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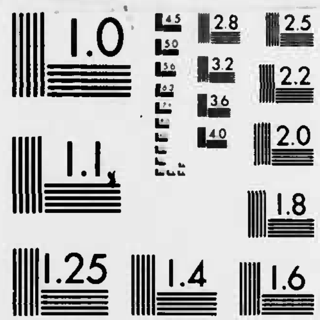

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A Method For Evaluating The Surface Concentrations of Two Like-Charged Ions Simultaneously Adsorbed At An Electrode-Solution Interface

by

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A METHOD FOR EVALUATING THE SURFACE CONCENTRATIONS OF TWO LIKE-CHARGED IONS SIMULTANEOUSLY ADSORBED AT AN ELECTRODE-SOLUTION INTERFACE

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A recent preliminary report by Gonzales and co-workers highlights the experimental difficulties in determining the amounts of specific adsorption of two types of ions simultaneously present at a mercury-aqueous interface. The authors note that the elegant analysis of Lakshmanan and Rangarajan requires such a large amount of data that the method has scarcely ever been employed. There are additional difficulties with this analysis when employed at solid electrode surfaces. The Rangarajan approach involves the determination of overall surface excesses from the ionic strength dependence of the interfacial tension at a constant electrode potential or charge. However, accurate absolute, or even relative, values of the interfacial tension at different ionic strengths are largely inaccessible at solid surfaces. Thus an absolute value of the electrode charge, q^m, is required to evaluate even relative values of the surface tension, γ_{rel}, by doubly integrating capacitance-potential curves. Although approximate values of the potential of zero charge (p.z.c.), and hence q^m, can be obtained for some single crystal surfaces from capacitance-potential curves in dilute nonspecifically adsorbing electrolytes,[3] these quantities are difficult to determine for polycrystalline surfaces. Furthermore, any errors in the resulting interfacial tension values will likely depend upon the ionic strength, thereby yielding unknown systematic errors in the derived surface excesses. Values of q^m are also required to estimate specifically adsorbed concentrations from the surface excesses by using diffuse-layer theory.

Cont'd

These difficulties severely restrict the applicability of Rangarajan's method at solid surfaces. (Similar factors also make the Grahame-Soderberg analysis for single electrolytes[4] unsuitable at polycrystalline solid surfaces, despite statements to the contrary.[5]) Additionally, a knowledge of at least relative ionic activities in electrolyte mixtures over a range of ionic strengths is necessary. ~~Clearly~~ it is ~~would be~~ desirable to find a method that could readily be applied at polycrystalline solid, as well as liquid, electrodes.

~~In~~ this reports ~~communication we wish to~~ outline such an analysis for determining the simultaneous adsorption of like-charged ions, based on a simple extension of the well-known "Hurwitz-Parsons" approach.[6,7] These authors demonstrated independently that the amount of specific adsorption of, for example, an anion X^- can be assessed from differential capacitance-potential data for a series of mixed electrolytes containing varying proportions of the salts BX and BY at a constant total ionic strength, where Y^- is an anion that is not specifically adsorbed. The electrocapillary equation can be written in terms of salt chemical potentials[8]

$$-d\gamma = \sigma_m dE^+ + \Gamma_X \, d\mu_{BX} + \Gamma_Y \, d\mu_{BY} \qquad (1)$$

where γ is the interfacial tension, σ_m is the electrode charge, E^+ is the electrode potential with respect to a reference electrode reversible to the cation B^+, Γ_i is the total surface excess of component i and μ_j is the chemical potential of the salt j. Parsons showed that the required surface concentration of specifically adsorbed X^-, Γ'_X, could be obtained from these data using several differential relationships including

$$-(1/RT)(\partial\gamma_{rel}/\partial \ln m_{BX})_E = \Gamma'_X \qquad (2)$$

where E is the potential with respect to a fixed reference electrode, m_{BX} is the mole fraction of X^-, and where γ_{rel} again denotes the relative interfacial tension obtained by double integration of the capacitance-potential data.[8,9] In contrast to the variable ionic strength analyses noted above,[2,4] the dependence of γ_{rel} upon electrolyte composition [Eq. (2)] is not subject to serious systematic errors. This is because the values of γ_{rel} can usually be obtained from back integration from a potential where the extent of ionic specific adsorption is negligible, i.e. where the double-layer structure does not significantly depend upon m_{BX}. This constitutes a fundamental advantage of the constant ionic strength approach.

However, if Y^- is also specifically adsorbed all that can be obtained is a combination of the surface excesses of specifically adsorbed X^- and Y^-, since[7]

$$-(1/RT)(\partial\gamma_{rel}/\partial \ln m_{BX})_E = \Gamma'_X - \frac{m_{BX}}{1-m_{BX}}\Gamma'_Y \qquad (3)$$

or

$$-(1/RT)(\partial\gamma_{rel}/\partial \ln m_{BY})_E = \Gamma'_Y - \frac{m_{BY}}{1-m_{BY}}\Gamma'_X \qquad (4)$$

(Note that Eqs. 3 and 4 are not independent since Eq. 4 follows from Eq. 3 given that $m_{BX} + m_{BY} = 1$).

If a third salt BZ is present in the solution the electrocapillary equation becomes

$$-d\gamma = \sigma_m dE^+ + \Gamma_X d\mu_{BX} + \Gamma_Y d\mu_{BY} + \Gamma_Z d\mu_{BZ} \qquad (5)$$

If two of the anions, say X^- and Y^-, are specifically adsorbed while the third, Z^-, is not, it is possible to determine Γ'_X independently of Γ'_Y by obtaining relative surface tension versus potential data for a series of constant ionic strength solutions having the composition x_1 BX + $(1-x_1)$BZ + y_1BY. The concentration variable x_1 equals $c_{BX}/(c_{BX} + c_{BZ})$; $(c_{BX} + c_{BZ})$ is held constant as well as the solution concentration of co-adsorbed Y^-. For the salt BX (and similarly for the others) we can write:

$$d\mu_{MX} = RTd\ln a_{BX} \simeq RTd\ln c_{BX} \qquad (6)$$

where a_{BX} is the activity of BX and c_{BX} is its molar concentration. Following Parson's derivation[7] and noting that $d\ln c_{BX} = d\ln x_1$ and $d\ln c_{BY} = d\ln y_1$, Eq. 5 can be reformulated as

$$-d\gamma = \sigma_m dE^+ + \{\Gamma_X - [x_1/(1-x_1)]\Gamma_Z\} \; RTd\ln x_1 + \Gamma_Y \; RTd\ln y_1 \qquad (7)$$

Provided that the components of Γ_X and Γ_Z in the diffuse layer are present in the same proportions as the concentrations of these anions in the bulk solution, then Eq. 7 can be rewritten as

$$-d\,\gamma = \sigma_m dE^+ + \{\Gamma'_X + [x_1/(1-x_1)]\Gamma'_Z\} \; RTd\ln x_1 + \Gamma_Y \; RTd\ln y_1 \qquad (8)$$

If c_{BY} is invariant, then the term Γ_Y $RTd\ln y_1$ will disappear when the dependence of γ_{rel} upon x_1 is evaluated, *regardless* of whether specific adsorption of Y^- occurs. Similarly to the conventional analysis we obtain

$$-(1/RT)(\partial\gamma_{rel}/\partial\ln c_{BX})_{E,c_{BY}} = \Gamma'_X - [x_1/(1-x_1)]\Gamma'_Z \qquad (9)$$

which enables Γ'_X to be evaluated provided that $x_1/(1-x_1)]\Gamma'_Z$ is small compared to Γ'_X.

Similarly, Γ'_Y can be determined from measurements in a series of solutions having the composition $[y_2BY + (1-y_2)BZ + x_2BX]$, where $y_2 = c_{BY}/(c_{BY} + c_{BZ})$ and $(c_{BY} + c_{BZ})$ is constant, as is x_2. The values of Γ'_Y in the presence of co-adsorbing X^- can be obtained from

$$-(1/RT)(\partial\gamma_{rel}/\partial \ln c_{BY})_{E,c_{BX}} = \Gamma'_Y - [y_2/(1-y_2)]\Gamma'_Z \qquad (10)$$

By performing two sets of experiments at the same total ionic strength, Γ'_X can be obtained in mixed electrolytes having the same composition as in solutions used to determine Γ'_Y. Thus values of both Γ'_X and Γ'_Y can be extracted using this analysis by employing electrolytes that also contain a third anion Z^- which is not specifically adsorbed, or at least is much less strongly adsorbed than either X^- or Y^-.

As an alternative to the use of Eqs. 9 and 10, Γ'_X and Γ'_Y may be obtained from the displacement of relative electrode charge-potential curves obtained by singly integrating the capacitance-potential data.[9,10] However, although this latter procedure is often more sensitive to small amounts of specific adsorption[7,9] it is difficult to apply when the adsorption isotherms are highly noncongruent, as expected for the coadsorption of two like-charged ions. The evaluation of γ_{rel}-E data as the route to Γ'_X and Γ'_Y via Eqs. 9 and 10 is therefore preferred for most systems.

The total number of capacitance, charge or interfacial tension measurements required to evaluate Γ'_X and Γ'_Y via Eqs 9 and 10 is perhaps no fewer than the number required for the Rangarajan analysis. However, the need for extensive auxiliary information regarding ionic activities and absolute electrode charges is obviated. Also, in the present analysis the cumbersome E^+ scale is replaced with potentials measured against a fixed reference electrode since the cation activity is anticipated remain nearly constant for anion mixtures at a constant ionic strength. If Γ'

values are needed for only one of two simultaneously adsorbed ions this analysis is more straightforward since considerably fewer data are required than in the Rangarajan approach.[2] It should be noted that Γ' for the simultaneous adsorption of cations and anions can also be obtained individually by using the conventional Hurwitz-Parsons procedure[11] in a more straightforward manner than using the Rangarajan approach. In addition, the present analysis could be extended to treat the simultaneous adsorption of more than two like-charged ions, although the quantity of data required would become rapidly prohibitive as the number of coadsorbing ions increases.

The present analysis involves essentially the same assumptions as are required in the usual Hurwitz-Parsons approach.[6,7] Thus in addition to the assumption already made concerning diffuse-layer composition, the activity coefficients of all three salts are presumed to remain constant in the various constant ionic strength solutions. This is perhaps more tenuous for mixtures of three salts than for two. In principle, it is possible to relax this assumption by reformulating the analysis in terms of activities. The chief disadvantage is one shared by the usual Hurwitz-Parsons analysis, namely, a relatively surface-inactive salt is needed or errors will be introduced into the results (Eqs. 3, 4, 9, 10).[12] Nevertheless, this difficulty may be less severe in the present case where a pair of like-charged ions are adsorbed since the repulsive interactions with the third, more weakly adsorbing, "reference" ion Z^- should maintain the adsorption of Z^- at lower levels than in the absence of the additional surface-active ion.

It is hoped that the comparatively less extensive experimental effort required in order to utilize the present analysis coupled with its wider applicability will spur research on the topic of simultaneous ion adsorption.

We intend to employ the analysis of our ongoing studies of ionic adsorption at metal-solution interfaces that exhibit Surface-Enhanced Raman Scattering (SERS).[9,13-16] In Raman studies of adsorbed anions, chloride supporting electrolytes which themselves are strongly adsorbed are often employed in order to facilitate the mild electrochemical surface roughening that is conducive to the observation of SERS. The extended Hurwitz-Parsons analysis should enable the surface concentrations of chloride and other anions to be assessed independently. A forthcoming report will describe the analysis of simultaneous adsorption of perchlorate and iodide ions at solid electrodes and the application of the results in unraveling double-layer effects on electrode kinetics.

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REFERENCES

1. L. A. Avaca, E. A. Gonzáles, R. C. Rocha Filho, J. Electroanal. Chem., 147 (1983) 345.
2. S. Lakshmanan, S. K. Rangarajan, J. Electroanal. Chem., 27 (1970) 127.
3. D. I. Leikis, K. V. Rybalka, E. S. Sevastyanov, A. N. Frumkin, J. Electroanal. Chem., 46 (1973) 161.
4. D. C. Grahame, B.A. Soderberg, J. Chem. Phys., 22 (1954) 449.
5. B. Damaskin, U. Palm, M. Väärtnôu, J. Electroanal. Chem., 70 (1976) 103.
6. H. D. Hurwitz, J. Electroanal. Chem., 10 (1965) 35.
7. E. Dutkiewicz, R. Parsons, J. Electroanal. Chem., 11 (1966) 100.
8. G. Valette, A. Hamelin, R. Parsons, Z. Phys. Chem., N.F., 113 (1978) 71.
9. J. T. Hupp, D. Larkin, M. J. Weaver, Surf. Sci., 125 (1983) 429.
10. M. J. Weaver, F. C. Anson, J. Electroanal. Chem., 65 (1975) 737.
11. B. Baron, P. Delahay, D.J. Kelsh, J. Electroanal. Chem., 18 (1968) 187.
12. B. B. Damaskin, Sov. Electrochem., 7 (1971) 776.
13. D. Larkin, K. L. Guyer, J. T. Hupp, M. J. Weaver, J. Electroanal. Chem., 138 (1982) 401.
14. M.J. Weaver, F. Barz, J.G. Gordon II, M.R. Philpott, Surf. Sci., 125 (1983) 409.
15. M.J. Weaver, J.T. Hupp, F. Barz, J.G. Gordon II, M.R. Philpott, J. Electroanal. Chem., in press.
16. M. A. Tadayyoni, S. Farquharson, M. J. Weaver, J. Chem. Phys., in press.

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