there are initial concentration gradients in both phases at the beginning of the ripple experiments. We, therefore, first solved eq 10, 12, 13, 17, 20, and 21, respectively, for a flat interface starting with a fresh interface at $t = 0$, i.e., $C_1(x,y,0) = C_0$ and $C_2(x,y,0) = 0$. We then assumed that quantities like $C_1^{(0)}(y,t)$, which now depend on time and location because of evaporation, do not change significantly on the time scale of ripples and calculated the perturbed concentration profile by an appropriate linearization procedure. So we determined $C_1^{(1)}$ from the equation [see (12)]

$$\frac{\partial C_1^{(1)}(x,y,t)}{\partial t} =$$
$$D_1\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)C_1^{(1)}(x,y,t) - v(x,y,t)\frac{\partial}{\partial y}C_1^{(0)}(y,t_e) \quad (22)$$

where t_e is the time of observation.

For all practical situations, the initial concentration gradients lead to negligible deviations from the equilibrium results presented above. This can easily be understood: according to (14), perturbations of solute concentration decay on a length scale $|q_1|^{-1} \sim (D_1/\omega)^{1/2}$ while $C_1^{(0)}(t_0)$

changes on a length scale of $(D_1 t_e)^{1/2}$. Hence, initial gradients are of little importance for $(\omega t_e)^{1/2} \gg 1$ which holds for all experimental situations.

Conclusions

Our main result is expression 19 for the dilational index ϵ. We have shown that diffusion in the liquid dominates evporation as the mechanism for restoring gradients in solute concentration. But even diffusion is of minor importance: Lucassen and Hansen[5] have shown that it is already difficult to determine the diffusion coefficient from ripple experiments. Hence, our results suggest that it will be almost impossible to get reliable data on evaporation from studies of the ripple spectrum.

Similar equations can be applied to ripples at a liquid–liquid interface when discussing transfer of surfactant between the liquids. In that case, the additional terms in the expression for the dilational modulus will probably be more important, and the effect may be larger.

Thomson Equation Revisited in Light of Ion-Clustering Experiments

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Gas-phase ion-clustering data are used to assess the validity of the classical approach to nucleation by comparing experimental values for various positive ions to those predicted by Thomson's charged liquid drop expression at small cluster sizes for water, ammonia, pyridine, acetonitrile, and methanol. While some data for water compare favorably, those for the other ligands do not. In many systems, the experimental results for the entropies are sharply more negative than those predicted, suggesting that many cluster ions have a more ordered structure than can be accounted for in the classical approach. This effect is apparently due to orientation of ligand molecules about the ion. Possible adjustments to bulk parameters in the Thomson equation at small cluster sizes are considered, but it is concluded that such adjustments will not lead to significant improvements in the expression. This suggests that a fundamental inconsistency exists between the general form of the classical expression and the properties of many small cluster ions. It is also shown that the "effective size" of the ligand molecules has an important effect on the calculated results.

Introduction

Studies pertaining to various classes of nucleation phenomena comprise a very active area of current research. At the present time, an understanding of the molecular aspects of nucleation is far from complete, and basic theories are in a continuing state of development.[1-6] The Thomson equation has been a successful model in computing the energy barrier to nucleation about ions for some substances, but not for many others.[2c] The purpose of the present paper is to give much more extensive and general

consideration to this relationship than that given previously[5] in terms of recent findings from experimental ion-clustering studies. Such an assessment is especially relevant now, in view of recently developed models based on statistical mechanical[7] and electrostatic[8] corrections to the

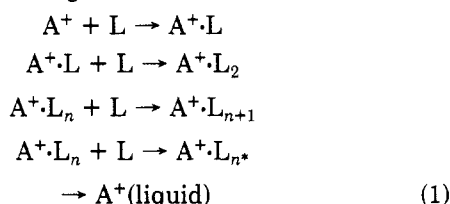[†] Present address: The Procter and Gamble Co., Miami Valley Laboratories, Cincinnati, OH 45247.
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form of the classical Thomson expression. The corrections incorporated in these models are most significant at the smallest cluster (or droplet) sizes where the macroscopic parmeters of the Thomson equation would be expected to fail. Recent theoretical developments[9] have now demonstrated that precise treatment of properties such as surface tension is possible down to the smallest cluster sizes. Whether any such corrections to the macroscopically based Thomson equation can lead to substantial improvement in this expression is a question of considerable interest.

High-pressure mass-spectrometric techniques[10,11] provide an experimental means of investigating the free energy, enthalpy, and entropy changes associated with individual ion-clustering reactions. When concentration and temperature are appropriately varied, it is possible to examine the thermodynamics of a variety of individual clustering reaction steps and, therefore, stepwise molecular details of the nucleation process enhanced by the presence of ions. In this context, these small ion clusters represent the prenucleation embryos from which an ion-induced nucleation process commences. Direct comparison with such experimental results allows the classical and other theoretical relationships which are proposed to account for the energy barrier to nucleation to be assessed at small cluster sizes.

A series of clustering reactions

$$A^+ + L \rightarrow A^+ \cdot L$$
$$A^+ \cdot L + L \rightarrow A^+ \cdot L_2$$
$$A^+ \cdot L_n + L \rightarrow A^+ \cdot L_{n+1}$$
$$A^+ \cdot L_n + L \rightarrow A^+ \cdot L_{n*}$$
$$\rightarrow A^+(\text{liquid}) \qquad (1)$$

where A represents the ion, L the clustering molecule, can be envisioned as leading progressively beyond the critical cluster size, $n*$, to an ion solvated in bulk liquid.

The classical liquid drop formulation of Thomson[5,12]

$$\Delta G_{0,n} =$$
$$-nRT \ln S + 4\pi N r^2 \sigma + (q^2 N/2)(1 - 1/\epsilon)(1/r - 1/r_i) \qquad (2)$$

is commonly used to evaluate the free energies of the nth cluster. The first term accounts for the change in free energy due to the condensation of n molecules at a saturation ratio S (where S is the ratio of the partial pressure of the ligand to its normal vapor pressure at the same temperature). The second represents the work done in forming a droplet of radius r (where σ is the surface tension and N is Avogadro's number). The final term gives the change in field energy due to the condensation of a dielectric about the ion (where ϵ is the dielectric constant of the solvent, q the ionic charge, and r_i the ionic radius). It should be noted that, in the Thomson equation, the ion is accounted for only by its radius and total charge.

The Thomson equation can be rewritten in terms of the number of molecules by using the relation based on the volume of the droplet

$$n = \tfrac{4}{3}\pi(r^3 - r_i^3)\rho N/M \qquad (3)$$

where M and ρ are the molecular weight and the bulk density of the liquid, respectively. In this form the

Thomson equation can be used to calculate the total free energy of the nth cluster as a function of both cluster size and saturation ratio.

This expression is often employed as the starting point for deducing the energy barrier to nucleation. In the case of a finite rate of nucleation, the distribution of clusters departs from the equilibrium one and requires introduction of the well-known Zeldovich factor.[2] Therefore, the energy barrier cannot be directly determined via a summation of the classical expression for the contributing free energy terms. Nevertheless, the final expression contains the same parameters for treating the physical properties of the clusters, hence, a determination of its range of validity is germane to an understanding of current theoretical approaches to nucleation.

The free energy change per molecule, $\Delta G_{n-1,n}$, can be obtained by taking the derivative of the Thomson equation with respect to cluster radius, giving

$$\Delta G_{n-1,n} = RT \ln p^\circ + (32\pi NM^2/3\rho^2 n)^{1/3}\sigma -$$
$$\frac{q^2}{8\pi}\left(1 - \frac{1}{\epsilon}\right)\left(\frac{4\pi N}{3n}\right)^{4/3}\left(\frac{\rho}{M}\right)^{1/3} \qquad (4)$$

where p° is the vapor pressure of the condensing molecules at the temperature of the system. It should be noted that this removes the explicit dependence on the radius of the central ion. However, a residual dependence on the radius of the ion can be retained by including the radius of the ion in the total volume of the droplet. In the case of atomic positive ions, the volume of the ion itself is usually small compared to the bulk volume calculated for a single ligand molecule. For negative ions, sizes are typically larger and thus this residual dependence can be somewhat more evident. But, in either case this effect is very small beyond the first few ligand molecules. For the purpose of comparing the Thomson results to experimental data for a number of different ions, residual dependence on the radius of the central ion is ignored.

Further differentiation of the above expression with respect to T gives an expression for the stepwise entropy change

$$-\Delta S_{n-1,n} = R \ln p^\circ + RT\frac{\mathrm{d} \ln p^\circ}{\mathrm{d}T} +$$
$$\left(\frac{32\pi NM^2}{3n}\right)^{1/3}\left(\rho^{-2/3}\frac{\mathrm{d}\sigma}{\mathrm{d}T} - \frac{2}{3}\sigma\rho^{-5/3}\frac{\mathrm{d}\rho}{\mathrm{d}T}\right) -$$
$$\frac{q^2 N}{6n}\left(\frac{4\pi N}{3Mn}\right)^{1/3}\left(\frac{1}{3}\rho^{-2/3}\left(1 - \frac{1}{\epsilon}\right)\frac{\mathrm{d}\rho}{\mathrm{d}T} + \rho^{1/3}\epsilon^{-2}\frac{\mathrm{d}\epsilon}{\mathrm{d}T}\right) \qquad (5)$$

From this, the enthalpy change can be obtained by using the thermodynamic relation

$$\Delta H_{n-1,n} = \Delta G_{n-1,n} + T\Delta S_{n-1,n} \qquad (6)$$

These expressions allow the classical charged liquid drop model of Thomson to be directly compared to the experimental results obtained in ion-clustering studies.

The motivation for this comparison is severalfold. First, since the Thomson equation is frequently used to calculate ion-induced nucleation, a direct comparison with experimental results at the small cluster sizes or prenucleation embryos from which nucleation would occur provides a stringent test of its validity. Second, the comparison of a model based on the macroscopic properties of the liquid may provide useful information about how far such macroscopic models can be pushed and still retain some validity. Third, by examining a variety of different systems, one can test the generality of the model. In this regard, it is of particular interest to ascertain whether or not

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TABLE I: Parameters Used in Charged Liquid Drop Calculations for Water, Ammonia, Pyridine, Acetonitrile, and Methanol

parameters[a]	water[b]	ammonia[c]	pyridine[d]	acetonitrile[e]	methanol[f]
T, K	313.15	233.15	353.15	293.15	293.15
M	18.015	17.031	79.10	41.05	32.04
σ	69.56	35.46	29.30	29.10	22.61
$d\sigma/dT$	-0.1635	-0.25	-0.1425	-0.132	-0.086
ϵ	73.15	22.10	10.60	37.67	33.70
$d\epsilon/dT$	-0.335	-0.100	-0.033	-0.200	-0.190
ρ	0.99224	0.6900	0.9211	0.782	0.7916
$d\rho/dT$	-0.00038	-0.00097	-0.00103	-0.0011	-0.00094
$\ln P°$	-2.62	-0.34489	-1.1591	-2.381	-2.149
$d \ln P°/dT$	0.053	0.05357	0.03893	0.0477	0.05224

[a] See text; cgs units where applicable except for $P°$ (atm). [b] From ref 22. [c] From ref 23-25 and 27. [d] From ref 22-24. [e] From ref 23, 24, and 26. [f] From ref 22-24.

modifications to some of the parameters such as surface tension or dielectric constant, as a function of cluster size, are capable of leading to any significant improvement in the model. Finally, differences between systems may shed light on differing degrees of interaction between the ion and liquid, liquid-liquid interactions, and solvation effects.

Comparison with Experimental Results

Comparison of the results of experiments to predictions based on the charged liquid drop formulation of Thomson can be made for the clustering of a number of different ligands about positive ions. These include water[13-15] and ammonia,[15-18] for which the greatest amount of experimental data is available, and pyridine,[15,19] methanol,[20] and acetonitrile.[21] It should be emphasized that these ligand molecules exhibit a considerable range of variation in their macroscopic properties such as vapor pressure, density, surface tension, and dielectric constant on which the charged liquid drop formulation is based and in molecular properties such as the molecular weight, size, and dipole moment. For example, the dipole moments of ammonia,[22] methanol,[23] water[24] pyridine,[23] and acetonitrile[23] are 1.47, 1.70, 1.87, 2.19, and 3.92 D, respectively.

As a result of the availability of clustering data for systems with such widely varying properties, an examination of these systems should provide a good test of the generality of the charged liquid drop approach and give insight into differences in the behavior of these systems. In the calculations reported here the necessary data for the surface tension, density, dielectric constant, and natural logarithm of the vapor pressure (in atmospheres) together with their temperature coefficients are available from a number of different sources and are summarized in Table I.[23-28]

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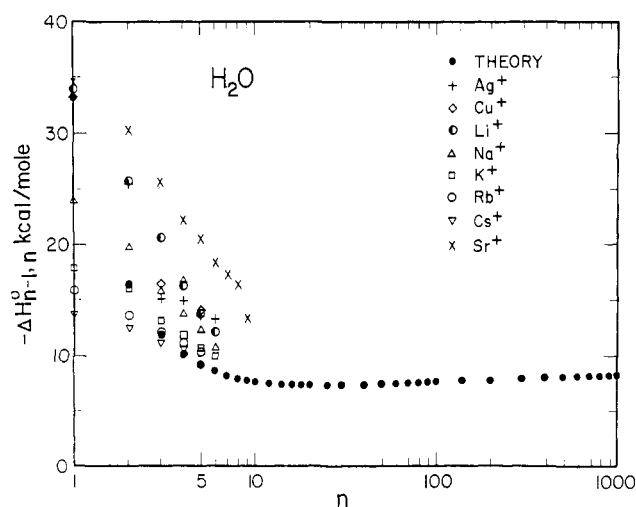(26) R. A. Stairs and M. J. Sienko, *J. Am. Chem. Soc.*, **78**, 920 (1956).

Figure 1. Gas-phase hydration enthalpies for the clustering of water about ions. The theoretical points are calculated on the basis of the classical Thomson equation (see text) at 313.15 K. The experimental points shown are for the Ag^+ and Cu^+ ions (ref 15), alkali-metal ions (ref 13), and Sr^+ ion (ref 14).
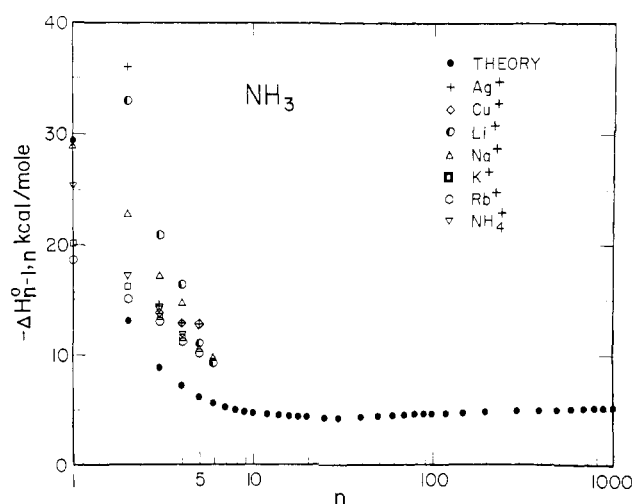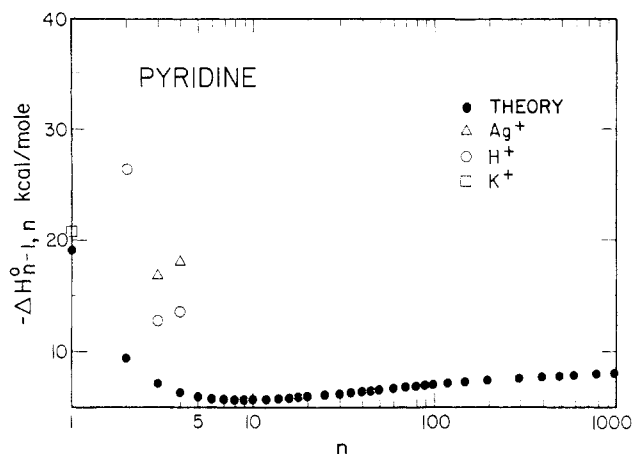

Figure 2. Gas-phase ammoniation enthalpies for the clustering of ammonia about ions. The theoretical points are calculated on the basis of the classical Thomson equation (see text) at 233.15 K. The experimental points shown are for the Ag^+ and Cu^+ ions (ref 15), Li^+ and Na^+ ions (ref 17), K^+ and Rb^+ ions (ref 16), and NH_4^+ ion (ref 18).

Of the substances considered, water is undoubtedly of the greatest interest and practical importance. Calculated results from the Thomson equation for stepwise enthalpy changes for water are plotted in Figure 1 together with experimental results for a number of different metal ions. As might be expected, the greatest differences between

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Figure 3. Gas-phase reaction enthalpies for the clustering of pyridine about ions. The theoretical points are calculated on the basis of classical Thomson equation (see text) at 353.15 K. The experimental points shown are for the Ag^+ and H^+ ions (ref 15) and K^+ ion (ref 19).

Figure 4. Gas-phase reaction enthalpies for the clustering of acetonitrile about ions. The theoretical points are calculated on the basis of the classical Thomson equation (see text) at 293.15 K. The experimental points shown are for the alkali-metal ions (ref 21).

metal ions occur at the smallest cluster sizes, and the values tend to converge at larger cluster sizes where the nature of the central ion should become progressively less important. Ultimately, of course, $\Delta H°$ should approach the value for condensation of the bulk liquid. The closed-shell alkali-metal-ion data coverge quickly to an enthalpy value in fairly good agreement with the calculated values even at small cluster sizes. The open-shell Sr^+ ion, clustered with water, shows unusually strong bonding out to nine ligands; however, it does appear that the $\Delta H°$ values will also approach the predicted ones somewhat beyond cluster size 10. Results plotted for the Ag^+ and Cu^+ ions fall between those for the larger alkali-metal ions and the Sr^+ ion.

A similar plot for the clustering of ammonia about positive ions is shown in Figure 2. While the experimental data strongly converge with increasing cluster size, agreement with the Thomson values is clearly not as good as in the case of water. It should be noted that the Thomson equation predicts water clusters to be more strongly bound than those of ammonia at the smallest cluster sizes, whereas experimental results show that ammonia binds more strongly than water for the first few clusters.[11,17]

Results for pyridine are shown in Figure 3. Here, agreement between experiment and the Thomson equation is fortuitously good for the first cluster with K^+ ion while not good for the others. A comparison with the Thomson results for ammonia reveals that, contrary to experiment, at large cluster sizes pyridine is predicted to bind more strongly than ammonia while at small sizes the opposite is indicated. This prediction is apparently due in part to a "size" effect in the Thomson equation which will be discussed in the following section.

A comparison of experimental data[21] of another nitrogen base, acetonitrile, with the Thomson results is given in Figure 4. Here, as with water and ammonia, convergence of the alkali-metal data to a single value is seen by the fifth cluster. However, the experimental data do not converge to the predicted result. Thus, agreement between theory and experiment for the alkali-metal ions is fairly good for water, but not as good for ammonia and acetonitrile.

Figure 5 shows experimental and calculated results for the methanol system. Again, it can be seen that agreement between the macroscopically based theory and experiment is not particularly good.

Another factor which must be considered in testing the validity of the Thomson equation is its success in pre-
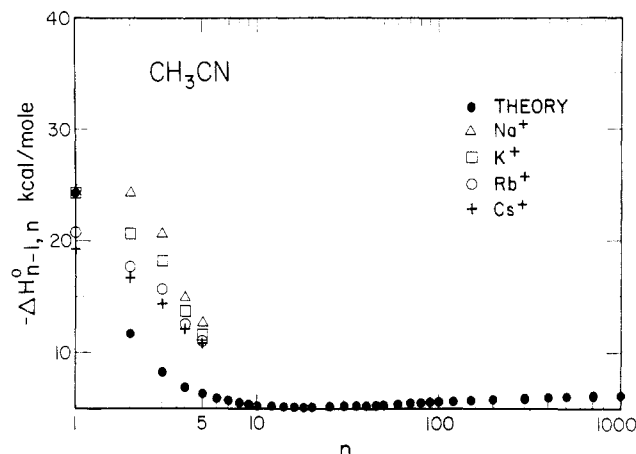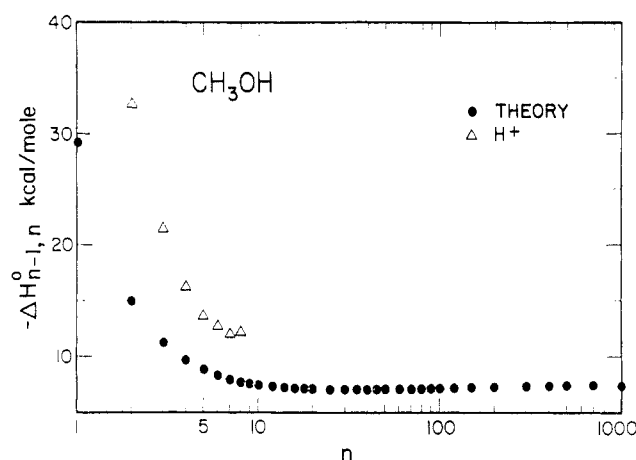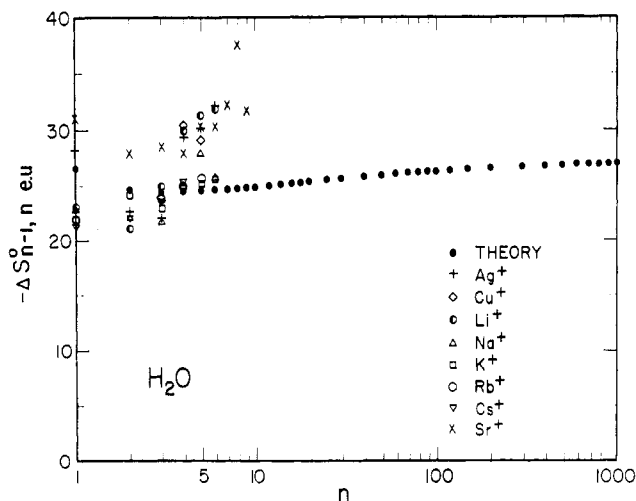

Figure 5. Gas-phase reaction enthalpies for the clustering of methanol about ions. The theoretical points are calculated on the basis of classical Thomson equation (see text) at 293.15 K. The experimental points shown are for the H^+ ion (ref 20).

dicting the entropy of small clusters. While entropy is closely related to structure, calculations based on the Thomson equation do not explicitly take the structure of ion clusters into account. As a result, experimental entropies provide a stringent test for the classical charged liquid drop formulation at small cluster sizes.

Entropy data[13-15] for the water system is shown in Figure 6. The data appear to fall into two fairly distinct groupings. The alkali-metal-ion data (with the exception of Li^+ ion) tend to converge, at about cluster size 5, to a value in fairly good agreement with the Thomson result. The results for the Ag^+, Cu^+, and Sr^+ ions have sharply more negative values at larger cluster sizes, which suggest greater "structuring" in these cluster ions.

Comparison of the Thomson results with experimental entropies for ammonia clusters (Figure 7) shows a sharp disagreement for all ions. For instance, at cluster size 5, the experimental results are more negative than predicted ones by 5–15 eu; furthermore, theory and experiment seem to diverge as cluster size increases. Clearly the experimental results suggest more ordered cluster ions than can be accounted for by the Thomson equation. Ammonia with its single "lone pair" of electrons would be expected to be a highly directional ligand in terms of interaction with an ion.

In Figure 8, experimental entropies are compared with the Thomson equation for pyridine. A very sharp diver-

Figure 6. Gas-phase hydration entropies for the clustering of water about ions. The theoretical points are calculated on the basis of the classical Thomson equation (see text) at 313.15 K. The experimental points shown are for the Ag^+ and Cu^+ ions (ref 15), alkali-metal ions (ref 13), and Sr^+ ion (ref 14).
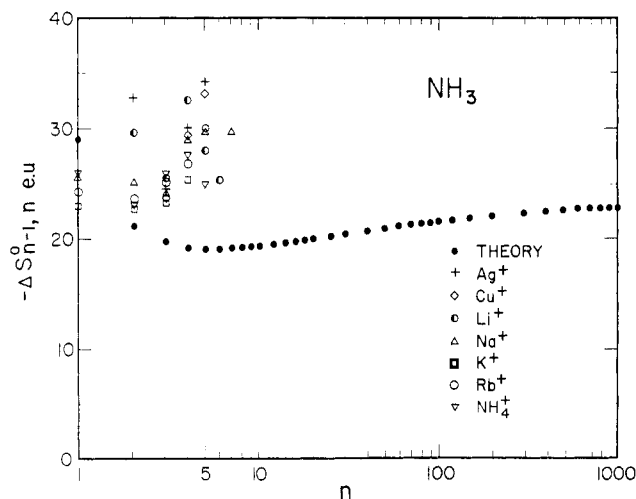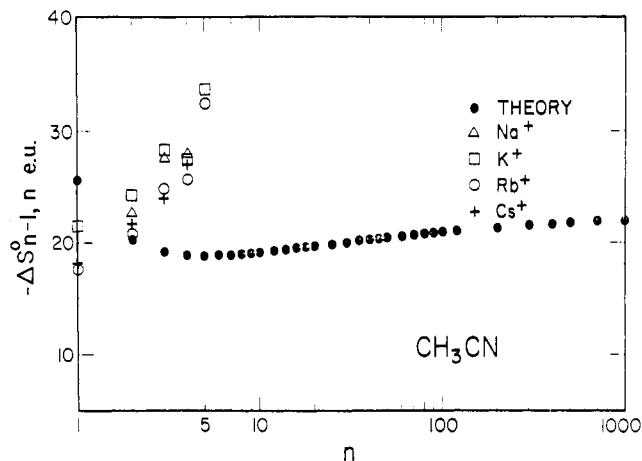

Figure 7. Gas-phase ammoniation entropies for the clustering of ammonia about ions. The theoretical points are calculated on the basis of the classical Thomson equation (see text) at 233.15 K. The experimental points shown are for the Ag^+ and Cu^+ ions (ref 15), Li^+ and Na^+ ions (ref 17), K^+ and Rb^+ ions (ref 16), and NH_4^+ ion (ref 18).
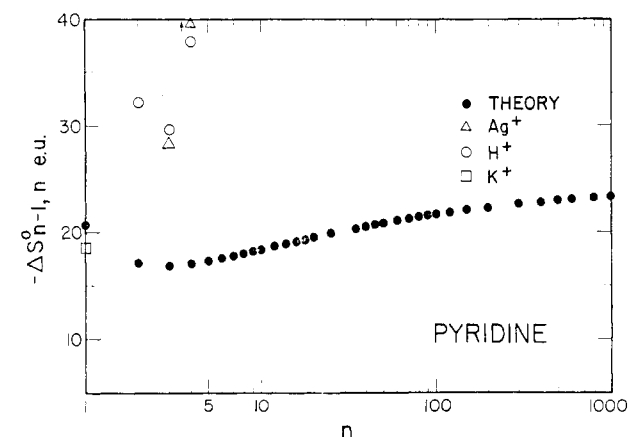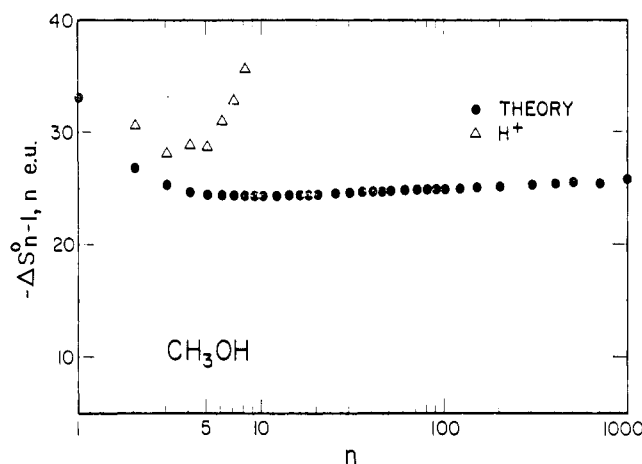

Figure 8. Gas-phase reaction entropies for the clustering of pyridine about ions. The theoretical points are calculated on the basis of classical Thomson equation (see text) at 353.15 K. The experimental points shown are for the Ag^+ and H^+ ions (ref 15) and K^+ ion (ref 19).

gence between calculation and experiment with increasing cluster size is also evident for this system. At cluster size 4 there is a difference of 20 eu between the calculated and

Figure 9. Gas-phase reaction entropies for the clustering of acetonitrile about ions. The theoretical points are calculated on the basis of the classical Thomson equation (see text) at 293.15 K. The experimental points shown are for the alkali-metal ions (ref 21).

Figure 10. Gas-phase reaction entropies for the clustering of methanol about ions. The theoretical points are calculated on the basis of the classical Thomson equation (see text) at 293.15 K. The experimental points shown are for the H^+ ion (ref 20).

experimental values. This large negative discrepancy at cluster size 4 correlates with the size where both Ag^+ and H^+ show very strong evidence of an ordered "solvation shell".[15]

Data for acetonitrile clustered to alkali-metal ions are shown in Figure 9. Here, although agreement with the Thomson equation is fairly good at the smallest cluster sizes, there is a sharp negative divergence by cluster size 5 of nearly 15 eu from the Thomson values. The more negative experimental values again suggest more order than can be accounted for by the Thomson equation.

Figure 10 shows experimental entropies for the H^+-$(CH_3OH)_n$ system. Again, a very sharp divergence from the Thomson values is seen with increasing cluster size. Although methanol might be expected to be the most "water-like" of the ligands examined, a comparison of the results for the two ligands does not show any special resemblance.

The experimental entropies are in most cases sharply more negative than those predicted, suggesting that these cluster ions have a more ordered structure than can be accounted for in the classical approach. This effect is observed for many cluster ions and is apparently due to orientation of ligand molecules about the ion. Such results support the view that structure is important in cluster ions. A more detailed discussion of experimental evidence for solvation structure in cluster ions is given elsewhere.[15]

TABLE II: Comparison of Enthalpies and Entropies of Condensation Calculated from Charged Liquid Drop Expression (at Infinite Size) with Literature Values

	heat of condn, kcal/mol		entropy of condn, eu	
	this work[a]	other	this work[a]	other
water	10.3	10.5[b]	27.8	28.4[b]
ammonia	5.8	6.0[c]	24.1	
pyridine	9.6	9.7[c]	25.0	
acetonitrile	8.2	8.1[b]	23.1	22.9[b]
methanol	8.9	9.1[b]	26.2	27.0[b]

[a] From charged Liquid drop expression at infinite size (see text). [b] At 298 K from ref 29. [c] From ref 23.

Evaluation of the Charged Liquid Drop Model

Inspection of the Thomson equation and appropriate derivatives shows that, in the limit of large cluster size (as n approaches infinity), only the vapor pressure terms contribute to the calculated results. The calculated values under these conditions should be those for condensation to the bulk phase, thus providing a consistency check for the Thomson formulation. These calculated and literature values[23,29] are compared in Table II. It can be seen that agreement is quite good for each of the ligands. Since the vapor pressure terms do not vary (for stepwise reactions), all of the variations in the Thomson values as a function of size are due to the terms representing the work done in forming the droplet (which contains the surface tension) and for the solvation of the ion (which contains the dielectric constant).

The validity of using bulk-phase parameters such as dielectric constant and surface tension at cluster sizes of only a few molecules is clearly questionable. Sinanoğlu has recently demonstrated[9] that precise treatment of properties such as surface tension is possible down to the smallest cluster sizes. His results[9] indicate microscopic values of surface tension for pure polar liquids to be greater by about 60%. Effects due to the presence of a solvated ion in the droplet are more difficult to assess. Surface tensions of dilute (electrically neutral) solutions of electrolytes would be expected to increase with concentration.[30] When one goes to higher electrolyte concentrations, it is more complicated; for example, the surface tension of water is known to increase while that of ethanol decreases.[31] Regarding the dielectric constant, dielectric saturation effects about the solvated ion would be expected to cause a significant decrease in the effective dielectric constant for small clusters. In the context of such effects, it is of interest to consider whether any reasonable adjustments to the macroscopic parameters at small cluster sizes can lead to significant improvement between the calculated and experimental values.

For each of the ligands except water, the experimental entropy values are from 5 to 20 eu more negative than those predicted by theory. While no change in the dielectric constant can account for this discrepancy, an increase in surface tension at small sizes improves agreement. However, the enthalpy data show that, for each of the ligands except water, experimental values are approximately 5 kcal/mol more negative than the predicted ones. Thus, to obtain improved agreement with the experimental results, the Thomson equation must predict both the stepwise entropy and the enthalpy changes at small sizes

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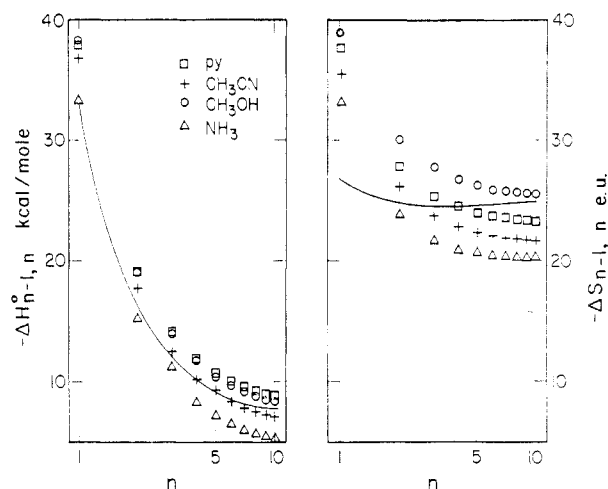(31) W. Drost-Hansen, *Ind. Eng. Chem.*, **57**, 18 (1965).

Figure 11. Charged liquid drop calculations of various ligands with the same "effective size" as water (see text).

to be more negative. An examination of the signs and relative magnitudes of the parameters used in calculating the entropy and enthalpy changes (see Table I) shows that, although an increase of surface tension at small sizes will improve agreement for the predicted entropy values, agreement for the predicted enthalpies will worsen. This suggests that a fundamental inconsistency exists between the general form of the classical expression and the properties of small ion clusters. In any case, it seems clear that no reasonable adjustments or corrections to the values of surface tension or dielectric constant at small cluster sizes will lead to a substantial improvement in the Thomson formulation.

The remaining elements in the Thomson formulation, which may have a bearing on the results at small cluster sizes, are volume, density, and number of molecules. Together, these constitute the relationships which determine the "effective size" of the cluster. It is readily seen that, on the basis of bulk densities and molecular weights, the different ligand molecules have quite different effective sizes. In the Thomson equation these effective sizes are taken into account in the calculated radius of the droplet for a cluster of n molecules.

In order to assess the extent to which the effective size influences the calculated results of the Thomson equation (at small cluster sizes), we made a series of calculations in which each of the ligands was constrained to have the same effective size as the water molecule. This was accomplished by assigning a "pseudo molecular weight" to each ligand, leaving all other parameters intact. The results for each ligand are shown in Figure 11 compared with those for water (solid line). It can be seen that, at the same effective size, the calculated enthalpies agree fairly well. This suggests that the calculated results at small sizes may be more dependent on the bulk relationships that are used in determining the effective sizes of the ligand molecules than on differences in the other macroscopic parameters. For the entropies, a similar trend is shown for all of the ligands except water, which behaves in a qualitatively different fashion.

In the case of water an examination of the relative magnitudes of the terms contributing to the entropy shows that the non-vapor-pressure terms contribute much less than those of the other ligands at small cluster sizes. This is also true in the calculations where no "size" adjustments were made. Examination of the parameters used in the calculation (Table I) suggests that the greatest effect is due to the temperature derivative of the density for water (about one-third that of the other ligands). As a result,

the calculated values for the entropy of water do not differ greatly from the −27.8 eu calculated at infinite cluster size.

Since the Thomson equation can be viewed as an expression for evaluating the gas-phase solvation of ions, a comparison to the Born expression for ion solvation in liquids is germane. It should be noted that, when the radius of the droplet becomes infinite, the third term in the Thomson equation for $\Delta G_{0,n}$ corresponds in form to the Born expression for ion solvation.[32]

$$\Delta G_{solv} = -\frac{q^2 N}{2r_i}\left(1 - \frac{1}{\epsilon}\right) \qquad (7)$$

As in the Thomson equation, the sign of the charge does not affect the result; thus, the effects of ligand structure about the ion are ignored. Since the identical form and the same classical assumptions are used in both expressions, any defects noted in the more extensively studied Born expression should also apply to the Thomson equation.

In the Born equation the free energy of solvation is calculated to be the difference between the work of charging an ion of radius r in a uniform dielectric and a vacuum. A weakness of the Born equation lies in unambiguously determining the appropriate radius of the ion. Although radii based on crystal lattices are commonly used, it is now recognized that the radius of an ion depends on its environment. For example, gas-phase radii are larger than those in condensed phases.[33]

A more fundamental weakness of the Born equation involves the assumptions that are made regarding the solvent.[34,35] For example, the Born equation ignores dielectric saturation effects which are known to occur about solvated ions. These effects cause a reduction in the dielectric constant near the ion and are mainly due to hindered rotation of molecules in the primary hydration shell.[36] This leads to an inconsistency since it has been shown that, if no dielectric saturation occurs, the work of charging an ion is actually equal to the Helmholtz free energy[37] and thus only approximates the Gibb's free energy. The solvent is also assumed to be incompressible, although electrostriction about ions is a well-known fact. As a result, the Born equation (and by implication the Thomson equation) has some fundamental weaknesses which limit its ability to deal with ion solvation. Extensions of the Born equation with the inclusion of dielectric saturation effects and empirical adjustments to the ionic radii have led to improvements.[38] However, the discrete nature of the ion–solvent interaction region must ultimately limit the effectiveness of any continuous theory for ion solvation. In the case of the Thomson equation, effects on the calculated values should not be as significant since the "ion-solvation" term is not large compared to other terms in the expression. In particular, the effect of errors due to the ion-solvation term should be quite small in the case of stepwise reactions at larger cluster sizes since the explicit dependence on the radius of the central ion is absent for the stepwise reactions.

Two very recent models based on statistical mechanical[7] and electrostatic[8] corrections to the form of the Thomson expression have been applied to the problem of calculating the excess free energy for water about both positive and negative ions. The first of these by Chan and Mohnen[7] incorporates a discrete molecular "core" region inbedded in a modified Fisher liquid drop model. The second, by Suck,[8] includes the contribution of higher-order electric moments and polarization effects. Each of these approaches has been applied with some success to clusters of water molecules about ions. Comparison with the classical (Thomson) results shows that the magnitude of the corrections incorporated in these models is large for an ion with a single ligand but that the differences diminish very rapidly as the first few ligands are added. Since the Thomson equation itself seems to represent the *stepwise* thermochemical properties of small clusters of water molecules about ions reasonably well, this suggests that other approaches based on the general form of the Thomson equation are likely to do as well as the classical expression (or better) in this regard when applied to water. However, the Thomson equation clearly fails to account for the observed stepwise thermochemical properties of clusters of ammonia, pyridine, acetonitrile, and methanol about ions. As a result it is not clear that approaches based on the general form of the Thomson equation can be successfully extended to these systems. This suggests that the calculation of the excess free energy of solvated ions in non-water systems will provide a more rigorous test for such models.

Conclusions

The classical charged liquid drop expression is based on macroscopic properties of the bulk condensed phase and therefore is independent of the discrete nature of matter. A direct comparison of results calculated from the classical formulation with experimental results for stepwise enthalpies and entropies of clustering about ions provides a test of the classical expression down to small cluster sizes. While the results for water are found to compare rather favorably, those for ammonia, pyridine, acetonitrile, and methanol do not. In general, the classical expression is somewhat better in its description of enthalpies than entropies of clustering.

The validity of using bulk-phase parameters is clearly questionable at small cluster sizes. However, no reasonable adjustments of parameters such as the dielectric constant or surface tension for small cluster sizes lead to any significant general improvement in the classical expression. For example, it has been shown that, while an increase of surface tension at small sizes will improve agreement for the entropies, it will worsen agreement for the enthalpies. This suggests that a fundamental inconsistency exists between the general form of the classical expression and the properties of small cluster ions. The major reason seems to be that small clusters develop with an ordered structure while the Thomson relationship assumes a disordered liquidlike structure.

The "effective size" of the molecules in the droplet (via density and molecular weight considerations) is shown to have a significant effect on the calculated results. When this effect is removed by constraining each of the ligand molecules to have the same effective size, calculated enthalpies and entropies behave in a very similar way except for the entropy of water. This is shown to be due to the relatively small non-vapor-pressure terms in the classical expression for entropy in the case of water compared to the other ligands.

The classical charged liquid drop expression is able to represent reasonably well the stepwise thermochemical properties of small clusters of water molecules about ions.

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However, the classical expression fails for small clusters of ammonia, pyridine, acetonitrile, and methanol about ions. This suggests that general application of the Thomson formulation to non-water systems will not be valid, at least at small cluster sizes.

Interaction of Organic Molecules with the Surface of Zinc Oxide

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Adsorption isotherms of organic molecules, n-BuOH, n-BuCl, n-C_7H_{16}, and CH_3NO_2, on ZnO surfaces hydroxylated to varying degrees were measured at 25 °C, which allowed an estimation of the amounts of irreversibly and reversibly adsorbed molecules. Irrespective of the differences in polarity and functional group of the organic molecules, the amount of irreversibly adsorbed molecules decreased linearly, while that of reversibly adsorbed ones increased, with increasing surface hydroxyl content of the sample. This implies that hydroxyl groups on the metal oxide surface inhibit the chemisorption of organic molecules but act as effective sites for reversible physisorption of them. The infrared spectroscopic method was applied to identify the adsorbed species on surfaces of both strongly dehydroxylated and fully hydroxylated ZnO samples. n-BuOH molecules were found to be chemisorbed dissociatively to form surface alkoxyl and hydroxyl groups on the dehydroxylated surface, which resulted in the formation of an autophobic surface layer. It seemed likely that there was a strong interaction, which might be regarded as chemisorption, between n-BuCl molecules and the dehydroxylated ZnO surface. Nonpolar, n-C_7H_{16} molecules with no functional group, however, were held on the surface simply by physical interaction. For CH_3NO_2, surface hydroxyl groups were produced on the dehydroxylated ZnO sample, which was interpreted in terms of the electron-attractive effect of nitro groups in this molecule.

Introduction

A study of the interaction between metal oxide surfaces and organic molecules is a fundamental subject in the field of catalyst chemistry as well as an attractive one in the surface chemistry of solids. The surface properties of a solid can be best appreciated by studying the interaction with organic molecules which have different properties such as molecular size, polarity, and kind of functional groups. At this time, special regard should be paid to the role of surface hydroxyl groups on metal oxides, because they are held tenaciously on the surface even after degassing the sample at higher temperatures.[1-4] Actually, some cases are known where the presence of optimum amounts of water enhance a catalytic activity of metal oxides.[5,6] Therefore, it will be useful in the characterization of solid surfaces to understand the adsorption of organic molecules on metal oxide surfaces as a function of the surface hydroxyl content of the sample.

In the previous work,[7] the adsorption of a series of normal aliphatic alcohols (C_1–C_3) on ZnO with a controlled number of surface hydroxyls has been measured to investigate the effect of hydroxyl groups on the adsorption of alcohol molecules. The results showed that the dissociative chemisorption of alcohols occurred on the dehydroxylated ZnO surface to produce both alkoxyl and hydroxyl groups, but on the fully hydroxylated surface reversible physisorption took place predominantly through hydrogen bonding. It was also revealed that the amount of irreversibly adsorbed alcohol molecules decreases, while that of the reversibly adsorbed ones increases, with increasing hydroxyl content of the sample.

In the present work, as an extension of the previous study, the interaction of ZnO surfaces with four kinds of organic molecules which have different functional groups was investigated in connection with the effect of surface hydroxyls on the adsorption of these organic molecules.

Experimental Section

Materials and Pretreatment. The original ZnO sample used in this study was Kadox 15 produced by New Jersey Zinc Co., being the same as that used in the previous work.[7] The sample was first degassed at 600 °C for 4 h under vacuum at 1×10^{-3} N m^{-2} in order to remove surface contaminations which might be present. This sample was then kept for 15 h at room temperature in contact with saturated water vapor to ensure complete hydroxylation. We obtained ZnO samples covered with a different number of surface hydroxyls by evacuating the fully hydroxylated sample at various temperatures between 25 and 600 °C under vacuum at 1×10^{-3} N m^{-2}.

The organic compounds used as adsorbated were 1-butanol (n-BuOH), 1-chlorobutane (n-BuCl), heptane (n-C_7H_{16}), and nitromethane (CH_3NO_2), all of which were guaranteed grade reagents of Nakarai Chemicals. These adsorbates, except CH_3NO_2, were purified by distillation in the usual way. CH_3NO_2 was dried over molecular sieves 4A dehydrated at 350 °C, since it was liable to be decom-

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