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ELECTROCAPILLARY CURVES OF CHLORIDE IONS
IN WATER-HYDROGEN FLUORIDE MIXTURES.

KEY WORDS : electrocapillary curves, mercury electrode, chloride ions, water-hydrogen fluoride mixtures.

Hugues Ménard*, Francine Leblond-Routhier*
Jean-Luc Roux* and Jacques Devynck**

* Département de Chimie, Université de Sherbrooke
Sherbrooke, Québec J1K 2R1 (CANADA).

** Laboratoire d'Electrochimie Analytique et Appliquée
Associé au CNRS (LA 216), E.N.S.C.P., Université
Pierre et Marie Curie, Paris (FRANCE).

ABSTRACT

We have determined the electrocapillary curves of the mercury electrode with a mixture of hydrogen fluoride and water containing 40% (by weight) of HF, using the mercury electrode drop time formation technique. The addition of KCl at concentrations from 0.01 to 0.5 M provokes a displacement of the electrocapillary curves showing a possible specific adsorption of HCl at the electrode.

Several polarographic studies of metallic ions in water-hydrogen fluoride mixtures between 0 and 100% of HF have been reported. Recently¹, a study of Sb(III) reduction in HF-H₂O containing 40% in HF has led to the suggestion that the variations in the double layer parameters were at the origin of the kinetic variations of electrochemical systems when chloride ions were added. A study of electrocapillary curves was undertaken to confirm this hypothesis.

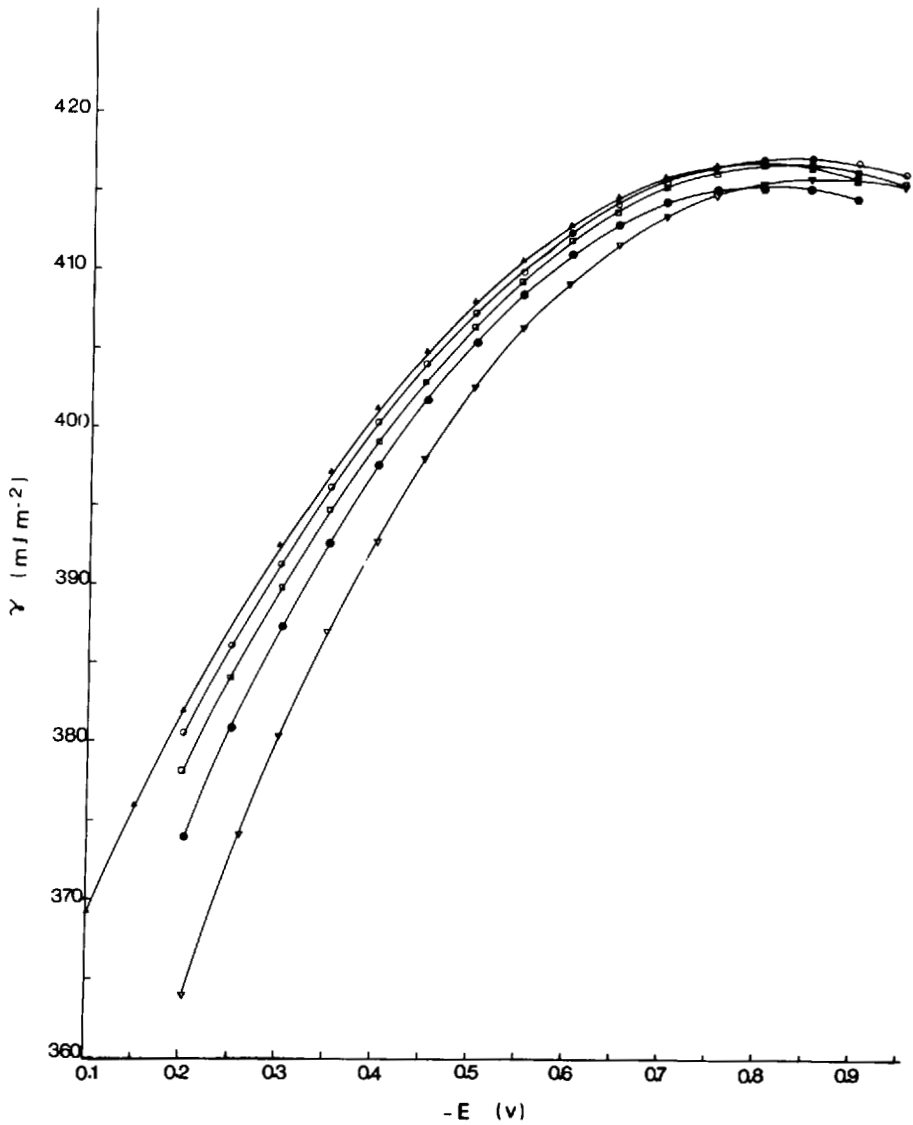
The values of the interfacial tension were calculated from the formation time of the mercury drop² measured at potential intervals of 50 mV, in solutions containing KCl between 0.01 and 0.5 M (Figure). The potential of the mercury drop is fixed with a three-electrode potentiostatic system, the reference electrode being an aqueous saturated calomel electrode, separated from the HF media by a Kel-F junction. The polarographic capillary was a polyethylene³.

The values of the capillary dropping time were employed according to the method previously described⁴. The reference tension was that of a 0.4 M KF aqueous solution : $426.2 \text{ dynes cm}^{-1}$ ⁵.

Corrections of density were made using the values of DESNOYER et al. for KF solutions⁶ and these of DOMANGE for HF⁷. The reproducibility of the interfacial tension under our experimental conditions was better than $\pm 0.3 \text{ dyne cm}^{-1}$.

Results for HF + H₂O⁸ without chloride ions are in good accord with these of RAAEN⁸ obtained with a teflon capillary. With reference to the potential of the electrocapillary maximum (observed at - 0.8 V) the reduction potential of the greater part of metallic ions is in the anodic region of the electrocapillary curve ; addition of KCl provokes a lowering of the interfacial tension. This decrease is induced by a specific adsorption of chloride ions (which are in the protonated form of HCl because of the high acidity level⁹). The adsorption enhances the kinetic of the electrochemical reduction of metallic ions. Thus the reduction of Sb(III), irreversible in HF + H₂O without HCl, is reversible when KCl (or HCl) concentration is higher than 1 M ¹.

This study shows also that simple polyethylene capillaries, which are relatively easy to build³, function well for very precise measurements in glass-corroding media.



FIGURE

Electrocapillary curves of water-HF mixtures
(HF 40% by weight).

(▲) pure HF-H₂O mixture ; after addition of KCl :
(O) 0.01 M ; (■) 0.05 M ; (●) 0.1 M ; (Δ) 0.5 M.

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