HOMOGENEOUS NUCLEATION OF SUPERSATURATED VAPORS. A COMPARISON OF EXPERIMENTAL RESULTS WITH THEORY

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Some theories of homogeneous nucleation based on liquid droplet model were tested by comparing with experimental supersaturations of naphthalene, phthalic anhydride, stearic acid, bis(2-ethylhexyl) phthalate, and bis(2-ethylhexyl) sebacate required to bring about the rate of homogeneous nucleation of about 5 drops/cm^3 s^{-1}. It was found that except for highly polar substance phthalic anhydride, the classical (Becker–Döring) theory of homogeneous nucleation, if suitably scaled, yielded fairly good predictions of the nucleation behavior.

Homogeneous nucleation from the vapor might play an important role in many natural and technological condensation processes leading to the aerosol formation. Therefore, it has been the subject of many theoretical and experimental investigations. Among various theoretical approaches to this problem, the droplet model is often used which combines molecular kinetics with thermodynamics of cluster formation. The simplest droplet model where cluster is treated as a microscopic liquid droplet having bulk properties, is the basis of the classical (Becker–Döring) nucleation theory[1]. The fact that the classical theory is able to describe the nucleation process only qualitatively led to various modifications of the droplet model. Assuming the cluster as a spherical giant molecule, Lothe and Pound[2] used the methods of statistical mechanics to include contributions of translational and rotational degrees of freedom to the free energy of cluster formation. Their theory predicts the homogeneous nucleation rate about 10^{17} greater than the classical one. The fluctuations of the center of mass of a spherical droplet with fixed boundaries were considered by Reiss, Katz and Cohen[3]. In comparison with the classical theory the nucleation rates predicted by this model are greater by a factor $10^3 - 10^6$. Numerous nucleation theories based on the droplet model can be found in the literature[4] but none of them is able to predict, in a correct manner, the experimentally determined nucleation rates for all substances investigated. Recently, a new refined droplet approach suggested by Dillman and Meier has appeared in the literature[5]. The model relates the real gas behavior of the superheated vapor and nucleation behavior of the supersaturated vapor to obtain the Gibbs free energy of cluster formation. It has three free parameters which account for the surface free energy variation with the surface curvature and for various mechanical degrees of freedom. By using the appropriate values of these parameters, the results of all the droplet models mentioned above can be obtained. Yet, the kinetic approach to the theory of nucleation was developed by Katz and Wiedersich[6]. In this model the evaporation rate is obtained with reference to the stable equilibrium of a saturated vapor instead of to the constrained and metastable (and physically unrealizable) equilibrium in supersaturated vapor. By extending the kinetic theory of nucleation of Katz and Wiedersich[6], Girshick and Chiu[7] obtained a new expression for the rate of homogeneous nucleation. It exhibits a slightly different dependence of the rate of nucleation on supersaturation but a substantially different dependence on temperature compared to the classical theory.

In our laboratory we measured supersaturations of vapors of various organic compounds which are necessary to cause the rate of homogeneous nucleation of about 5 drops/cm^3 s^{-1}. They include nonpolar substance naphthalene[8], highly polar substance phthalic anhydride[8] and high molecular mass and polar substances stearic acid[9], bis(2-ethylhexyl)phthalate[10], and bis(2-ethylhexyl) sebacate[11]. The experimental results were compared with the predictions by the classical theory[1]. It was found[8 – 11] that the classical theory usually predicted higher supersaturations for the measured rate of nucleation and that the theoretical predictions varied with temperature more steeply than observed in experiments. Since the corrections considered in both the Dillmann–Meier[5] and Girshick–Chiu[7] theories might explain the deviations from the classical theory we observed, we compared in this paper our experimental results with predictions of these theories.

EXPERIMENTAL

The supersaturations of vapors of individual compounds mentioned above, required for the rate of homogeneous nucleation of about 5 drops/cm^3 s^{-1}, were measured by using the conventional thermal diffusion cloud chamber. Since the detailed description of the chamber[8,10] as well as principles of its operation[12] can be found elsewhere, it will not be repeated here. Therefore, we will describe only the basic principle of the experimental method.

The typical cloud chamber consists of two metal circular plates connected by a glass cylinder. The bottom plate with shallow pool of working liquid is heated, vapor diffuses through an inert gas and condenses on the cooler top plate. At a steady state temperature T and partial vapor pressure P_v decrease from the bottom to the top almost linearly. But the equilibrium vapor pressure $P_{v,eq}$, which is approximately an exponential function of temperature, decreases with the axial coordinate more rapidly than the actual partial vapor pressure P_v. The vapor in the chamber is therefore supersaturated. The supersaturation $S = P_v/P_{v,eq}$ equals unity both at the surface of liquid evaporated from the bottom plate and at the surface of condensate on the top plate. But it is greater than unity in the volume of the chamber, with maximum supersaturation reached close to the top plate. By increasing the temperature difference between both plates, one can arrange the state where the supersaturation is high enough for homogeneous nucleation to begin.

To observe the droplets generated by homogeneous nucleation, the interior of the chamber is illuminated by a thin laser beam. Counting by eye the number of droplets falling through the known cross-section of laser beam during a certain period of time, one can determine the rate of nucleation. So determined rate of nucleation is a mean integral value in a so-called nucleation zone. Since both temperature and supersaturation vary across the nucleation zone considerably, it is difficult to specify some characteristic values of both variables. The experimental conditions are therefore usually presented as a peak of supersaturation $S = S(T)$ across the nucleation zone. The variation of supersaturation with temperature over all experiments that can be compared with theoretical predictions is then obtained as an envelope to the individual peaks of supersaturation[8].

RESULTS AND DISCUSSION

By using the described method, we measured the supersaturations of naphthalene[8], phthalic anhydride[8], stearic acid[9], bis(2-ethylhexyl) phthalate[10], and bis(2-ethylhexyl) sebacate[11] which are necessary to cause the rate of homogeneous nucleation of about 5 drops/cm^3 s^{-1}.

The nucleation experiments were carried out with helium or hydrogen as inert gases. It was found that except for bis(2-ethylhexyl) sebacate the experimental supersaturations were independent of the inert gas used. In case of bis(2-ethylhexyl) sebacate, the experimental supersaturations we obtained with helium were about 20% lower than those we obtained with hydrogen. The variation of supersaturation with temperature for each of these compounds was fitted to the empirical formula[8]

$$\ln S = (A + B/T)^{1.5} . \qquad (1)$$

The parameters A and B for the individual compounds are given in Table I. The experimentally determined temperature dependences of supersaturations were compared with the predictions by the classical Becker–Döring (B–D) theory[1], Dillmann–Meier (D–M) theory[5], and Girshick–Chiu (G–C) theory[7] calculated for the same rate of homogeneous nucleation. The physical properties needed for such predictions are: surface tension of liquid, equilibrium vapor pressure, liquid density, and molecular mass.

TABLE I
Results of fitting experimental data to empirical formula (*1*)

Compound	A	B, K	ΔT, K
Naphthalene	−1.9934	1 301.4	360 – 410
Phthalic anhydride	−1.9466	1 353.8	400 – 440
Stearic acid	−1.6200	1 554.8	330 – 410
Bis(2-ethylhexyl) phthalate	−1.4450	1 497.9	330 – 410
Bis(2-ethylhexyl) sebacate in H_2	−1.5620	1 625.0	360 – 440
Bis(2-ethylhexyl) sebacate in He	−1.5711	1 590.4	360 – 440

Further, for the D–M theory, the thermodynamic variables of state at the critical point and the second virial coefficient are also required. Most of these data were taken from our previous papers[8 – 11]. The rest of them was estimated by some reliable theoretical or empirical methods. Thus, critical properties of stearic acid, bis(2-ethylhexyl) phthalate, and bis(2-ethylhexyl) sebacate were estimated by the method proposed by Somayajulu[13], the second virial coefficients were calculated by means of the corresponding states relation of Tsonopoulos[14] and the low-temperature surface tension data were extended to higher temperatures by using the Macleod–Sugden correlation[15].

The experimentally determined temperature dependences of supersaturations of individual substances are compared with theoretical predictions in Fig. 1*a* – 1*e*. It is appar-

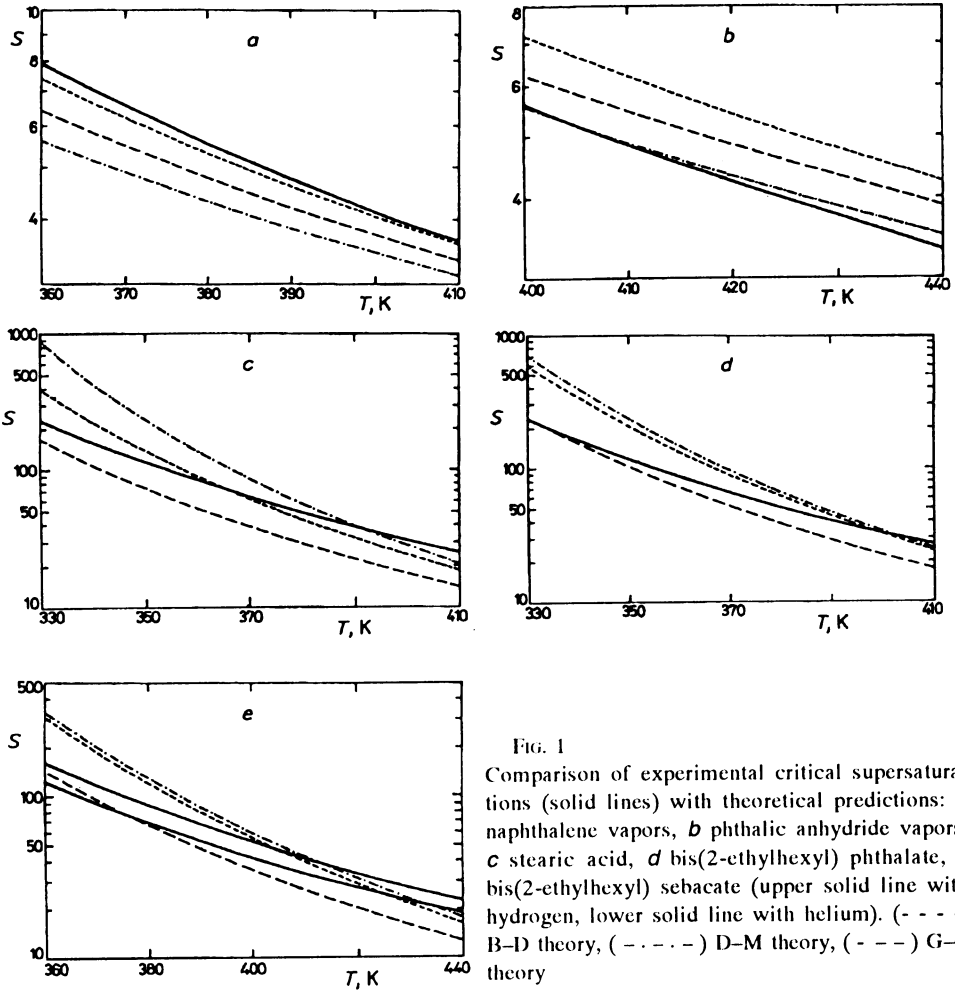

FIG. 1

Comparison of experimental critical supersaturations (solid lines) with theoretical predictions: *a* naphthalene vapors, *b* phthalic anhydride vapors, *c* stearic acid, *d* bis(2-ethylhexyl) phthalate, *e* bis(2-ethylhexyl) sebacate (upper solid line with hydrogen, lower solid line with helium). (- - - -) B–D theory, (– · – · –) D–M theory, (- — —) G–C theory ent that both the new theories do not offer any special improvement except for highly polar phthalic anhydride where the agreement of the experiment with the Dillmann–Meier theory is surprisingly good. Similar agreement was also found for other polar substances[5]. Further, the results of comparison confirm the findings of other authors[5] that the classical theory describes nucleation process fairly well at higher temperatures while at lower ones some corrections to this theory are needed.

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