The Entropy of Formation of the Liquid Gallium−Water Interface

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The entropy of formation of the interface, $S*$, between liquid gallium and aqueous solutions of the nonspecifically adsorbed Na_2SO_4 was calculated from interfacial tension measurements carried out by a wholly computerized sessile drop technique. The advantages of nonisothermal conditions over isothermal conditions for a direct estimate of $S*$ are pointed out on the basis of thermodynamic arguments. The entropy of formation of the inner layer at the gallium|water interface, as estimated at 36 °C upon correction for the small diffuse-layer contribution, increases monotonically with an increase in the charge density σ_M on the metal over the accessible charge range and is about 1 order of magnitude greater than that at the mercury|water interface at 25 °C. This difference in behavior is explained on the basis of the notable difference in hydrophilicity between the two metals.

Introduction

The temperature dependence of the parameters of electrified interfaces may provide useful information on their molecular structure. The thermodynamic quantity that measures the dependence of the interfacial tension γ of a metal|solution interface upon temperature T at constant pressure and composition is the entropy surface excess, Γ_s, which can be estimated on the basis of the electrocapillary equation. A more structure-sensitive quantity is the entropy of formation of the interface, $S*$, which measures the difference in entropy of the components when they are present at the interface and in the bulk of the adjoining phases. This quantity was first introduced by Harrison et al.[1] In defining $S*$, these authors disregarded the contribution from metal electrons.[2] Unfortunately, $S*$ is not a thermodynamic quantity, since bulk partial molar entropies of single ions and of electrons enter in its calculation. A number of extrathermodynamic assumptions are therefore required.

Absolute values of $S*$ require interfacial tension measurements, which can only be carried out on liquid electrodes, either by the capillary electrometer or by drop shape techniques. Curves of $S*$ against the charge density σ_M on the metal for the Hg|(aqueous NaF) interface were reported by Harrison et al.[1] The entropy of formation of the inner layer, $S*_{M-d}$, was obtained from $S*$ by correcting for the diffuse-layer contribution on the basis of the Gouy−Chapman theory. The resulting curves of $S*_{M-d}$ versus σ_M attain a maximum value of ≈ 0.15 mJ K^{-1} m^{-2} in the proximity of $\sigma_M = -50$ mC m^{-2}. A further approximate correction for the contribution from metal electrons increases the maximum by ≈ 0.03 mJ K^{-1} m^{-2}, shifting it to ≈ -90 mC m^{-2}.[2] On solid electrodes, only the differential capacity C (or the charge density σ_M) and the potential of zero charge (pzc) are experimentally accessible, as well as their temperature dependence. Consequently, only relative values of $S*$ are available. Usually, $S*$ is referred to its value at $\sigma_M = 0$, $S*_{\sigma=0}$, taken conventionally equal to zero. Plots of $(S*-S*_{\sigma=0})$

versus σ_M were reported on Au(210),[3] Au(100),[4] Ag(111),[5] and Ag(100).[6] On Au(210), Ag(111), and Ag(100) these plots show a flat maximum at a relatively high negative charge, and then a decrease with an increase in σ_M. A monotonic decrease of $(S*-S*_{\sigma=0})$ with increasing σ_M is observed on Au(100). The same behavior is shown by the plots of $(S*_{M-d}-S*_{\sigma=0})$ versus σ_M on Ag(111) and Ag(100), as obtained from the corresponding $(S*-S*_{\sigma=0})$ versus σ_M plots upon subtracting the entropy of formation of the diffuse layer. The temperature coefficient of the potential difference across the interface, $\Delta\phi^{M-S}$, at the pzc was found to be positive on all of the above single-crystal faces, thus showing the same qualitative behavior as on Hg.[7] The temperature coefficients of the interfacial parameters of the Au-(111)|water interface were found to be strongly dependent on the choice of the potential-time programs adopted in the experiments,[4] whereas irreproducibilities due to the interference of hydrogen evolution prevented a reliable estimate of $\Delta\phi^{M-S}$ at the pzc on Ag(110).[6]

In nature only two metals are liquid in the proximity of room temperature, namely mercury and gallium, the latter melting at 31 °C. Hence gallium is the only pure metal, besides mercury, which may allow interfacial tension measurements at different temperatures, yielding absolute values of $S*$ for the Ga|water interface. Mercury and gallium differ notably in one of the main distinguishing figures of metals, namely hydrophilicity: mercury is hydrophobic, whereas gallium is strongly hydrophilic.[8] A comparison between $S*$ versus σ_M curves on Hg and Ga seems, therefore, particularly attractive. From a practical point of view, the use of liquid electrodes avoids a number of complications that are encountered with solid metals (surface reconstruction, stresses, surface roughness, etc.). Only very few measurements of the temperature dependence of interfacial parameters of Ga are available in the literature. Timofeevicheva and Pugachevich[9] measured the temperature dependence of the surface tension γ of Ga at the interface with its own saturated vapor by the maximum drop pressure method, whereas Nizhenko et al.[10] and Karashaev et al.[11] carried out analogous measurements by drop shape techniques. In particular, the latter authors obtained a constant temperature coefficient $d\gamma/dT = -0.1$ mJ K^{-1} m^{-2}

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for the Ga|(Ga vapor) interface over the temperature range from 120 to 360 °C, using gallium of 99.9998% purity.[11] Grigor'ev et al.[12] reported curves of the differential capacity C against the applied potential E for the interface between Ga and aqueous 0.5 M Na_2SO_4 + 0.005 M H_2SO_4 at three different temperatures. An increase in *C* with temperature was observed in the proximity of −1.0 V/SCE. No data analysis was attempted, in view of the conclusion by Frumkin and Grigor'ev[13] that the Gouy−Chapman theory does not apply to a Ga electrode. Szabó and Mika[14] measured the temperature dependence of the differential capacity *C* at the Ga|(aqueous $HClO_4$) interface and found that *C* varies slightly with temperature at constant σ_M.

In contrast with the early results of the Russian school,[13] accurate chronocoulometric measurements carried out in this laboratory have shown that the Gouy−Chapman theory is satisfied at the interfaces between Ga and aqueous $NaClO_4$[15] or aqueous Na_2SO_4.[16] Moreover, both these salts are nonspecifically adsorbed on Ga. This work reports an investigation of the temperature dependence of the interfacial tension at the Ga|-(aqueous Na_2SO_4) interface. Nonisothermal conditions were adopted, in that an external saturated calomel electrode (SCE) maintained at constant temperature was used as a reference. The advantages of these nonisothermal conditions over isothermal conditions for the estimate of the entropy of formation of the interface, *S**, will be pointed out. *S** turns out to be about 1 order of magnitude greater on Ga|Na_2SO_4 than on Hg|NaF.

Thermodynamic Analysis

Consider the interface, M|solution (w,+,−), between a pure metal M and a solution of a cation (+) and an anion (−) in water (w). The entropy of formation of this interface is defined by:

$$S^* = s_{ex} - \Gamma_M s_M - \Gamma_e s_e - \Gamma_w s_w - \Gamma_+ s_+ - \Gamma_- s_- \quad (1)$$

where s_{ex} is the entropy of the real system minus that of the ideal Gibbs system per unit surface of the interface; Γ_i and s_i, with i = M, e, w, +, −, are the absolute surface excesses of the various constituents and their partial molal entropies in the bulk of the respective phases. As distinct from the definition by Harrison et al.,[1] *S** also includes the contribution $\Gamma_e s_e$ from metal electrons, which must be considered on the same footing as the other charged constituents of the interface.[2]

If the ideally polarized electrode under study and the reference electrode are kept at the same temperature (isothermal conditions), *S** is obtained from electrocapillary measurements on the basis of the equation:

$$S^* = -\left(\frac{\partial \gamma}{\partial T}\right)_{E_+,m} + \frac{\sigma_M}{F}\left[s_e + s_+ - \left(\frac{\partial K}{\partial T}\right)_m\right] \quad (2)$$

This equation differs from eq 20 of ref 1 by the presence of the contribution from metal electrons, that is, $-\Gamma_e s_e = \sigma_M s_e/F$. *K* is a temperature-dependent parameter determined by the type of reference electrode employed, which is considered to be reversible to the cation of the solution under study. The subscript *m* denotes a constant molality. In practice, for temperature changes that are not too large, the requirement of constant molality can be regarded as fulfilled to a sufficient degree of accuracy by keeping the molarity constant. While $\partial K/\partial T$ is thermodynamically accessible, the estimates of s_e and s_+ (or s_- if an electrode reversible to the anion is adopted) require extrathermodynamic assumptions. The contribution of these entropic terms to *S**, which is clearly linear in σ_M, is usually non negligible[1,2] and introduces a certain degree of uncertainty

in the estimate of *S**. Thus, in the presence of a maximum in the $-(\partial \gamma/\partial T)_{E+,m}$ versus σ_M plot, it may shift the maximum appreciably in a direction that depends on the sign of $(s_e + s_+)$. Similar conclusions apply to the determination of $(S^* - S^*_{\sigma = 0})$ from differential capacity measurements under isothermal conditions. Thus, upon introducing the contribution from metal electrons in the expression for *S** in eq 13 of ref 1 or eq 16 of ref 17, we get:

$$S^* = S^*_{\sigma_M = 0} - \int_0^{\sigma_M}\left[\int_0^{\sigma_M}\left(\frac{\partial(1/C)}{\partial T}\right)_{\sigma_M,m} d\sigma_M + \frac{\partial E_+}{\partial T}\right]d\sigma_M + \frac{\sigma_M}{F}\left[s_e + s_+ - \left(\frac{\partial K}{\partial T}\right)_m\right]$$

Thus, no matter whether electrocapillary or differential capacity measurements are carried out, the estimate of *S** or $(S^* - S^*_{\sigma = 0})$ requires a reasonable guess as to the extrathermodynamic quantities s_e and s_+ (or s_-).

In this respect, working under nonisothermal conditions appears more advantageous. Consider the cell, Cu|M|solution (w,+,−)||Me$^+$|Me|Cu′, in which the ideally polarized electrode under study is kept at a variable temperature *T*, while the reference electrode of constant composition, Me|Me$^+$, is kept at a fixed temperature T_0. Me is generally different from M, and the two copper leads, Cu and Cu′, have different electrical states. The temperature gradient is distributed along a salt bridge containing the same solution as in the polarized electrode. If the temperature range explored is narrow, as in the present case, the potential difference arising from this temperature gradient can be roughly estimated via the approximate equation $E_{sb} = (RT/F) \ln[\Lambda(T)/\Lambda(T_0)]$, where Λ is the equivalent conductance of the electrolyte.[1,18] The Λ value for Na_2SO_4 varies by a few percent over the temperature range from 32 to 45 °C. Consequently, E_{sb} amounts to a few mV, and can be safely neglected. With this approximation, any change ΔE in the potential applied between the two leads is transferred exclusively to the M|solution (w,+,−) interface. Application of the Gibbs adsorption equation to this interface yields:

$$-d\gamma = s_{ex}dT + \Gamma_M d\mu_M + \Gamma_e d\tilde{\mu}_e + \Gamma_w d\mu_w + \Gamma_+ d\tilde{\mu}_+ + \Gamma_- d\tilde{\mu}_- \quad (3)$$

If we split the various electrochemical potentials formally into their chemical and electrical parts and we then differentiate, we obtain:

$$d\mu_M = -s_M dT; \ d\tilde{\mu}_e = -s_e dT - Fd\phi^M \quad (4)$$

$$d\tilde{\mu}_+ = -s_+ dT + RTd \ln a_+ + Fd\phi^s$$
$$\text{with: } s_+ = s^0_+ - R \ln a_+ \quad (5)$$

$$d\tilde{\mu}_- = -s_- dT + RTd\ln a_- - 2Fd\phi^s$$
$$\text{with: } s_- = s^0_- - R\ln a_- \quad (6)$$

Here a_+ and a_- are the activities of anion and cation, whereas s^0_+ and s^0_- are their standard partial molal entropies; ϕ^M and ϕ^S are the electrical potentials of the metal and solution phases. Eqns 5 and 6 apply to a monovalent cation such as Na$^+$ and a divalent anion such as SO_4^{2-}, but the final conclusions hold for any electrolyte composed of only two ions. The differential, $d\mu_w$, of the chemical potential of water is expressed via the Gibbs−Duhem equation for the bulk aqueous phase:

$$d\mu_w = -\frac{x_\pm}{x_w}d\mu_\pm - \frac{s_{sol}}{x_w}dT = -2\frac{x_\pm}{x_w}d\tilde{\mu}_+ - \frac{x_\pm}{x_w}d\tilde{\mu}_- - s_wdT -$$
$$2\frac{x_\pm}{x_w}s_+dT - \frac{x_\pm}{x_w}s_-dT \quad (7)$$

where $\mu_\pm = (2\tilde{\mu}_+ + \tilde{\mu}_-)$ is the chemical potential of the electrolyte, $s_{sol} = [x_ws_w + x_\pm(2s_++s_-)]$ is the mean molal entropy of the solution, and x_w, $x_\pm$ are the mole fractions of water and electrolyte. Upon substituting the differentials of the various chemical and electrochemical potentials from eqns. 4−7 into eq 3, after straightforward calculations we get:

$$-d\gamma = S^*dT + \sigma_MdE + \Gamma_{+,w}RTd\ln a_+ + \Gamma_{-,w}RTd\ln a_- \quad (8)$$

where $dE = d(\phi^M - \phi^S)$ is the differential of the applied potential, while $\Gamma_{+,w} \equiv \Gamma_+ - (2x_\pm/x_w)\Gamma_w$ and $\Gamma_{-,w} \equiv \Gamma_- - (x_\pm/x_w)\Gamma_w$ are the relative surface excesses of cation and anion. In deriving eq 8 use has been made of the electroneutrality condition for the entire interface:

$$\sigma_M = -F\Gamma_e = 2F\Gamma_- - F\Gamma_+ = 2F\Gamma_{-,w} - F\Gamma_{+,w} \quad (9)$$

The form of eq 8 is symmetrical with respect to cation and anion, as expected in view of the fact that our cell makes use of a reference electrode of constant composition. Moreover, eq 8 does not contain the entropic term for the reference electrode, dK/dT, since the latter is kept at a constant temperature T_0. Making use of eq 9, eq 8 can also be written in the alternative form:

$$-d\gamma = S^*dT + \sigma_M[dE - (RT/F)d\ln a_+] + 3RT\Gamma_{-,w}d\ln a_\pm \quad (10)$$

where $a_\pm \equiv (a_+^2a_-)^{1/3}$ is the mean ionic activity of the 1,2-valent electrolyte. The only extra-thermodynamic differential in eq 10 is $d\ln a_+$. Setting the activity a_+ of the cation equal to the mean ionic activity $a_\pm$ of the electrolyte amounts to postulating the validity of the Debye−Hückel theory over the concentration range explored. With this assumption, from eq 10 it follows that:

$$S^* = -\left(\frac{\partial\gamma}{\partial T}\right)_{E,m} - \frac{\bar{L}_\pm}{3FT}(\sigma_M - 3\Gamma_{-,w}) \quad (11)$$

where $\bar{L}_\pm = -3RT^2(\partial\ln f_\pm/\partial T)_m$ is the relative partial molal heat content of the 1,2-valent electrolyte and $f_\pm$ is its mean ionic activity coefficient. From eq 11 it is apparent that the entropy of formation of the interface can be directly obtained from electrocapillary measurements under nonisothermal conditions. This equation implies the reasonable assumption of a negligible thermodiffusion potential, but does not require any guesses as to the partial entropies of single ions and electrons.

Within the limits in which the thermodiffusion potential can be disregarded and the activity of the single cation can be equated to the corresponding mean ionic activity, the entropy S^* of formation of the interface obtained via eq 11 under nonisothermal conditions can be regarded as a pure thermodynamic quantity, namely a quantity that is experimentally accessible without recourse to extrathermodynamic assumptions. As such, S^* does not depend on the position of the dividing surface in the ideal Gibbs system, even though the single absolute surface excesses in eq 1 do. Analogous conclusions were drawn by Defay et al. for a quantity defined as in eq 1 and relative to a nonelectrified interface populated exclusively

by neutral components (eq 20.67 of ref 19). Evidently, in this case, no reference electrode is required to define the whole system, and consequently the question of isothermal or nonisothermal conditions does not arise.

The Entropy of Formation of the Diffuse Layer. The entropy of formation of the diffuse layer, S^*_{d-s}, can be estimated within the range of validity of the Gouy−Chapman theory[1,20] by using the equation:

$$S^*_{d-S} = -\int_0^{\sigma_M}\left(\frac{\partial\phi_d}{\partial T}\right)_{m,\sigma_M}d\sigma_M \quad (12)$$

where ϕ_d is the potential difference across the diffuse layer. For a 1,2-valent electrolyte at negative charge densities, the Gouy−Chapman expression of ϕ_d as a function of σ_M takes the form:[16,21]

$$\phi_d = \frac{RT}{F}\ln x; x = -2Q^{1/2}\cos\left(\frac{\theta + 4\pi}{3}\right); Q = 1 + \frac{\sigma_M^2}{3A^2};$$
$$\theta = \arccos(Q^{-3/2}) \quad (13)$$

where $A\equiv(2RT\epsilon_r\epsilon_0c)^{1/2}$, ϵ_r is the relative dielectric constant of bulk water and c is the electrolyte concentration. Under the quite reasonable assumption that the change of ϵ with T is negligible over the temperature range investigated, differentiation of ϕ_d with respect to T at constant σ_M and $c\approx m$ yields:

$$\left(\frac{\partial\phi_d}{\partial T}\right)_{\sigma_M,c} = \frac{R}{F}\ln x + \frac{RT\sigma_M^2}{3FxA^2T}\left[\frac{1}{Q^{1/2}}\cos\left(\frac{\theta + 4\pi}{3}\right) - \frac{1}{Q^2(1 - Q^{-3})^{1/2}}\sin\left(\frac{\theta + 4\pi}{3}\right)\right] \quad (14)$$

S^*_{d-S} for $\sigma_M < 0$ is obtained by numerical integration of eq 14 over σ_M. In practice, the resulting curve of S^*_{d-S} versus σ_M is almost coincident with that obtained from the analytical expression for a 1,1-valent electrolyte of concentration $2c$, obtained once again from eq 12 using the Gouy−Chapman theory and assuming a temperature independent ϵ:

$$S^*_{d-S} = -\frac{2R}{F}\left[\sigma_M\operatorname{arcsinh}\left(\frac{\sigma_M}{2A}\right) + 3A\left(1 - \sqrt{\frac{\sigma_M^2}{4A^2} + 1}\right)\right]$$

Taking into account that the relative surface excess $\Gamma_{+,w}$ of the cation of a 1,2-valent electrolyte is expressed by the equation:[21]

$$F\Gamma_{+,w} = A[(1 + 2/x)^{1/2} - 3^{1/2}]$$

from eqs 9 and 11 we obtain the following expression of S^*:

$$S^* = -(\partial\gamma/\partial T)_{E,m} + (\bar{L}_\pm/6FT)\{\sigma_M + 3A[(1 + 2/x)^{1/2} - 3^{1/2}]\} \quad (15)$$

Experimental Section

Merck suprapur Na_2SO_4 and H_2SO_4 were used without further purification. All solutions were prepared from distilled water treated with the milli-Q water system. Johnson Matthey & C. gallium of 99.9999% purity was employed.

Interfacial tension measurements were carried out by the sessile drop method using the computerized system and the procedure described in refs 22 and 23, with a few slight modifications required by the use of Ga instead of Hg. Thus,
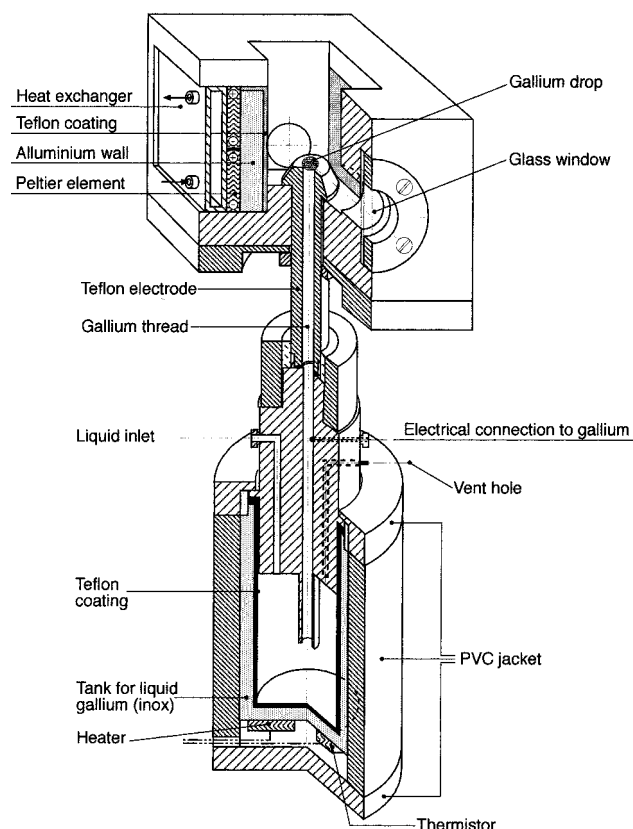
S* of Liquid Gallium−Water Interface

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Figure 1. Gallium sessile drop electrode. The upper cube is the electrochemical cell, while the lower cylinder is the gallium reservoir.

Figure 2. Plots of γ versus E for 0.1 M (*a*) and 0.01 M sulfate (*b*) on Ga at 32, 36, 40, and 44 °C. The right-hand scale refers to set *a*, the left-hand one to set *b*. Within each set the lower curves correspond to the higher temperatures.

Figure 3. The dashed curve is a plot of $-(\partial\gamma/\partial T)_{E,c}$ versus σ_M for 0.01 M sulfate on Ga at 36 °C. The solid curves are plots of the entropy of formation of the inner layer, S^*_{M-d}, against σ_M at the Ga|(aqueous Na_2SO_4) interface at 36 °C and at the Hg|(aqueous NaF) interface at 25 °C.[1] The error bar in the curve relative to Ga accounts for the propagation of errors in the differentiation with respect to T of the γ versus E curves fitted to a third-degree polynomial.

the Ga sessile drop was extruded from a Teflon tube, rather than from a glass one, since gallium tends to stick to glass walls. Moreover, the inox reservoir for liquid gallium, shown in Figure 1, was coated with a Teflon layer 0.3 mm thick to ensure good thermal exchange with the heater; the reservoir was kept at a constant temperature of 36 °C. The cubic aluminum cell was also coated with a Teflon layer 0.3 mm thick and heated with Peltier elements covering two sides of the cubic cell; the other four sides were thermally insulated with Teflon walls 10 mm thick. Temperature control of the cell was accomplished as decribed in ref 23. The gallium drop was extruded by injecting water on top of the pool of liquid gallium inside the reservoir. To obtain accurate results the top of the tube on which the sessile drop stands must be flat and the edge of the orifice must be extremely sharp, without curls. Great care was required to fulfill this requirement using a soft material such as Teflon. Good results were obtained by lathe machining, moving the cutting tool first inside the hollow cylinder parallel to its axis and then, with no pause, perpendicular to it. No further polishing was attempted, since it would unavoidably leave some curls on the sharp edge of the orifice. The quality of the top of the Teflon tube was checked visually with a microscope. The reference electrode consisted of a saturated calomel electrode (SCE), which was kept at a constant temperature of 36 °C and was connected to the electrochemical cell via a salt bridge containing the same solution as in the cell. The error of the interfacial tension measurements amounts to 0.5−0.8 mJ m^{-2}; it is largely systematic within each γ versus E curve in Figure 2, whereas it is random in passing from one curve to another.

The double-layer region at a gallium|water interface shifts toward less negative potentials and becomes narrower with a progressive decrease in pH. In fact, a decrease in pH shifts both hydrogen discharge and Ga oxidation toward less negative
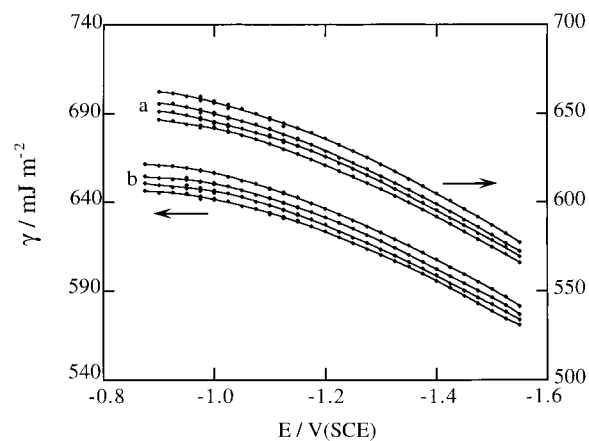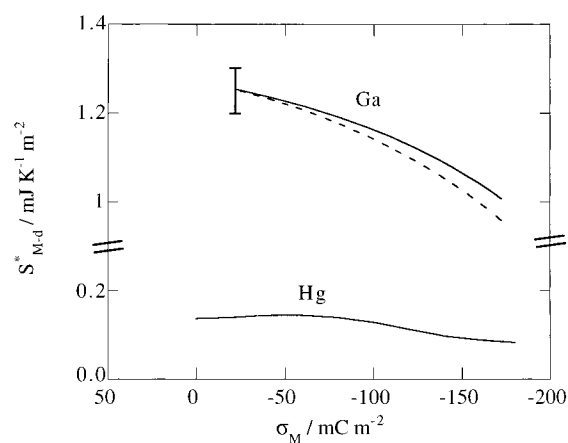
potentials. The potential region undisturbed by faradaic currents ranges from −1.55 to −1.10 V in a pH 7.6 neutral Na_2SO_4 solution, from −1.15 to −0.98 V in a sulfate solution acidified with H_2SO_4 at pH 3, and from −1.025 to −0.90 V at pH 2.2. To cover the largest possible potential range, interfacial tension measurements at 32, 36, 40, and 44 °C were carried out in neutral Na_2SO_4 solutions and in solutions of the same sulfate concentration acidified at pH 3 and 2.2. Solutions of overall sulfate concentration equal to 0.01, 0.0316, and 0.1M were examined.

Results

Figure 2 shows plots of γ versus E at four different temperatures and at two different sulfate concentrations. Each curve results from the combination of measurements carried out at pH 7.6, 3, and 2.2. The sets of γ versus E plots relative to the three different sulfate concentrations are very similar, thus pointing to a small contribution from the entropy of formation of the diffuse layer. The dashed curve in Figure 3 is a plot of $-(\partial\gamma/\partial T)_{E,c}$ versus σ_M for c = 0.01 M at 36 °C, as obtained from the plots in Figure 1 by numerical differentiation with respect to T. The charge density σ_M reported on the abscissas

was obtained by numerical differential of the relative γ versus E plot. To obtain the entropy of formation of the interface, S^*, as a function of σ_M from $-(\partial\gamma/\partial T)_{E,c}$, this quantity must be corrected for the temperature dependence of the mean ionic activity coefficient of the electrolyte by using eq 15. The $\bar{L}_\pm$ value for 0.01 M Na_2SO_4 at 25 °C amounts to 732 J mol^{-1}.[24] Hence, the multiplying factor ($\bar{L}_\pm/6FT$) in eq 15 is $\approx 4 \times 10^{-6}$ J C^{-1} K^{-1}. In practice, this makes the second term in eq 11 entirely negligible with respect to the first over the whole charge range.

By definition, the entropy of formation of the inner layer, S^*_{M-d}, is the difference between S^* and the entropy of formation of the diffuse layer, S^*_{d-S}. The latter quantity was calculated as a function of σ_M by numerical integration of eq 14 over σ_M, in accordance with eq 12. The solid curve in Figure 3 is a plot of $S^*_{M-d} = (S^* - S^*_{d-S})$ versus σ_M. It is evident that the contribution from the diffuse layer to S^* is small with respect to that from the inner layer. For comparison, the plot of S^*_{M-d} versus σ_M for the Hg|(aqueous 0.1M NaF) interface at 25 °C is also shown in Figure 3.[1] While the S^*_{M-d} versus σ_M plot for Hg exhibits a rounded maximum in the proximity of -5 μC cm^{-2}, that for Ga increases with an increase of σ_M over the whole experimentally accessible charge range. Moreover, the S^*_{M-d} values on Ga are almost 1 order of magnitude greater than those on Hg. It might be argued that the S^*_{M-2} values estimated by Harrison et al.[1] on Hg are not corrected for the contribution, $s_e\sigma_M/F$, from metal electrons. However, the notable difference in S^*_{M-2} values between Ga and Hg is also present in the proximity of $\sigma_M = 0$, where the above contribution vanishes. Hence, this difference is real.

Discussion

Taking into account the definition of eq 1 for the entropy of formation S^* of the interface as well as the significance of the absolute surface excess of entropy, s_{ex}, it immediately follows that the entropy of formation S^*_{M-d} of the inner layer, obtained upon correcting S^* for the diffuse layer contribution, is given by:

$$S^*_{M-d} = \Gamma_M \Delta s_M + \Gamma_e \Delta s_e + \Gamma_w \Delta s_w \qquad (16)$$

where the various Δs's denote differences in the partial molal entropy of the given constituent between the inner layer and the corresponding bulk phase. Equation 16 differs from eq 35 in ref 1 by the presence of the term relative of metal electrons. At any rate, in the proximity of the potential of zero charge, this term is expected to be negligible. A comparison between the S^*_{M-d} values for Ga in the proximity of zero charge ≈ 1.2 mJ K^{-1} m^{-2}, and the entropy of formation of the Ga|(Ga vapor) interface, $-d\gamma/dT = 0.1$ mJ K^{-1} m^{-2}, strongly suggests that the major contribution to S^*_{M-d} for the Ga|water interface stems from the interfacial water molecules.[11] An analogous conclusion was drawn by Harrison et al.[1] for the Hg|water interface.

The entropy of formation S^*_{M-2} on Ga being about 1 order of magnitude greater than on Hg can be justified by considering the different hydrophilicity of the two metals. Thus, while Hg is the most hydrophobic metal, Ga is one of the most hydrophilic.[8] Stated differently, Ga interacts with the oxygen atom of the adsorbed water molecules much more strongly than does Hg. Therefore, with respect to hydration effects, Hg and Ga behave like a nonpolar molecule and an ion in aqueous solution, respectively. Near nonpolar molecules or nonpolar groups, there is a reinforcement of the hydrogen bonds of water which, on a time average, is expected to extend over a few

molecular diameters. This shell of structured water has been ascribed to icelike clusters,[25] to clathrate hydrates,[26] or to the solute molecules acting as fifth-coordination neighbors to the tetrahydrogen-bonded water molecules.[27] Whatever the nature of this shell, it is generally accepted that the hydration does not stem from strong solute−solvent interactions, but rather from a strengthening of the solvent−solvent interactions brought about by the nonpolar molecule. This is the reason why this hydration is often termed hydrophobic. This effect might be envisaged as an increase in the average life of the short-range tetrahedral configurations that are also present in pure water at room temperature, due to the reluctance of the nonpolar molecule to get out of the way.[25,28] The situation of water structuring around ions is quite different, in view of the strong electrostatic solute−solvent interactions. The resulting hydration has been, therefore, termed hydrophilic.[29] Hydrophilic hydration is commonly divided in two main types. Primary hydration refers to rather firmly oriented water molecules, probably four in number for most of the monatomic and monovalent ions. Secondary hydration does not depend on specific ion−water interactions, and is usually accounted for by classical electrostatics upon treating water as a continuous medium.

From the temperature dependence of solubility it was possible to estimate the entropy lost in the process of solution of both nonpolar gas molecules and ions in water. A particularly illuminating example of these entropy data was provided by Frank and Evans.[25] The standard entropy loss per mole of potassium chloride, whose constituent ions both have the argon structure, is 217 J K^{-1} mol^{-1}, whereas the corresponding quantity for two gram-atoms of argon is 253 J K^{-1} mol^{-1}. Therefore, the presence of ionic charges reduces the entropy loss, that is, it increases disorder in the water. To justify this behavior, Frank and Evans made a rough estimate of the contributions to the entropy of solution in water from primary and secondary hydration, as well as from the reduction of the free volume when the solute molecule enters the solution. Upon subtracting the sum of these three entropy losses from the experimental entropies of solution, a positive remainder was found for the majority of inorganic ions, with the only exceptions being the small fluoride and lithium ions. This was called structure-breaking entropy by Frank and Evans.[25] This structural entropy term corresponds to an appreciable disorder, which increases with an increase in the ion size. Thus, the structure-breaking entropy increases from $+42.7$ to $+74.9$ J K^{-1} mol^{-1} in passing from Cl$^-$ to I$^-$, and from $+16.7$ to $+65.7$ J K^{-1} mol^{-1} in passing from Na$^+$ to Cs$^+$. This entropy gain is explained by the incompatibility of the structure imposed by the strong electric field of an ion on its primary hydration sheath with the structure of ordinary water. Thus, a highly disordered, structure-broken region is envisaged outside the primary solvation sheath, in which the orienting influence of the ion becomes of the same order of magnitude as the normal structural influence of the neighboring water molecules.[25,30] No such an incompatibility exists between the icelike structure around nonpolar molecules and the structure of ordinary water.

For comparison with a Ga electrode, to be regarded as a macro-cation, the structure-breaking entropy of I$^-$, 75 J K^{-1} mol^{-1}, can be expressed in mJ K^{-1} m^{-2} by dividing it by the surface area of a gram-ion of I$^-$ ions, $4\pi r^2 N_{av}$, where $r = 2.2$ Å is the radius of I$^-$. The resulting value, 0.21 mJ K^{-1} m^{-2}, is about five times smaller than the difference, ≈ 1.1 mJ K^{-1} m^{-2}, between the entropies of formation, S^*_{M-d}, of the inner layer on Ga and on Hg in the proximity of zero charge. Naturally, the comparison between iodide ion and Ga, regarded as a macro-

cation, is quite crude, since the electric fields created by a metal electrode and by an ion are quite different. Thus, the surface electron density at Hg can only be varied between about −0.12 and +0.18 electrons/atom by varying the applied potential over the accessible range.[31] Moreover, the ion-H_2O quadrupole interaction has a different sign at anions and cations.[32] At any rate, since a certain increase in structure-breaking entropy is to be expected with an increase in radius from that of I$^-$ to the comparatively infinite radius of a Ga dropping electrode, it is reasonable to ascribe the difference in S^*_{M-d} between Ga and Hg primarily to the notable difference in their degree of hydrophilicity. Thus, the primary hydration sheath adjacent to the Ga surface, with the oxygens of the practically "frozen" water molecules directed toward the metal, is expected to be followed by a "thawed," or "depolymerized," sheath of disordered water, as compared with ordinary water. Conversely, the hydrophobic Hg surface may allow preformed water aggregates (icebergs in the picturesque words of Frank and Evans) to find their way to this surface, with a resulting stabilization and, possibly, an increase in their average size. The pratically infinite radius of curvature of a Hg electrode, as compared with that of an ion, also decreases the frequency with which these aggregates escape from the electrode surface. Since the structure of these icebergs is analogous to that of ordinary water, the thawed region, and the resulting structure-breaking entropy, are expected to be much less on Hg than on Ga. It should be noted that the concept of hydrophilicity is a relative concept. In this respect, mercury can be regarded equally well as the most hydrophobic metal or the least hydrophilic one. The hydrophilicity of a metal reflects the extent by which the structured metal/(water dipole) coplane opposes overlapping with the solvation co-sphere of a given ion.[31] Thus, for instance, sulfate[16] and perchlorate ions[15] are nonspecifically adsorbed on Ga, whereas they are appreciably adsorbed on mercury.[33,34] Hydrophilicity also reflects the extent by which amphiphilic molecules tend to turn their hydrophilic portion toward the metal upon adsorption. Thus, upon self-assembling, phospholipid monolayers turn their hydrophobic hydrocarbon tails toward Hg,[35] whereas phospholipid bilayers turn their hydrophilic polar heads toward freshly cut Ag,[36] whose hydrophilicity is comparable with that of Ga.

The absence of an S^*_{M-d} maximum on Ga, at least at negative charges, can be justified on the basis of the above considerations. If an increasing orientation of the water molecules in direct contact with the Ga surface with their negative end toward the electrode causes an increase, rather than a decrease, in S^*_{M-d} due to an increase in the thawed sheath of disordered water, then the maximum entropy will be reached at the minimum charge density σ_M at which the water molecules in direct contact with the Ga surface attain an almost full alignment along the direction of the external electric field: this charge density is expected to be positive. Conversely, on Hg a maximum entropy has been predicted[37] at a negative charge, where the water dipoles in direct contact with the electrode have a more horizontal orientation.

According to Trasatti,[38] metal hydrophilicity increases in the order Hg < Au < Ag < Ga. Hence, a parallel increase in the entropy of formation of the inner layer at these metals should be expected. Unfortunately, there is no way to determine absolute values of S^*_{M-d} at solid metals. Only the potential dependence of S^*_{M-d} on Au and Ag relative to its value at the potential of zero charge is available.[3−6]

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