three cycles of freeze–pump–thaw treatment at a pressure of 4.0×10^{-6} Torr.

3.2   Direct Photoisomerization

Z–Benzalpyrrolinone (Z-1) (0.084 mg, 3.7×10^{-4} mmoles) was dissolved in 10 ml methanol. The solution (2.8 ml) in uv cell (1 cm path) were irradiated at the absorption maximum wavelength (323 mn) using 10 mn bandpass monochromatic light from a Bausch and Lomb monochromator (Model 33–86–07) equiped with a Hg–lamp(200W). The results were reported in Table 1.

Z-5–Benzylidene-4–methyl-3–vinyl-3–pyrrolin-2–one(Z-2). The procedure was the same as *Z*-1 except the excitation wavelength differed (342 nm).

5'–Oxo-3',4'4–triethyl-3,5–dimethyl-1',5'–dihydro–(2.2')–dipyrromethene (3). The oxodipyrromethene 3 (7.1 mg, 2.6×10^{-2} mmoles) was dissolved in methanol in a 10 ml volumetric flask. When the solution was irradiated at 417 nm (λ_{max} of $3=417$) by monochromatic light, (Hg–lamp) the disappearance peak at 417 nm and appearance peaks at 320 nm and 265 nm were monitored (see Table 3). After 8 hrs irradiation the reaction mixture was allowed to reverse in the dark and monitored. To determine the solvent effect on reaction rate (initial rate) the above concentration of the solution 3 was irradiated in several different solvents. The results are reported in Table 4.

To check the effect of oxygen on the photoisomerization, the oxodipyrromethene 3 in methanol was examined under aerobic and anaerobic condition (see Table 5).

5'–Oxo-3',4'–diethyl-5–methyl-1',5'–dihydro–(2.2')–dipyrromethene (4). Procedure is the same as above (see also Table 6).

Bilirubin IX–α. See Table 7 and the procedure in Section of Results.

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The Significant Structure Theory of Liquids Applied to Homogeneous Nucleation Theory

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The surface tensions, the chemical potentials and the densities of various liquids such as argon, nitrogen, helium, ammonia, and water are calculated using the significant structure theory of liquids. And using these calculated values, the critical supersaturation ratios and the radii of the above materials are determind according to the classical Becker–Döring and the revised Lothe–Pound theories. The results are compared with the experimental values and well agreed with the available experimental data.

Introduction

Most of the homogeneous nucleation theories of the vapor–liquid condensation make use of the capillarity approximation in which the free energy of formation of a droplet is described in terms of the experimental surface tension and the density of the bulk liquid.

Among them, the classical Becker–Döring[1] and the revised Lothe–Pound theories are known as the most useful ones.

Using the capillarity approximation, the Helmholtz free energy of n–cluster droplet in Becker–Döring theory is given by

$$F_{B-D}(n) = F_{cap}(n) = \mu_{exp} n + \sigma_{exp} 4\pi \left(\frac{3}{4\pi\rho}\right)^{2/3} n^{2/3} \qquad (1)$$

were μ_{exp}, σ_{exp}, and ρ are the chemical potential, flat–plane surface tension, and density of the macroscopic liquid state, respectively.

And in Lothe–Pound theory, that is given by

$$F_{L-P}(n) = F_{cap}(n) + F_{trans}(n) + F_{rot}(n) - f_{rep} \qquad (2)$$

The translational free energy is given in terms of the partition function as

$$F_{trans}(n) = -kT \ln\left[\left(\frac{2\pi \, nmkT}{h^2}\right)^{3/2} \frac{V}{C_1}\right] - kT \qquad (3)$$

where m, V, and C_1 are the mass of a single molecule, the volume of the system, and the monomer concentration, respectively. The rest of the notation has the usual meaning.

The rotational free energy is given by

$$F_{rot}(n) = -kT \ln\left[\sqrt{\pi}\left(\frac{8\pi^2 IkT}{h^2}\right)^{3/2}\right] \qquad (4)$$

where I is the moment of inertia of the cluster and taken to $I = \frac{2}{5}nmr^2$. Here, r is the radius of the spherical droplet.

The replacement free energy for a liquid cluster, f_{rep}, has been estimated to be $\sim 10\ kT$.

In various theories, the law of mass action is written in the following form

$$C_n = C_1 \cdot \exp(-[F(n) - n\mu_1(T, P)]/kT) \qquad (4)$$

in which C_n and μ_1 (T, P) are the concentration of the n-clusters and the chemical potential of the monomer at T and P in the vapor phase.

In the rate theory of homogeneous nucleation, the steady state current I_s which is defined as the number of clusters forming per second in a unit volume of vapor, is derived by Becker and Döring[3] and Zeldovich[4] as

$$I_s = Z(4\pi r^{*2})\frac{P}{(2\pi mkT)^{1/2}}C_1\exp(-\Delta F^*/kT) \qquad (6)$$

in which the so-called Zeldovich factor Z accounts for the departure of steady state from equilibrium concentration of critical nuclei.

The free energy of formation of the critical nucleus ΔF^* and the critical radius r^* are given by

$$\Delta F^* = \frac{4\pi}{3}\sigma_{exp}r^{*2} \qquad (7)$$

$$r^* = 2\sigma_{exp}v_l/(kT\ln S) \qquad (8)$$

where v_l and S are the molecular volume of the liquid phase and the supersaturation ratio $(P/P_\infty$; P is the actual pressure and P_∞ is the equilibrium vapor pressure at temperature $T)$.

The critical supersaturation ratio S_c is defined as that at which the steady state current I_s, is one droplet per cubic centimeter per second.

In this paper, we have calculated the density, vapor pressure suface tension, and chemical potential of the liquid phase by using the significant structure theory of liquids for various materials.

And the critical supersaturation ratio and the critical radius are also determined according to the Becker–Döring and the Lothe–Pound theories.

Calculation

In the significant structure theory of liquids, the partition function for N molecules (1 mole) is generally written as

$$f_N = f_s^{N\frac{V_s}{V}} f_g^{N\left(\frac{V-V_s}{V}\right)} \qquad (9)$$

in which f_s and f_g are the partition functions of the solid-like and the gas-like molecules, respectively. N, V_s, and V

are the Avogadro's number and the molar volumes of the solid-like molecules and liquid, respectively.

The partition functions for argon[6], nitrogen[7], helium[8], ammonia[9] and water[10] are adopted from the previous works. And the parametric values used for the calculation are the same as those in the above partition functions.

Density and Vapor Pressure. The Helmholtz free energy is given by

$$A = -kT \ln f \qquad (10)$$

If A is plotted as a function of volume at constant temperature and the common tangent of the graph is obtained, the calculated vapor pressure equals to the slope of the common tangent and the abscissas of the two points of common tangency are the molar volume of the liquid V_1 and that of the vapor V_g, respectively.

And the corresponding ordinates are the Helmholtz free energies of the liquid and vapor. The chemical potential is given by

$$\mu = A/N \qquad (11)$$

Surface Tension. In order to calculate the surface tension, we used the iteration method in which the sublimation energy and density are changed at each iteration step.

The sublimation energy E_{si} of the i-th surface layer has the following relationship

$$E_{si} = E_s\left(\frac{6}{12}\ \frac{\rho_i}{\rho_i} + \frac{3}{12}\ \frac{\rho_{i+1}}{\rho_i} + \frac{3}{12}\ \frac{\rho_{i-1}}{\rho_i}\right) \qquad (12)$$

where ρ_i, ρ_{i+1}, and ρ_{i-1} are the densities of the i-th layer and the layers immediately below and above.

To determine the value of ρ_i, the iteration method by Chang et al.[11] is used.

The surface tension of a liquid σ is the excess Gibbs free energy per unit area over that of the bulk liquid.

Therefore, the surface tension is given by

$$\sigma = \sum_i (G_i - G) \cdot \frac{d}{V_i} \qquad (13)$$

in which G_i, G, d, and V_j are the Gibbs free energies of the i-th layer and bulk liquid, the layer thickness, and the molar volume of the i-th layer, respectively.

The layer thickness d becomes

$$d = 0.9165\left(\frac{V_i}{N}\right)^{1/3} \qquad (14)$$

In evaluating the surface tensions of polar molecules[12], we considered the orderliness of the top layer.

Using these calculated values of the chemical potentials, densities, vapor pressures, and surface tensions of liquids, the critical supersaturation ratios and radii are computed and the results are presented in Table 1 and compared with the available experimental data.

Discussion

So far, the fact that polar and strongly hydrogen bonded liquids follow the Becker–Döring theory while non–polar

TABLE 1: Critical Supersaturation Ratios, Radii, and Droplet Sizes.

Vapor	Temperature T (°K)	No. of molecules in the nucleus		Critical radius, r^*(A)		Critical supersaturation ratio, S_c		
		B–D	L–P	B–D	L–P	B–D	L–P	Exp.
Argon	80	109	100	10.7	10.4	3.34	2.76	(2.97)[a]
Nitrogen	63.3	92	83	10.5	10.2	4.17	3.30	—
Helium	1.0	55	50	8.44	8.19	9.65	8.37	—
Helium	2.0	122	108	11.0	10.6	1.98	1.89	—
Ammonia	195.45	94	85	9.52	9.21	3.84	2.99	2.56[b]
Ammonia	239.75	189	171	12.25	11.85	1.97	1.74	1.72[b]
Water	275.2	78	69	8.19	7.88	4.55	3.33	4.2±0.1[c]
Water	261.0	67	60	7.87	7.59	5.50	3.38	5.0[c]

[a]From Burton[14]; [b]from Jaeger et al.[15]; [c]from Volmer et al.[16];

liquids follow the Lothe–Pound therory has been generally known. As shown in Table 1, the results are consistent with the known facts.

Even though the experimental critical supersaturation ratios in the case of argon, nitrogen, and helium, have not been known, it is expected that they follow the Lothe–Pound theory because they are the typical non–polar liquids. The value of argon in parenthesis in Table 1 is taken from Burton[14] and agrees with that of Lothe–Pound theory well.

While ammonia is considered as a polar and hydrogen bonded liquid, it has no net dipole moment in the surface due to the "inversion–vibration" and, hence, it follows the Lothe–Pound theory.[15]

The surface tension of a small droplet is obviously different from that of bulk liquid, therefore, a correction should be made for the curvature dependence of surface tension.

We have tried to account for the curvature dependence of surface tension by applying the Tolman equation,[17] but as pointed out by himself, the equation is not applicable if the radius of a droplet is smaller than 10^{-6}cm.

Moreover, recently Nishioka[18] proposed a empirical equation for the size-dependence of surface tension using the data of the free energy calculation of argon by Monte Carlo method at various temperatures.

In this equation, the surface tension is decreasing as the curvature is increasing in the same manner in Tolman equation but if the cluster is smaller than certain size, the surface tension is rater increasing while in Tolman equation it is still decreasing. Hence, the curvature dependence of surface tension can't be considered analytically at this stage.

In this paper, we have found that the significant structure theory of liquids is successfully applicable to explaining the homogeneous nucleation phenomena.

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