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Growth of vapour bubbles in boiling polymer solutions—I. Rheological and diffusional effects

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Abstract—Effects of elastic viscosity and diffusion resistance during the growth of vapour bubbles in a superheated polymer solution are investigated. Based on the approximate solutions of the equations of interphase interaction, the influence of the relaxation behaviour of a fluid, diffusion phenomena and thermodynamic non-ideality of the solution on the rate of the expansion of vapour bubbles is analysed.

INTRODUCTION

The evolution of vapour bubbles in a superheated liquid plays a crucial role in the processes of boiling. In particular, the rate of growth of bubbles is one of the parameters that determines the intensity of heat removal from a heating surface. For low-molecular fluids, including binary solutions [1], the phenomenon has been investigated well, in contrast to polymer systems, the boiling of which is accompanied by manifestation of a number of specific factors. Theoretical investigation of their role and effect is of special interest in view of the scarcity of available experimental data and differences in the interpretation of results obtained. Note that knowledge of the rate of expansion of vapour cavities is also important for predicting the rate of solvent removal in certain technological processes for obtaining high-molecular compounds. This determines one more applied aspect of the problem.

If the superheat throughout a volume is produced by pressure reduction, the initial stage in the growth of a vapour bubble is determined by the added inertia of the liquid. At this stage of the process an essential role can be played by the rheological properties of the liquid, the effect of which on the dynamics of spherically symmetric interphase interaction was investigated in refs. [2–5]. The specific feature of the dynamic stage in the growth of the cavity, the duration of which can be evaluated with the help of the Rayleigh time scale $t_R = R_0(\rho_2/p_{20})^{1/2}$, is a change of the pressure in a bubble and the possibility of oscillations. After the equalization of pressure in phases, a thermal stage sets in when the rate of growth of the inclusion is determined by the ability of the liquid to supply heat for phase transition. The expansion of the vapour cavity in the thermal regime is described by Scriven's self-similar solution [6]. Also considered in ref. [6] was the case when the carrier phase was a binary solution. Later publications on the dynamics of vapour bubbles in binary systems were reviewed in ref. [7]. A numerical analysis of the collapse of vapour bubbles in a binary solution with thermal and inertial stages can be found in ref. [8]; small oscillations were investigated in ref. [9].

The present work is aimed at extending the basic results pertaining to the growth of vapour bubbles to the case of a polymer solution. Certainly, a complete solution of the non-linear thermal and dynamic problem concerning the growth of a vapour bubble in a relaxing two-component liquid is possible only with the help of numerical methods [10]: however, approximate analytical solutions that reflect the basic features of the evolution of inclusions are also of interest. In the following, two solutions of this type are considered that allow one to isolate solvent in a pure form and perform a successive analysis of the role of rheological effects and diffusional transport of a solvent during the expansion of bubbles in a polymer solution.

EFFECTS OF VISCOELASTICITY

Radial flows in the vicinity of a spherical bubble are classified as elongational [11]. The available data [12, 13] point to the possibility of the use of the following types of equations for describing the rheological behaviour of polymer fluids in such flows

NOMENCLATURE

c_2	specific heat of fluid
D^*	reduced coefficient of diffusion, D/D_0
D/Dt	Jaumann derivative
$\mathbf{e}$	rate-of-strain tensor
j	intensity of phase transitions
Ja	Jacob number, $c_2 \Delta T \rho_2 (\rho_1 l)^{-1}$
k	mass concentration of solvent in liquid phase
K_ρ	density ratio of solvent and polymer
l	specific heat of evaporation
Le_2	Lewis number for liquid phase, a_2/D_0
p	pressure
p_{v0}	pressure of pure solvent vapours
$\bar{p}_{v0}$	pressure of saturated vapours of solvent above solution
r	radial axis of spherical coordinate system with origin at the bubble centre
R	bubble radius
Re_p	Reynolds number based on Newtonian viscosity of solution, $R_0(\rho_2\|\Delta p\|)^{1/2}/(4\eta)$
Re_s	Reynolds number based on Newtonian viscosity of solvent, $R_0(\rho_2\|\Delta p\|)^{1/2}/(4\eta_s)$
Sn	Scriven number, $\Delta T/\Delta T_*$
t	time
T	temperature
v	radial velocity component.

Greek symbols

η	Newtonian viscosity of polymer solution
η_s	shear viscosity of solvent
κ	thermal conductivity coefficient
λ	relaxation time
ρ	density
σ	surface tension coefficient
τ	extra-stress tensor
φ_1	volumetric condensation of solvent in solution
χ	Flory–Huggins constant.

Subscripts

R	phase interface
s	solvent saturation state
1	vapour
2	liquid
0	equilibrium state.

$$\boldsymbol{\tau} = \sum_k \boldsymbol{\tau}^{(k)} + 2\eta_s \mathbf{e}$$

$$\boldsymbol{\tau}^{(k)} + \lambda_k [D\tau^{(k)}/Dt - \alpha(\boldsymbol{\tau}^{(k)} \cdot \mathbf{e} + \mathbf{e} \cdot \boldsymbol{\tau}^{(k)})] = 2\eta_k \mathbf{e}. \quad (1)$$

The use of more complex versions of the generalized Maxwellian model with the character of variation in longitudinal viscosity similar to equation (1) does not cause any fundamental changes in the results of the calculations [14]. For the analysis to be more clear, only one non-linear relaxing oscillator in model (1) will be taken into account, with the assumption that

$$\tau = \tau^{(1)} + \tau^{(s)} \quad \tau^{(s)} = 2\eta(1-\beta)e. \quad (2)$$

Here β characterizes the contribution of the Maxwellian element to the effective viscosity of the solution η, whereas the parameter $1/2 < \alpha \leqslant 1$ regulates the effect of non-linear terms. Then, the Rayleigh generalized equation [15] that describes the radial motion of the spherical phase interface can be presented in the form

$$J + \Delta p + T = S. \quad (3)$$

$$S_1 = J_\alpha = -\frac{2\beta\eta}{\alpha\lambda R^{4\alpha}} \int_0^t \mathrm{e}^{-(\xi - t)/\lambda} (\nu^{2\alpha} - v^{2\alpha})$$

$$\times (\nu - v)^{-1} \cdot R^{2(1-\alpha)}(\xi) \dot{R}(\xi) \, \mathrm{d}\xi$$

$$\nu = R^3(\xi) \quad v = R^3(t) \quad S_2 = -4\eta(1-\beta)\dot{R}R^{-1}$$

$$S = S_1 + S_2 \quad T = 2\sigma R^{-1} \quad J = \rho_2(R\ddot{R} + 3/2\dot{R}^2)$$

$$\Delta p = p_2(\infty) - p_1. \quad (4)$$

Equation (3) reflects the balance of the forces of inertia J, pressure Δp, surface tension T and 'rheological' force S. Note that the integral $J_\alpha(t)$, which in equation (3) characterizes the influence of the relaxing portion of the stress tensor, can be determined from the system of first-order differential equations at the boundary values of the parameter α from the region of its variation ($\alpha = 1/2$, 1), for which there are the following equations equivalent to equation (4):

$$\dot{J}_{1/2} + (\lambda^{-1} + 2\dot{R}R^{-1}) J_{1/2} = -4\beta\eta\lambda^{-1}\dot{R}R^{-1} \quad (5)$$

$$J_1 = J_{11} + J_{12}$$

$$\dot{J}_{11} + (\lambda^{-1} + 4\dot{R}R^{-1}) J_{11} = -2\beta\eta\lambda^{-1}\dot{R}R^{-1}$$

$$\dot{J}_{12} + (\lambda^{-1} + \dot{R}R^{-1}) J_{12} = -2\beta\eta\lambda^{-1}\dot{R}R^{-1}. \quad (6)$$

For $\alpha = 1/2$, equations (2) and (5) yield $J_{1/2}(t) = \tau_{rr}^{(1)}(\mathrm{R}, \mathrm{t})$. This means that at $\alpha = 1/2$, similarly to conventional viscosity for a Newtonian fluid, the rheological properties of a polymer solution during the evolution of a bubble (growth, collapse, oscillations) manifest themselves only in the zone adjacent to the phase interface and can be taken into account only in the boundary condition when deriving an equation for $R(t)$. When $\alpha = 1$, $J_1(t) < \tau_{rr}^{(1)}(R, t)$, and accounting for the rheology of the medium only via the boundary condition leads to a certain acceleration in the expansion of the inclusion as compared with the solution of the exact system of equations (3) and (6).

For the initial portion of the growth of a bubble from its equilibrium state, relations (4) yield $R_p(t) < R(t) < R_s(t)$, where $R_p(t)$, $R_s(t)$ is the law of the expansion of a cavity in a Newtonian fluid with the viscosity of the solution and solvent, respectively. A similar result for the Oldroyd model fluid was obtained somewhat differently in ref. [3], and for a fluid with a spectrum of relaxation times in ref. [5]. To investigate the non-linear stage of the process, write a system of equations (3), (5) ($\alpha = 1/2$) in the inertialess approximation assuming the Reynolds number Re based on the effective longitudinal viscosity η_l to be small [$Re = (\eta/\eta_l)Re_p$]. After the result was rendered dimensionless with the assumption that $\Delta p =$ const. and capillary pressure was neglected (for bubbles with $R \gg 10^{-6}$ m), the following relations were obtained:

$$\dot{z}+2(z-z_1)(z-z_2) = 0 \quad z = \dot{x}x^{-1}$$
$$z_{1,2} = -A/4 \mp (A^2/16+B/2)^{1/2} \quad x = x(\tau) = R/R_0$$
$$A = \lambda^{*-1}(1-\beta)^{-1}(1-2k\lambda^* Re_p)$$
$$B = k\,Re_p\,\lambda^{*-1}(1-\beta)^{-1} \quad k = -\operatorname{sgn}(\Delta p)$$
$$\tau = t/t_0 \quad t_0 = R_0(\rho_2/|\Delta p|)^{1/2} \quad \lambda^* = \lambda/t_0. \tag{7}$$

Analysis of equation (7) on the phase plane for a growing bubble ($k = 1$) shows that in the non-linear stage also, a cavity expands faster than in a Newtonian fluid with equivalent viscosity: $z_p \leqslant z_1 \leqslant z_s$, $z_p = Re_p$, $z_s = Re_s$, where z_p, z_s is the asymptotic rate of growth of a cavity in a Newtonian fluid with the viscosity of solution (η) and solvent [$\eta_s = (1-\beta)\eta$], respectively. For $\lambda^* \ll 1$

$$z_1 = z_p + 2\beta\lambda^* Re_p^2$$

and for $\lambda^* \gg 1$

$$z_1 = z_s - 1/2\beta\lambda^{*-1}(1-\beta)^{-1}.$$

Thus, polymer additives slow down the growth of a bubble in an infinite liquid, but because of the manifestation of elastoviscous effects the rate of growth turns out to be higher than in a Newtonian fluid with the viscosity of a solution.

Note that collapse of a cavity ($k = -1$) leads to the opposite result [16]: $z \to z_1$ when $\tau \to \infty$ (the quiescent point z_2 is unstable) and the speed of closure of a cavity in the asymptotic regime satisfies the inequality $z_p \leqslant z_1 \leqslant 0$, where $z_p = -Re_p$. This is explained by the different behaviour of the stress tensor component $\tau_{rr}^{(1)}$ which determines the effect of viscoelastic properties of the liquid on the dynamics of the cavity in compression and extension flows. According to ref. [14], the quantity $|\tau_{rr}^{(1)}|$ may attain substantially higher values in the second case than in the first. Results similar to those given follow from equations (3) and (6) for $\alpha = 1$.

THERMAL REGIME OF THE GROWTH OF BUBBLES

The evolution of vapour inclusions in a polymer solution at the thermal stage is specifically due to the following three factors. First, because of the great difference in molecular masses, phase transitions in the system considered occur only with a low-molecular solvent. Second, polymer solutions are usually substantially non-ideal and therefore in practice one observes substantial deviations in the volatile component saturated vapour pressure above the solution from Raoult's law. Finally, in the process investigated one can observe the dependence of the velocity of diffusional transport of a low-molecular component to the liquid–vapour interface on concentration, resulting from the changes in the binary diffusion coefficient [17]. The significance of the factors listed increases with boiling systems which have the lower critical temperature of mixing, and which can laminate on increasing temperature in the region $T < T_S$. In the latter case, the polymer-enriched phase, which usually has a higher density, finds itself near the heating surface (with heating from below), as a result of which the growth of vapour bubbles occurs under conditions of deficit of the volatile component.

Let us investigate the thermal stage in the expansion of a vapour cavity in a superheated polymer solution [$T_{20} > T_S(k_0)$], assuming the pressure and temperature in the vapour phase to be steady:

$$p_1 = p_{20} \quad T_1 = T_s(p_{20}, k_R) = T_{2R} \quad k_R = k(R,t). \tag{8}$$

SELF-SIMILAR SOLUTION

Equations of heat conduction and diffusion in a fluid have the form

$$\frac{\partial T_2}{\partial t^2} + v_{2R}R^2r^{-2}\frac{\partial T_2}{\partial r} = r^{-2}\frac{\partial}{\partial r}\left(a_2 r^2\frac{\partial T_2}{\partial r}\right) \tag{9}$$

$$\frac{\partial k}{\partial t} + v_{2R}R^2r^{-2}\frac{\partial k}{\partial r} = r^{-2}\frac{\partial}{\partial r}\left(Dr^2\frac{\partial k}{\partial r}\right). \tag{10}$$

Since within the ranges $T_S(k_R) < T_2 < T_{20}$ and $k_R < k < k_0$ the thermal conductivity of the solution a_2 changes less [18] with variation in temperature and concentration than the coefficient of binary diffusion D, it is assumed in what follows that $a_2 \approx$ const. Moreover, since the thermal boundary layer is much thicker than the diffusional one, it can be assumed that within the latter $D = D(k, T_{2R})$.

Boundary conditions for equations (9) and (10) are

$$T_2 = T_{20} \quad k = k_0 \quad r = \infty \tag{11}$$

$$\dot{R} - v_{2R} = \rho_2^{-1}j \quad \dot{R} = \rho_1^{-1}j \tag{12}$$

$$j = (\dot{R}-v_{2R})\rho_2 k_R + \rho_2 D\frac{\partial k}{\partial r} \tag{13}$$

$$jl = \kappa_2\frac{\partial r_2}{\partial r} \quad r = R. \tag{14}$$

Equations (12) and (13) yield

$$j = \frac{\rho_2}{1-k_\mathrm{R}} D \left.\frac{\partial k}{\partial r}\right|_{r=R}. \tag{15}$$

For conditions which have little in common with critical conditions, $\varepsilon = \rho_1/\rho_2 \ll 1$ and then it is possible to assume that $v_{2\mathrm{R}} = \dot{R}(1-\varepsilon) \approx \dot{R}$.

Let us introduce the variable $\eta = rR^{-1}$ and obtain the solution of equations (9) and (10) of the form $T = T(\eta)$, $k = k(\eta)$. The dependence of the diffusion coefficient on concentration will be given in the form $D = D_0\ [1+f(k)]$. The self-similar solution of the problem exists if

$$h = R\dot{R}a_2^{-1} = \text{const} \quad h_1 = R\dot{R}D_0^{-1} = \text{const}. \tag{16}$$

Let $\bar{T} = T/T_{2\mathrm{R}}$, then equation (9) yields [10]

$$\bar{T} = 1 + c_1^{-1} \int_1^\eta \eta^{-2} \exp\left[-h(\eta^2/2 + (1-\varepsilon)/\eta)\right] \mathrm{d}\eta$$

$$C_1 = (\bar{T}_{20} - 1)^{-1} \int_1^\infty \eta^{-2}$$

$$\times \exp\left[-h(\eta^2/2 + (1-\varepsilon)\eta^{-1})\right] \mathrm{d}\eta$$

$$\bar{T}_{20} = T_{20}/T_\mathrm{R}. \tag{17}$$

In contrast to equation (9), equation (10) is non-linear. It does not have an analytical solution when the function $D = D(k(\eta))$ is arbitrary. Note that for a plane case of non-linear diffusional transport under self-similarity conditions, the field of concentrations can be defined in quadratures at specific forms of the function $D = D(k)$ (for example, linear, exponential, power-law, etc. [19]). However, the resulting relations are rather cumbersome and usually have a parametric character, and their investigation requires using a computer. Now, an approximate expression for the function $k = k(\eta)$ is to be obtained. Introduce a new variable $\bar{k} = k/k_\mathrm{R}$. The solution of equation (10) will be sought in the form [20] $\bar{k} = \bar{k}^0 + \bar{k}^*$, where $\bar{k}^0$ is the solution of a linear problem and $\bar{k}^*$ is the first approximation which takes into account non-linear effects. The following boundary-value problems are used for determining $\bar{k}^0$ and $\bar{k}^*$:

$$\frac{\mathrm{d}^2\bar{k}^0}{\mathrm{d}\eta^2} + [h_1\eta + 2/\eta - h_1(1-\varepsilon)\eta^{-2}]\frac{\mathrm{d}\bar{k}^0}{\mathrm{d}\eta} = 0. \tag{18}$$

$$\bar{k}^0(1) = 1 \quad \bar{k}^0(\infty) = \bar{k}_0 \equiv k_0/k_\mathrm{R}$$

$$\frac{\mathrm{d}^2\bar{k}^*}{\mathrm{d}\eta^2} + [h_1\eta + 2/\eta - h_1(1-\varepsilon)\eta^{-2}]\frac{\mathrm{d}\bar{k}^*}{\mathrm{d}\eta} = -F(\bar{k}^0(\eta))$$

$$F(\bar{k}^0(\eta)) = \eta^{-2}\frac{\mathrm{d}}{\mathrm{d}\eta}\left(\eta^2 f(\bar{k}^0(\eta))\frac{\mathrm{d}\bar{k}^0}{\mathrm{d}\eta}\right)$$

$$\bar{k}^*(1) = \bar{k}^*(\infty) = 0. \tag{19}$$

Equations (18) and (19) yield

$$\bar{k} = 1 + (A + C_2^{-1}) \int_1^\eta K(\eta)\,\mathrm{d}\eta$$

$$-\left(\int_1^\eta K(\eta)\,\mathrm{d}\eta\right) \int_1^\eta F(\bar{k}^0(\eta))K^{-1}(\eta)\,\mathrm{d}\eta$$

$$+ \int_1^\eta F(\bar{k}^0(\eta))K^{-1}(\eta)\left[\int_1^\eta K(u)\,\mathrm{d}u\right]\mathrm{d}\eta$$

$$\bar{k}^0(\eta) = 1 + C_2^{-1}\int_1^\eta K(\eta)\,\mathrm{d}\eta$$

$$K(\eta) = \eta^{-2}\exp\left[-h_1(\eta^2/2 + (1-\varepsilon)\eta)\right]$$

$$A = \int_1^\infty F(\bar{k}^0(\eta))K^{-1}(\eta)\,\mathrm{d}\eta - \left[\int_1^\infty K(\eta)\,\mathrm{d}\eta\right]^{-1}$$

$$\times \int_1^\infty F(\bar{k}^0(\eta))K^{-1}(\eta)\,\mathrm{d}\eta\left[\int_1^\eta K(u)\,\mathrm{d}u\right]\mathrm{d}\eta. \tag{20}$$

The solutions obtained involve unknown parameters: the constant h which determines the rate of bubble growth ($h_1 = h\,Le_2$), the phase interface temperature $T_{2\mathrm{R}}$ and the solvent concentration k_R. In contrast to a one-component fluid, the temperature $T_{2\mathrm{R}}$ is unknown *a priori* and is associated with the surface concentration k_R by the phase equilibrium equation. Equations (12), (14) and (15) yield the following equations for determining k_R and h:

$$h = \rho_2 c_2 T_\mathrm{R}\left(\frac{\mathrm{d}\bar{T}}{\mathrm{d}\eta}\right)_{\eta=1}(\rho_1 \mathrm{l})^{-1} \tag{21}$$

$$h_1 = \rho_2 k_\mathrm{R}\rho_1^{-1}(1-k_\mathrm{R})^{-1}\left(\frac{\mathrm{d}\bar{k}}{\mathrm{d}\eta}\right)_{\eta=1}. \tag{22}$$

Formal substitution of solutions (17) and (20) into equations (21) and (22) with the use of relation $T_{2\mathrm{R}} = T_\mathrm{S}\,(\mathrm{p}_{20}, k_\mathrm{R})$ allows one to obtain easily a closed system of equations for determining h, but this requires a laborious numerical investigation. The problem can be simplified for the case $Ja \gg 1$ (the member Ja is determined from the factual superheating of the fluid $\Delta T = T_{20} - T_{2\mathrm{R}}$). Physically, the approximation considered corresponds to a thin thermal boundary layer around a growing bubble. Since in polymer solutions $Le_2 \gg 1$, here the condition of the small thickness of diffusional boundary layer δ_D is also complied with. Investigation of the asymptotics of the obtained solutions in the region $Ja \gg 1$ leads to the relations

$$\bar{T} = 1 + (\bar{T}_{20} - 1)\,\mathrm{erf}\left[(\sqrt{3h/2})(\eta - 1)\right]$$

$$\bar{k}_0 = 1 + (\bar{k}_0 - 1)\,\mathrm{erf}\left[(\sqrt{3h_1/2})(\eta - 1)\right]$$

$$C = \sqrt{2a_2\,Ja} = \sqrt{2D_0\,Di} \quad Ja \ll 1 \quad Di \ll 1.$$

Since here $Ja < Ja_0$, the rate of the growth of bubbles in a polymer solution is always smaller than in an equivalent single-component fluid.

To close the relations obtained, it is necessary to use the phase equilibrium equation [22]

$$\bar{p}_{v0}/p_{v0} = \varphi_1 \exp\,[1-\varphi_1+\chi(1-\varphi_1)^2].$$

The dependence of the pressure of pure solvent vapours on temperature is described with the aid of the following approximation:

$$p_{v0} = A \exp\,(-B/T).$$

Simplify the expression for M_1 by assuming a linear dependence of diffusion coefficient on concentration in the interval (k_R, k_0). When $f = \bar{\alpha}(\bar{k}-\bar{k}_0)$, $M_1 = \bar{\alpha}(1-\pi^{-1})(\bar{k}_0-1)$. The accuracy of the linear approximation of the function $f(\bar{k})$ employed can be improved, if one first determines $\bar{k}_R = \bar{k}'_R$, assuming $\bar{\alpha} = (\mathrm{d}D^*/\mathrm{d}\bar{k})_{\bar{k}=\bar{k}_0}$ and then refines the value obtained by drawing a straight line through a point with the abscissa $\bar{k}_m = 1/2(\bar{k}_0+\bar{k}'_R)$. Thus, the second iteration is executed with the value $\bar{\alpha} = (D^*_m-1)(\bar{k}_m-\bar{k}_0)^{-1}$, where $D^*_m = D^*(\bar{k}_m)$. Simultaneously the temperature correction for D^* is taken into account by T_{20} in the argument of the function $D_0 = D_0(T_{20})$ for the T'_{2R} value found in the first iteration. For calculations it is convenient to represent equation (24) in the form

$$Sn = \kappa G^{-1}(1+\alpha_1 x)(1-\alpha x)/(1+x-k_0)$$
$$G = \varepsilon\,Ja_o\,Le_2^{1/2} \quad x = k_o - k_R \quad \alpha_1 = \alpha(1-\pi^{-1})$$
$$\alpha = \bar{\alpha}k_R^{-1} \quad Sn = \Delta T/\Delta T_*. \tag{29}$$

The data of numerical investigation of equation (29) are presented in Figs. 1–3. The thermophysical parameters of the solution were estimated taking into account the corresponding values for a solvent and recommendations given in ref. [18].

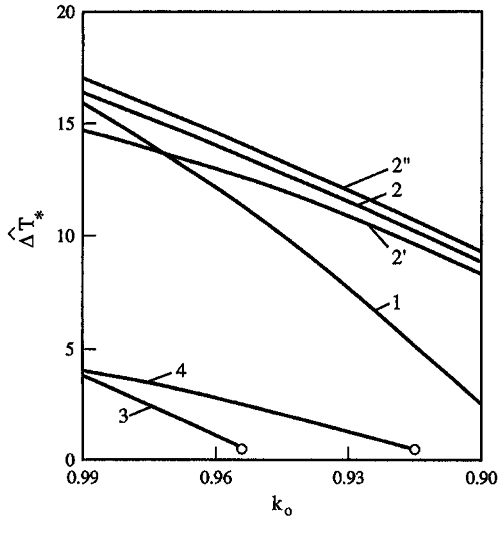

Fig. 1. Limiting superheating during the growth of vapour bubbles. 1, 2, 2′, 2″: $l = 2.3\times10$ J^6 kg^{-1}; $c_2 = 3\times10^3$ J kg^{-1} K^{-1}, $a_2 = 10^{-7}$ m^2 s^{-1}, $D_0 = 5\times10^{-11}$ m^2 s^{-1}; 3, 4: $l = 3.6\times10^5$ J kg^{-1}, $c_2 = 2\times10^3$ J kg^{-1} K^{-1}, $a_2 = 8\times10^{-8}$ m^2 s^{-1}, $D_0 = 5\times10^{-11}$ m^2 s^{-1}; 1–4: $\alpha = 0$; 2′, 2″: $\alpha = 1, -1$; 1, 3: $\chi = 0.1$; 2, 4: $\chi = 0.4$; $K_\rho = 0.7$. o, $J\hat{a}_o = 1$.

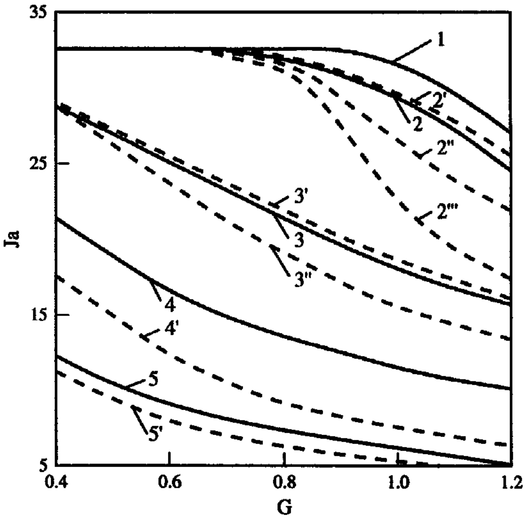

Fig. 2. Dependence of the effective Jacob number for a vap our bubble growing in a superheated aqueous solution of a polymer on the parameter G. $\Delta T_* = 15$ K, $\chi = 0.1$, $K_\rho = 0.7$; 1–5: $k_o = 0.99, 0.95, 0.7, 0.5, 0.3$; 2′–2‴: $k_o = 0.95$; 3′–3″: $k_o = 0.7$; 4′, 5′: $k_o = 0.5, 0.3$; 1–5; 2′, 3′; 2″; 2‴, 3″, 4′, 5′: $\alpha = 0, -0.5, 0.8; 2$.

A characteristic feature of the curves of the liquid–vapour phase equilibrium for polymer solutions in the coordinates p, k or T, k is the presence of almost a plateau in the region of rather small contents of the polymer ($k_* \leqslant k_o \leqslant 1$). For the k_o values in this interval it is possible to determine such a number $\hat{J}a_o$, at which, when $1 < Ja_o < \hat{J}a_o$, diffusional retardation of the growth of vapour bubbles does not show up due to a weak dependence of T_s (or p_s) on k_R. Let us evaluate $\hat{J}a_o$ or the corresponding superheat $\Delta\hat{T}_*$ from the condition $Sn = 0.99$ (the deviation of the effective superheat ΔT from the volumetric one ΔT_* does not exceed 1%). The results of the calculation are presented in Fig. 1. As can be seen, the thus obtained conventional limiting superheat $\Delta\hat{T}_*$ decreases with a decrease in k_o and increases in the non-linearity parameter α, whereas with the growth of the Flory–Huggins constant it increases. The increase in χ also leads to the extension of the range $k_* \leqslant k_o \leqslant 1$. The value $\Delta\hat{T}_*$ depends substantially on the diffusion transfer rate: as the latter falls, a decrease in the limiting superheat is observed below which bubbles in a polymer fluid grow as in a pure solvent. For polymer solutions in volatile organic solvents, $\Delta\hat{T}_*$ is lower than the value for an aqueous solution of the same concentration.

When $Ja_o > \hat{J}a_o > 1$, one can see that diffusion retards the growth of vapour bubbles in a solution. Note that in low-molecular binary systems with a clearly observed dependence $T_s = T_s(k_o)$, a similar effect is absent in the entire range of the values of k_o.

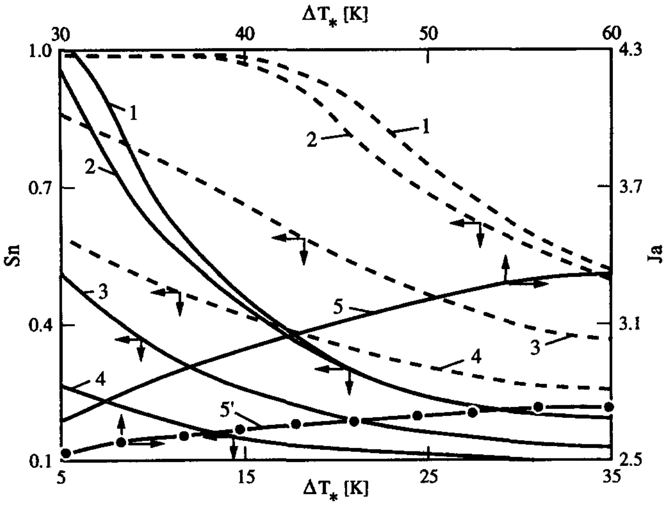

Fig. 3. Effect of the volumetric superheat of a solution on the Scriven and Jacob numbers. (—) Polymer solution in toluol; (---) aqueous solution; 1–5: $\alpha = 0$, $k_o = 0.99$, 0.95, 0.7, 0.5, 0.3; 1–4: $\chi = 0.1$; 5, 5′: solution of polystyrole in toluol at $k_o = 0.3$; 5′: $\alpha \neq 0$, calculation with the use of the function $D = D(T, \varphi_1)$ from ref. [24]. Thermophysical parameters are the same as for the curves in Fig. 1.

It should be emphasized that the scale of the effect is closely associated with the deviation of the behaviour of a solution from an ideal one: the larger the deviation, the less is the effect. This can be easily understood, since in the case of a very large difference between the molecular masses of a solvent and solved substance, typical for a polymer solution, the graph of the function $T_s = T_s(k_o)$ plotted on the basis of Raul's law passes virtually along the coordinate axes [23]. For this reason, the rate of growth of vapour bubbles in a polymer solution in compliance with the Flory–Huggins equation is always smaller than for an equivalent ideal solution.

Analysis of the curves in Fig. 2 shows that a decrease in the rate of diffusional transfer $[G \sim (Le_2)^{1/2}]$ under the conditions of a fixed superheat ΔT_* leads to a substantial decrease in the effective Jacob number Ja. The growth of the content of a polymer in a solution leads to the same result. The influence of the non-linearity of diffusional transport is higher for diluted solutions. This is explained by a decrease in the deviation of the surface concentration k_R from the volumetric one k_0 when k_0 falls because of the typical growth of the derivative $|\partial T_S/\partial k|$ in polymer fluids. The presence of an almost horizontal portion on the curve $Ja = Ja\ (G)$ when $k_0 \geqslant 0.95$ is explained by the existence of the limiting superheat ΔT_* dependent on the Lewis number.

The role of diffusional retardation with the growth of the volumetric superheating increases. This reveals itself in a decrease of the number Sn with a growth in ΔT_* (Fig. 3). For solutions involving volatile organic liquids as solvents the effect is higher than for aqueous systems. For concentrated solutions the differences between the effective ΔT and volumetric ΔT_* superheats leads to the impossibility of substantially increasing in practice the rate of growth of vapour bubbles by increasing volumetric superheat. Curves 5 and 5′ are typical in this case.

CONCLUSIONS

The analysis carried out shows that the growth of bubbles in a large volume of a polymer solution occurs more slowly than in a solvent but faster than in a similar pure viscous fluid. Investigation of viscoelastic effects during the growth, collapse and pulsations of bubbles in a polymer medium can be conveniently carried out on the basis of differential equations of the dynamics of a cavity. These equations can be obtained by transformation of the Rayleigh non-linear generalized integrodifferential equation. The possibility of such a transformation is physically associated with the fact that rheological specific features of carrying phase and dissipative losses attributable to these features are substantial mainly in the vicinity of the phase interface—the zones of maximal velocity gradients.

The rate of the expansion of vapour bubbles in a superheated solution of a high-molecular compound is lower than in a pure solvent due to diffusion resistance. In diluted solutions at rather small superheats (nevertheless satisfying the condition $Ja_o > 1$) the mechanism of diffusional retardation can be suppressed due to a weak dependence of T_s on k_o, characteristic for macromolecular systems in this concentration range. It is convenient to characterize this effect with the aid of the conventional limiting superheat $\Delta \hat{T}_*$ below which the difference in the rates of growth of bubbles in a solution and a pure solvent can be neglected. The value of $\Delta \hat{T}_*$ falls with the growth in the content of a polymer in the solution, increase in the deviation from ideal behaviour, increase in the number Le_2 and with an increase in the non-linearity parameter of diffusional transfer. For binary systems containing as solvents organic liquids with low vapour generation enthalpy, the $\Delta \hat{T}_*$ value is much smaller than for aqueous solutions.

A criterion of the display of diffusion resistance during the growth of vapour bubbles in a solution—the number *Sn*—decreases with an increase in the volumetric superheat (Le_2 number) in the heat of vapour generation. The effect of diffusional non-linearity with a decrease in the content of a polymer in a solution and with a decrease in the content of a solvent becomes weaker due to the narrowing of the interval (k_R, k_o) and to the increase in the saturation temperature on the phase interface. Calculations also showed that in concentrated solutions it is practically impossible to attain the values $Ja \gg 1$ by increasing the superheat because of the smallness of the corresponding *Sn* numbers.

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