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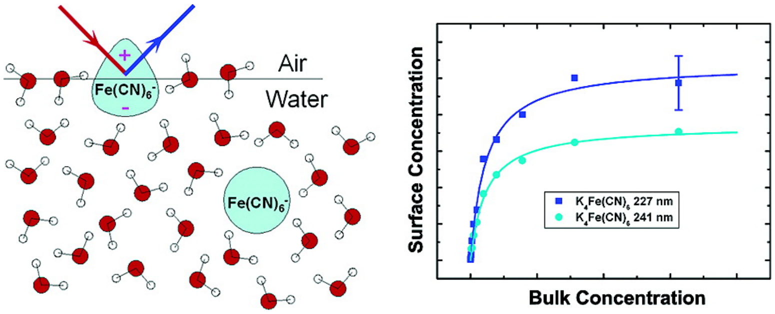

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Adsorption of Ions to the Surface of Dilute Electrolyte Solutions: The Jones−Ray Effect Revisited

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Abstract: The controversial observation of a minimum in the surface tension of dilute aqueous electrolyte solutions by Jones and Ray in the 1930s is confirmed by new resonance-enhanced second harmonic generation (SHG) experiments demonstrating surface enhancement of simple inorganic anions in the same concentration range. New experiments show that the quadruply charged ferrocyanide, $Fe(CN)_6^{4-}$, anion is not surface active at high concentrations, as expected, but at dilute concentrations, the anion is strongly attracted to the interface with a Gibbs free energy of adsorption of −6.8 kcal/mol. Using this value, the original Jones and Ray data are fit to a simple model of the surface tension with qualitative agreement, although better agreement is found for all 13 Jones and Ray salts with an even stronger surface adsorption.

1. Introduction

In the period 1935−42, Jones and Ray published five controversial papers in this journal concerning the surface tension of aqueous electrolyte solutions at dilute concentrations.[1−5] Using the capillary rise method, they measured a minimum in the surface tension near 1 mM for 13 different inorganic salts. A decreasing surface tension implies a net surface excess of the ions, contrary to the accepted theories, which hold that electrolytes are repelled from the interface and the outermost surface layer of water is completely devoid of ions. The original papers have been followed by others both supporting and refuting the finding, but the "Jones−Ray effect" remains today an unresolved controversy.

In 1934, Onsager and Samaras had just published their model of the surface tension effects, based on a continuum dielectric media and describing the ions as point charges.[6] The ions were repelled from the surface by image charge forces, as first proposed by Wagner,[7] leaving the outermost surface layer virtually free of ions. Moreover, Langmuir had already proposed a model in 1917 for the surface of electrolyte solutions with the outermost layer of the interface (∼4 Å) being pure water atop of a uniform solution.[8] He was thus quick to dismiss the Jones−Ray findings as an artifact due to the experimental technique, viz. adding ions to water changes the thickness of the wetting layer inside the capillary by several hundred Å, effectively altering the capillary radius.[9,10]

Others were more receptive. Bikerman proposed a model for the surface tension involving three contributions that could account for the surface tension minimum.[11] Dole first presented his model for the surface tension[12,13] and then, with Swartout, reproduced the experimental minimum in the surface tension for KCl using an advanced version of the ring method that is unaffected by the artifacts proposed by Langmuir.[14] The theoretical model of Dole is close to the one we present here.

An alternative approach to measuring the surface tension is the maximum bubble pressure method, wherein gas bubbles of an inert gas are formed at the end of a capillary tube at a given rate. The method is thus a dynamic measurement, with bubble lifetimes ranging from one to hundreds of seconds. The first bubble pressure experiment on dilute electrolyte solutions failed to observed a minimum for all bubble lifetimes (5−120 s).[15] A second study reproduced the surface tension minimum at long bubble lifetimes (120 s) but not at short (15 s) times and attributed the Jones−Ray effect to organic contaminations building up at the surface, although identical results were obtained for samples prepared from both a powdered and single-crystal salt.[16] A third study first dismissed the Jones−Ray effect on a thermodynamic basis[17] but later observed a minimum in the surface tension with the bubble pressure method, for all bubble lifetimes.[18] In this case, the surface tension minimum was greatest at short times (12 s) but still observable at longer times (250−500 s), and the authors attributed the observation to nonequilibrium electrification dynamics of the surface.

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(1) Jones, G.; Ray, W. A. *J. Am. Chem. Soc.* **1935**, *57*, 957−958.
(2) Jones, G.; Ray, W. A. *J. Am. Chem. Soc.* **1937**, *59*, 187−198.
(3) Jones, G.; Ray, W. A. *J. Am. Chem. Soc.* **1941**, *63*, 288−294.
(4) Jones, G.; Ray, W. A. *J. Am. Chem. Soc.* **1941**, *63*, 3262−3263.
(5) Jones, G.; Ray, W. A. *J. Am. Chem. Soc.* **1942**, *64*, 2744−2745.
(6) Onsager, L.; Samaras, N. N. T. *J. Phys. Chem.* **1934**, *2*, 528−536.
(7) Wagner, V. C. *Phys. Z.* **1924**, *15*, 474−477.
(8) Langmuir, I. *J. Am. Chem. Soc.* **1917**, *39*, 1848−1906.
(9) Langmuir, I. *Science* **1938**, *88*, 430−432.
(10) Langmuir, I. *J. Chem. Phys.* **1938**, *6*, 873−896.
(11) Bikerman, J. J. *Trans. Faraday. Soc.* **1938**, *34*, 1268−1274.
(12) Dole, M. *Nature* **1937**, *140*, 464−465.
(13) Dole, M. *J. Am. Chem. Soc.* **1938**, *60*, 904−911.
(14) Dole, M.; Swartout, J. A. *J. Am. Chem. Soc.* **1940**, *62*, 3039−3045.
(15) Long, F. A.; Nutting, G. C. *J. Am. Chem. Soc.* **1942**, *64*, 2476−2482.
(16) Passoth, G. *Z. Phys. Chem.* **1959**, *211*, 129−147.
(17) Rusanov, A. I.; Faktor, E. A. *Russ. Chem. Rev.* **1974**, *43*, 933−950.
(18) Kochurova, N. N.; Rusanov, A. I.; Myrzakhmetova, N. O. *Dokl. Phys. Chem.* **1991**, *316*, 176−178.

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Langmuir's theoretical treatment was, like the Onsager and Samaras model, based on solving the Poisson–Boltzmann equation for a continuum system under certain simplifying approximations. His model precipitated a further discussion of the problem. First, it was criticized as not adequately describing the system, and a more complete treatment was made.[19] Then, with precise measurements of the zeta potential, the "Langmuir correction" (viz. the change in capillary radius with salt concentration) was calculated for different salts and first found to remove the observed surface tension minimum[20] and then later to increase it[21] and finally remove it again.[22] Considering changes in the contact angle further increased the complexity of the problem.[23]

The reason for the discrepancies between the various theoretical treatments of the problem is the nature of the approximations that have to be made in order to solve the problem analytically. Such approximations depend on knowing the short-range interactions between ions and water molecules at interfaces. A recent review has shown that the nature of these short-range forces is still not well described.[24] However, recent complex electrostatic models have been able to reproduce the Jones–Ray effect by including an ambient surface layer of hydroxide.[25,26]

This interest in surface adsorption of inorganic anions has recently been revived. To explain the chemical reactions observed to occur on aqueous sea salt particles, on ocean surfaces, and in laboratory aerosol experiments, surface ions had to be invoked.[27–29] This claim inspired molecular dynamics simulations using polarizable potentials, which clearly showed the affinity of polarizable anions for the liquid surface.[28,30–34] Several indirect experimental investigations using Sum-Frequency Generation (SFG) have examined the change in the water structure due to the presence of the ions but disagree on the interpretation of the measurements.[35–37] Ghosal et al. used photoemission spectroscopy to study the anion-to-cation ratio at the surface of concentration electrolyte solution on a crystal surface above the deliquescence point.[38] These experiments clearly showed an enhanced anion-to-cation ratio that approached unity at longer probing depths.

Our approach is to directly and selectively probe the anion concentration at the surface using SHG that is resonantly enhanced through the strong charge-transfer-to-solvent (CTTS) transitions of the anions in the UV. This technique is not affected by Langmuir's correction and thus provides an independent and direct measurement of anion surface adsorption. We have recently reported the surface enhancement of dilute iodide solutions,[39] which agree with the Jones–Ray effect, as well as the atmospherically relevant high concentration adsorption of azide (N_3^-)[40] and thiocyanide (SCN^-).[41] Here we present measurements of the SHG intensity of aqueous potassium ferrocyanide ($K_4Fe(CN)_6$) over a large range of concentrations. At high concentration the anions are not attracted to the surface, as expected due to the quadruple negative charge, whereas the dilute concentration range shows surface *enhancement* similar to the iodide solutions and in reasonable agreement with the Jones–Ray surface tension experiments. In addition, a simple model of the surface tension at dilute concentrations is presented. This model is slightly different from the model presented by Dole[13] and, using the experimentally obtained Gibbs free energies, agrees qualitatively with the surface tension data. However, more quantitative agreement is obtained with Gibbs free energies of adsorption which are larger than those obtained from the SHG experiments.

2. Experimental Details

The laser system and experimental design are described in detail elsewhere,[42] and only a brief description is given here. A home-built femtosecond oscillator is used to pump a commercial regenerative amplifier (Spectra Physics, Spitfire, 1 kHz, 90 fs, 2 mJ), after which two optical parametric amplifiers (Light Conversion, TOPAS) provide tunability. The laser light is purified by dichroic mirrors and optical filters before being focused onto the sample at 45°. After the sample, the copropagating fundamental and SHG beams are recollimated by another lens and separated by dichroic mirrors and a prism. The SHG light is collected on a solar blind PMT (Hamamatsu, R7154PHA). To prevent perturbation of the water surface, 10 μJ/pulse or less is used for the experiments and the surface is gently stirred by flowing nitrogen over the sample. Each data point is an average over 80 000 laser shots and reproduced over at least 2 different days.

During data acquisition, the sample is kept in a box purged with nitrogen. The concentration profiles are generated by sequentially diluting the sample. All glassware in contact with the solution is soaked in Nochromix (a chromic acid substitute) for an hour and rinsed with excessive ultrapure water (18.2 MΩ, $\leq$4 ppm total organic content) from a Millipore system (Milli-Q gradient). All samples are made fresh with reagent grade salt (99%) and ultrapure water before each experiment.

3. Results

3.1. SHG Measurements. As an even-order process, SHG is forbidden in bulk centrosymmetric media within the dipole approximation and is thus a surface specific technique for aqueous solutions.[43–46] The SHG intensity is given by the norm

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(19) Jones, G.; Frizzel, L. D. *J. Chem. Phys.* **1940**, *8*, 986–997.
(20) Jones, G.; Wood, L. A. *J. Chem. Phys.* **1945**, *13*, 106–121.
(21) Wood, L. A. *J. Chem. Phys.* **1945**, *13*, 429–439.
(22) Wood, L. A.; Robinson, L. B. *J. Chem. Phys.* **1946**, *14*, 258–262.
(23) Cassel, H. M. *J. Chem. Phys.* **1946**, *14*, 462.
(24) Kunz, W.; Lo Nostro, P.; Ninham, B. W. *Curr. Opin. Colloid Interface Sci.* **2004**, *9*, 1–18.
(25) Karraker, K. A.; Radke, C. J. *Adv. Colloid Interface Sci.* **2002**, *96*, 231–264.
(26) Manciu, M.; Ruckenstein, E. *Adv. Colloid Interface Sci.* **2003**, *105*, 63–101.
(27) Hu, J. H.; Shi, Q.; Davidovits, P.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. *J. Phys. Chem.* **1995**, *99*, 8768–8776.
(28) Knipping, E. M.; Lakin, M. J.; Foster, K. L.; Jungwirth, P.; Tobias, D. J.; Gerber, R. B.; Dabdub, D.; Finlayson-Pitts, B. J. *Science* **2000**, *288*, 301–306.
(29) Laskin, A.; Gaspar, D. J.; Wang, W.; Hunt, S. W.; Cowin, J. P.; Colson, S. D.; Finlayson-Pitts, B. J. *Science* **2003**, *301*, 340–344.
(30) Jungwirth, P.; Tobias, D. J. *J. Phys. Chem. B* **2001**, *105*, 10468–10472.
(31) Dang, L. X.; Chang, T.-M. *J. Phys. Chem. B* **2002**, *106*, 235–238.
(32) Jungwirth, P.; Tobias, D. J. *J. Phys. Chem. B* **2002**, *106*, 6361–6373.
(33) Salvodor, P.; Curtis, J. E.; Tobias, D. J.; Jungwirth, P. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3752–3757.
(34) Yang, X.; Kiran, B.; Wang, X.-B.; Wang, L.-S.; Mucha, M.; Jungwirth, P. *J. Phys. Chem. A* **2004**, *108*, 7820–7826.
(35) Schnitzer, C.; Baldelli, S.; Shultz, M. J. *J. Phys. Chem. B* **2000**, *104*, 585–590.
(36) Raymond, E. A.; Richmond, G. L. *J. Phys. Chem. B* **2004**, *108*, 5051–5059.
(37) Liu, D.; Ma, G.; Levering, L. M.; Allen, H. C. *J. Phys. Chem. B* **2004**, *108*, 2252–2260.
(38) Ghosal, S.; Hemminger, J. C.; Bluhm, H.; Mun, B. S.; Hebenstreit, E. L. D.; Ketteler, G.; Ogletree, D. F.; Requejo, F. G.; Salmeron, M. *Science* **2005**, *307*, 563–566.
(39) Petersen, P. B.; Johnson, J. C.; Knutsen, K. P.; Saykally, R. J. *Chem. Phys. Lett.* **2004**, *397*, 46–50.
(40) Petersen, P. B.; Saykally, R. J. *Chem. Phys. Lett.* **2004**, *397*, 51–55.
(41) Petersen, P. B.; Saykally, R. J.; Mucha, M.; Jungwirth, P. *J. Phys. Chem. B*, in press.
(42) Petersen, P. B.; Saykally, R. J., in preparation.

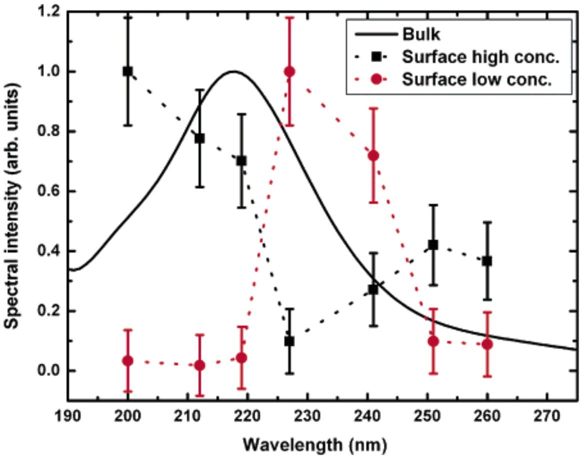

Figure 1. Spectral response. The line shows the bulk adsorption spectrum, and the black squares and the red circles are the second-order nonlinear response at high and low concentrations, respectively.

squared of the second-order susceptibility, $\chi^{(2)}$, which contains the sum of the contributions from both water and the anions (assuming a negligible contribution from the nonpolarizable cations):

$$I_{2\omega} \propto |\chi^{(2)}|^2 I_\omega^2 \tag{1}$$

$$\chi^{(2)} = \chi^{(2)}_{\mathrm{water}} + \chi^{(2)}_{\mathrm{anion}} \tag{2}$$

For the wavelength range studied in this work, the water susceptibility is nonresonant and thus real, but the ferrocyanide contribution contains a complex phase depending on the wavelength. This will lead to partial destructive or constructive interference with the nonresonant background, depending on the wavelength, as previously observed.[39]

Ferrocyanide exhibits a broad CTTS transition at 218 nm, shown in Figure 1. By tuning the laser on and off this resonance, the water and anion contribution to the total SHG intensity can be separated. The SHG intensity of aqueous ferrocyanide solutions as a function of the bulk concentration is shown in Figure 2 for various SHG wavelengths. The SHG intensity can be divided into two distinct regimes, a dilute ($<$10 mM) and a concentrated ($>$10 mM) range. The top and bottom panel show the same data on a linear and logarithmic scale, respectively, allowing the details of the dilute and concentrated ranges to be observed. The SHG intensity variation in the dilute (mM) range is due to anion adsorption, which saturates and becomes constant before 10 mM, causing an initial offset for the concentrated range. The initial decrease in the total SHG intensity is due to the destructive interference between the water background and the anion adsorption, as previously described.[39] The increased SHG intensity in the concentrated range is due to both anions in the interfacial layer and a change in the water background due to the presence of the ions, as evident from the SHG response at on- and off-resonant wavelengths.

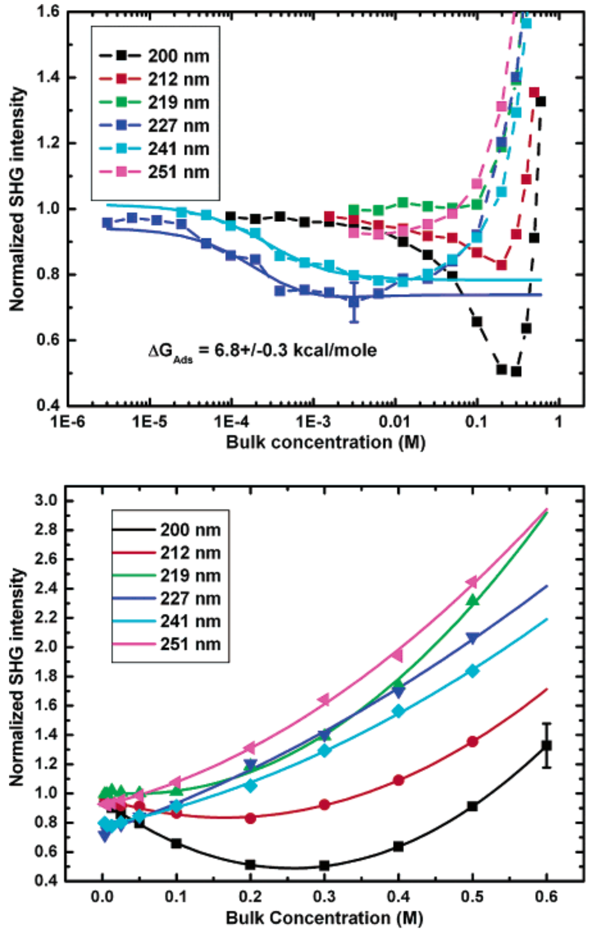

Figure 2. SHG intensity with varying $K_4Fe(CN)_6$ concentration. Panels a and b show the SHG intensity normalized to pure water at a logarithmic and linear scale for better viewing of the low and high concentration range, respectively. The solid lines are fits to a model describing surface enhancement at dilute concentrations but no surface preference at high concentrations, as described in the text.

At two wavelengths (227 and 241 nm), the SHG intensity at dilute concentration exhibits a decrease, which is large enough to be modeled. The anion adsorption is represented by the simple Langmuir adsorption isotherm:

$$N_{\mathrm{S}} = \frac{N_{\mathrm{S}}^{\max} \times KC}{C_{\mathrm{w}} + KC} \approx \frac{N_{\mathrm{S}}^{\max} \times C}{C + 55.5M \times \exp(\Delta G_{\mathrm{Ads}}/RT)} \tag{3}$$

Here, N_{S} is the surface concentration of the anion, $N_{\mathrm{S}}^{\max}$ is the maximum obtainable surface concentration, K is the equilibrium constant for occupying a surface site, C and C_{w} are the bulk anion and water concentrations, respectively, and ΔG_{Ads} is the Gibbs free energy of adsorption. The SHG intensity at the two wavelengths is fit simultaneously to yield a Gibbs free energy of adsorption of -6.8 ± 0.3 kcal/mol. The fitted lines are shown along with the data points in Figure 2a.

At high concentrations, the contributions from the anions and the water background must be separated. The change in the water background is obtained from the off-resonant wavelengths. However, to directly compare the SHG response at the different wavelengths and extract the change in the water SHG background, the initial offset from the dilute concentration adsorption must be removed.[42] The resulting linear increase in the water background with bulk anion concentration is shown in Figure 3. The determined initial offset and linear increase in the water

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(43) Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley: New York, 1984.
(44) Boyd, R. W. *Nonlinear Optics*, 2nd ed.; Elsevier: Amsterdam, 2003.
(45) Eisenthal, K. B. *Chem. Rev.* **1996**, *96*, 1343−1360.
(46) Richmond, G. L. *Annu. Rev. Phys. Chem.* **2001**, *52*, 357−389.

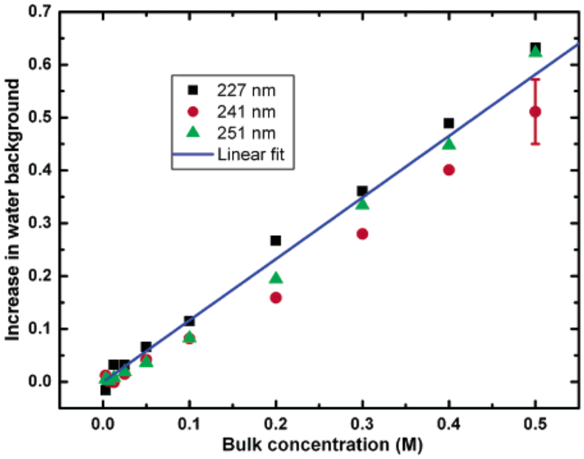

Figure 3. Increase in the water SHG background due to the presence of the ions. The data points are the increase in the second-order electric field normalized at the nonresonant wavelengths, generated by the water background. The line is a linear fit to the average of the data points.

background can then be incorporated into the expression for the total SHG intensity to extract the anion contribution in the concentrated range. In this range, the anion surface concentration is modeled to increase linearly with the bulk, implying no energetic difference between surface and bulk solvation. Experimentally, it is difficult to distinguish between the anion having no energetic difference between the surface and the bulk or being repelled from the surface. The data are thus consistent with the anions being repelled from the surface at high concentrations. The lines in Figure 2b show the resulting fit.

The magnitudes of the anion response at both dilute and high concentrations are shown in Figure 1 along with the linear bulk spectrum. The dilute concentration SHG spectrum exhibits a small red-shift with respect to the bulk due to the lower polarity of the interface,[47] as previously observed for iodide.[39] At high concentrations, the spectrum is broadened due to the increased interionic interactions, and the SHG response increases to the blue. This has been observed for all the examined ions (iodide, azide, thiocyanide, and ferrocyanide) and so far seems to be a general trend.

3.2. Surface Tension Model. To compare the results of our SHG experiments directly with the surface tension data of Jones and Ray, a model of the surface tension is derived. This model is similar to that derived by Dole in 1938 but differs in the definition of the Langmuir adsorption isotherm.

The model for the surface structure invokes a surface layer, wherein the anion concentration follows the Langmuir adsorption isotherm. A sketch showing the relevant parameters of the model is shown in Figure 4. The blue curve is the water density profile that, for the case of pure water, has a thickness of about 5 Å, when defined as the distance where the water density changes from 90% to 10% of the bulk density.[48] The red and green curves are the anion and cation density profiles, respectively, which are generally broader than the water density profile. These profiles are adapted from MD simulations at high concentrations,[32] showing the surface enhancement of the anion at the Gibbs dividing surface and depletion in the surface sublayer, where the cations are enhanced. The exact shape of the curve does not affect the surface tension model, however. The vertical lines at *a* and *b* are placed in the solution and air side of the interface, respectively, where the density profiles reach bulk values and thus define the boundaries of the interfacial region. The vertical line at *g* indicates the Gibbs dividing surface, which is roughly the midpoint of the water density profile and defined rigorously in the following. The surface concentration (ions per area) of the anion is thus given by

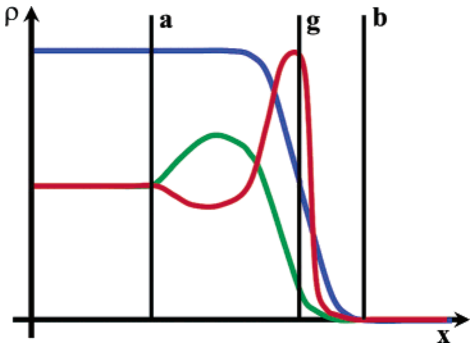

Figure 4. Surface density profiles. The blue curve is the water density profile showing a narrow 90−10 region. The red and green curves are the anion and cation density profile, respectively. The vertical black lines define the positions a, b, and g, which are the boundaries for bulk solution and vapor and the Gibbs dividing surface, respectively.

$$N_{\mathrm{S}}^{\mathrm{anion}} = \int_a^b C^{\mathrm{anion}}(x)\,\mathrm{d}x \qquad (4)$$

The surface concentration of the anion is modeled by the Langmuir adsorption isotherm (eq 3). However, the relevant quantity for the surface tension is not the surface *concentration* but the surface *excess* (Γ), defined with respect to the Gibbs dividing surface:

$$\begin{aligned}\Gamma_- &= N_{\mathrm{S}}^{\mathrm{anion}} - \int_a^g C_{\mathrm{bulk}}^{\mathrm{anion}}\,\mathrm{d}x\\ &= N_{\mathrm{S}} - dC\nu_-\\ &= \frac{N_{\mathrm{S}}^{\max}K'C\nu_-}{1+K'C\nu_-} - dC\nu_- \end{aligned} \qquad (5)$$

Here, N_{S} is the surface anion concentration, *d* is the interfacial depth (N.B. *not* the entire interfacial width, which is the distance between *a* and *b*), ν_- is the stoichiometric number for anions in the salt, *C* is the bulk salt concentration, and $K' = K/55.5$ M is the Langmuir constant.

The interfacial region is electrically neutral, so the surface concentration of the cation is given by $N_{\mathrm{S}}^{\mathrm{cation}} = \nu_+/\nu_- N_{\mathrm{S}}^{\mathrm{anion}}$ and the surface excess of the cation then becomes

$$\begin{aligned}\Gamma_+ &= \frac{\nu_+}{\nu_-}N_{\mathrm{S}} - dC\nu_+\\ &= \frac{N_{\mathrm{S}}^{\max}K'C\nu_+}{1+K'C\nu_-} - dC\nu_+ \end{aligned} \qquad (6)$$

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(47) Wang, H.; Borguet, E.; Eisenthal, K. B. *J. Phys. Chem. B* **1998**, *102*, 4927−4932.
(48) Sokhan, V. P.; Tildesley, D. J. *Mol. Phys.* **1997**, *92*, 625−640.

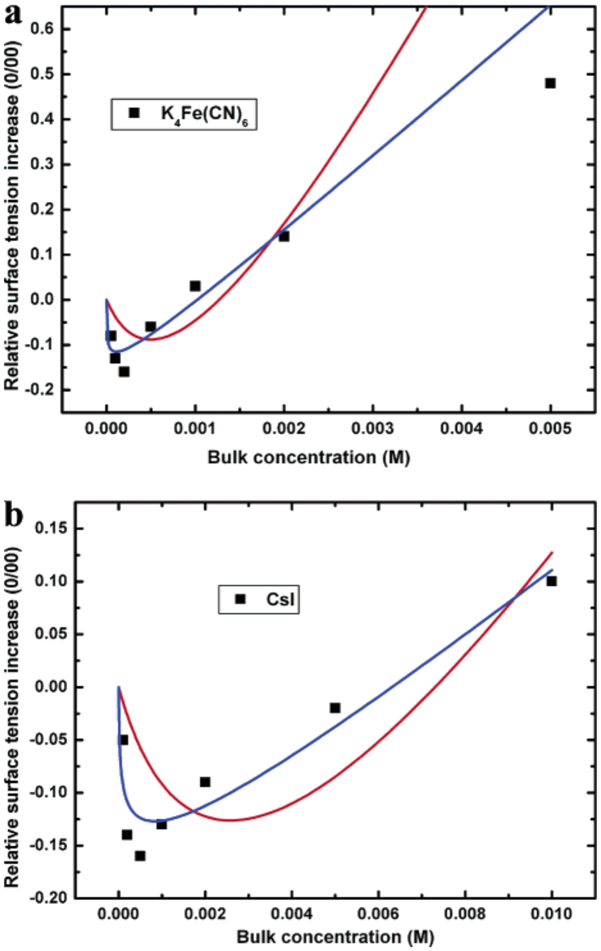

Figure 5. Surface tension of $K_4Fe(CN)_6$ and CsI solutions. The points are the original Jones and Ray data, and the red and blue lines are constrained and unconstrained fits to the proposed model, respectively.

We can now find the change in the surface tension ($\Delta\gamma$) by integrating the Gibbs adsorption equation:

$$\Delta\gamma = RT\int_0^{C'}\sum_i \Gamma_i \mathrm{d}\ln C$$

$$= RT\int_0^{C'}\left(\frac{N_S^{\max}K'C(\nu_- + \nu_+)}{1 + K'C\nu_-} - dC(\nu_- + \nu_+)\right)\mathrm{d}\ln C$$

$$= -RTN_S^{\max}\left(\frac{\nu_- + \nu_+}{\nu_-}\right)\ln(1 + K'C\nu_-) + RTdC(\nu_- + \nu_+) \tag{7}$$

The model has three adjustable parameters: The number of active surface sites ($N_S^{\max}$), the Langmuir constant ($K' = 1/55.5$ M $\exp(-\Delta G_{Ads}/RT)$), and the interfacial depth (d). The model does not account for deviations due the activities of the ions and is thus only applicable at dilute concentrations.

The Gibbs free energies of adsorption of iodide and ferrocyanide have been measured in our recent SHG experiments, yielding −6.2 ± 0.2 kcal/mol and −6.8 ± 0.3 kcal/mol, respectively. Figure 5 shows the Jones and Ray surface tension data for bulk concentrations up to 0.01 M that have been fit to the above model, with and without constraining the Gibbs free energy of adsorption to the SHG values. Whereas qualitative agreement is observed in both cases, the unconstrained fit achieves better quantitative agreement. The fitted Gibbs free energies are larger (more negative) than the SHG values. This implies that either the SHG experiments must have measured a lower bound of the Gibbs free energy (from either a larger probing depth or a weighted average through the interfacial region favoring the low energy side), or the adopted model for the surface tension is too simple, or perhaps the surface tension measurements are obscured by the capillary effect described by Langmuir.[9,19]

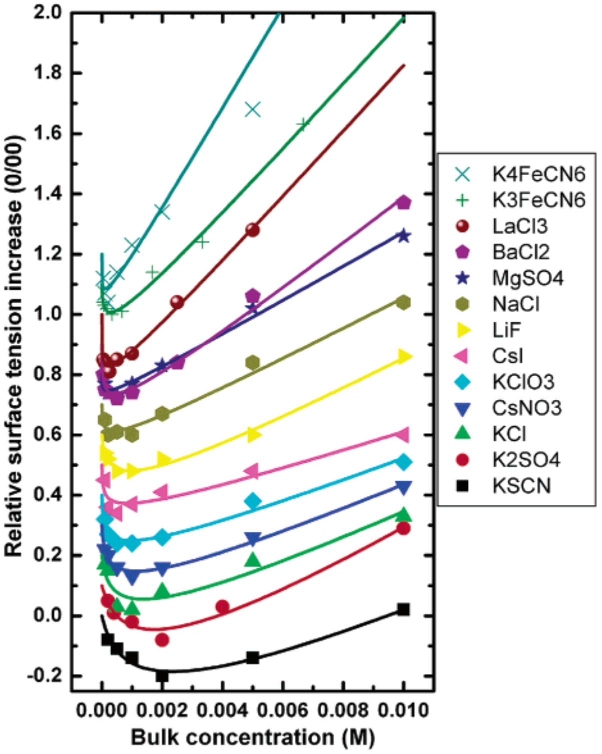

Figure 6. Surface tension data for all 13 Jones−Ray electrolyte solutions. The points are the original data from Jones and Ray, and the lines are the fits to the proposed model.

Table 1. Fitted Parameters and Derived Quantities: the Interfacial Width (d), Maximum Surface Coverage ($N_S^{\max}$), Langmuir Constant (K), Gibbs Free Energy of Adsorption (ΔG_{Ads}), Number of Water Molecules Per Active Site (N_{water}/N_{ion}), and Mean Anion Separation in the Surface Layer (D)

salt	d (Å)	$N_S^{\max}$ (10^{10}/cm^2)	K (M)	ΔG_{Ads} (kcal/mol)	N_{water}/N_{ion}	D (Å)
KSCN	7.6	12	3900	−7.1	21 000	140
K_2SO_4	6.8	8.4	3300	−7.0	27 000	170
KCl	7.5	6.5	14 000	−7.8	39 000	190
$CsNO_3$	6.8	4.8	40 000	−8.5	48 000	230
$KClO_3$	6.0	3.5	140 000	−9.2	58 000	270
LiF	8.3	4.9	23 000	−8.1	56 000	220
NaCl	7.9	1.8	490 000	−9.9	140 000	360
$MgSO_4$	8.7	0.96	2 100 000	−10.7	300 000	500
$BaCl_2$	15.9	2.0	820 000	−10.2	260 000	350
$LaCl_3$	25.1	1.1	15 000 000	−11.9	770 000	470
$K_3Fe(CN)_6$	8.5	1.5	150 000	−9.2	190 000	400
CsI	5.0	2.5	300 000	−9.6	66 000	310
CsI[a]	11.8	28	730	−6.2	14 000	93
$K_4Fe(CN)_6$	12.9	0.84	12 000 000	−11.8	510 000	540
$K_4Fe(CN)_6$ [a]	32.2	18	2200	−6.8	58000	120

[a] Fit constrained to the experimentally determined ΔG_{Ads}.

All 13 Jones−Ray salts have been fit to the proposed model with good agreement, as shown in Figure 6. The fitted parameters and derived quantities are given in Table 1. The fitted parameter values are quite reasonable, with Gibbs free energies falling in the range −7 to −10 kcal/mol and interfacial widths of 6−9 Å for most of the salts, which agrees well with MD simulations.[32] The maximum surface coverage is 10^{10}−10^{11}/cm^2, which corresponds to one binding site per 20.000−300.000 water molecules or interanionic distances of 100−500 Å. The variations in the fit parameters can be explained by a proposed molecular mechanism behind the Jones−Ray effect presented in the discussion, though caution has to be taken in relying too much on the exact values obtained in this simple model.

4. Discussion

The newly discovered surface enhancement of anions in the outermost layer of the water surface at *molar* bulk concentrations seems fairly well understood. The surface tension increases, and the *total* ion concentration, as integrated over the entire surface region, is depleted with respect to the bulk as it must be, according to the Gibbs Adsorption Equation. The electrostatic interactions act to repel the ions from the interface, but the dipole−induced dipole interaction due to the polarizability of the ions will attract them to the surface, where the net electric field is largest due to the asymmetry of the interface. For weakly polarizable anions, the electrostatics dominate and the anions are repelled from the surface, thus behaving classically with a monotonic surface distribution. Highly polarizable anions, however, are enhanced in the outermost surface layer but depleted in the sublayer, where the cations, in turn, are enhanced, thus engendering a nonmonotonic surface distribution of both anions and cations.[41] The Gibbs free energies of adsorption at molar concentrations due to the polarizability of the anions are ca. −1 to −2.5 kcal/mol.[31,32,40,41] Cations are, in general, repelled from the surface, but new evidence reveals that the hydronium cation is also enhanced at the surface due to its lower coordination number.[49−51]

At *dilute* concentrations, the picture is different and not yet complete. Since the surface tension data exhibit a minimum at dilute concentrations, the total surface excess must be positive, and the ion concentrations integrated over the entire surface region are actually larger than the bulk value. This behavior is quite distinct from the high concentration adsorption, where the total surface excess is negative and enhancement in the outermost surface layer is compensated by depletion in the sublayer.

Our simple model for the surface tension incorporates a surface layer of thickness 6−9 Å in which the anions are enhanced with Gibbs free energies around −7 to −10 kcal/mol, above the bulk. The SHG experiments reported here and previously[39] show a strong adsorption of the anions to the water surface with Gibbs free energies of −6.2 ± 0.2 kcal/mol and −6.8 ± 0.3 kcal/mol for iodide and ferrocyanide, respectively. This is a much stronger binding than at high concentrations and reflective of a different molecular mechanism that governs the effect. As macroscopic measurements, the surface tension experiments are sensitive to the entire surface region. The SHG experiments measure a weighted average of the squared (since SHG is a coherent optical phenomena) anion concentration over the surface region, preferentially probing the outermost surface layer. It thus seems unlikely that the SHG experiments should have measured a lower bound of the surface energy. The discrepancy between the Gibbs free energies measured in the surface tension and SHG experiments could be due to Langmuir's correction or our perhaps oversimplified model of the surface tension data that is used to extract the energy.

The role of contamination as a possible origin of the Jones−Ray effect needs to be addressed. Possible contaminations could originate both from sample preparation, and thus be present in the bulk, and from surface adsorption of gas phase molecules from the atmosphere. Although trace contaminations offer an easy explanation, this would, however, not explain the consistency found between the various experiments and samples. One would expect the amount and type of contaminants to vary between experiments in a nonsystematic manner. Furthermore, when great care is taken to eliminate bulk contamination in sample preparation, many previous SHG and SFG experiments have successfully studied static liquid surfaces under a protective atmosphere for long times without observing a noticeable effect of contaminations.[45,46] This is particularly noteworthy for SFG experiments where most possible organic contaminations would show up directly in the CH-stretching region of the spectrum.

The mechanism underlying the strong surface adsorption of anions at dilute bulk concentrations, which seems to be a general feature of simple aqueous electrolytes, remains unclear. Molecular dynamics simulations are currently unable to simulate the dilute concentrations (∼1 mM), but recent continuum models have been able to reproduce the Jones−Ray effect.[25,26] These models postulate a small ambient surface layer of hydroxide that depends on the pH of the solution and a cutoff distance of closest approach for the other ions. In this case, the surface tension minimum occurs due either to the competition between the positive adsorption of hydroxide and the negative adsorption of the other ions[25] or to the positive adsorption of cations due to the negative charge of the hydroxide.[26] These continuum models, however, suffer from the description of the dispersion forces. They predict that this interaction will repel the ions from the surface, and anions more than cations. This is in strong contrast to the MD simulations and surface potential measurements, which show that anions approach closer to the surface than cations.

The SHG experiments have verified the Jones−Ray effect for iodide and ferrocyanide, both spherical anions. For the linear conjugated anions, azide[40] and thiocyanide,[41] no positive adsorption at dilute concentration was observed. This indicates that these anions do not bind to the surface at dilute concentrations or that something in the experimental technique (e.g., orientational effects) prevents the Jones−Ray effect from being observed. Jones and Ray observed a minimum in the surface tension for thiocyanide but did not examine azide. The surface tension minimum for thiocyanide, however, is the smallest and broadest of the 13 salts examined, and could possibly be completely removed by Langmuir's correction.

Furthermore, the SHG experiments on hydroiodic acid (HI) showed a much weaker Jones−Ray effect compared to sodium and potassium iodide.[50] This indicates that the surface adsorption at dilute concentrations is sensitive to the pH of the solution. If the Jones−Ray effect is due to an ambient surface layer of hydroxide, as the recent continuum models postulate, this would

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(49) Petersen, M. K.; Iyengar, S. S.; Day, T. J. F.; Voth, G. A. *J. Phys. Chem. B* **2004**, *108*, 14804−14806.
(50) Petersen, P. B.; Saykally, R. J. *J. Phys. Chem. B* **2005**, *109*, 7976−7980.
(51) Mucha, M.; Frigato, T.; Levering, L.; Allen, H. C.; Tobias, D. J.; Dang, L. X.; Jungwirth, P. *J. Phys. Chem. B* **2005**, *109*, 7617−7623.

indeed be the case. However, recent MD simulations and SFG experiments show that hydroxide, unlike hydronium, is repelled from the surface at molar bulk concentrations.[51] The low ambient surface coverage of hydroxide could, like the proposed strong anion binding, be due to a yet undetermined molecular mechanism occurring at dilute concentrations and would be unlikely to show up in an MD simulation.

It remains, then, to postulate the actual mechanism of the Jones−Ray effect. Suggestive evidence accumulated thus far includes the above pH dependence and a systematic increase of the free energies of adsorption and interfacial depths with cation charge (for NaCl, $MgCl_2$, and $LaCl_3$, Table 1). This suggests that the Jones−Ray effect may be induced by the *cations*, viz. that the cations are repelled from the interface by their image charges, accumulate below the surface, and generate a charge induced at the surface. The more polarizable anions adsorb to the outermost surface layer to compensate for the charge excess, since they are less strongly repelled or even attracted to the surface because of induced dipole effects. The stronger binding of the multiply charged ion pairs is then due to the increased electrostatic interaction, which also accounts for the lower surface coverage observed for multiply charged cations due to their increased mutual repulsion. Hydrated protons (hydronium) can compete with the cations at the interface, exhibiting a positive adsorption in the outermost surface layer, as described earlier. Hence, the Jones−Ray effect is reduced at low pH. If this proposed general mechanism is correct, a question remains regarding the surface potential of pure water, generally accepted to be small and positive.[52] If hydrated protons positively adsorb, one would instead expect a negative surface potential, recognizing, however, that the fractional surface coverage due to ions is very small ($>10^5$ waters per ion). Hence, dipole ordering effects could compete and dominate the effect of positive adsorption, yielding the observed small, positive surface potential.[52]

5. Conclusions

Using the surface specific technique of SHG, we have measured the surface enhancement of ferrocyanide at dilute concentrations, finding Langmuir adsorption behavior with a Gibbs free energy of −6.8 kcal/mol. This, along with previous measurements on iodide, confirms the controversial Jones−Ray effect with a direct method that is not affected by the Langmuir correction.

Furthermore, we have constructed a simple model that fits the surface tension data for the Jones−Ray salts at dilute concentrations. The model postulates a thin (6−9 Å) surface layer, wherein the concentration of the anions follows Langmuir isotherms. Qualitative agreement of the model with Jones and Ray's original surface tension data is found, although stronger Gibbs free energies of −7 to −10 kcal/mol are needed for quantitative agreement. The maximum surface coverage of the ions is low ($10^{10}-10^{11}/cm^2$), corresponding to one anion per 20.000−300.000 water molecules or interanionic distances of 100−500 Å. Finally, a general mechanism explaining the origin of the Jones−Ray effect is proposed.

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(52) Koczorowski, Z. *Bull. Pol. Acad. Sci., Chem.* **1997**, *45*, 225−242.