J. Phys. Chem. A **2002,** *106,* 982−987

Adsorption of Atmospheric Gases at the Air−Water Interface. 4: The Influence of Salts

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Received: July 24, 2001; In Final Form: October 26, 2001

We have measured the standard free energies and standard enthalpies of adsorption as well as saturated surface coverages for hexanoic acid and 1-propanol adsorbed at the air−aqueous interface of sodium chloride (NaCl) and ammonium sulfate ($(NH_4)_2SO_4$) solutions of concentrations between 0 and 4 mol L^{-1}. Temperature-dependent surface tension measurements are used to obtain $\Delta G^0_{aq\to\sigma}$ and $\Delta H^0_{aq\to\sigma}$; using known Henry's law constants and estimated values of the salting-out coefficient we calculate the gas−interface adsorption parameters $\Delta G^0_{g\to\sigma}$ and $\Delta H^0_{g\to\sigma}$. A small (∼1−2 kJ mol^{-1}) decrease in $\Delta G^0_{aq\to\sigma}$ with increasing salt concentration is accompanied by an increase (∼10−30%) in saturated surface coverage, consistent with the expected "salting-out" behavior. Adsorption from the gas phase becomes somewhat less favorable with increasing salt concentration for both organic species. The standard enthalpy of adsorption from the gas phase decreases with increasing salt concentration for hexanoic acid, but not for 1-propanol. This may be a consequence of acid dimer formation at the interface becoming important at higher coverages.

Introduction

Recent studies of the structure and chemical composition of atmospheric aerosols have indicated that a substantial mass fraction of both tropospheric and stratospheric aerosol particles consists of organic species.[1−3] In the atmosphere, hygroscopic salt particles, such as NaCl or $(NH_4)_2SO_4$, often act as condensation nuclei for aerosol formation. However, the exact concentration, composition, and formation mechanisms of multicomponent aerosol particles are not well understood.[4] The presence of organic species dissolved in or on the surface of atmospheric aerosols can alter the surface and bulk thermodynamic and chemical properties, and therefore the role of particles in the environment. For example, there is evidence that suggests that particle-phase organic aerosols in nonurban areas are hydrophilic and enhance water uptake, whereas those in urban areas are hydrophobic and inhibit water uptake.[5]

Chemical reactions and uptake at particle surfaces will certainly depend on the surface composition of the particles. To explain observed oxidation rates of Cl^- in sea-salt aerosol, Knipping et al.[6] conclude that in highly concentrated aqueous solutions of inorganic salts, the large polarizable anions cover a greater fraction of the air−solution interface than the small nonpolarizable cations. In particular, those authors suggest that negative chloride ions, at the surface of saturated NaCl solutions, strongly attract gas-phase reactive particles. If this is true, the degree of surface exposure of each ion present in solution could influence the interfacial reactivity toward gas-phase reactants and the degree to which absorption and adsorption occurs.

In recent work probing the effects of various ions on the structure of the air−water interface, Schnitzer et al.[7] use results of surface sum-frequency generation (SFG) experiments to conclude that the alignment and orientation of surface water molecules in aqueous salt solutions is independent of the presence of salts. In the same paper, the orientation and ratio of "free" to hydrogen-bonded OH groups of surfacial water molecules is reported to change with changes in solution pH. The addition of acids apparently disrupts the first layer of surface water molecules, allowing ions to approach the surface more easily. This might lead to a change in reactivity toward certain molecules.

In addition to potentially changing the surface composition and reactivity directly, the presence of salts in aqueous solution also affects the ability of organic molecules to dissolve, through the salting-out effect.[8] The salting-out effect refers to the decrease in aqueous solubility and increase in the activity coefficient observed for neutral nonpolar compounds by dissolved inorganic salts. Ions in solution tightly bind several water molecules into hydration shells. This process, known as electrostriction, results in a reduction of the volume of the aqueous solution. A smaller aqueous volume means that there is less available water to form cavities, and hence accommodate organic molecules; their solubility decreases as a consequence. Therefore, the propensity for soluble atmospheric gases to adsorb and/or react at the air−water interface could be altered.

The purpose of the present study is to extend our previous work[9−11] on the adsorption of soluble atmospheric gases at the air−water interface to investigate adsorption on the surfaces of salt solutions. We report the adsorption thermodynamics of two semivolatile organic species, 1-propanol and hexanoic acid, at the air−aqueous interface of solutions of NaCl and $(NH_4)_2SO_4$. These salts were chosen in order to study the possible processes occurring in marine and continental aerosols.

Experimental Section

Equilibrium surface tensions of aqueous and salt solutions of 1-propanol and hexanoic acid were measured at 278, 288, 298, and 308 K using the capillary rise method.[12] This method allows measurement of the surface tension when equilibrium has been established among the vapor, solution, and surface phases. Capillary rise was measured using a capillary tube of inner diameter 0.0185 cm suspended inside a sealed tube of inner diameter 2.4 cm which contained the solution of interest.

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10.1021/jp0128628 CCC: $22.00

TABLE 1: Standard Adsorption Thermodynamic Parameters for the Aqueous-to-Surface Process

	hexanoic acid			1-propanol		
solvent	K_H[a]	$\Delta G^0_{aq\to\sigma}$[b]	$\Delta H^0_{aq\to\sigma}$[b]	K_H[a]	$\Delta G^0_{aq\to\sigma}$[b]	$\Delta H^0_{aq\to\sigma}$[b]
water	1400[c]	−27.9 ± 0.5	−6.9 ± 1.5	138[c]	−17.1 ± 0.5	3.5 ± 1.5
1 M NaCl	900	−28.1	−6.1	110	−17.4	3.2
3 M NaCl	400	−28.3	−5.4			
4 M NaCl	200	−28.9	−5.1	55	−17.0	3.6
1 M $(NH_4)_2SO_4$	900	−29.1	−6.3	110	−15.6	5.0
4 M $(NH_4)_2SO_4$	200	−29.1	−4.7	55	−17.2	3.4

[a] K_H units in mol L^{-1} atm^{-1}. [b] In kJ mol^{-1}. [c] Henry's law constants for pure water from ref 13.

About one-quarter of the 22-cm length of the capillary was immersed in the solution. The rise of solution in the capillary was between 2 and 5 cm. The solution in the capillary was assumed to have the same temperature as the bulk solution. Temperature was maintained using a commercial recirculating water bath with a stated temperature stability of ±0.2 K. All solutions were made up volumetrically, using analytical grade organic and inorganic reagents and high purity water. Glassware was cleaned prior to use with concentrated nitric acid and high purity water. Surface tension as a function of organic concentration of aqueous solutions of 1-propanol and hexanoic acid was measured in 0 M, 1, 3, and 4 M NaCl, and 1 and 4 M $(NH_4)_2SO_4$ solutions. The surface tensions of aqueous solutions of 1-propanol and NaCl were compared to literature values and were in good agreement.

Data Analysis

The thermochemistry of adsorption onto water surfaces appropriate for soluble atmospheric gases has been developed in previous papers from this group.[9−11] Briefly, the surface concentration of species "i" is expressed in terms of the surface pressure, π_i, defined as $\pi = \sigma^* - \sigma$, where σ^* is the surface tension of the pure solvent, and σ represents the surface tension of the solution. The standard state appropriate for the adsorbed species, π^0 ($= 0.06084$ dyn cm^{-1}), was first proposed by Kemball and Rideal,[13] and has been used in our previous work. The chemical potential of species "i" in the surface phase is

$$\mu_i^{\sigma} = \mu_i^{0,\sigma} + RT\ln(\gamma_i^{\sigma}\pi_i/\pi^0)$$

where nonidealities at the surface are included by use of a surface activity coefficient, γ_i^{σ}.

In each of the two bulk phases the chemical potential of species "i" is

$$\mu_i^{g} = \mu_i^{0,g} + RT\ln(p_i/p^0)$$

$$\mu_i^{aq} = \mu_i^{0,aq} + RT\ln(a_i/a^0)$$

where p^0 and a^0 are the standard pressure (1 bar) and standard activity (which is taken as 1 M), respectively. The solution activity, a_i, is: $a_i = \gamma_i M_i$, where the γ_i are concentration-dependent activity coefficients and M_i represents the solute concentration in mol L^{-1}. Here ideal gas behavior of the vapor is assumed, which is quite reasonable in atmospheric applications.

The free energy for transferring 1 mole of species "i" from the solution phase to the surface (the molar free energy of adsorption from solution) is

$$\Delta G_{aq\to\sigma} = \mu_i^{\sigma} - \mu_i^{aq} = (\mu_i^{0,\sigma} - \mu_i^{0,aq}) + RT\ln\{(\gamma_i^{\sigma}\pi_i/\pi^0)/(a_i/a^0)\}$$

At phase equilibrium $\Delta G_{aq\to\sigma} = 0$, and so from the above,

$$\Delta G^0_{aq\to\sigma} = -RT\ln\{(\gamma_i^{\sigma}\pi_i/\pi^0)/(a_i/a^0)\}_{eq}$$

The surface activity coefficients are unknown functions of the surface coverage (and hence, surface pressure, π). However, they are defined such that all of the $\gamma_i^{\sigma} \to 1$ as $\pi_i \to 0$. Therefore, a plot of $RT\ln\{(\pi_i/\pi^0)/(a_i/a^0)\}_{eq}$ vs (a_i/a^0) extrapolated to zero solution activity will yield the "ideal" value of $\Delta G^0_{aq\to\sigma}$, which is independent of the concentration of "i" in any of the phases.

As well, at equilibrium,

$$\Delta G^0_{aq\to\sigma} = \Delta G^0_{g\to\sigma} - \Delta G^0_{g\to aq}$$

from which the gas−surface adsorption free energy may be calculated:

$$\Delta G^0_{g\to\sigma} = -RT\ln K_H + \Delta G^0_{aq\to\sigma}$$

where K_H represents the appropriate Henry's law constant. The Henry's law constants and their temperature dependencies (given as the standard enthalpy of solution) were obtained from the NIST tabulation[14] and are reported in Table 1.

The present work involves studies of adsorption onto the surface of solutions of different salt concentrations and therefore of differing ionic strength. An empirical relation for the effect of ionic strength on a compound's Henry's law constant in aqueous solution was given by Setchenow:[15]

$$\log(K^0_H/K_H) = k_S\,[\text{salt}]$$

where K^0_H is the Henry's law coefficient in pure water, [salt] is the concentration of the ionic solution expressed in mol L^{-1} and k_s is the Setchenow salting-out coefficient in units of L mol^{-1}. Values of k_S for hexanoic acid and 1-propanol in NaCl and $(NH_4)_2SO_4$ solutions have not been reported. By inspection of reported values of other, similar compounds,[16] we estimate a value of 0.2 L mol^{-1} for hexanoic acid, and 0.1 L mol^{-1} for 1-propanol. The values of K_H used here were calculated using these estimates for k_S, and are reported in Table 1.

Over a reasonable temperature range the standard entropy and standard enthalpy of adsorption are essentially constant, so may be calculated from the temperature dependence of ΔG° as:$\Delta S^\circ = -(\partial\Delta G^0/\partial T)$, and then $\Delta H^\circ = \Delta G^\circ + T\,\Delta S^0$.

The surface coverage as a function of solution concentration was also determined from the surface tension data. At equilibrium among all three phases the chemical potentials are equal, $\mu_i^{g} = \mu_i^{\sigma} = \mu_i^{aq}$, and from the Gibbs equation,[17] the relative surface excess of species "i" over water may be written as:

$$\Gamma_{H_2O,i} = (\partial\sigma/\partial\mu_i)_{T,\mu j\neq 1} = -(a_i/RT)(\partial\sigma/\partial a_i)$$

for adsorption from solution. (In the following, $\Gamma_{H_2O,i}$ will be

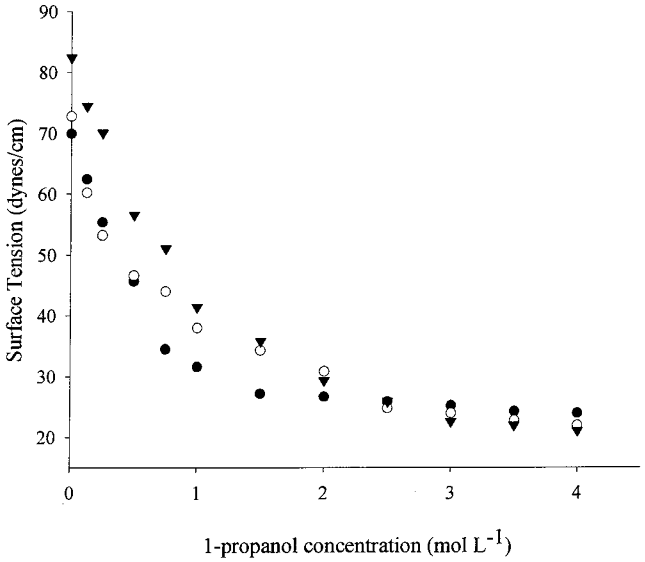

Figure 1. Surface tension of aqueous solutions of 1-propanol at 298 K as a function of alcohol concentration. Three different salt concentrations are shown: 0 mol L^{-1} (filled circles), 1 mol L^{-1} (hollow circles), and 4 mol L^{-1} NaCl (filled triangles). The estimated error on each surface tension measurement is ±(0.25−0.49) dyn/cm.

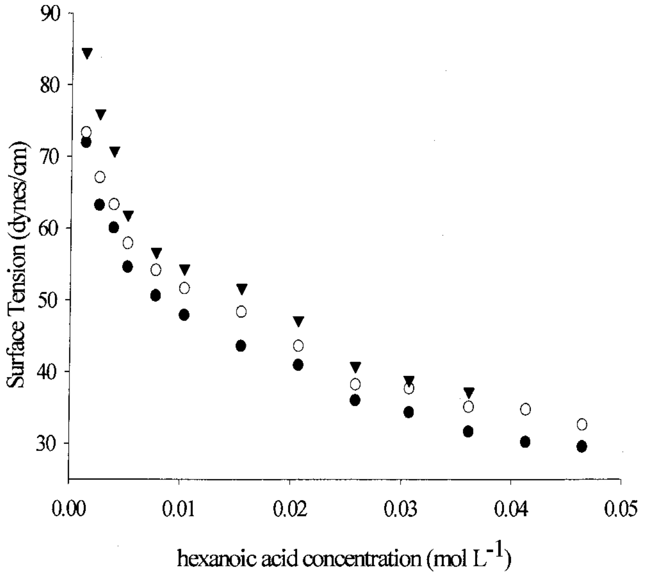

Figure 2. Surface tension of aqueous solutions of hexanoic acid at 298 K as a function of the acid concentration. Three different salt concentrations are shown: 0 mol L^{-1} (filled circles), 1 mol L^{-1} (hollow circles), and 4 mol L^{-1} NaCl (filled triangles). The estimated error on each surface tension measurement is ±(0.25−0.49) dyn/cm.

abbreviated to Γ). A plot of Γ as a function of solution activity can often be fit to a Langmuir adsorption isotherm,[17] to obtain adsorption parameters:

$$\Gamma = \Gamma^{sat}\, c/(b + c)$$

where c represents the concentration in solution, b is a parameter related to the rate constants for adsorption and desorption from both bulk phases,[9] and Γ^{sat} gives the saturated surface coverage.

Results

1. Adsorption Thermodynamics. Figures 1 and 2 show representative plots of the 298 K surface tension versus organic concentration for 1-propanol and hexanoic acid, respectively, in solutions of various NaCl concentrations. The accuracy of determining the surface tensions of the various solutions was tested by completing repetitive measurements with pure water at 298 K. The experimental results agreed with the values in the *CRC Handbook of Chemistry and Physics* with a relative error of 0.11%. The precision of the measurements was between 0.25 and 0.49 dyn cm^{-1}. This was determined by completing at least four measurements for each sample. Similar results were obtained for all the solutions studied. With increasing salt concentration, the surface tensions of the solutions at a given organic concentration increase, as expected. As well, the decrease in surface tension with increasing organic concentration is more rapid in the salt solutions than in pure water.

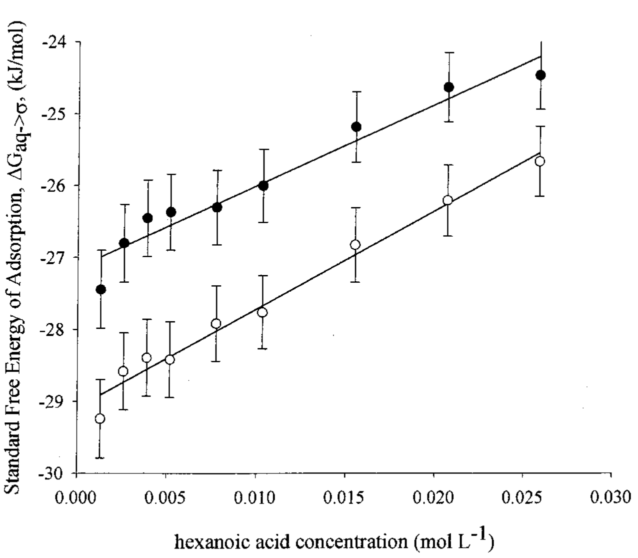

Figure 3. Adsorption free energy of hexanoic acid at the air−water interface as a function of acid concentration at 278 K (filled circles) and 298 K (hollow circles) in a 1 mol L^{-1} $(NH_4)_2SO_4$ solution. The lines show linear fits to the data.

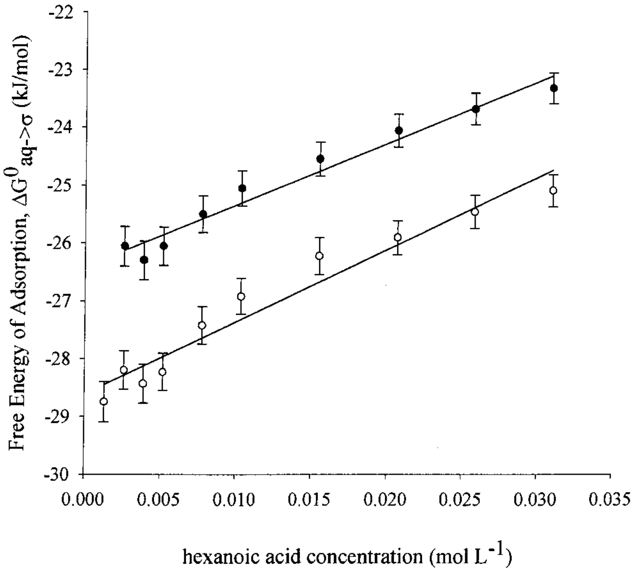

Figure 4. Same as for Figure 3, but for a 4 mol L^{-1} NaCl solution.

The standard free energy of adsorption from solution was plotted as a function of concentration for each of the solutions and temperatures used. We assume that the solution activity coefficients remain essentially constant over the range of low organic solute concentrations used here.[10,11] All solutions show a linear dependence of $\Delta G^0_{aq\to\sigma}$ on concentration at low organic solute concentrations. Figures 3 and 4 show representative plots

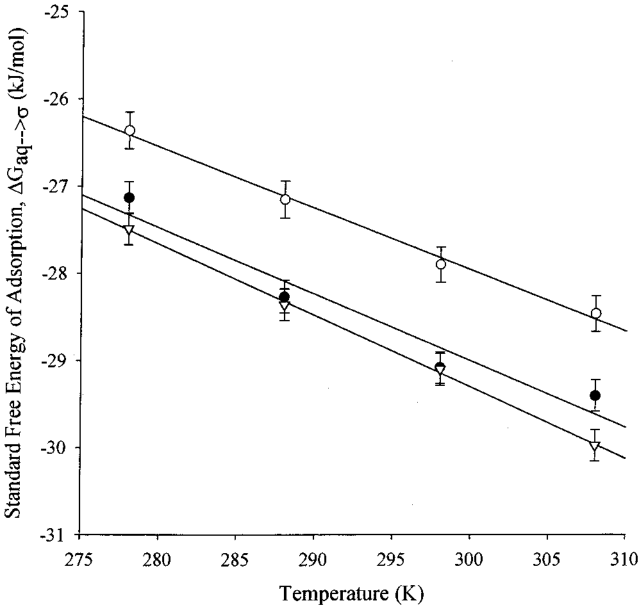

Figure 5. Standard free energy of adsorption of hexanoic acid from the bulk to the surface as a function of temperature in various salt concentrations. The solutions are: water (filled circles); 1 mol L^{-1} $(NH_4)_2SO_4$ (hollow triangles); 4 mol L^{-1} $(NH_4)_2SO_4$ (hollow circles). The lines show linear fits to the data.

TABLE 2: Standard Adsorption Thermodynamic Parameters for the Gas-to-Surface Process

	hexanoic acid		1-propanol	
solution	$\Delta G^0_{g\to\sigma}$[a]	$\Delta H^0_{g\to\sigma}$[a]	$\Delta G^0_{g\to\sigma}$[a]	$\Delta H^0_{g\to\sigma}$[a]
water	−45.8 ± 0.7	−57.6 ± 1.9	−29.1 ± 0.8	−58.8 ± 1.9
1 M NaCl	−44.9	−56.8	−28.9	−59.1
3 M NaCl	−43.2	−55.1		
4 M NaCl	−42.3	−54.2	−26.8	−58.7
1 M $(NH_4)_2SO_4$	−45.9	−57.0	−27.1	−57.3
4 M $(NH_4)_2SO_4$	−42.5	−55.4	−27.0	−58.9

[a] In kJ mol^{-1}.

of $\Delta G^0_{aq\to\sigma}$ as a function of hexanoic acid concentration at different temperatures in, respectively, 1 mol L^{-1} $(NH_4)_2SO_4$ and 4 mol L^{-1} NaCl solutions. Results for 1-propanol are of similar quality. The zero-concentration intercept provides the “ideal” $\Delta G^0_{aq\to\sigma}$ for adsorption from solution onto the air–aqueous interface. The values of $\Delta G^0_{aq\to\sigma}$ we determine here are given in Table 1. The precision of these measurements was approximately the same for all solutions and calculated as ±0.5 kJ mol^{-1}. Using Henry’s law and salting-out constants also shown in Table 1, we calculate the standard free energy of adsorption for the gas phase, $\Delta G^0_{g\to\sigma}$, for each solution at each temperature. These results are displayed in Table 2.

Figure 5 shows the temperature dependence of $\Delta G^0_{aq\to\sigma}$ for hexanoic acid in the various salt solutions. The slopes of linear fits to these data provide the standard entropies of adsorption from the solution onto the surface, $\Delta S^0_{aq\to\sigma}$, from which the corresponding standard enthalpies of adsorption from solution, $\Delta H^0_{aq\to\sigma}$ were calculated. Table 1 contains these results as well. The standard enthalpies of adsorption from the gas phase, $\Delta H^0_{g\to\sigma}$, were calculated from the following relation:

$$\Delta H^0_{g\to\sigma} = \Delta H^0_{g\to aq} + \Delta H^0_{aq\to\sigma}$$

as well as from the temperature dependence of the $\Delta G^0_{g\to\sigma}$. The two methods gave the same results; these are shown in Table 2.

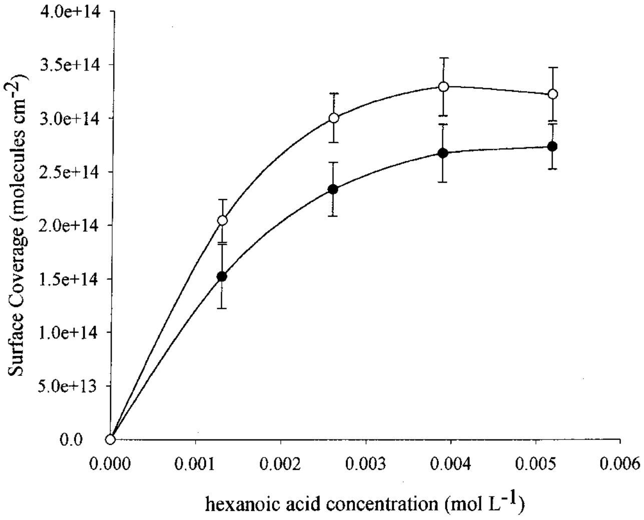

Figure 6. Surface coverage of hexanoic acid as a function of acid concentration in a 0 mol L^{-1} NaCl (filled circles) and a 4 mol L^{-1} NaCl (hollow circles) solution. The lines show fits of the data to Langmuir isotherms.

2. Surface Coverages. An exponential-polynomial function of the form[10,11]

$$\sigma = \sigma_0 e^{-a_1 c} + a_2 c + a_3 c^2 + a_4 c^3$$

where c is the concentration of the organic solute in mol L^{-1} and σ_o is the surface tension of the aqueous solution without organic solute present, was used to fit all the surface tension data at 278 and 298 K. The derivative of this function was then used in the Gibbs equation to calculate the relative surface excesses, Γ. Figure 6 displays the resulting Γ as a function of hexanoic acid concentration in NaCl solutions of 0 and 4 mol L^{-1} at 298 K, as well as Langmuir isotherms which were fit to these data. Although the exact values of the parameters in the Langmuir isotherms depend on the function used to fit the surface tension data,[10,11] in every instance the value of Γ^{sat} calculated for salt solutions is larger than that for pure water, increases with increasing salt concentration and is somewhat smaller at 278 K than at 298 K. The error in these measurements was estimated to be ±(2–3) × 10^{13} molecules cm^{-2}. Similar results hold for both organic species in each of the salts used here. At 298 K, there is an increase of approximately 10–30% in Γ^{sat} as the salt concentration is increased from 0 to 4 mol L^{-1}.

Discussion

1. Adsorption Thermodynamics and the Salting-Out Effect. The results shown in Table 1 indicate a slight increase in the solution-to-surface partitioning of hexanoic acid with increasing salt concentration. The magnitude of this effect (about 1 kJ mol^{-1} at [salt] = 4 mol L^{-1}, independent of the identity of the salt) is small, but somewhat greater than the uncertainty. It is similar to that reported for *p*-nitrophenol in LiCl solution (about 2 kJ mol^{-1} at [LiCl] = 3 mol L^{-1}).[18] By contrast the 1-propanol data show somewhat more scatter than do the hexanoic acid results; within this scatter there seems to be little change in $\Delta G^0_{aq\to\sigma}$ with increasing salt concentration. This difference between the two molecules in their partitioning out of solution is consistent with the difference in salting-out coefficients assumed here.

The standard entropies of adsorption of hexanoic acid from solution, $\Delta S^0_{aq\to\sigma}$, increase slightly with increasing salt con-

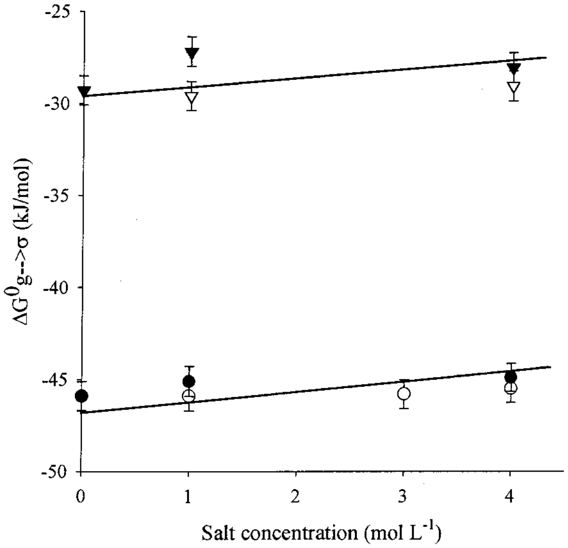

Figure 7. Standard free energy of adsorption from the gas phase to the surface for hexanoic acid (circles) and 1-propanol (triangles) as a function of salt concentration. The filled symbols represent NaCl solution and the hollow symbols represent $(NH_4)_2SO_4$ solution. The lines are present to guide the eye.

centration, from about +69 J K^{-1} mol^{-1} in pure water to about +82 J K^{-1} mol^{-1} in 4 mol L^{-1} salt solution. The standard adsorption enthalpies, $\Delta H^0_{aq\to\sigma}$, also show a small trend with increasing [salt], varying from about −7 kJ mol^{-1} for pure water to −5 kJ mol^{-1} for 4 mol L^{-1} salt solutions. The estimated error in these measurements, from the $\Delta G^\circ_{aq\to\sigma}$ calculations, temperature reading, and entropy, was ±1.5 kJ mol^{-1}. Thus, transfer from solution to the surface becomes a little more favorable entropically and somewhat less favorable enthalpically as the salt concentration is increased.

For 1-propanol, no such trends are apparent. The temperature dependence of $\Delta G^0_{aq\to\sigma}$ shows considerable scatter, but little or no dependence on the nature or concentration of the salt in solution. Combined with the independence of $\Delta G^0_{aq\to\sigma}$ on [salt], this yields a near constant standard enthalpy of adsorption from solution as the concentration of the salt is varied. The calculated values of $\Delta H^0_{aq\to\sigma}$ for the 1-propanol solutions are all approximately +3.5 kJ mol^{-1}. In this case, the partitioning to the surface must be driven entirely by entropic considerations, whereas in hexanoic acid, the partitioning is favored both by entropy and enthalpy. These differences are probably reflective of the much greater solubility of 1-propanol in water.

The adsorption behavior from the gas phase to the surface also shows differences between the two organic species. Both hexanoic acid and 1-propanol display a reduction in the propensity for gas−surface partitioning as the salt concentration is increased. Numerically, the increase in $\Delta G^0_{g\to\sigma}$ is larger for hexanoic acid than for 1-propanol; however, as a fraction of the corresponding $\Delta G^0_{g\to\sigma}$ value for pure water, the change is about the same for each. Figure 7 shows the dependencies of $\Delta G^0_{g\to\sigma}$ at 298 K on salt concentration we calculate. Our results do not indicate any dependence on the identity of the salt for either organic species. A possible explanation for the free energy change is provided by Warszynnski and Lunkenheimer,[19] who point out that, whereas an unrestricted hydrophobic chain can assume practically any conformation at the interface, adsorption of other molecules restricts the conformational possibilities, thereby changing the conformational free energy. If the surface of the salt solutions studied here is “enriched” in anions, as suggested by Knipping et al.,[6] their presence at (or near) the interface might influence the adsorption thermodynamics. Such changes might be expected to appear most strongly in the entropy terms, however, and we observe no dependence of the adsorption entropies on salt concentration.

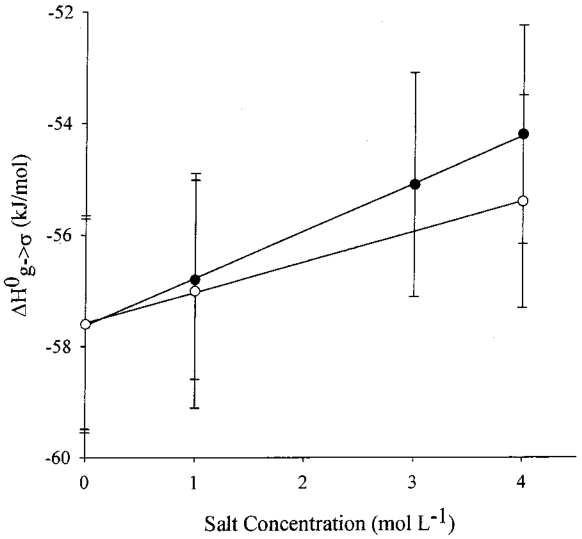

Figure 8. Standard free enthalpy of adsorption from the gas phase to the surface for hexanoic acid as a function of salt concentration. The lines show linear fits to the data.

The standard enthalpies of adsorption from the gas phase do show some interesting differences, however. We calculate that $\Delta H^0_{g\to\sigma}$ is essentially independent of the identity and concentration of salt in the case of 1-propanol, but depends weakly upon both parameters in the case of hexanoic acid. Figure 8 displays $\Delta H^0_{g\to\sigma}$ for hexanoic acid as a function of salt concentration. A decrease in the binding enthalpy to the surface is observed with increasing salt concentration. The dependence of $\Delta H^0_{g\to\sigma}$ on [NaCl] is about 50% larger than that on $[(NH_4)_2SO_4]$.

The standard enthalpy of adsorption from the gas phase is expected to reflect the nature of the binding at the surface. Our previous work has shown that for molecules such as 1-propanol and hexanoic acid, the primary interactions are 1−3 hydrogen bonds with surfacial water,[9−11] forming a “proto-solvated” species, or “critical complex”[20] at the surface. A dependence of $\Delta H^0_{g\to\sigma}$ on the identity and concentration of the salt in solution suggests a change in the nature of the binding at the surface.

One possibility might be that as the ionic strength of the solution increases the water molecules are increasingly bound in water−salt hydration complexes and so become less available to make hydrogen bonds with the acid. Ab initio calculations of Aloisio et al.[21] indicate that formic acid forms strong complexes with 1, 2, and 3 water molecules. The strongest complexes occur when water molecules are bound to the acid in cyclic hydrogen-bonded complexes. Such complexes are predicted to possess binding energies of approximately 20 kJ mol^{-1} per hydrogen bond. If such acid−water complexes exist at the air−water interface, they may be responsible for the strong binding enthalpies we observe for hexanoic (and other organic) acids. In salt solutions, the surfacial water molecules could be involved in strongly bound hydration complexes with the ions present near the interface, and so reduce the number of “free” waters available for binding to the carboxylic acid, giving rise to weaker binding at the interface.

However, the results of surface sum-frequency generation experiments reported by Shultz and co-workers,[7] suggest that the presence of (nonprotonated) ions in solution does not strongly perturb the structure of surfacial water. The relative numbers of free and hydrogen-bonded water hydrogens at the surface do not change greatly as the ionic strength of the solution is increased, even to fairly high levels. Certainly our finding that $\Delta H^0{}_{g\rightarrow\sigma}$ for 1-propanol does not depend on the presence of salts in solution is consistent with this finding. The dependence we observe for hexanoic acid must therefore arise from some other source.

One clue might come from the increase in surface coverage with increasing salt concentration. Carboxylic acids are known to form strongly bound dimers via cyclic hydrogen bonding between the acid functionalities of two molecules.[22,23] If this is occurring as the acid number density on the surface increases, then the standard adsorption enthalpy may contain contributions from dimers, as well as from the monomer. Since 1-propanol is not expected to form dimers as its surface concentration is raised, this will not influence the binding of this molecule at the surface.

A final possibility is that the decrease in adsorption enthalpy with increasing salt concentration may be due to repulsive forces between anions lying near the surface[6,7] and ionized hexanoic acid anions. Although the acid constant for hexanoic acid is small, we expect some ionized species to dwell at the air−water boundary. If this is the case, the negatively charged carboxyl group and the negatively charged surface would repel each other, decreasing the observed (average) binding enthalpy. Again, this effect will not be present in solutions of 1-propanol.

2. Atmospheric Implications. The coverage of atmospheric particles by organic molecules may have important atmospheric consequences for the reactivity, potential for growth, and optical properties of the aerosol. Elsewhere,[10] we have argued that urban aqueous aerosol particles in the submicron size regime are most probably coated with partially oxidized organic species. The present results suggest that aqueous aerosols consisting of concentrated salt solutions (such as those formed by deliquescing NaCl or $(NH_4)_2SO_4$ particles) are less likely to have an organic coating formed by uptake from the atmosphere. For example, assuming a gas-phase concentration of 1 ppb of hexanoic acid, our results predict that a 100 nm diameter droplet of pure water will have approximately 150 hexanoic acid molecules on its surface, compared with about 30 for the corresponding droplet formed from a 4 mol L^{-1} NaCl solution. These numbers increase to 1.4×10^4 and 450, respectively, for a 1-μm-diameter droplet. For the smaller particles, essentially all of the acid resides upon the surface in both pure water and concentrated salt solution; even the 1-μm-diameter droplets have surface-to-bulk concentration ratios of 31 and 41, respectively, for the pure water and saltwater solutions. This may have significant consequences for the reactivity of organic species associated with such particles: reactions (such as oxidation by OH or ozone) may show different rates and mechanisms on the aqueous surface than in the bulk solution or the gas phase.[24,25] Future work from this laboratory will address this issue more fully.

For involatile, aqueous-phase species, such as the long-chain fatty acids found at the ocean surface, the salting out effect can only give rise to an increased surface concentration, without affecting the partitioning to the gas phase. Therefore, for aerosol formed from ocean spray, there could well be a significant propensity for organic coatings, as suggested elsewhere.[26,27]

Conclusions

The presence of dissolved salts affects the solution−surface−gas-phase partitioning for soluble atmospheric gases. The most common atmospheric salts, NaCl and $(NH_4)_2SO_4$, both exhibit a "salting-out" effect toward organic species, increasing the surface concentration of organics for fixed solution concentration, but decreasing it for fixed gas-phase concentration.

Acknowledgment. This work was funded by NSERC. The authors thank Professor B. J. Finlayson-Pitts for many stimulating discussions, and D. Gentleman and L. Ng for their contributions in the preliminary stages of this work.

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