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Study of prenucleation ion clusters: Correlation between ion mobility spectra and size distributions

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Additional studies regarding our earlier electrothermodynamic theory are presented. Comparisons to recent expansion cloud chamber ion mobility measurements are made, indicating general agreement with observations. This theory predicts more stable and ordered structure for prenucleation ion-water cluster systems than accounted for by the classical Thomson's theory. In the limiting case of the dielectric constant $\epsilon = 1$, our monopole electrostatic energy term contributed by the foreign ion center precisely converges to that of Thomson. Predicted ion cluster size distributions are found to correlate well with ion cluster size spectra obtained from the ion mobility measurements of hydrated ion clusters and Champman-Enskog theory. In view of good correlation between the theory and observation, we believe that ion mobility study at sufficiently low electric field is a powerful tool for studying prenucleation dynamics.

I. INTRODUCTION

The importance of hydrated ion clusters is manifold. An understanding of ion nucleation, solvation, and atmospheric electricity require a knowledge of structure, binding energy, stability, concentration, and reaction kinetics of these clusters. Recently, several theoretical studies of heteromolecular clusters (i. e., ion clusters) with varying degrees of emphasis have been reported by researchers in the field; they include SCF Hartree-Fock molecular orbital methods,¹ molecular dynamics and Monte Carlo calculations,² semimolecular model theory,³ and "molecular electrothermodynamic"⁴ and statistical mechanical⁵ theories.

Extensive experimental and theoretical studies regarding various small ion clusters at thermal equilibrium have been reported by Castleman and co-workers.^{1(b),6-9} Their studies⁶ revealed that there exists great discrepancy between their entropy data for small ion clusters (5 to 10 water molecule systems) and entropy change predicted by Thomson's electrothermodynamic theory, showing that the structure of actual clusters are more ordered than the "Thomson ion clusters." Other experimental studies of ion clusters have been made with the use of various jet expansion methods.¹⁰⁻¹² The size distribution of the ion clusters observed in various nozzle experiments showed a peak at the 21 water molecule cluster. Unlike nozzle expansion methods (dynamic flow experiments) which may cause nonequilibrium of the clusters with the noncondensable gas as was pointed out by Searcy and Fenn,¹¹ expansion cloud chamber ion mobility measurements at sufficiently low electric field provide ions which must be much closer to thermal equilibrium with the gas, and thus their velocity distribution is nearly Maxwellian as is well known.¹³ In the present study, we introduce some

new discussions and applications of our earlier electrothermodynamics theory⁴ of small clusters (droplets). We compare our predicted size distributions of the ion clusters with those deduced from ion mobility spectra measured at low electric field using a Chapman-Enskog mobility theory.¹³ In addition, we stress that the low field ion (hydrated ion cluster) mobility study will prove highly useful for understanding ion nucleation processes.

II. COMPARISON OF THOMSON'S THEORY WITH OUR MOLECULAR ELECTROTHERMODYNAMIC THEORY

Thomson's electrostatic energy term¹⁴ was derived from the assumption that the foreign charged particle has no structure, i. e., a point charge centered in a drop or a cluster. On the other hand in our (S. H. S.) recent study⁴ we introduced a more realistic picture for describing the foreign particle by considering it as an electronic charge cloud system. This then takes into account the effects of its permanent dipole moment and polarizability on the determination of the total electrostatic energy. For the sake of consistency, we considered the medium surrounding the foreign ion as a system made of dipolar and polarizable molecules. For this reason, we will term it as a "molecular electrothermodynamic theory."

The electrostatic energy term derived from the consideration mentioned above is written⁴

$$E_s = -f_s(\epsilon) \left[q_I^2 \left(\frac{1}{R_I} - \frac{1}{R} \right) + \frac{2}{3} \mu_I^2 \left(\frac{1}{R_I^3} - \frac{1}{R^3} \right) \right] - \frac{4}{3} \pi n [3\epsilon/(2\epsilon + 1)] \alpha_I \mu_s^2 \left(\frac{1}{R_I^3} - \frac{1}{R^3} \right), \quad (\text{II. 1})$$

where

$$f_s(\epsilon) = \lambda f'_s(\epsilon) \quad (\text{II. 2a})$$

with

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$$f'_s(\epsilon) = \frac{9}{2} [\epsilon(\epsilon - 1)/(2\epsilon + 1)(\epsilon + 2)] . \quad (\text{II. 2b})$$

Here ϵ is the dielectric constant which depends on temperature and the size of the clusters. q_I and α_I are the charge and electric polarizability of the foreign ion. μ_I° and μ_s° are the electric dipole moments of the ion and surrounding molecules, respectively. R_I and R are the radii of the foreign ion and the ion cluster. n is the water molecule number density in the cluster. λ is the scaling or calibration factor that was introduced⁴ to compensate only for possible failure due to approximations or inaccuracy in the estimation of the size dependent dielectric constant particularly for small clusters. Otherwise we have to set the value of λ equal to unity, i. e., if the value of ϵ is reliable, this parameter should be removed from Eq. (II. 2a) above. For the sake of rigorous comparison with Thomson's theory, we set $\lambda = 1$ in the following discussions.

Thomson's electrostatic energy term which takes into account only the electric monopole of the foreign ion center is written¹⁴

$$E_T = -f_T(\epsilon) q_I^2 \left(\frac{1}{R_I} - \frac{1}{R} \right) , \quad (\text{II. 3})$$

where

$$f_T(\epsilon) = \frac{\epsilon - 1}{2\epsilon} . \quad (\text{II. 4})$$

It is noted from Eq. (II. 4) that the free energy change of the ion clusters is relatively insensitive to the variation of the dielectric constant ϵ , compared to that [Eq. (II. 1) above] of Suck's theory. This is due to the relatively small range of the Thomson's factor $f_T(\epsilon)$ [Eq. (II. 4)] given by

$$f_T(\epsilon = 1) = 0 \leq f_T(\epsilon) \leq f_T(\epsilon = \infty) = 1/2 \quad (\text{II. 5})$$

compared to the range predicted by Suck's theory,⁴

$$f_S(\epsilon = 1) = 0 \leq f_S(\epsilon) \leq f_S(\epsilon = \infty) = 2.25 . \quad (\text{II. 6})$$

In the limiting case of vanishing dipole moment and electric polarizability of the foreign ion, we obtain from Eq. (II. 1),

$$E_S = -f_S(\epsilon) q_I^2 \left(\frac{1}{R_I} - \frac{1}{R} \right) . \quad (\text{II. 7})$$

Note that in the charge monopole term, both Thomson's and Suck's theories have exactly identical functional dependencies on the charge and size of the foreign ion and ion clusters. As ϵ approaches the value of 1, we find $f_S(\epsilon) \approx f_T(\epsilon)$ [or at $\epsilon = 1$, $f_S(\epsilon) = f_T(\epsilon) = 0$]. Thus for a small dielectric constant ϵ close to the value of 1, our electrostatic energy term converges to Thomson's term (II. 3) above, that is $E_S \rightarrow E_T$.

Castleman and co-workers⁶ pointed out the relative insensitivity of Thomson's theory [Eq. (II. 3)], to the variation of the dielectric constant ϵ in accounting for observed free energy changes (in particular, entropy change). In general, ϵ is expected to be small for small clusters and tends to approach a bulk value for sufficiently large clusters or droplets. Due to this relative insensitivity of the electrostatic free energy change or entropy change, Thomson's theory is expected to be

inadequate for predicting discrepancies between small clusters made of different substances surrounding the same foreign ion center. On the other hand, our theory is sensitive to the variation of the dielectric constant, and thus of the physical properties of the media surrounding the parent ion. The electrostatic term is significant particularly for small clusters since it diminishes with cluster size.

We find for $\epsilon \geq 1$, the inequality relations

$$f_S(\epsilon) \geq f_T(\epsilon) , \quad (\text{II. 8})$$

and thus

$$E_S \geq E_T . \quad (\text{II. 9})$$

Now it is evident from Eq. (II. 1) that with Suck's theory, cluster stability is increased. Earlier calculations (see Figs. 1 and 2 in Ref. 4) showed that this theory predicts consistently lower magnitude in the free energy change at each cluster size increment than in the case of Thomson's theory. This difference comes only from the difference in the electrostatic terms between the two theories. This suggests more tightly bound (ordered) structures for the ion clusters than accounted for by the Thomson's classical theory. This trend is consistent with the recent study of Castleman and co-workers⁶ who examined various experimental data^{9,15,16} for the small ion clusters.

The electrostatic energy term (II. 1) above has the additional merit of describing even electrically neutral heteromolecular clusters involving uncharged foreign particle species. Our theory predicts that the charge sign difference between positive and negative ions in the electrostatic free energy change does not necessarily come from the charge monopole q_I , but rather from the differences in the dipole μ_I and polarizability α_I of the foreign ion. The polarizability of atomic ions significantly differs between the positive and negative species. Thus in general, the negative atomic ions have higher polarizabilities than the positive ones. This could be one of the main reasons for more ordered structures with the negative foreign ions, and differences in structural correlations caused by the difference of charge sign.

III. COMPUTED RESULTS OF SIZE DISTRIBUTIONS AND DISCUSSIONS

In computing the electrostatic free energy change, there exists uncertainty in the evaluation of $f(\epsilon)$ due to inadequate information on the dielectric constant ϵ of small clusters. However, to evaluate the size dependent dielectric constant ϵ , we used the theory of Glueckauf.¹⁸ To the best of our knowledge there exists no direct experimental verification regarding his theoretical validity for small clusters. Thus in our earlier works,^{4,17} we introduced the scaling factor or calibration factor λ as shown in Eq. (II. 2a) to correct for errors which we believe are inherent in ϵ . Calibration of λ for hydrated ion clusters was made with respect to the molecular dynamics calculations of Briant and Burton^{2(b)} who reported the free energy change of $C_S^+(H_2O)_i$ and $F^-(H_2O)_i$ against the cluster size i . The

choice of one value, $\lambda = 1/3$ consistently fitted their free energy calculations for both positive and negative ion clusters remarkably well. For the sake of consistency, in our present calculations, we used the same values of $\epsilon^{3,18}$ and λ that fitted the molecular dynamics calculations of the free energy change made by Briant and Burton.^{2(b)} Our earlier computed results¹⁷ were in reasonable agreement with the semimolecular model theory of Chan and Mohnen.³

The total free energy change can be written

$$\Delta\Phi = -\frac{4}{3}\pi(R^3 - R_i^3)nkT \ln S + 4\pi R^2\sigma + E_s, \quad (\text{III. 1})$$

where n is the water molecule number density in the cluster (which is assumed to be the bulk liquid number density); k , Boltzmann constant; T , absolute temperature; S , saturation ratio; and σ , surface tension. Our computed results of normalized cluster distributions will now be compared with those obtained from the ion mobility spectra measurements of Stoddard¹⁹ and Chapman-Enskog theory.¹³

The Chapman-Enskog theory¹³ we employ yields, in first approximation, the ion mobility

$$K = \frac{3e}{16} \left(\frac{1}{m} + \frac{1}{M} \right)^{1/2} \left(\frac{2\pi}{kT} \right)^{1/2} (N\Omega)^{-1}, \quad (\text{III. 2})$$

where m and M are the ionic and molecular masses, e the ionic charge, and N the number density of a neutral gas. Ω , the collision integral is given by¹³

$$\Omega(T) = [2(kT)^3]^{-1} \int_0^\infty \exp(-E/kT) E^2 Q(E) dE, \quad (\text{III. 3})$$

where the cross-section $Q(E)$ is

$$Q(E) = 2\pi \int_0^\infty [1 - \cos \theta(b, E)] b db, \quad (\text{III. 4})$$

with the deflection angle given by

$$\theta(b, E) = \pi - 2b \int_{R_0}^\infty \frac{R^2 dR}{[1 - b^2/R^2 - V(R)/E]^{1/2}}. \quad (\text{III. 5})$$

Equation (III. 2) is used to convert the measured ion mobility spectra into the size distribution of the ion clusters, i. e., the mass (size) of the ion cluster m is determined from Eq. (III. 2), using the value of the observed ion mobility K . b is the impact parameter, and R_0 the distance of closest approach. E is the relative kinetic energy, and $V(R)$ the ion-molecule potential energy.^{5,13,20,21}

Although our primary objective of this paper is a theoretical analysis, a brief account of the ion mobility experiment is given below to substantiate our discussions below. The expansion cloud chamber technique for measuring ion mobilities was developed in this laboratory by Yue^{20,21} who used the method to measure the mobilities of intermediate ions. In this experiment the ambient environment is held at saturation when hydrated ions are injected from an ion source into the chamber at a known point and time and are then allowed to drift across the chamber in the presence of a small electric field for a specific time. Then a fast expansion nucleates drops on the ions, their positions

are photographed, and their mobilities are calculated from the observed drift distances, time, and field strength. In such an experiment the ion concentrations are held to extremely low values so that space charge effects are essentially absent. This technique has been further refined by Stoddard,¹⁹ and measurements have been made of the mobilities of small cluster ions in an environment of argon and saturated water vapor. An ion source using alpha radiation from polonium 210 for ionization was developed along with a field wire cage which provided a satisfactorily uniform electric drift field. Argon was frozen in a liquid nitrogen cold trap in the presence of an activated charcoal filter. The argon vapor, which was then introduced into the chamber by warming the cold trap in such a way that impurities with lower vapor pressures were effectively retained in the trap.

Measurement of positive ion mobilities were conducted at seven temperatures in a range from 3.2 to 24.5 °C. It should be noted that the water vapor pressure increases with increasing temperature since all of the mobility measurements occur at saturation vapor pressures. Positive ions showed a trend of decreasing in mobility as the temperature was increased. Measurements of negative ion mobilities were conducted over a temperature range from 13.2 to 35 °C. The location of two peaks in the negative ion mobility distribution did not shift with changes in temperature. The positive ions are believed to be $\text{H}_3\text{O}^+(\text{H}_2\text{O})_i$.⁷ The negative ions have not been identified. Oxygen was added to the chamber at 13.2 and 24.5 °C, resulting in a definite predominance in the mobility distribution for the slow group of negative ions. It is likely that this group of ion clusters is $\text{O}_2^-(\text{H}_2\text{O})_i$. The ion mobility measurements were conducted at the electric field of $E \approx 20$ V/cm to reasonably ensure thermal equilibrium. Detailed experimental descriptions¹⁹ of the ion mobility measurements will appear elsewhere.

Figures 1 and 2 show the size distributions of the positive and negative ion clusters respectively. The dotted curves represent the cluster size distributions obtained from the Chapman-Enskog fit to the experimental mobility spectra and the solid curves, our theoretical predictions. The smaller cluster size mode (dotted curve) of the negative ions appears to shift with temperature as shown in Fig. 2. For the positive ions, the mobility spectra broaden significantly with temperature and a small glitch is present around size 22 at 13.2 °C and the double peak at 3.2 °C appears to change to a shoulder and peak (which did not shift with temperature) at 13 °C. The increasing size of the positive ion clusters with temperature may imply that $-\Delta\phi_{\text{clusterization}} > \Delta\phi_{\text{vaporization}}$ or possibly that the clustering species changes with temperature. We find from Fig. 1 that at lower temperatures ($T = 3.2$ and 13.2 °C) the size distributions (dotted lines) of positive hydrated ion clusters obtained from the observed ion mobility spectra at the saturation ratio of 1 and Chapman-Enskog theory show the occurrence of peaks at the cluster size i (number of water molecules) of 10 to 13 in close agreement with our predicted value around $i = 12$. At the higher temperature of $T = 21.7$ °C, agreement between the Chapman-

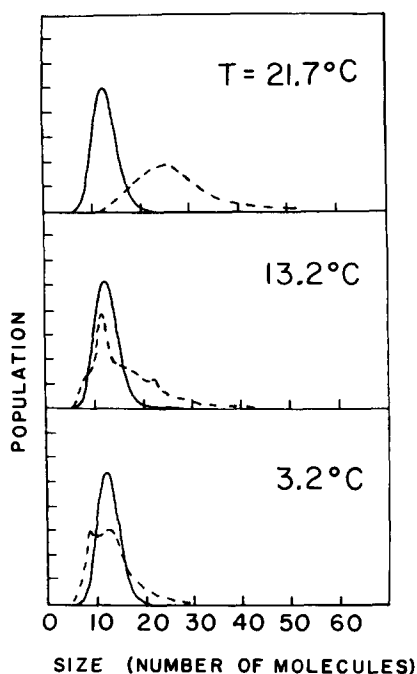


FIG. 1. Positive ion cluster size distributions at various temperatures and at the water vapor saturation ratio of 1. Solid curves are predicted by our theory. Dotted curves represent Chapman-Enskog fit to the ion mobility spectra measurements of Stoddard (Ref. 19).

Enskog fit and our results became poor.

Markedly different structures (dotted curves) in the size distributions with two distinctively separated peaks are observed for the negative ion clusters as shown in Fig. 2. Interestingly, our results show peak positions at $i = 13$ for both $T = 13.2$ and 24.5 °C. They are located nearly halfway between the two peaks, thus representing the average values. In the calculations above, the ion cluster species we assumed were $\text{H}_3\text{O}^+(\text{H}_2\text{O})_i$ and $\text{O}_2^-(\text{H}_2\text{O})_i$.

The ions in the mobility measurements were not spectroscopically identified, as mentioned earlier. It is possible that in the mobility measurements, different cluster structures or ion species might have been present causing the multimodal (bimodal) distributions. Due to lack of experimental knowledge concerning the true identity of the ion species and the possibility of mixed ion species, we decided to assess the influence of variation in the values of the effective radius R_i , polarizability α_i , and dipole moment μ_i^o for foreign ion centers. To the best of our knowledge, the values of α_i for the ionic molecules H_3O^+ and O_2^- are not currently available. We found a relatively slow change in peak position, with the range of R_i from 1 to 3 Å, of α_i from 0.0 to 2.4 Å³, and of μ_i^o from 0.0 to 2.0 D. Particularly the variation of α_i in the above range did not affect the peak positions. However, the total free energy change (due to the electrostatic term) varies with α_i . Such moderate variations yielded only minor relative shifts in peak positions ($i = 9$ to 13) at the saturation ratio of $S = 1$ and at the temperatures shown in Figs. 1 and 2. Thus it appears unlikely that ion species

which coincide with the above mentioned range of ionic radius, of dipole moment, and of polarizability will not significantly alter our discussions made earlier. However, we found stronger sensitivity of peak position to the variation of the dielectric constant ϵ . For instance, the peak position is shifted to $i = 4$ for positive ions and $i = 5$ for negative ions with the choice of $\epsilon = 3.4$. We would like to point out that, in general, the magnitude of the electrostatic free energy change varies more noticeably with R_i , μ_i^o , and α_i , compared to the size (peak position) of stable clusters, showing stronger dependency on the choice of ion species.

The criterion needed to insure the negligible field energy compared to the thermal energy is $E/p < 2$ V/cm Torr where p is the gas pressure.¹³ The ion mobility measurements were conducted at reasonably low field as mentioned earlier. Thus the observed ion clusters are expected to be in near thermal equilibrium with the ambient gas, H_2O and Ar. The Chapman-Enskog fit to the positive ion mobility spectra of Stoddard¹⁹ at 21.7 °C showed a peak at the cluster size around $i = 25$ compared to our prediction of $i = 12$. In general, the Chapman-Enskog theory based on the assumption of the dominance of elastic collisions tends to be less accurate as the temperature of the system increases, because the contribution of inelastic collisions increases. At high temperatures, energy transfer to the relatively loosely bound ion clusters may readily occur to decrease the kinetic energy of the clusters, thus reducing mobility even without the size increase of the hydrated ion clusters. If this indeed happens, the true peak position may lie at a cluster size less than $i = 25$ at the high temperature of 21.7 °C. If the negative ions are able to pack the water molecules more tightly with less repulsive (more attractive) interaction than the positive ones as discussed by Kebarle and co-workers,²² it is possible that the

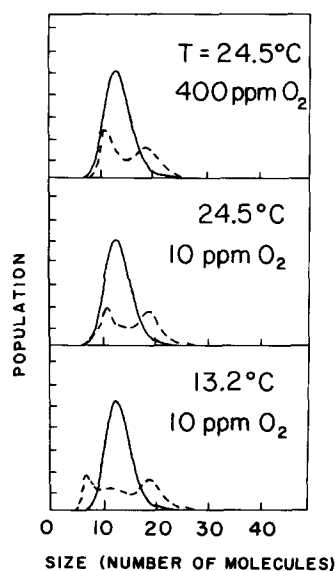


FIG. 2. Negative ion cluster size distributions at the temperatures of 13.2 and 24.5 °C. Note that a relatively small change in size distribution is observed with the variation of O_2 concentrations introduced into the expansion chamber of having the water vapor saturation ratio of 1.

negative ion clusters are subject to less internal excitation and thus to more elastic scattering than in the case of the positive ones.

Finally we would like to point out that Thomson's theory predicts peak positions at much smaller cluster sizes around $i=7$ and 8, for both the positive and negative ion clusters, showing marked disagreement with the predictions made by the Chapman-Enskog fit and by the present molecular electrothermodynamic theory.⁴ Variation of the dielectric constant in Thomson's theory will not improve the fit of size distributions both the positive and negative ion clusters shown in Figs. 1 and 2.

IV. CONCLUSION

In the present paper, we presented additional interpretation of our earlier molecular electrothermodynamic theory⁴ and comparison of the computed size distributions of hydrated ion clusters with those obtained from the measurements of ion mobility spectra¹⁹ and Chapman-Enskog theory.¹³ The following summary is in order:

(1) as the dielectric constant ϵ approaches 1, the most important monopole electrostatic energy term in Eq. (1) converges to Thomson's theory [Eq. (II. 3)].

(2) Thomson's electrostatic energy term is relatively insensitive to the variation of the dielectric constant compared to our theory. Our theory is expected to better account for dependency on the dielectric properties of media.

(3) Our theory predicts more stable (and ordered) structures of ion clusters than accounted for by the Thomson's theory in agreement with observation,⁶ and the molecular dynamics calculations^{2(b)} by showing larger negative electrostatic free energy change.

(4) Our predicted ion cluster size distributions are in relatively good correlation with ion mobility spectra measured at low electric field, and these peaks in the ion mobility spectra at the saturation ratio $S=1$ correspond to the stable clusters which are associated with the minimum "well" of the total free energy change.

(5) In view of good correlation between theory and observation, low field ion mobility measurements in combination with the use of Chapman-Enskog theory¹³ and the molecular electrothermodynamic theory⁴ will prove highly useful for understanding ion nucleation processes.

We would like to recall that in our present calculations, we did not change the values of the dielectric constants to fit the present ion cluster size distributions. For the exercise of varying ϵ to fit theory to observed data, it would be necessary to set λ [in Eq. (II. 2a)] as 1. The present theory shows insensitivity with temperature variation in predicting the peak positions of the negative ion cluster size distributions, in agreement with the ion mobility spectra. However for the positive ion clusters, it did not agree with the peak position at the higher temperature of 21.7°C. The cause of this difference needs further attention in the future. The variation of the

polarizability α_i of the ions affects only the magnitude of free energy change. The peak positions of the cluster size distributions were found to be relatively insensitive to the variation of α_i for both positive and negative ions. Finally, we would like to stress that ion-mobility spectra studies at sufficiently low electric field to insure thermal equilibrium may prove highly important for studying the dynamics and structures of small hydrated ion clusters to sharpen the understanding of nucleation processes involving ion species.

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