

Preliminary note

THE PIEZOELECTRIC MEASUREMENT OF ELECTROCAPILLARY CURVES

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Techniques currently available for obtaining double-layer information at solid electrode-solution interfaces are either not generally applicable (e.g., capacitance techniques require integration constants which may be difficult to obtain [1,2]) or are experimentally very difficult (e.g. surface stress [3–5] or meniscus rise [6] techniques). In a recent paper [7, this issue, pp. 171–180] we demonstrated that a piezoelectric ceramic disk, attached to a platinum foil electrode could be used to follow changes of the derivative of the electrode surface stress with potential, permitting the observation of such electrode surface processes as adsorption and film formation. This communication reports preliminary results of the application of this technique to the measurement of electrocapillary curves of a gold electrode in sodium fluoride and sodium fluoride/sodium bromide solutions. The technique has been fully described [7] and bears similarities to that of Gokhshtein [5] but employs a simplified electrode design and commercial instrumentation. The electrode was constructed by bonding a ceramic piezoelectric disk to 0.09 mm gold foil with epoxy cement, taking care to insure that the Au electrode was insulated from the piezoelectric disk and the disk from the solution by the epoxy. A linear potential ramp with a superimposed small amplitude sinusoidal signal was applied to the electrode and the resulting signal from the piezoelectric disk synchronously detected at the above frequency with a lock-amplifier.

In 0.8 M NaF, with a superimposed 230-Hz, 10-mV sinusoidal signal as before [7] a positive potential scan from -0.4 V (SCE) typically gave the piezoelectric signal shown in Fig. 1 (as its magnitude and phase angle). The piezoelectric signal magnitude is proportional to $|d\sigma/dE|$ (where σ = surface stress; E = electrode potential). The minimum in magnitude at -0.03 V accompanied by a phase change of close to 180° indicates a change of sign in $d\sigma/dE$ and integration of the piezoelectric signal magnitude, taking the sign change into account, yields a plot of Σ against E , as before (Fig. 2). The quantity Σ is linearly related to σ and thus by previous argument [3] to the interfacial tension, γ ; therefore the Σ vs. E plot constitutes an "electrocapillary" curve with maximum equal to the p.z.c.

Table 1 shows the values of E_{pzc} obtained from experiments at three different NaF concentrations. The values appear to be independent of concentration and have a mean, -0.05 ± 0.08 V (SCE), in fair agreement with previous results [1,2,8]. The variation in the values was dependent on the history of the elec-

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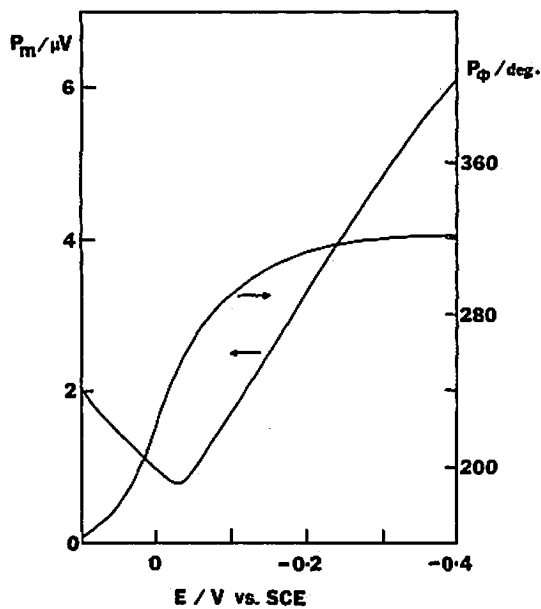


Fig. 1. Piezoelectric signals for an Au electrode in 0.8 M NaF. Potential scan positive from -0.4 V (SCE) at 2 mV s^{-1} ; P_m = piezoelectric magnitude, P_ϕ = piezoelectric phase angle.

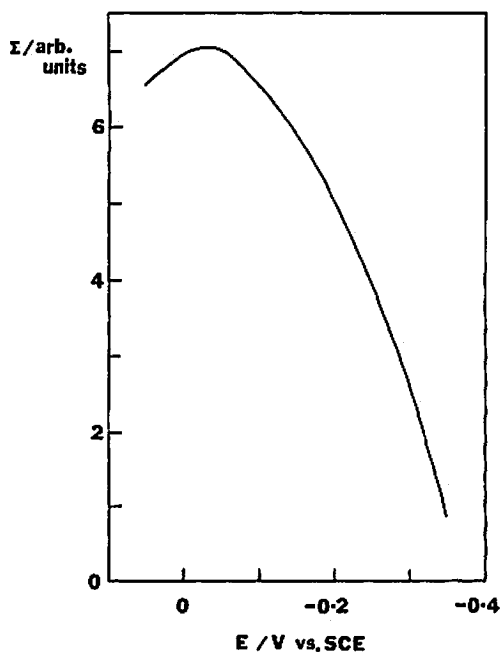


Fig. 2. Σ vs. E plot for Au in 0.8 M NaF.

TABLE 1

Experimentally obtained E_{pzc} values for an Au electrode in NaF solution, where c = concentration of NaF (pH 7) and f , the frequency of the applied alternating 10 mV signal; E_{pzc} is in V vs. SCE

c/M	E_{pzc}/V	f/Hz
0.8	+0.04	230
	-0.03	230
0.1	+0.09	41
	-0.06	41
	-0.11	23
	-0.11	7.5
0.01	0.00	7.3
	-0.10	7.5
	-0.20	7.5

trode and solution and was probably caused by the presence of organic impurities, which are most strongly adsorbed near the pzc and are known to affect the interfacial tension. Careful attention to solution purity, including modifying the electrode design to eliminate the solution-epoxy contact, appears necessary to improve reproducibility. In dilute solutions low frequency signals were needed to obtain a sufficient piezoelectric response. Near the pzc the electrode capacitance,

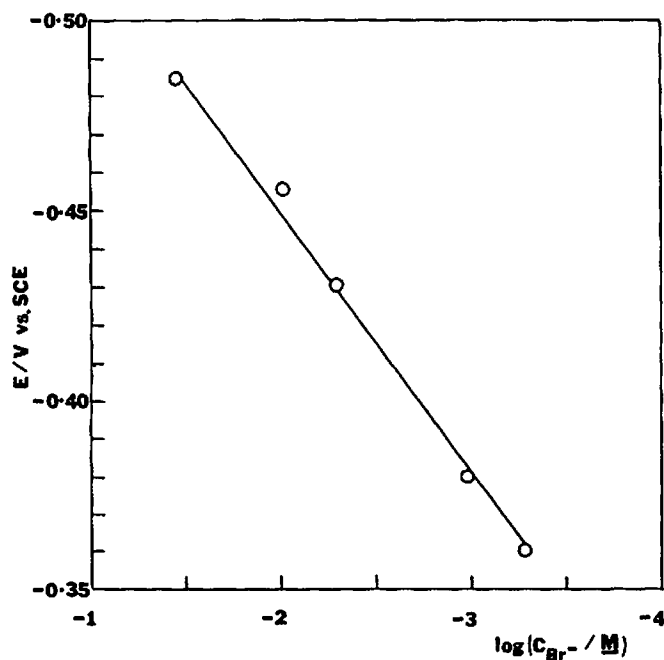


Fig. 3. Change in the pzc on addition of bromide ion to 0.8 M NaF, where c_{Br^-} is the concentration of bromide ion.

C , is dominated by the diffuse-layer contribution and varies as the square root of the electrolyte concentration while the solution resistance R varies approximately inversely. At low electrolyte concentrations the time constant, RC , of the cell is increased and thus the frequency must be reduced to permit the electrode capacitance to change producing the maximum change in σ and therefore the piezoelectric response. Note that the piezoelectric signal observed here due to double-layer effects is approximately a factor of three times smaller than that observed previously for adsorption or film formation [7].

The change in the pzc of the electrode in 0.8 M NaF on addition of bromide ion (as NaBr) is shown in Fig. 3. Increasing bromide ion concentration shifts the pzc further negative as expected and the observed linear logarithmic dependence is in agreement with the Esin-Markov effect [9,10]. The unintegrated piezoelectric magnitude is by the above reasoning and the Lippmann equation, proportional to the electrode charge density, $-q_m$. Fig. 4 shows the concentration dependence of the change in piezoelectric magnitude, and therefore Δq_m , on sweeping the potential from a region where no bromide adsorption occurs (-0.7 V, SCE) to potentials where adsorption is possible.

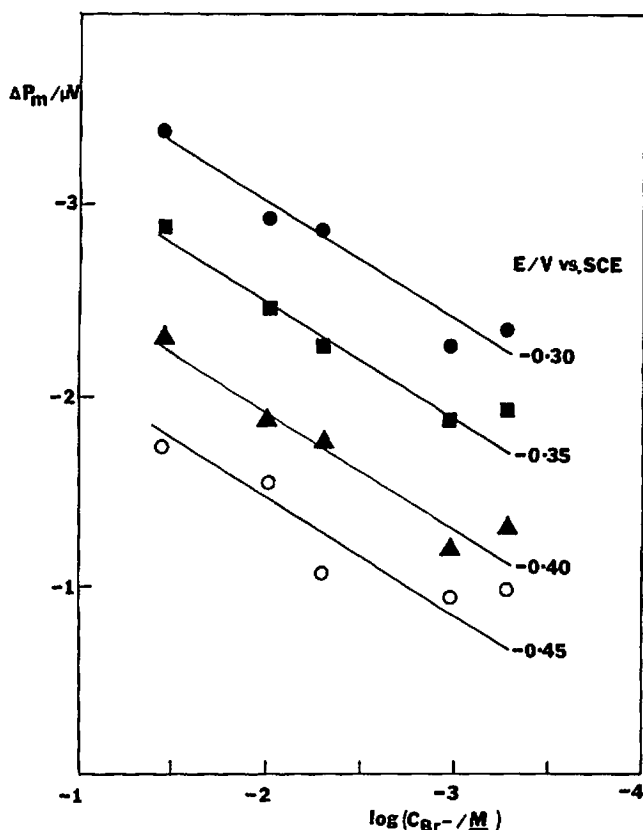


Fig. 4. ΔP_m vs. $\log c_{Br^-}$ plot for the system in Fig. 3. ΔP_m at -0.30 V denotes (piezoelectric magnitude at -0.70 V) - (piezoelectric magnitude at -0.30 V) with the piezoelectric magnitudes at potentials negative of the pzc being assigned negative values.

between concentration and piezoelectric magnitude is observed as before [11], strong evidence that the piezoelectric element is detecting changes in double-layer properties.

Finally we note that an absolute value of q_m can be obtained by integration of the electrode capacitance (using the value for E_{pzc} obtained from the above measurements). Thus simultaneous capacitance and piezoelectric measurements enable a further check to be made on the validity of the technique as a constant proportionality should exist between q_m (from the former measurement) and the piezoelectric magnitude. Knowledge of q_m also permits the transformation of Σ into $\Delta\gamma$ from which complete double-layer data may be obtained by experimentation over a range of electrolyte concentrations.

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