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EXTRACTION OF GALLIUM(III) FROM ALKALINE SOLUTIONS BY ALKYLATED HYDROXYQUINOLINE

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The distribution equilibrium of gallium(III) between aqueous sodium hydroxide solutions and solutions of 7-(5,5,7,7-tetramethyl-1-octen-3-yl)-8-hydroxyquinoline (KELEX 100) in kerosene has been examined under different conditions. As a result, it is confirmed that the extraction of gallium(III) proceeds in a cation exchane reaction.

It has been recently reported[1,2] that the recovery of gallium from sodium aluminate solutions in Bayer process is effectively carried out by solvent extraction with the mixture of 7-(5,5,7,7-tetramethyl-1-octen-3-yl)-8-hydroxyquinoline (KELEX 100, HQ) and decanol in kerosene. However, since the fundamental results are not yet issued, further informations for its extraction system are presented in this paper.

Aqueous gallium hydroxide solution was prepared by dissolving the freshly precipitated gallium hydroxide gel, obtained by adding sodium hydroxide to gallium chloride solution,[3] in the sodium hydroxide solution of selected concentration. KELEX 100 (Schering AG) purified by distillation under a pressure (0.25 mmHg) at 147-159 °C was diluted with kerosene. The concentration of KELEX 100 was determined by the copper loading experiment on the basis of the literature.[4]

Dependence of the time to attain to the equilibrium in the extraction by KELEX 100 on [NaOH] in aqueous phase is reversed as follows in the presence of alcohol in organic phase: in the extraction by 0.05 mol dm^{-3} KELEX 100 the equilibria at 0.6 and 6 mol dm^{-3}NaOH are complete in 1 and 8 hrs, respectively, while in the extraction in the presence of 10 vol% 2-ethylhexylalcohol those at 0.6 and 6 mol dm^{-3} NaOH in 32 and 8 hrs, respectively. In contrast the distribution isotherm for gallium(III) by KELEX 100 resembles that by the mixture of KELEX 100 and 10 vol% 2-ethylhexylalcohol (Fig.1), although alcohol prevents the formation of the third phase at stripping. The distribution coefficient of gallium (the ratio of the equilibrium concentration of gallium in the organic phase to that in the aqueous phase, E_a^o) decreases gradually with increasing [NaOH] except that the decrease in E_a^o for the extraction in the presence of alcohol becomes steep at [NaOH] > 4 mol dm^{-3}.

As the gallium ion in sodium hydroxide solution exists as the tetrahydroxo species $Ga(OH)_4^-$,[5] it is inferred that the decrease in the E_a^o is governed by a cation exchange reaction

$$Ga(OH)_4^-(aq) + nHQ(org) \rightleftharpoons GaQ_nH_{n-3}(org) + OH^-(aq) + 3H_2O(aq) \qquad (1)$$

This leads the relationship

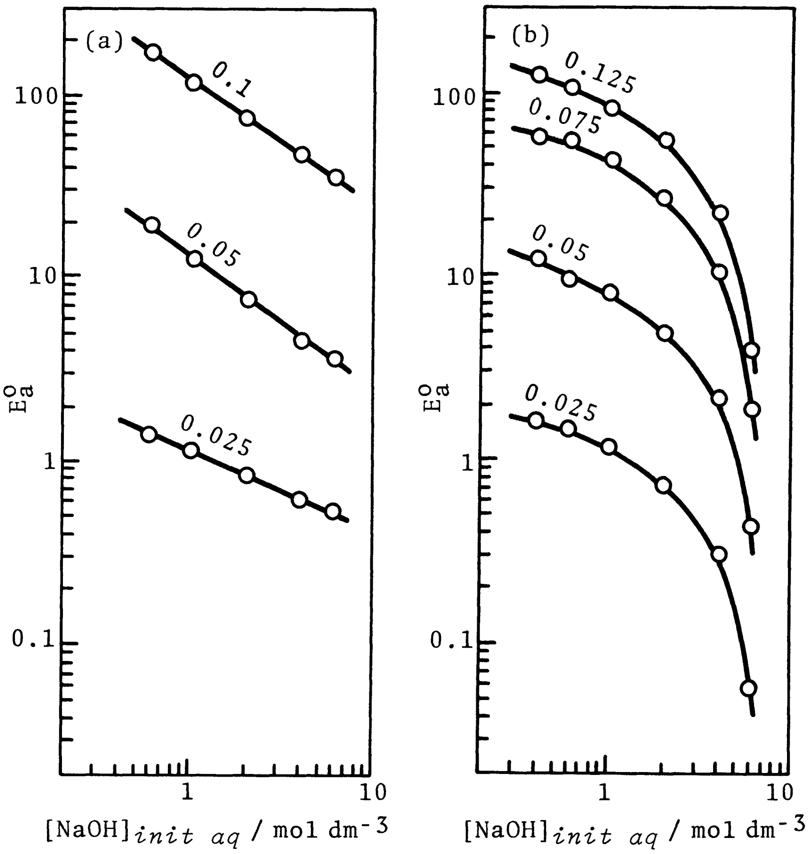

Fig.1 Distribution isotherms of gallium (III) from sodium hydroxide solutions by (a) KELEX 100 in kerosene and (b) by the mixture of KELEX 100 and 10 vol% 2-ethylhexylalcohol in kerosene at 30 °C (numerals on curves are KELEX 100 concentrations / mol dm^{-3}).

$$\log E_a^o = \log K + n\log[HQ] - \log[OH^-]. \qquad (2)$$

Assuming n = 3, the log-log plots of E_a^o vs. [HQ] at constant [NaOH] give straight lines with slope of ~3. Hence it is deduced that the extraction of gallium(III) from sodium hydroxide solutions by KELEX 100 is dominated by the equilibrium

$$Ga(OH)_4^-(aq) + 3HQ(org) \rightleftharpoons GaQ_3(org) + OH^-(aq) + 3H_2O(aq). \qquad (3)$$

This is also supported by the continuous variation method at a constant [NaOH] in 1 mol dm^{-3}: at a fixed total concentration of initial aqueous gallium and KELEX 100 in 0.1 mol dm^{-3}, the gallium concentration in the organic phase shows a maximum at molar fraction of $[Ga]_{init\ aq} / ([Ga]_{init\ aq} + [HQ]_{init}) = 0.25$, implying the formation of the complex GaQ_3 in the organic phase.

A rise in temperature does not always facilitate the extraction rate of gallium contrary to the results by Leveque et al.[1] The detailed data for the present extraction system will be published elsewhere.

References

1) A.Leveque and J.Helgorsky,"Proc. Int. Solvent Extraction Conf., 1977, Toronto", Vol.2,439(1977).
2) J.Helgorsky and A.Leveque, German Patent 2,530,880(1976); French Patent 2,307,047(1976); German Patent 2,743,475(1978); French Patent 2,397,464(1979).
3) T.Sato and T.Nakamura, J.Chem.Tech.Biotechnol.,32(3),1982.
4) D.S.Flett, J.Inorg.Nucl.Chem.,37,1967(1975).
5) B.Daniel, Rev.Chim.Miner.,6,499(1969).

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