On the Growth of a Non-Ideal Gas Bubble in a Solvent-Polymer Solution

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A model for the growth of an ideal and a non-ideal spherical gas bubble in a quiescent viscous liquid is presented. The growth of the bubble is assumed to be controlled by both mass transfer and viscous forces. Using the integral method, the differential momentum and binary mass balances were transformed into ordinary differential equations, which were numerically solved. Some analytical solutions for simple cases are also presented. The relevance of this work to the process of polymer melt devolatilization is discussed.

INTRODUCTION

The problem of bubble growth can be found in many areas of chemical engineering science. For example, one of the elementary steps in polymer processing is that of polymer melt devolatilization. In this industrial process, low concentrations of volatile components (unreacted monomers, solvents, water) are removed from the polymer melt. This boiling process conducted at high temperatures and under vacuum, results in the nucleation and the growth of bubbles (1, 2).

A large number of mathematical models for bubble growth were presented in the literature. Some models have been written for bubble growth assumed to be governed by mass transfer alone, while others assumed momentum transfer alone. Using an integral method, the combination of these phenomena was presented by Rosner and Epstein (3), Patel (4) and others. Heat transfer at the low concentrations at which devolatilization is conducted is probably not a controlling factor (5, 6).

Most of the models have been focused on the liquid outside the growing bubble. Very little is known, for example, about the pressure within the bubble. This is due to the fact that most of the investigators present their results in terms of the bubble radius as a function of time. It will be shown that for the case in which both mass transfer and viscous forces control the bubble growth, the pressure inside the bubble can increase to extremely high values before it decreases to a value close to the ambient pressure. If, for example, the value of this maximum pressure is above the saturation pressure of the vapor inside the bubble, then a wrong physical situation is obtained.

In a previous work (4), the growth of a spherical bubble in a quiescent liquid has been theoretically studied. In his work it was assumed that both mass transfer and viscous forces (creeping flow) controlled the process. The concentration boundary layer thickness was assumed to be very small compared to the radius of the bubble, the gas within the bubble was assumed to obey the ideal gas law and Henry's law was applied. The present paper extends Patel's numerical work by presenting some approximated analytical solutions to his work. Furthermore, and in order to avoid the wrong physical situation discussed above, the present work connects between the thermodynamic properties of the solvent-polymer solution and an equation of state for the gas inside the bubble capable to predict phase change.

THE BASIC GOVERNING EQUATIONS

A review of fundamentals of bubble growth, where all the basic equations are presented and developed, is given by Favelukis and Albalak (7). We shall present here only the main results. The equation of continuity in the liquid phase in spherical coordinates, assuming constant density and spherical symmetry, may be integrated to give the radial velocity of the liquid:

$$v_r = \left(\frac{R}{r}\right)^2 \frac{dR}{dt} \tag{1}$$

where R(t) is the radius of the bubble and t is time. Note that $Eq \ l$ is valid when the density of the liquid is much greater than that of the bubble and when both phases are incompressible.

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The Navier-Stokes equation in the radial direction assuming creeping flow and spherical symmetry may be combined with the radial velocity of the liquid and a force balance at the surface of the bubble to give:

$$P_{\rm B} - P_{\infty} - \frac{2\sigma}{R} = \frac{4\mu}{R} \left(\frac{dR}{dt}\right) \tag{2}$$

where $P_B(t)$ is the pressure in the bubble, P_{∞} is the ambient pressure (a constant in this work), σ is the surface tension and μ is the liquid viscosity. The initial condition for the last equation is:

$$R = R_0 \quad \text{at} \quad t = 0 \tag{3}$$

According to Eq 2, and for bubble growth (dR/dt > 0), the initial radius of the bubble must be greater than a critical value of:

$$R_{cr} = \frac{2\sigma}{P_B - P_{\infty}} \tag{4}$$

A differential mass balance in a binary system assuming spherical symmetry, constant density and diffusion coefficient (D) is of the form:

$$\frac{\partial c}{\partial t} + v_r \frac{\partial c}{\partial r} = D \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right) \right]$$
(5)

where c is the molar concentration of the volatile solvent in the liquid. The boundary and initial conditions for Eq 5, in this work, are:

$$c = c_s(t)$$
 at $r = R(t)$ (6)

$$c = c_{\infty}$$
 at $r = \infty$ (7)

$$c = c_{\infty}$$
 at $t = 0$ (8)

If only the volatile solvent is present within the bubble, which is in chemical equilibrium with the liquid at the bubble surface, then we may apply Henry's law:

$$P_B = Kc_s \tag{9}$$

where *K* is Henry's constant (molar base). In order to solve the problem another boundary condition is required. A mass balance for the solvent in the bubble gives:

$$\frac{1}{4\pi R^2} \frac{dn}{dt} = D\left(\frac{\partial c}{\partial r}\right)_{r=R}$$
(10)

where n is the number of moles of the volatile solvent in the bubble. *Equation 10* requires the following initial condition:

$$n = n_0$$
 at $t = 0$ (11)

As mentioned by Patel (4), constant gas density is assumed in the derivation of Eqs 1 and 2 but it will be left as a variable in Eq 10. For the case of variable gas density, also Eq 10 need to be modified, but this would not cause a significant change in the results. Finally, the ideal gas equation of state is:

$$P_B V = n R_q T \tag{12}$$

here V is the volume of the bubble, R_g is the universal gas constant and T is the absolute temperature. Constant temperature will be assumed in this work.

CONSTANT PRESSURE AND TEMPERATURE INSIDE THE BUBBLE

Before we start to solve the complete problem, it is interesting to see first the simple case in which the pressure and the temperature within the bubble are constant. Although this is not true, this assumption leads to analytical solutions, which may be later compared to the numerical results. For this case the momentum and the binary mass balances can be solved independently.

Assuming that viscous forces alone control the bubble growth, Eq 2 may be integrated using the initial condition given in Eq 3 to give (7, 8):

$$R(t) = R_{cr} + (R_0 - R_{cr}) \exp\left[\frac{(P_B - P_{\infty})t}{4\mu}\right]$$
(13)

However, if the growth is controlled by mass transfer alone, then the solution of Eqs 1 and 5 together with the boundary conditions described by Eqs 6-8and 10 is given by Birkhoff *et al.* (9), and Scriven (10):

$$R(t) = 2\lambda \sqrt{Dt} \tag{14}$$

where λ is the dimensionless growth constant. For an ideal gas inside the bubble, the following asymptotic cases may be obtained. For small values of λ (slow growth rates):

$$R(t) = \sqrt{2 \frac{R_g T(c_{\infty} - c_s)}{P_B}} Dt$$
(15)

and for large values of λ (fast growth rates):

$$R(t) = 2\sqrt{\frac{3}{\pi}} \frac{R_g T(c_{\infty} - c_s)}{P_B} \sqrt{Dt}$$
(16)

Note that when viscous forces alone control the growth of the bubble, the radius changes as an exponential function of time. However, if mass transfer controls the growth, then the radius of the bubble changes as the square root of the time.

THE INTEGRAL METHOD

The integral method, that was used by Rosner and Epstein (3), Patel (4) and others, will be applied also in the present work. First, Eq 5 is multiplied by r^2 followed by an integration with respect to r from r = R(t) to $r = R(t) + \delta(t)$, where δ is the concentration boundary layer thickness. The result, together with Eq 10, is then integrated with respect to time. Two important assumptions are made: (a) A parabolic profile, given in Rosner and Epstein (3), is assumed for the solvent

concentration; and (b) That the concentration boundary layer thickness is much smaller than the radius of the bubble ($\delta/R \ll 1$). After a long algebraic procedure, the final result is:

$$\frac{dn}{dt} = \frac{32\pi^2}{3} \frac{D(c_{\infty} - c_s)^2 R^4}{n - n_0}$$
(17)

which is valid, only if the following ratio:

$$\frac{\delta}{R} = \frac{3}{4\pi} \frac{n - n_0}{(c_{\infty} - c_s)R^3}$$
(18)

is much smaller than 1. Note that the results here differ somewhat from the earlier works since we refer here to molar concentrations rather than mass concentrations.

It is interesting to check the approximated expression, given by Eq 17, with the exact solution for the case of constant pressure inside the bubble. Equation 17 can be integrated under the assumption of an ideal gas inside the bubble and that $n_0 = 0$ ($R_0 = 0$) at t = 0 to give:

$$R(t) = 2 \frac{R_g T (c_{\infty} - c_s)}{P_B} \sqrt{Dt}$$
(19)

This result (thin concentration boundary layer thickness) should be compared to the case of fast growth rates given by Eq 16. Note that the two equations are similar in form. Also the numerical constant 2 is very close to the numerical value of 1.95 of Eq 16.

DIMENSIONLESS EQUATIONS

We define the following dimensionless variables:

$$R^* = \frac{R}{R_0} \tag{20}$$

$$n^* = \frac{n}{n_0} \tag{21}$$

$$P_B^* = \frac{P_B}{P_{B_0}}$$
(22)

$$t^* = \frac{(P_{B0} - P_{\infty})}{4\mu} t$$
 (23)

and the following dimensionless numbers:

$$P_{\infty}^{*} = \frac{P_{\infty}}{P_{B0}}$$
(24)

$$R_{cr0}^{*} = \frac{R_{cr0}}{R_0}$$
(25)

$$A = \frac{R_0^3 c_\infty}{n_0} \tag{26}$$

$$B = \frac{P_{B0}}{Kc_{\infty}}$$
(27)

$$F = \frac{4\mu D}{R_0^2 (P_{B0} - P_{\infty})}$$
 (28)

Note that P_{B0} can be obtained by substituting R_0 , n_0 and the temperature of the system into the ideal gas equation. A characteristic "viscous" time was chosen instead of the usual "diffusion" time. This is because by looking at the published results so far, it appears that for short times the radius of the bubble changes as something similar to an exponential function of time, whether for long times the bubble radius looks to be proportional to the square root of time. We shall see later that the pressure inside the bubble increases to extremely high values only at the beginning of the process. Therefore, a characteristic "viscous" time seems to be the reasonable choice.

The two governing equations, Eqs 2 and 17, are given in a dimensionless form by:

$$\frac{dR^*}{dt^*} = \left(\frac{P_B^* - P_\infty^*}{1 - P_\infty^*}\right) R^* - R_{cr0}^*$$
(29)

$$\frac{dz}{dt^*} = \frac{(8\pi)^2}{3} FA^2 (1 - BP_B^*)^2 R^{*4}$$
(30)

As suggested by Patel (4), a dimensionless variable $z = (n^* - 1)^2$ was introduced in order to avoid the singularity of Eq 17 at t = 0 where $n = n_0$. The last two eqs need to be solved simultaneously with the following initial conditions:

$$R^* = 1$$
 at $t^* = 0$ (31)

$$z = 0$$
 at $t^* = 0$ (32)

The dimensionless pressure, according to the ideal gas equation is:

$$P_B^* = \frac{1 + \sqrt{z}}{R^{*3}}$$
(33)

Finally, the following condition must be met:

$$\frac{\delta}{R} = \frac{3}{4\pi} \frac{\sqrt{z}}{A(1 - BP_B^*)R^{*3}} < <1$$
(34)

Note that this complicated problem has been transformed into two, first order, ordinary, non-linear, differential equations. Five dimensionless numbers govern the physical situation.

IDEAL GAS

In order to simplify the problem we start with the simplest case in which $P_{\infty}^* = R_{cr0}^* = B = 0$, which probably represents a case of maximum growth rate.

FA² >> 1

In Fig. 1 we examine the influence of varying the value of A for a constant value of F = 1. Figure 1a shows that, as expected from Eq 30, bubble growth increases as A increases. Note also that for this case

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Fig. 1. The effect of the parameter A on bubble growth, for the case of F = 1 and $P_x^* = R_{cr0}^* = B = 0$. (a) the radius of the bubble; (b) the number of moles in the bubble; (c) the pressure in the bubble; (d) the ratio δ/R .

the radius of the bubble changes as something similar to an exponential function of time. We could not check cases for which the value of *A* is smaller than 1, since already at A = 1 the ratio δ/R is above 0.6 and according to our assumptions Eq 34 is not valid any more (see Fig. 1d). Note also that if $B = c_s(0)/c_{\infty} = 0$, then the ratio $c_s(t)/c_{\infty}$ will be equal to zero at all times.

The most interesting observation is, of course, the behavior of the pressure, as it can be seen in *Fig. 1c*. The pressure increases to a maximum (at a relative short time) before it decreases to a value close to the ambient pressure (at long times). As the value of A increases, this maximum pressure increases and depending upon the physical situation it can reach extremely large values. Therefore the two most common assumptions found in the literature, ideal gas or constant pressure within the bubble, may not be valid.

The reason for the increase in the pressure, at relative short times, is very simple. At t = 0, and according to the boundary and initial conditions defined in this problem, the thickness of the concentration boundary layer is zero and therefore there is an infinity

flux to the bubble. Since the bubble does not expand "relatively" fast, then the pressure within the bubble must increase. Fortunately, all this happens at t = 0.

Two observations can be made from the numerical results. At the maximum pressure $n^* >> 1$ $(\sqrt{z} >> 1)$ and that the maximum occurs always at an asymptotic value of $R^* = 1.24$. With those observations we shall now try to obtain an analytical expression for the maximum pressure for the simple case where $P_x^* = R_{cr0}^* = B = 0$. First Eq 30 can be divided by Eq 29 to give an expression for dz/dR^* which, combined with Eq 33, may be later integrated to give the following algebraic expression valid at all times:

$$z\left(\frac{2}{3}\sqrt{z}+1\right) = \frac{(8\pi)^2}{3} FA^2\left(\frac{R^{*7}-1}{7}\right)$$
(35)

Then, Eq 33 may be differentiated with respect to t^* and evaluated under the condition that $dP_B^*/dt^* = 0$. The result may be combined with Eqs 29 and 30 to give a second algebraic equation valid only when the pressure is at its maximum:

$$6\sqrt{z}(\sqrt{z}+1)^2 = \frac{(8\pi)^2}{3} FA^2 R^{*7}$$
 (36)

Solving Eqs 35 and 36 simultaneously, we get complicated expressions which may be simplified when $FA^2 >> 1$:

$$R^* = \left(\frac{9}{2}\right)^{1/7} = 1.24 \tag{37}$$

$$P_{B,max}^{*} = \frac{2^{37/21} \pi^{2/3}}{3^{6/7}} (FA^2)^{1/3} = 2.84 (FA^2)^{1/3} \quad (38)$$

Using a similar procedure it can be shown that at this same value for R^* , δ/R obtains its maximum, which is equal to:

$$\left(\frac{\delta}{R}\right)_{max} = \frac{3^{1/7}}{2^{5/21}\pi^{1/3}} \left(\frac{F}{A}\right)^{1/3} = 0.677 \left(\frac{F}{A}\right)^{1/3}$$
 (39)

Therefore, for the present case, in order to assure a thin concentration boundary layer thickness at all times, the condition $(F/A)^{1/3} << 1$ must be met.

FA² << 1

Next, we examine the case of varying the value of F for a constant value of A = 1. Again, we choose the simple case of $P_{\infty}^* = R_{cr0}^* = B = 0$. Figure 2a shows that, as expected from Eq 30, bubble growth decreases as F decreases. Figure 2c shows that, again, there is a maximum pressure. As F decreases P_{Bmax}^* decreases to an asymptotic value of 1. The radius in which this maximum is obtained is very close to 1 and also decreases as F decreases. Figure 2d shows that for values greater than F = 1 the condition $\delta/R <<1$ would not be met.

$\mathbf{R_{cr0}}^* \geq 1$

According to the momentum equation, for the bubble to grow, the radius of the bubble at t = 0 must be greater than the initial critical radius ($R_{cr0}^* < 1$). However, no such condition is required for the mass equation where the initial radius can be zero. The question to be asked is what is the new condition when we solve both equations simultaneously. Figure 3a shows some numerical results for the case of A = 1, $F = 10^{-5}$, $P_{\infty}^* = B = 0$, and $R_{cr0}^* \ge 1$.



Fig. 2. The effect of the parameter F on bubble growth, for the case of A = 1 and $P_{\infty}^* = R_{cr0}^* = B = 0$. (a) the radius of the bubble; (b) the number of moles in the bubble; (c) the pressure in the bubble; (d) the ratio δ/R .



Fig. 3. The effect of the parameter R_{cr0}^* on bubble growth, when $R_{cr0}^* \ge 1$. (a) A = 1, $F = 10^{-5}$, $P_{x}^* = B = 0$; (b) A = 100, F = 1, $P_{x}^* = B = 0$.

For the cases where $R_{cr0}^* > 1$, the radius of the bubble decreases to some minimum value before it increases. Thus we have an interesting situation where there is mass transfer to the bubble, but the radius of the bubble decreases. Again, we shall try an analytical expression for this unusual situation. At the minimum radius, $dR^*/dt^* = 0$, Eq 29 (when $P_{\infty}^* = 0$) together with Eq 33 results in:

$$R_{min}^{*} = \left(\frac{1+\sqrt{z}}{R_{cr0}^{*}}\right)^{1/2}$$
(40)

For the cases where $FA^2 << 1$, the numerical results show that at the minimum radius $\sqrt{z} << 1$, leading to the following expression for the minimum radius:

$$R_{min}^{\star} = \frac{1}{\sqrt{R_{cro}^{\star}}} \tag{41}$$

However, when $FA^2 >> 1$, the numerical results indicate that very large values R_{cr0}^* are needed in order to obtain a significant reduction in the value of the minimum radius (see Fig. 3b). When $R_{cr0}^* > 1$, according to the momentum equation, there are conditions for bubble collapse and the radius of the bubble decreases with time. But because there are also conditions for mass transfer to the bubble, eventually the bubble will grow. Clearly that for large values of FA^2 (large diffusion coefficients) the minimum radius will be larger, and the recovering time (the time in which the bubble will obtain again its initial value) will be smaller.

NON-IDEAL GAS

It was shown that when $FA^2 >> 1$ the pressure inside the bubble can increase to extremely high values before it decreases to a value close to the ambient pressure. Therefore, the common assumption of an ideal gas inside the bubble may not be valid at all times. Furthermore, we can imagine that there can be a certain pressure in which beyond it dissolution or even condensation may occur. This last point will be explained in the next two figures.

Figure 4 shows a typical behavior of a solvent-polymer solution. The x-axis represents the volume fraction of the solvent (ϕ) while the y-axis is the pressure of the bubble (P_B) since we assume that the bubble contains only the volatile solvent and that the vapor pressure of the polymer is zero. As usual, Henry's law may be assumed for the low solvent concentration regime.

Suppose we have a system originally at some solvent volume fraction at the bubble's surface of $\phi_s(0)$ represented by the point A, while the point B represents the (constant) solvent volume fraction at infinity (ϕ_{α}) . At the beginning of the process, the pressure inside the bubble increases, point A moves towards point B, the concentration difference decreases and the concentration boundary layer thickness increases. If the maximum pressure is below $P_{B,B}$ then there is no problem at all. However, if the maximum pressure is above $P_{B,B}$, then at some time $P_{B,A}(t) > P_{B,B}$ or $\phi_s(t)$ $> \phi_{x}$ and mass transfer from the bubble to the liquid will happen. Also, when A approaches B the concentration boundary layer thickness becomes very large and the solution is not valid any more. Therefore, our model cannot predict the physical situation close and beyond point B.

Now, suppose that ϕ_{∞} is at point *B*' where Henry's law is not applicable anymore. But our ideal gas model does not know that since Henry's law is assumed only for ϕ_s (at the moving point *A*). Now the pressure in the bubble increases and assume a situation where point *A* reaches point *C*' in which the pressure in the bubble is equal to the equilibrium pressure of the solvent ($P_{B,sat}$). Thus we have a wrong physical situation where condensation takes place before dissolution. The pressure in the bubble should follow the *AB*' path (and perhaps *AB*'*C*) but certainly not the *AC*' path.



Fig. 4. The vapor pressure of a solvent-polymer system, as a function of the volume fraction of the solvent in the liquid.

In order to avoid a wrong physical situation, we need to connect the solvent pressure and the solvent volume fraction with an equation of state for the gas phase capable of predicting phase change. The simplest choice is, of course, the van der Waals equation of state given by:

$$\left(P_B + \frac{n^2 a}{V^2}\right)(V - nb) = nR_gT$$
(42)

where a and b are parameters of the van der Waals equation that can be calculated from the critical properties as follows:

$$a = \frac{27R_g^2 T_c^2}{64P_c}$$
(43)

$$b = \frac{R_g T_c}{8P_c} \tag{44}$$

here T_c and P_c are the critical temperature and critical pressure respectively.

Figure 5 shows a typical van der Waals fluid at some constant temperature below the critical temperature. As before, point A represents the concentration at the surface which moves (at the beginning) towards the fixed point B, which represents the constant concentration at infinity. In general, the solvent may even be at a pressure above the equilibrium pressure (in the line *CD*) without undergoing condensation. However, this is an unstable situation and we shall assume that it does not happen here. The equilibrium pressure $P_{B,sat}$ (at points *C* or *E*) is the one where the integral (along *EC*) vanishes. An approximated expression for the equilibrium vapor pressure of a van der Waals fluid is given by Wall (11):

$$P_{B,sat} = \frac{a}{b^2} \exp\left(-\frac{a}{bR_gT}\right) \tag{45}$$

Using Flory-Hugins theory, the volatile pressure can be connected to the equilibrium pressure and the volume fraction at the surface of the bubble by (1) and (2):

$$P_B = P_{B,sat}\phi_s \exp[(1-\phi_s) + \chi(1-\phi_s)^2] \qquad (46)$$

where χ is the interaction parameter. Note that $\chi \leq 0.5$, otherwise a wrong physical situation is obtained $(P_B > P_{B,sal})$.

For typical devolatilization system the solvent concentration is very small ($\phi_s << 1$) and we obtain Henry's law:

$$P_B = P_{B,sat} \phi_s \exp(1 + \chi) \tag{47}$$

Finally, the solvent volume fraction may be related to the solvent molar concentration by the following approximated expression:

$$\phi = \frac{Mc}{\rho} \tag{48}$$

where *M* is the molecular mass of the solvent and ρ is the density of the pure solvent.



Fig. 5. A van der Waals fluid at some constant temperature below the critical temperature.

With the new definitions Eq 30 becomes now:

$$\frac{dz}{dt^*} = \frac{(8\pi)^2}{3} FA^2 \left(1 - \frac{\phi_s}{\phi_\infty}\right)^2 R^{*4}$$
(49)

the ideal gas Eq 33 is replaced by the van der Waals eq., which its dimensionless form is:

$$P_B^* = \frac{1 + \sqrt{z}}{\gamma [R^{*3} - \beta (1 + \sqrt{z})]} - \alpha \left(\frac{1 + \sqrt{z}}{R^{*3}}\right)^2 \quad (50)$$

where the following dimensionless parameters are defined as:

$$\alpha = \frac{n_0^2 a}{P_{B0} V_0^2}$$
(51)

$$\beta = \frac{n_0 b}{V_0} \tag{52}$$

and γ is given by:

$$\gamma = \frac{P_{B0}V_0}{n_0 R_g T} = \frac{1}{(1+\alpha)(1-\beta)}$$
 (53)

Note that $\alpha \ge 0$ and $0 \le \beta \le 1$, so that $\gamma \ge 0$. For the simple case of an ideal gas inside the bubble $\alpha = \beta = 0$ leading to $\gamma = 1$.

The two differential governing equations are now Eqs 29 and 49 together with Eqs 50–53, and the combination of Eqs 45 and 46 given by:

$$P_{B}^{*} = \frac{\alpha}{\beta^{2}} \phi_{s} \exp\left(-\frac{\alpha\gamma}{\beta}\right) \exp\left[(1 - \phi_{s}) + \chi(1 - \phi_{s})^{2}\right]$$
(54)

The dimensionless numbers remain the same except that *B* (*Eq.* 27) does not exist any more. Instead, we have four new dimensionless numbers: α , β , ϕ_{α} and χ .

Finally, the condition given in Eq 34 has to be modified to:

$$\frac{\delta}{R} = \frac{3}{4\pi} \frac{\sqrt{z}}{A\left(1 - \frac{\Phi_s}{\Phi_\infty}\right)R^{*3}} << 1$$
(55)

Note that we have now a total of eight dimensionless numbers that govern the physical situation.

Consider a devolatilization system initially containing 30% volume fraction of solvent at 200°C and 1 mmHg. Some typical values for an organic solvent are: $T_c = 600 \text{ K}$, $P_c = 4 \cdot 10^6 \text{ Pa}$ leading to $a = 2.62 \cdot 10^6 \text{ Pa} \cdot \text{m}^6/\text{kgmol}^2$, $b = 0.156 \text{ m}^3/\text{kgmol}$ and $P_{B,sat} = 1.49 \cdot 10^6 \text{ Pa}$. Assuming that: $\mu = 100 \text{ Pa} \cdot \text{s}$, $D = 10^{-8} \text{ m}^2/\text{s}$, $\sigma = 10^{-3} \text{ N/m}$, $\chi = 0.5$, M = 50 kg/kgmol and $\rho = 800 \text{ kg/m}^3$. If we chose $R_{cr0} = 0.5 \mu\text{m}$ and $R_0 = 5 \mu\text{m}$ then $P_{B0} = 4.13 \cdot 10^3 \text{ Pa}$ and $n_0 = 5.51 \cdot 10^{-19} \text{ kgmol}$. The eight dimensionless numbers are: $P_x^* = 0.0323$, $R_{cr0}^* = 0.1$, A = 1090, F = 40, $\alpha = 7.02 \cdot 10^{-4}$, $\beta = 1.64 \cdot 10^{-4}$, $\phi_\infty = 0.3$ and $\chi = 0.5$.



Fig. 6. The growth of an ideal gas bubble (with Henry's law) compared to the growth of non-ideal gas bubble (with the complete Flory-Hugins theory) for a typical devolatilization system. (a) the radius of the bubble; (b) the pressure in the bubble; (c) the ratio δ/R ; (d) the ratio ϕ_S/ϕ_∞ . The dashed line is the ideal gas and the solid line is the non-ideal gas.

Figure 6 compares the growth an ideal gas using Henry's law (Eq 47) with a non-ideal gas bubble using the complete Flory-Huggins theory (Eq 46) for the chosen system. Figure 6a shows that the radius of the bubble using Henry's Law is always greater. From Figs. 4 and 6d it can be seen that for the same P_B , ϕ_s is greater and $(\phi_{\infty} - \phi_s)$ is smaller leading to a lower growth rate (lower driving force) using the new formulation. Figure 6b shows that it is possible to obtain a wrong physical situation ($P_B > P_{sat}$) when using Henry's law. Finally, the validity of the solution is checked in Fig. 6c.

SOME LIMITATIONS OF THE MODELS

The models presented here assumed that the solvent concentration at infinity (c_{∞}) is constant. In a real process the amount of solvent is limited, and therefore as time passes the concentration at infinity must decrease. According to our models, the pressure in the bubble reaches high values at relative short times. Since this situation appears at the beginning of the process, when the solvent concentration at infinity

cannot change so much, the assumption of constant infinity concentration can still describe this phenomenon. At long times, we cannot justify any more this assumption, and a more realistic picture can be obtained using the cell model (12). In that model, not only the concentration at infinity can be treated as a variable, but it also can deal with a large number of bubbles in a limited amount of polymer.

For reasons of simplicity we have assumed constant physical properties although it is well known that they are a strong function of the solvent concentration. At the beginning of the process, the pressure in the bubble increases, and so does the solvent concentration at the surface of the bubble (c_s) . As a result, not only the viscosity decreases but also the surface tension decreases (13), resulting from Eq 2 in a pressure decrease. On the other hand, as the pressure and the surface concentration increase, the diffusion coefficient will increase dramatically (14), and this time, according to Eqs 10 and 12 the pressure will increase. We observe that some parameters tend to decrease the pressure, while others tend to increase the pressure. Since the governing equations are valid for constant physical properties, the value of the maximum pressure described in this work should be taken only as a first approximation.

CONCLUSIONS

A model for momentum and mass controlled spherical bubble growth in a quiescent viscous liquid is presented. Applying the integral method and assuming a thin concentration boundary layer thickness, the theoretical model presented by Patel (4) was improved by developing some analytical results. The model was further improved in order to deal with the pressure within the bubble, which under certain conditions may reach very large values that can lead to a wrong physical situation. This was done for a solvent-polymer mixture in a devolatilization process by connecting the van der Waals equation of state with Flory-Hugins theory.

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NOMENCLATURE

- a = Parameter of the van der Waals equation.
- A = Dimensionless number.
- b = Parameter of the van der Waals equation.
- B = Dimensionless number.
- c = Molar concentration.
- D = Diffusion coefficient.
- F = Dimensionless number.
- K = Henry's constant.
- M = Molecular mass of the solvent.
- n = Number of moles inside the bubble.
- P = Pressure.
- r = Radial coordinate.
- R = Radius of the bubble.
- $R_g =$ Universal gas constant.
 - t = Time.
- T = Absolute temperature.
- v = Velocity.
- V = Volume of the bubble.
- z = Dimensionless variable.

Greek letters

- α = Dimensionless parameter.
- β = Dimensionless parameter.

- γ = Dimensionless parameter.
- δ = Concentration boundary layer thickness.
- λ = Dimensionless growth constant.
- μ = Viscosity of the liquid.
- ρ = Density of the pure solvent.
- σ = Surface tension.
- ϕ = Volume fraction of the solvent.
- χ = Interaction parameter.

Subscripts

- B = In the bubble.
- c = Critical.
- cr = Critical.
- r = Radial direction.
- s = At the bubble's surface.
- sat = Saturation.
 - 0 = at t = 0
 - ∞ = Far away from the bubble.

Superscripts

* = Dimensionless.

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