Colloid & Polymer Science Colloid Polym Sci 272:181–183 (1994)

On the dependence of the critical supersaturation on the initial undersaturation in the reverse Wilson chamber

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Abstract: The dependence of the critical supersaturation on the degree of the initial undersaturation has been analyzed in detail.

This dependence is explained by means of the Richarch–Powell equation, taking into account the dependence of the γ-ratio upon the partial pressures of the inert gas and the liquid under investigation.

Key words: Line tension – reverse Wilson chamber – heterogeneous nucleation – nucleation on a substrate – condensation

In previous investigations [1, 2] the reverse Wilson chamber (RWC) method [3] has been used to measure the critical supersaturation in the case of nucleation from supersaturated water vapor on the surface of n-hexadecane substrate. In [1, 2] the dependence of the critical supersaturation $\ln S_c$ on the degree of initial undersaturation is investigated. The initial undersaturation is characterized by the ratio $P_e/P_0 < 1$, where P_0 was the saturated vapor pressure at the same temperature. The initial water vapor pressure P_e in the cell was fixed by equilibrating the space with aqueous solution of nonvolatile substances (inorganic salts – KJ, KNO_3, KCl, $Na_2SO_4 \cdot 10H_2O$, $(NH_4)_2SO_4$, $CuSO_4 \cdot 5H_2O$) [1, 2]. For the sake of clarity we shall reproduce again this dependence (Fig. 1) given previously in [1]. (The same dependence over a wider undersaturation range is demonstrated as Fig. 3 in [2]).

In Fig. 1 the undersaturation is presented in the form of $\ln(P_e/P_0) = -\ln S_0$. As can be seen from this figure the higher the partial water vapor pressure, the lower is the critical supersaturation measured. At small water vapor pressures (high undersaturations) the critical supersaturation reaches a constant ("plateau") value. This dependence has not been explained upto now, although some speculative explanations were put forward in [1, 2]. Even more surprising are the experimental findings reported in [4] (see Fig. 7), according to which the critical supersaturation is no longer dependent on the initial degree of undersaturation, when the critical supersaturation is recalculated from the calibration curves given in [4]. These curves recognize the deviations from the adiabatic regime postulated in [1–3].

The aim of the present paper is to explain the reason for the observed dependence of $\ln S_c$ on the initial undersaturation and to answer the question of why this dependence disappears when taking into account the real regime in the RWC [4].

In [1, 2] the critical supersaturation is calculated assuming that the compression, which produces the supersaturation, takes place as a strictly adiabatic process, i.e.,

$$\ln S_c - \ln(P_e/P_0) = \ln(1 + \Delta V/V)^\gamma , \qquad (1)$$

where $\gamma = C_p/C_v$ (C_p and C_v are the constant-pressure and constant-volume molar heat capacities, respectively), V is the total volume of camber, and ΔV is volume change in the course of compression. Equation (1) follows immediately from the application of Poisson's adiabatic law $PV^\gamma = \text{const}$.

In all calculations carried out in [1–3], γ is assumed to be constant, and not dependent on the

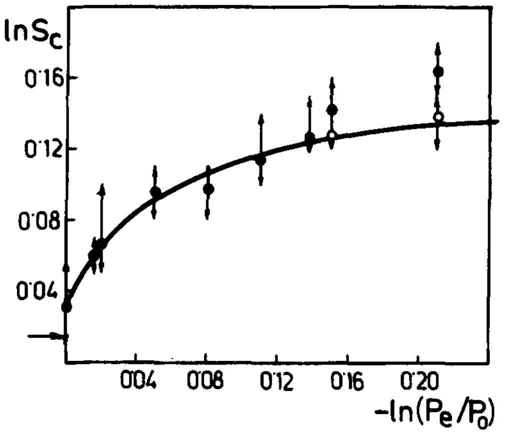

Fig. 1. Dependence of the critical supersaturation $\ln S_c$ on the initial undersaturation $\ln S_0$ in the case of water nucleation on *n*-hexadecane substrate. The most frequent results within each series of measurements are indicated by solid circles. Vertical arrowed bars mark the range of values of the experimental $\ln S_c$'s within each series of measurements ($-\ln S_0 = \text{const}$)

partial pressures of water and carrier gas. However, according to the equation first derived by Richarz [5] and later rederived by Powell [6] γ is related to the partial pressure of carrier gas, P_g, and the partial pressure of vapor, P_v, by means of the following expression

$$\frac{1}{\gamma - 1} = \frac{1}{\gamma_g - 1}\left(\frac{P_g}{P_t}\right) + \frac{1}{\gamma_v - 1}\left(\frac{P_v}{P_t}\right) . \tag{2}$$

For perfect gas the total pressure of carrier gas-vapor mixture is $P_t = P_g + P_v$.

In previous experiments [1, 2] the vapor pressure of water P_v is decreased by adding of inorganic salts, so that P_v has been changed.

If we recalculate the results presented in Fig. 1, taking into account the changes in P_v due to addition of a given amount of soluble nonvolatile compounds, we reach a constant (within the experimental uncertainty) $\ln S_c = 0.112$. Therefore, the use of γ values calculated by making use of Richarz–Powell equation (2) instead of constant value of γ as in [1, 2] leads to a value for $\ln S_c$ value which is no longer dependent on the initial degree of undersaturationln S_0.

Evidently, the neglect of the dependence of γ on P_v leads to an underestimation of $\ln S_c$ at higher initial water vapor pressures and overestimation of this quantity at lower humidities.

The approach presented above explains why the critical supersaturation becomes constant, when its value is recalculated from the calibration curves given in [3]. These curves give the relative pressure increase $(1 + \Delta P/P)$ as a function of the relative volume change $(1 + \Delta V/V)$, and are obtained by direct measurement of the pressure in the chamber. As is shown in [3] the regime in the RWC is intermediate between adiabatic ($PV^\gamma = \text{const}$) and isothermal ($PV = \text{const}$) depending upon the compression time τ. At compression times greater or equal to 0.4 s the regime in the RWC is isothermal and, as was experimentally established [7], no detectable condensation occurs. In all cases when $\tau < 0.4$ s the $(1 + \Delta P/P)$ versus $(1 + \Delta V/V)$ line lies closer to the adiabatic lines as the compression time becomes shorter [3]. In fact, when the calculation of $\ln S_c$ is carried out by making use of the calibration procedure described in [3], the $\ln S_c$ (or any other supersaturation value corresponding to a given change of V) is to be determined by the expression that follows

$$\ln S_c - \ln S_0 = \ln\left(1 + \frac{\Delta V}{V}\right)^{\gamma_{\text{eff}}} , \tag{3a}$$

or if $\ln S_0 = 0$, i.e., for pure liquid expression (3a) has to be reduced to

$$\ln S_c = \ln\left[1 + \Delta V/V\right]^{\gamma_{\text{eff}}} . \tag{3b}$$

In Eq. (3a) and (3b) γ_{eff} is an empirical parameter, which is a function of the compression time τ $[\gamma_{\text{eff}} = f(\tau)]$ and its value lies in the interval between $\gamma_{\text{eff}} = 1$ (isothermal regime) and $\gamma_{\text{eff}} = C_p/C_v$ (adiabatic regime). However, as it is pointed out in [3], we cannot realize a completely adiabatic regime since we are not able to produce sufficiently fast compression in reasonable time.

However, the Richarz–Powell equation (2) is derived under the assumptions that the carrier gas-water vapor mixture behaves as a perfect gas and that the compression is taking place as an adiabatic process. Therefore, the $\ln S_c$ value, recalculated by making use of Eq. (2) from the data graphically presented in Fig. 1, and that one reported in [4] for the same system will differ to some extent. The reason for this is that the value of γ_{eff} must be different from $\gamma = C_p/C_v$, because the regime in the chamber is far from being an adiabatic one. Although using Eq. (2) explains the observed dependence of $\ln S_c$ on $-\ln S_0$, the recalculation of final results for the critical supersaturation based upon the calibration curves given in [4] is obligatory.

Acknowledgements

The author would like to express his sincere thanks to Prof. A.D. Scheludko and Dr. B.V. Toshev for many helpful discussions.

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Received January 5, 1993;
accepted February 10, 1993

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