Hazen Research Inc.[20,21] has had two patents granted which cite alkylphosphoric acids and carboxylic acids as accelerators for the same reaction. Interfacial tension measurements at Warren Spring Laboratory have shown that addition of dinonylnaphthalenesulfonic acid (DNNSA) to LIX 65N causes total displacement of LIX 65N from the interface. Thus this accelerator mechanism obviously proceeds via interaction of the copper with ionized DNNSA (a strong acid) at the interface and formation of the copper LIX complex through a ligand-exchange reaction in the bulk organic phase. It would seem logical to conclude that the action of the alkylphosphoric and carboxylic acids would be similar but scaled in proportion to their acid strengths. This mechanism is identical with phase transfer catalysis.

(20) W. C. Hazen and E. L. Coltrinari, U.S. Patent 3 872 209 (1975).
(21) M. B. Goren and E. L. Coltrinari, U.S. Patent 3 927 169 (1975).

Conclusions

The extraction of copper by the proprietary chelating extractants LIX 65N and Kelex 100 cannot proceed by the classical mechanism involving sequential chelating reaction in the bulk aqueous phase between copper cations and the anions of the ionized extractant. The available physical chemical and kinetic data show that the site of the rate-controlling reaction is the aqueous organic interface. Solvent effects and physical organic interaction play an important role in determining the behavior of LIX and Kelex reagents in various diluents, and much remains to be done in this area. Unambiguous detailed mechanisms cannot as yet be produced from kinetic data. More work is required in this area, particularly with respect to the significance of pathways involving aqueous phase intermediates and the nature of the species adsorbed at the interface.

Additions and Corrections

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Noal Cohen: Asymmetric Induction in 19-Norsteroid Total Synthesis.

Page 416. The following corrections should be made to Table I: Entry 35, the product should read **25f**. Entry 36, the amino acid should read (*R*)-Tryptophan. Entry 37, the solvent should read CH_3CN. Entry 38, the amino acid should read (*R*)-Valine.