The Effect of Counter Ion Property on Surface Activity of Fe(III)-EDTA Complex (Graduate School of Science and Engineering, Saitama University) <u>M. Villeneuve,</u> M. Tanaka, and M. Abe

There are many biologically important metal complexes, however their interfacial behavior has not been well understood, yet. The influences of pH of the aqueous solution and the hydration property of the counterion on the adsorption of iron(III)-ethylenediamine-N,N,N',N'-tetraacetic acid complex (Fe-edta) at the air/water interface were studied by surface tension measurement. Experimental data were analyzed with thermodynamic equations derived for mixed aqueous solutions of an alkali hydroxide (MOH) and Fe-edta, in which the following dissociation and association equilibria [1, 2] of Fe-edta complex were taken into account.

| $[Fe(Hedta)(H2O)] = [Fe(edta)(H2O)]^{-} + H^{+}$ | ; $pKa_1 = 2.2^{[1]}$ | (1) |
|--|-----------------------|-----|
| $[Fe(edta)(H2O)]^{-} = [Fe(edta)(OH)]^{2-} + H^{+}$ | ; $pKa_2 = 7.6^{[1]}$ | (2) |
| $2[Fe(edta)(OH)]^{2-} = [(edta)Fe-O-Fe(edta)]^{4-} + H_2O$ | ; $pKd = -1.88^{[2]}$ | (3) |

The surface tension and pH of aqueous solutions of MOH / Fe-edta mixture were measured at 298.15 K under atmospheric pressure as functions of *m* and X_2 ($m = m_1 + m_2$; $X_2 = m_2 / (m_1 + m_2)$, m_1 : molality of MOH, m_2 : molality of Fe-edta), since at a given temperature and pressure, surface tension is expressed as a function of *m* and X_2 .

$$-\frac{d\gamma}{RT\Gamma_{t}^{H}} = \left(\frac{1}{m} + CX_{1}^{H} + DX_{2}^{H}\right)dm + m\left(\frac{X_{2}^{H} - X_{2}}{mX_{1}X_{2}} + EX_{1}^{H} + FX_{2}^{H}\right)dX_{2},$$
(4)

where *C*, *D*, *E*, *F* are determined by degrees of dissociation and association of Fe(III)-edta (eqs. (1) ~ (3)), *m* and *X*₂. Γ_{t}^{H} is the total surface density ($\Gamma_{t}^{H} = \Gamma_{c0}^{H} + \Gamma_{c1}^{H} + \Gamma_{c2}^{H} + \Gamma_{d}^{H} + \Gamma_{M+}^{H}$) and X_{2}^{H} is the interfacial composition of the Fe-edta ($X_{2}^{H} = (\Gamma_{c0}^{H} + \Gamma_{c1}^{H} + \Gamma_{c2}^{H} + \Gamma_{d}^{H}) / \Gamma_{t}^{H}$). Here, c0, c1-, c2-, and d represent the neutral species [Fe(Hedta)(H2O)], the monoanionic species [Fe(edta)(H2O)]⁻, the

dianionic species [Fe(edta)(OH)]²⁻, and the tetraanionic dimer

[(edta)Fe-O-Fe(edta)]⁴⁻, respectively.

The total surface density

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\Gamma_t^H vs. m curves at constant X_2 of the KOH / Fe-edta and the NaOH / Fe-edta systems were significantly different from each other as shown in the figure. The
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Fig. Γ_t^H vs. *m* curves at constant X_2 : KOH / Fe-edta system (left); NaOH / Fe-edta system (right).

structure breaker ion, K^+ brought Fe-edta to positive adsorption at most X_2 , whereas the structure maker ion Na⁺, negative adsorption at most X_2 . The counter ion effect on pH dependence of the surface density will be discussed in detail at the conference.

References: [1] J. L. Lambert, C. E. Godsey, L. M. Seitz, Inorg. Chem., 1963, 127-129.

[2] W. W. Frenier, Canadian Journal of Chemistry, 1980, 1999-2005.