

Propandiol Vapor Nucleation Rates

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Abstract. Consideration of vapor-gas nucleation as binary vapor nucleation (instead widely used the one component approximation for nucleation of this system now) may lead the progress in the development of nucleation theory. Observations of phase transitions initiated by the carrier gas in the critical embryos of condensate can be a sufficiently convincing argument in this discussion. In order to confirm the role of the carrier gases received in the recent research ¹, in present study 1,2-propanediol and 1,3-propanediol vapor nucleation rates were measured. Carbon dioxide ($T_c=304.2$ K, $P_c=7.39$ MPa) and sulfur hexafluoride ($T_c = 318.7$ K, $P_c= 3.75$ MPa) were chosen as the carrier gases, because of their low and convenient critical temperatures, T_c , and critical pressures, P_c . Analysis of the experimental data shows that gas-carrier molecules are involved in new phase embryo formation. Vapor nucleation of investigated substances in a carrier gas atmosphere can be considered as nucleation of binary system

INTRODUCTION

Vapor condensation, boiling, crystallization, or haze formation, polymerization, etc. – all of these events are examples of nucleation, i.e. new phase generation. Nucleation is a subject of multiple theoretical and experimental studies. Currently, the most significant progress in the theory and experiment has been for vapor nucleation. Classical nucleation theory is a significant step in the development of new phase formation description. But the agreement between experimental rates and theory predictions are satisfactory only for some experimental results on nucleation. This suggests that the theory have significant axiomatic inconsistencies. It is well known that any vapor or gas has a critical point. The critical line connects the critical points of two individual components. Obviously, the condition of a nucleation must be below the critical conditions, because there are no heterogeneous states at and above the critical conditions. Consideration of vapor-gas nucleation as binary vapor nucleation (instead widely used the one component approximation for nucleation of this system now) may lead to progress in the development of nucleation theory.

In order to alleviate these contradictions, it is necessary to carry out experiments under conditions where the influence of the carrier-gas is obvious. Observations of phase transitions initiated by the carrier gas in the critical embryos of condensate can be a sufficiently convincing argument in this discussion. It is known that at the first order phase transition temperature, the chemical potential of a condensed phase has a singularity. The free energy of critical embryo formation and therefore, the vapor nucleation rate, reflect this singularity. In other words, the chemical potential singularity is the basic reason to find experimentally a singularity of the nucleation rate surface at the condition of critical embryo phase transition. The vapor nucleation rate should have an experimentally detectable

response to the non-monotone temperature behavior of the free energy of new phase critical embryos. As can be seen in the example of glycerin-carbon dioxide system nucleation, a nucleation rate singularity can be experimentally observed¹. This singularity can be detected in the measurement of the vapor nucleation rates with high resolution in the nucleation rate and temperature.

In order to confirm the role of the carrier gases received in previous research¹, in present study 1,2-propanediol and 1,3-propanediol vapor nucleation rates were measured. Carbon dioxide ($T_c=304.2$ K, $P_c=7.39$ MPa) and sulfur hexafluoride ($T_c = 318.7$ K, $P_c= 3.75$ MPa) were chosen as the carrier gases, because of their low and convenient critical temperatures, T_c , and critical pressures, P_c . These parameters allowed variation of experimental conditions in the nucleation temperature from below to above the critical temperatures of the gases. It is known that these gases have no singularities of heat-mass transfer constants over the pressure interval $P = 0.1 \div 0.3$ MPa.

II. EXPERIMENTAL SET UP

Aerosol formation was experimentally studied in a flow diffusion chamber (FDC), which is suitable to measure the nucleation rate at different total pressures and nucleation temperatures of system under investigation. Description of FDC can be found, for example, in paper by Anisimov et al.¹ and briefly repeated here.

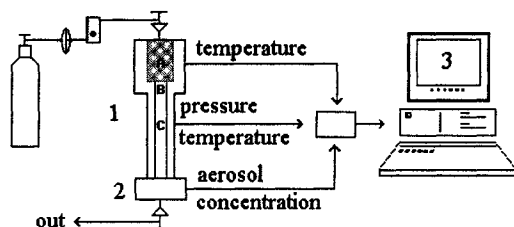


Fig. 1. The experimental setup scheme
 1 - Aerosol generator, containing hot thermostat with vapor saturation volume, A; Laminator, B; and Cooler, C; 2 - Laser aerosol counter; 3 - System for computer collection of experimental parameters.

The experimental setup (Fig. 1) contains an aerosol generator (1), which consists of hot (A, B) and cold thermostats (C). A high-pressure cylinder provided the inert carrier gas, which maintained the flow via a gas pressure reducer, filter, flow meter, and pressure regulator to the hot thermostat. The gas then passed through a chromatographic stationary phase, alumina (A), where the gas become saturated in the substance under investigation. Inside the second

thermostat (B), a steady state laminar flow was established. The vapor-gas mixture becomes supersaturated in the cooler (C) and aerosol particles are generated. Temperatures were measured with copper-constantan thermocouples, which were calibrated in the appropriate temperature range by using mercury thermometers with an accuracy of 0.1°C .

The aerosol concentration was measured by a laser photoelectric aerosol counter (2). The sensitivity of particle detection was sufficient to count particles such as $0.1 \mu\text{m}$ in diameter and bigger. Computer control of the aerosol concentration allowed collecting a sufficient statistical data in the complete range of the experimental aerosol nucleation rates achievable in these experiments. The standard deviation for measured aerosol concentration did not exceed 3% in these experiments. The sensor's signals were digitized and passed to a personal computer (3) for processing.

The carrier gas (with purity not less than 99.99 vol. %) passed through the chromatographic stationary phase soaked by 1,2-propanediol or 1,3-propanediol, where the carrier gas becomes vapor saturated in those vapors. The Reynolds number was around 100. The maximum rate of droplet formation was calculated using the algorithm

developed for the flow diffusion chamber by Wagner and Anisimov².

III. RESULTS AND DISCUSSION

A. Nucleation of 1,2-propanediol and 1,3-propanediol vapors in the sulfur hexafluoride atmosphere

Investigations of the influence of conditions in the vicinity of the critical line of the binary systems on the vapor nucleation of 1,2- and 1,3-propanediols in sulfur hexafluoride (SF_6) were carried out at total system pressures $P = 0.10; 0.20; \text{ and } 0.30 \text{ MPa}$.

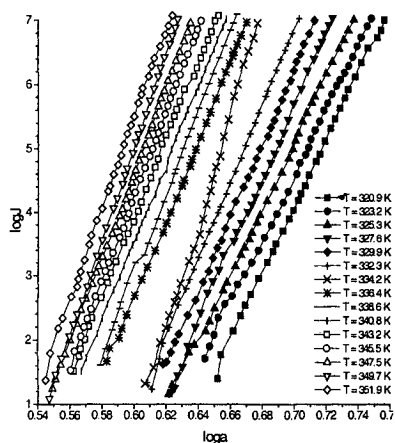


Fig. 2. Sulfur hexafluoride – 1,3 propanediol nucleation rate, J , on vapor activity, a , at total pressure $P=0.30\text{MPa}$

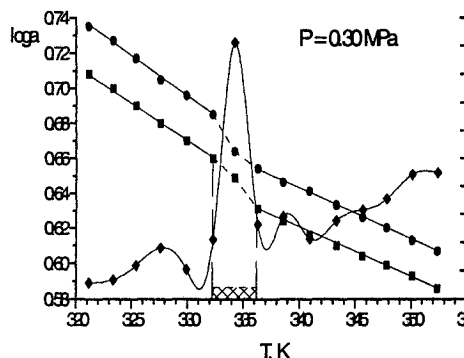


Fig. 3. Sulfur hexafluoride – 1,3 propanediol vapor activity, a , on nucleation temperature, T , at total pressure $P=0.30\text{MPa}$ and the critical embryo size, n^* (diamond-shaped points)

Figure 2 displays the experimental nucleation rates, $\log J$, versus the 1,3-propanediols vapor activities, $\log a$, at different nucleation temperatures and total pressure 0.3 MPa. As example of the temperature dependencies³ of $\log a$ on nucleation temperatures of 1,3-propanediol vapors in SF_6 is shown in fig.3 at two sections of nucleation rates ($\log J = 4.5$ and $\log J = 6.0$) and total pressure in the system at $P = 0.30 \text{ MPa}$. As one can see, the logarithms of activity at different binary system pressures exhibited breaks, which do not coincide with critical temperature of pure SF_6 . The temperature of the phase transition is shifted to lower temperatures as the carrier gas pressure grows. In other words, increasing the sulfur hexafluoride content shifts the phase transition temperature to the critical temperature of pure SF_6 .

B. Isothermal nucleation of 1,2-propanediol and 1,3-propanediol vapors in carbon dioxide atmosphere

Experimental investigations of 1,2- and 1,3-propanediol vapor nucleation in carbon dioxide in the vicinity of its critical temperature were carried out at total pressures $P = 0.10$; 0.20 ; and 0.30 MPa. The experimental 1,2- and 1,3-propanediol vapors activities, $\log a$, on nucleation temperature, T , (at constant nucleation rates, i.e. for the 1,2-propanediol – carbon dioxide at $\log J = 5.0$ and $\log J = 6.5$ and for the 1,3-propanediol – carbon dioxide at $\log J = 4.5$ and $\log J = 6.0$) are presented in our paper³.

One can see nonmonotone temperature behavior for activity logarithms³. With increasing the nucleation temperature, growth the $\log a(T)$ values falls monotonous, then breakup initiated by first order phase transition in critical embryos is appeared. These are phase transitions of the first order because the second order phase transitions have continuous first derivatives for chemical potential with respect to temperature, therefore the nucleation rate surface can not have the broken first derivative as the result of second order phase transitions. Further nucleation temperature growth leads the regular, monotonous changing of $\log a(T)$. It is remarkable that the temperatures of phase transitions in critical embryos are decreasing with increasing the total pressure in these systems. The system behavior can be explained by approximation of a binary system. The increasing of carbon dioxide contents in the system leads the shift of the phase transition temperature toward the critical temperature of pure CO_2 .

V. CONCLUSIONS

A phase transition initiated by critical lines of binary systems was found experimentally. The nucleation rate surface singularity and a gap in the number of molecules in critical embryos reflect the influence of the critical line on nucleation. Shifts of the phase transition temperatures were revealed by increasing the pressure (or concentrations) of the carrier gases. This behavior is peculiar to binary systems. Analysis of the experimental data shows that gas-carrier molecules are involved in new phase embryo formation. Vapor nucleation of investigated substances in a carrier gas atmosphere can be considered as nucleation of binary system⁴.

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4. Critical embryo compositions and comparison of the experimental and calculated temperatures of phase transitions are presented in Web Page:
<http://www.geocities.com/ResearchTriangle/System/7762/1.html>

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