation for two-component systems in the presence of an inert gas was developed based on the weight-not-time-counter Direct Simulation Monte Carlo method. The effect of the composition of the test liquid, the evaporating temperature, the condensing temperature, the distance between evaporator and condenser, the arrangement of distillation space, and the inert gas pressure on mass transfer and separation efficiency is discussed.

INTRODUCTION

Short-path distillation or molecular distillation is generally acknowledged to be the safest method to separate and purify thermally unstable compounds and substances having low volatility. In a previous communication (1) we presented the profiles of such macroscopic quantities as density, mean free path, mean velocities, kinetic temperature, frequency of molecular collisions at different positions in the distillation space, and the relation between mass transfer efficiency and distillation space geometry, evaporating temperature, and condensing temperature for a single component system.

Using a slip-diffusion model, Toei et al. (2) and Uyeha et al. (3) attempted to model the mass transfer between evaporating and condensing surfaces during molecular distillation using an analysis of the Boltzmann equation with a two-sided Maxwell velocity distribution function of molecules. They analyzed the influence of an inert gas on the mass transfer efficiency for single component liquids distilled at a low-level partial pressure of the inert gas. Baker and Olejniczak (4) published experimental results of the effect of inert gas on the distillation rate of a single component liquid. All the authors cited obtained similar results. They found the dependence of inert gas pressure on the distillation rate or mass transfer efficiency had a convex–concave curve shape (S-shape curve) with the value of the distillation rate near the theoretical rate for low levels of inert gas pressure.

We now present a one-dimensional model of molecular distillation for a two-component test liquid in the presence of an inert gas, based on the no-time-counter Direct Simulation Monte Carlo method. We used this model to explore the influence of some process parameters (composition, evaporator and condenser temperatures, inert gas pressure) and some construction parameters (distance between evaporator and condenser, and design of distillation space) on separation ability and mass transfer efficiency.

PROBLEM ANALYSIS

The rate of molecular evaporation from a surface is described by the Langmuir–Knudsen equation (5)

$$w_0 = p^0 \sqrt{\frac{1}{2\pi RTM}} \tag{1}$$

or for the evaporation of a two-component liquid with Components A and B

$$w_{0A} = p^0_A x_A \sqrt{\frac{1}{2\pi RTM_A}} \tag{2}$$

$$w_{0B} = p^0_B x_B \sqrt{\frac{1}{2\pi RTM_B}}$$

and for the total molecular evaporation rate

$$w_0 = w_{0A} + w_{0B} \tag{3}$$

The rate of molecular distillation is lower due to mutual collisions of evaporated molecules and collisions with molecules of the inert gas. When the inert gas pressure is increased, the distillation rate is depressed and the rate of distillation is controlled by diffusion.

We can apply

$$\eta = w/w_0 \tag{4}$$

as a criterion of mass transfer efficiency between evaporator and condenser surfaces and

$$\alpha = x_B y_A / x_A y_B \tag{5}$$

as the criterion of separation efficiency.

Using Raoult's law

$$\begin{aligned} p_A &= p_A^0 x_A \\ p_B &= p_B^0 x_B \end{aligned} \tag{6}$$

and Dalton's law

$$\begin{aligned} y_A &= \frac{p_A}{p_A + p_B} \\ y_B &= \frac{p_B}{p_A + p_B} \end{aligned} \tag{7}$$

we obtain the theoretical value of separation efficiency valid at conditions of ideal equilibrium distillation

$$\alpha_1 = p_A^0 / p_B^0 \tag{8}$$

Applying the Langmuir–Knudsen equation (2), we obtain the theoretical value of separation efficiency valid at conditions of molecular distillation

$$\alpha_2 = \frac{p_A^0}{p_B^0} \sqrt{\frac{M_B}{M_A}} \tag{9}$$

A suitable method for simulation of molecular distillation is the weight-not-time-counter direct simulation Monte Carlo (DSMC) method (6–8). Using this method, all velocity coordinates and the position coordinates of model molecules in the direction in which the change of characteristics occurs were stored in the memory of a computer. The modeled space was divided into cells. In general, the method follows the time evolution of the system from the initial to the final conditions. The time was changed at Δt steps, which were sufficiently small when compared to the average time of collisions between molecules. Macroscopic quantities, such as density, pressure, and temperature, were calculated from the positions and velocities of the modeled molecules.

The algorithm of the method is defined in Fig. 1. The action performed in one time step, Δt, is as follows.

1. All molecules are transported to a given distance, the distance being determined by their velocity $\bar{v}$ and the time step Δt.

   $$\bar{r}(t + \Delta t) = \bar{r}(t) + \Delta t\bar{v} \tag{10}$$

   An analysis is carried out in order to ascertain whether the molecules did cross the surface or the outer limits of flow. New molecules are randomly generated at the limits, through which molecules flow into the area of the cell (evaporation of molecules from an evaporator).
2. Collisions occur between molecules, which correspond to the time Δt. The velocities of molecules prior to collision are substituted by the velocities following the collision.

In our model we considered the evaporation and condensation processes occurring in a one-dimensional, high-vacuum distillation. The vaporized molecules emanating from the hot surface of an evaporator flow toward the cool surface of a condenser situated directly opposite. Some molecules leave the condenser surface in the reverse direction, toward the evaporator. Mutual collisions between the vaporized molecules occur in the distillation space together with collisions with inert gas molecules. All these collisions result in a dispersion process and change the rate and separation efficiency of the process.

The evaporating and condensing temperatures and the composition of the liquid on the evaporating surface are used as the input calculation data. These parameters are kept constant during the calculation. At the beginning of calculation the liquid is situated only on the evaporator surface. There is a vacuum in the distillation gap. The evaporated molecules gradually fill up the gap, collide with the condenser, and condense on it. The calculation output is the quantity of liquid condensed on the condenser and its composition at steady-state conditions.

The number of molecules evaporated from the evaporating surface during the time step Δt is determined using the Langmuir–Knudsen equation (2), where T is the temperature of evaporating surface and p_A^0 is the vapor pressure of Component A at temperature T. This number depends solely on time step Δt because either the evaporation temperature or the liquid composition is kept constant whereas time step Δt can be changed during the calculation.

The number of molecules evaporated from the condenser is determined analogically. In this case the composition of liquid on the condensing surface, y_A and y_B, is also changed. This composition is given as the difference between the number of condensed molecules and the number of reevaporated molecules.

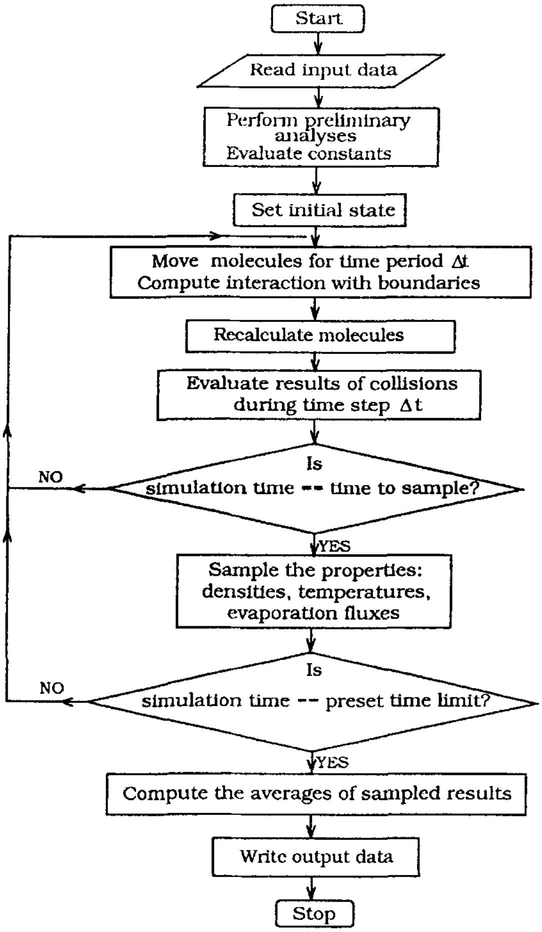

FIG. 1 Algorithm of the DSMC method.

The number of inert gas molecules is constant in the distillation space and is given by the initial inert gas pressure. If an inert gas molecule collides with the evaporating or condensing surface, the diffusion reflection is taken into consideration. By "diffusion reflection" we mean the condensation on the surface, equalization of the molecule "temperature" with the surface temperature, and the evaporation that follows.

According to the DSMC method it is necessary to attach a velocity vector to molecules that have experienced evaporation and/or diffusion reflection from either the evaporator or condenser surface. If v_x is the component of the velocity vector perpendicular to the evaporating surface, then the distribution functions of velocity vector components are as follows (9):

$$f(v_x) = \frac{m}{kT} v_x \exp\left(-\frac{mv_x^2}{2kT}\right) \tag{11}$$

$$f(v_y) = \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{mv_y^2}{2kT}\right) \tag{12}$$

$$f(v_z) = \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{mv_z^2}{2kT}\right) \tag{13}$$

Using three random numbers $\Re_1$, $\Re_2$, $\Re_3$ from interval $\langle 0;1)$, it is possible to generate the velocity components v_x, v_y, v_z according to the scheme

$$v_x = -\frac{2kT \ln \Re_1}{m} \tag{14}$$

$$B = -\frac{2kT \ln \Re_2}{m} \tag{15}$$

$$\phi = 2\pi \Re_3 \tag{16}$$

$$v_y = B \cos(\phi) \tag{17}$$

$$v_z = B \sin(\phi) \tag{18}$$

where T is the surface temperature and m is the molecular mass. Molecular movement is calculated according to Eq. (10) after the velocity vector components are generated. In this operation, instead of time step Δt, time step $\Re_4 \Delta t$ is used.

The number of collisions during time step Δt is calculated separately for every cell in which the distillation space is divided. The determination of the number of the collisions was based on the probability principle (6–8).

RESULTS AND DISCUSSION

We used dibutylphthalate (DBP, M = 278.35 g·mol^{-1}, $d = 7.5 \times 10^{-10}$ m, $\log(p^0) = 12.7 - 4450/T$) and dibutylsebacate (DBS, M = 314.46 g·mol^{-1}, $d = 8.0 \times 10^{-10}$ m, $\log(p^0) = 13.22 - 4850/T$) as model systems, and nitrogen N_2 (M = 28 g·mol^{-1}, $d = 3.16 \times 10^{-10}$ m) as the inert gas.

We performed the model study of molecular distillation by the DSMC method for various mole fractions (x_{DBP}, x_{DBS}), the pressure of the inert gas (p_{N_2}), the evaporating temperature (T_{evp}), the condensing temperature (T_{con}) (process parameters), and the geometry of the distillation space (construction parameters). From Relationship (4) we calculated the mass transfer efficiency η, and from Eq. (5) the separation efficiency α_3 of the process.

The simulations were carried out on an IBM RS/6000 computer, equipped with 64 MB RAM and operating under the AIX 3.2 operating system. The programs were written in the GNU C+ + language ver. 2.6.0.

Effect of the Process and Construction Parameters on the Mass Transfer Efficiency

Figure 2 displays the dependence of mass transfer efficiency η on the initial inert gas pressure as a parametric 2-D plot for $x_{\mathrm{DBP}} = 0.00, 0.50,$ and 1.00. In this case the temperatures on the evaporating and condensing surfaces were 373 and 273 K, respectively. The evaporator-to-condenser distance was 10 mm. The evaporator and condenser were formed by two parallel planes. The relationship $\eta = f(p_{\mathrm{N}_2})$ has the characteristic S-shape with an inflex for $p_{\mathrm{N}_2} \approx p^0_{\mathrm{A}}x_{\mathrm{A}} + p^0_{\mathrm{B}}x_{\mathrm{B}}$. This result is in agreement with theoretical studies (2, 3) and experimental results (4). If $p_{\mathrm{N}_2} \ll p^0_{\mathrm{A}}x_{\mathrm{A}} + p^0_{\mathrm{B}}x_{\mathrm{B}}$, then η approaches a value close to 1. If $p_{\mathrm{N}_2} > p^0_{\mathrm{A}}x_{\mathrm{A}} + p^0_{\mathrm{B}}x_{\mathrm{B}}$, then

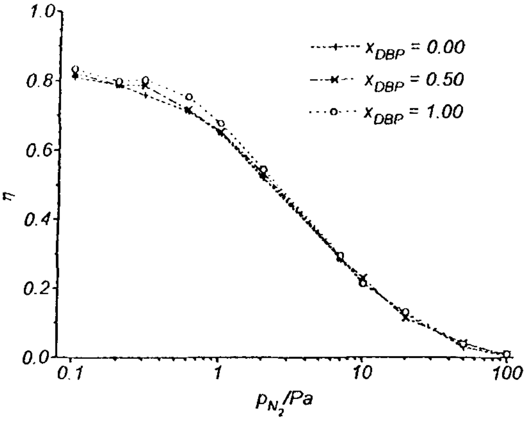

FIG. 2 Plot of mass transfer efficiency vs initial inert gas pressure for different mole fractions of DBP.

η is markedly low and the distillation rate is determined by diffusion. By increasing x_{DBP}, the value of η moderately increases.

Graphical representation of the relation $\eta = f(l, p_{N_2})$ is given in Fig. 3. In this case computations have been carried out at the evaporation temperature (373 K) and condensation temperature (273 K) at distances between the evaporating and condensing surface of 5, 10, 25, and 50 mm, with $x_{DBP} = 0.50$ and a parallel arrangement of the surfaces. The mass transfer efficiency η decreases when the width l between evaporator and condenser increases. However, an increase of the evaporator–condenser distance causes only a slow decrease of η. The same results were reached in our previous study dealing with a one-component system (1). A substantial increase in distillation gap width from 5 to 50 mm causes the mass transfer efficiency to drop from 84 to 66% at zero inert gas pressure. This result contradicts the demand often cited in connection with molecular distillation; namely, the evaporator–condenser distance should be lower than the mean free path of molecules in the distillation gap. However, our result is in good agreement with experimental observations.

Figure 4 shows plots of η vs inert gas pressure at various evaporating temperatures. Modeling conditions for this run were as follows: temperatures of the evaporating surface: 373, 393 and 413 K; temperature of the condensing surface: 273 K; evaporator–condenser distance, 10 mm; $x_{DBP} = 0.50$; evaporator and condenser as parallel planes. At higher evaporating temperatures the number of evaporated molecules increases and the relative portion of distilled molecules present in the distillation gap be-

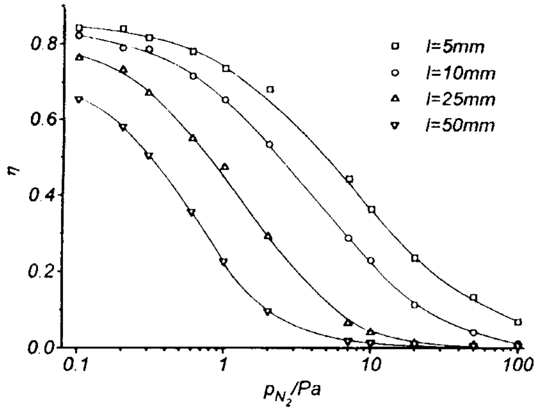

FIG. 3 Plot of mass transfer efficiency vs initial inert gas pressure for different distances between evaporating and condensing surfaces.

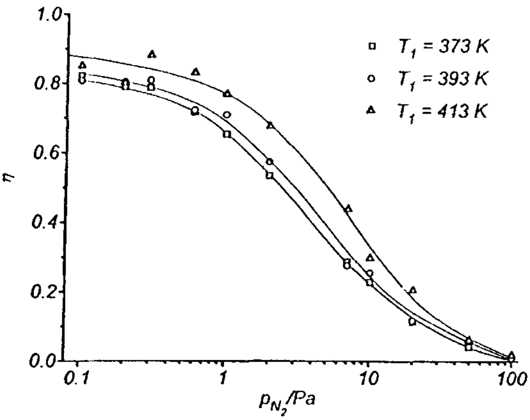

FIG. 4 Plot of mass transfer efficiency vs initial inert gas pressure for different evaporating temperatures.

comes larger. This fact causes an increase of η at higher evaporating temperatures.

The influence of condensing temperature on η can be deduced from Fig. 5. The evaporating temperature was 373 K; the condensing temperatures were 273, 333, and 353 K; the evaporator–condenser distance was 10 mm; x_{DBP} = 0.50; and the evaporator and condenser surfaces were parallel. Lower values of η at higher temperatures of the condensing sur-

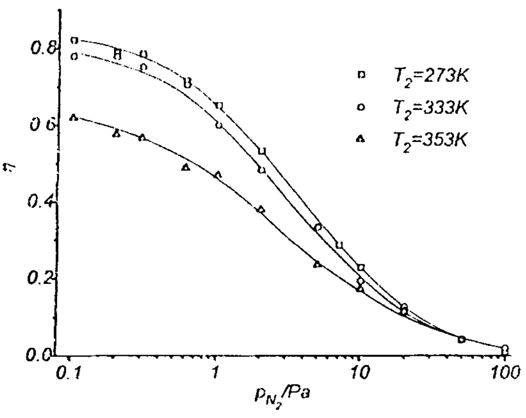

FIG. 5 Plot of mass transfer efficiency vs initial inert gas pressure for different condensing temperatures.

face are obviously caused by reevaporation of molecules from the condensing surface. As an additional effect, reevaporization causes an increase of molecular density and dispersion of molecular movement in the distillation gap, with the consequence that there is greater resistance toward mass transfer across the gap.

The evaporating and condensing surfaces are usually formed by two coaxial cylinders in practical technological equipment. There are two possible designs of molecular evaporators:

1. A convex evaporation surface (evaporation from the outer surface of the inner cylinder and condensation at the inner surface of the outer cylinder, Fig. 6a).
2. A concave evaporation surface (evaporation from the inner surface of the outer cylinder, Fig. 6b).

In a previous communication (1) we discussed a one-dimensional model of evaporation of the one-component system, and we found out that for $r_1 < 150$ mm the distillation rate was higher for the convex arrangement. The influence of design on η in a two-component system with an inert gas can be seen from Fig. 7. Computations have been carried out under the following conditions: evaporating temperature, 373 K; condensing temperature, 273 K; evaporator–condenser distance, 10 mm; $x_{DBP} = 0.50$; $r_1 = 5$ and 10 mm. Compared with the plane-parallel arrangement of the distillation space, the value of η was greater for the convex evaporation surface and smaller for the concave surface.

Effect of the Process and Construction Parameters on the Separation Efficiency

For an evaporation temperature of 373 K, $\alpha_1 = 3.56$, $\alpha_2 = 3.78$ (Table 1). α_3 calculated by the DSMC method at an initial inert gas pressure for the mole fraction of $x_{DBP} = 0.5$ is shown in Fig. 8. For $p_{N_2} < 10$ Pa, the

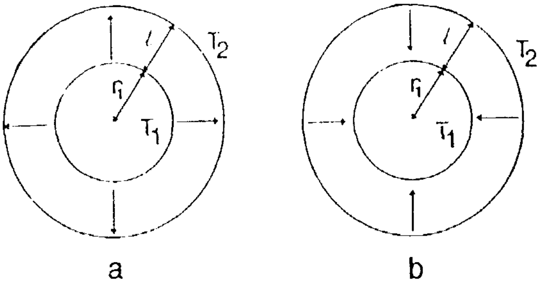

FIG. 6 Diagrams of the convex and concave surfaces.

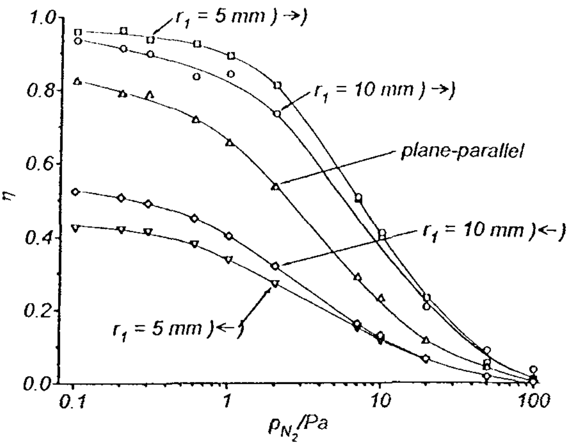

FIG. 7 Plot of mass transfer efficiency vs initial inert gas pressure for a cylindrical-shaped space with different radii of the smaller cylinder.

TABLE 1

α_1, α_2, and α_3 for Different Evaporating Temperatures

Temperature (K)	α_1	α_2	α_3
373	3.56	3.78	3.68
393	3.27	3.48	3.28
413	2.92	3.10	2.92

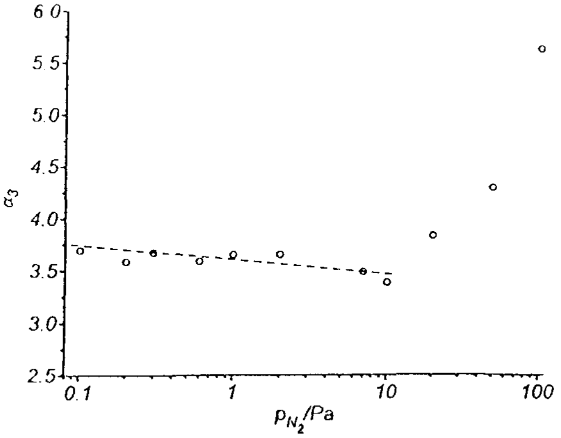

FIG. 8 Plot of separation efficiency α_3 vs initial inert gas pressure.

α_3 moderately decreases. For higher values of p_{N_2}, α_3 changes markedly. The deviations are connected with the increase of absolute error $\Delta\alpha_3$ of α_3 when the inert gas pressure increases. Applying the principle of absolute error accumulation to the equation (5) for the estimation of the absolute error $\Delta\alpha_3$ will be obtained

$$(\Delta\alpha_3)^2 = \left(\frac{\partial}{\partial w_A}\alpha_3\right)^2 (\Delta w_A)^2 + \left(\frac{\partial}{\partial w_B}\alpha_3\right)^2 (\Delta w_B)^2$$

$$= \frac{x_B^2}{x_A^2}\left[\frac{1}{w_B^2}(\Delta w_A)^2 + \frac{w_A^2}{w_B^4}(\Delta w_B)^2\right]$$

and if $x_A = x_B = 0.5$:

$$(\Delta\alpha_3)^2 = \frac{1}{w_B^2}\left[(\Delta w_A)^2 + \left(\frac{w_A}{w_B}\right)^2 (\Delta w_B)^2\right] \tag{19}$$

Although the absolute errors of Δw_A and Δw_B were kept at the same level, the computation time rose from ~20 minutes at zero inert gas pressure to 6–8 hours at an inert gas pressure equal to 100 Pa. With an increase of the inert gas pressure, the distillation rate decreases and at constant values of Δw_A and Δw_B the value of $\Delta\alpha_3$ grows. For higher values of p_{N_2} it will be possible to obtain results with better precision when very fast computers are used, e.g., one could obtain values of w_A and w_B with lower errors of Δw_A and Δw_B within reasonable computing times.

If the principle of absolute error accumulation is applied to Eq. (4), the error estimation of mass transfer efficiency is

$$(\Delta\eta)^2 = \left(\frac{\partial}{\partial w_A}\eta\right)^2 (\Delta w_A)^2 + \left(\frac{\partial}{\partial w_B}\eta\right)^2 (\Delta w_B)^2 = \frac{(\Delta w_A)^2 + (\Delta w_B)^2}{(w_{0A} + w_{0B})^2} \tag{20}$$

The absolute error $\Delta\eta$ depends only on Δw_A and Δw_B, and it is smaller than $\Delta\alpha_3$.

In Table 1 the average values of α_3 are compared with the theoretical values of α_1 and α_2 for various evaporation temperature values. The average values of α_3 were calculated from results obtained for inert gas pressures under 50 Pa. The α_3 values for higher inert gas pressures are greatly dispersed. By increasing the distillation temperature, the mean value of α_3 approaches the theoretical value α_1.

Theoretically, higher temperatures of the condenser surface preferentially deplete it of the more volatile component (DBP) by reevaporization. This has the consequence of lower values of α_3 (10). Figure 9 gives its

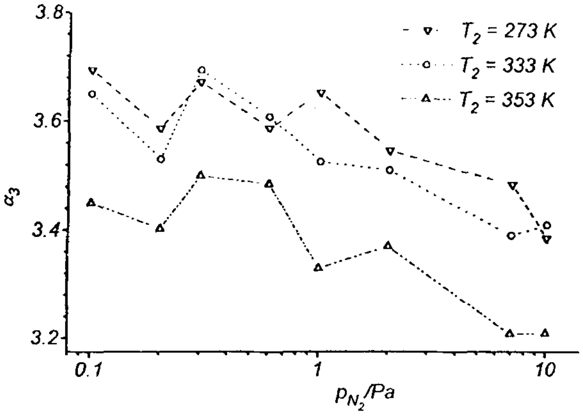

FIG. 9 Plot of separation efficiency vs initial inert gas pressure for different condensing temperatures.

relation to condensing temperature as a parameter. The effect of condensing temperature on α_3 is slight. Due to the collisions of molecules, some of the reevaporated molecules return to the condenser. It follows from the kinetic theory of gases that the probability of return is greater for lighter molecules (generally those of the more volatile component), and the resulting decrease of α_3 at a higher condensation temperature is then lower.

A dependence of α_3 on the geometry of the distillation space was not observed with either the convex or concave arrangement of distillation space or with evaporator–condenser distance.

CONCLUSIONS

A model study of the molecular distillation at inert gas pressure carried out using the DSMC method produced useful information on the influence of inert gas pressure on this nonequilibrium process.

The results proved that the effect of inert gas on mass transfer efficiency depends on its partial pressure. For inert gas pressures markedly lower than the vapor pressure of the liquid distilled, the effect of the inert gas is minimal. Its effect is marked in the opposite case, and it rapidly reduces the mass transfer efficiency to the value determined by diffusion.

We did not observe an unambiguous influence on the separation efficiency of the inert gas present.

Increasing of the distance between the evaporator and condenser brings about a slight decrease of the distillation rate. A marked decrease of the distillation rate is caused by an insufficiently cold condenser, and thus by reevaporation of molecules. In this case too, a slight decrease of separation efficiency is observed.

For small radii, the rate of distillation is higher for the convex arrangement. An influence by the convex or concave arrangement on separation efficiency has not been observed.

An efficient molecular distillation process requires a sufficiently cool condenser and a sufficiently low inert gas pressure in the evaporator.

The influence of other parameters on the molecular distillation process is smaller.

NOTATION

Variables and Constants Used

l	distance between evaporating and condensing surfaces (m)
M	molar mass ($\mathrm{kg \cdot mol^{-1}}$)
M_A	molar mass of Component A ($\mathrm{kg \cdot mol^{-1}}$)
p^0	saturation vapor pressure (Pa)
p_A^0	saturation vapor pressure of Component A (Pa)
p_A	partial pressure of Component A (Pa)
R	universal gas constant ($8.314\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)
T	temperature (K)
T_{evp}	evaporating temperature (K)
T_{con}	condensing temperature (K)
w_0	rate of evaporation ($\mathrm{mol \cdot m^{-2} \cdot s^{-1}}$)
w_{0A}	rate of evaporation of Component A ($\mathrm{mol \cdot m^{-2} \cdot s^{-1}}$)
w	rate of distillation ($\mathrm{mol \cdot m^{-2} \cdot s^{-1}}$)
w_A	rate of distillation of Component A ($\mathrm{mol \cdot m^{-2} \cdot s^{-1}}$)
x_A	mole fraction of Component A at evaporating surface
y_A	mole fraction of Component A at condensing surface $= w_A/(w_A + w_B)$

Greek Letters

α	separation efficiency
η	mass transfer efficiency
π	3.1415927

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