Separation of Ga^{3+} from a Ga^{3+}–Al^{3+} Solution using a Long-chain Alkylated Cupferron Membrane

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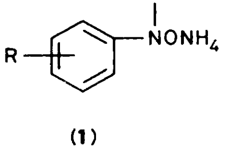
A porous membrane impregnated with a long-chain alkylated cupferron [*N*-(alkylphenyl)-*N*-nitrosohydroxylamine ammonium salt] kerosene solution almost completely concentrated Ga^{3+} from a Ga^{3+}–Al^{3+} binary solution against the concentration gradient, the counter flow of H^+ providing the driving force.

In recent years, the demand for gallium has increased rapidly in the expectation that new semiconductor devices would be based on materials such as GaAs and GaP. In general, gallium is found in ores with aluminium, *e.g.*, in bauxite. Most information on the separation of Ga^{3+} from Ga^{3+}–Al^{3+} binary solutions is available only through patents; electrolytic, carbonation and sedimentation, and chelation methods have been cited. Cupferron is a common chelating agent for multilvalent metal ions,[1—3] and it is known that Ga^{3+} forms a chelate with cupferron in a lower pH range than Al^{3+} does.[4—6]



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We have investigated the properties of highly hydrophobic long-chain alkylated cupferrons as adsorbing agents and carriers in membranes for Ga^{3+}, and have found that some are suitable for Ga^{3+} separation.

Long-chain alkylated cupferrons were synthesized as described previously.[7]† The solubilities of dodecyl- and octadecyl-cupferron in water were of the order of 10^{-2} wt%. Figure 1 shows the effect of pH on the adsorption of Ga^{3+} and Al^{3+} by octadecylcupferron. Each metal ion has its individual pH profile for adsorption. It is suggested that Ga^{3+} can be selectively separated from a Ga^{3+}–Al^{3+} binary solution at a

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† ^{1}H N.m.r. spectra of long-chain alkylated cupferrons showed peaks at δ 7.75 and 7.30 for phenyl protons; 3.10 for ammonium protons; 1.42, 1.00, and 0.72 for alkyl-chain protons. The peak areas at δ 7.75 and 7.30 were equally large, suggesting that the alkyl moiety was attached at the *para* position.

Table 1. Recovery of Ga^{3+} from a Ga^{3+}–Al^{3+} binary solution by octadecylcupferron.[a]

		Recovery solution				
		Ga^{3+}		Al^{3+}		Separation[d] factor
C_{18}-Cup.[b]/Ga^{3+} (molar ratio)	Adsorption time/h	Conc./p.p.m.[c]	Recovery, %	Conc./p.p.m.[c]	Recovery, %	Ga^{3+}/Al^{3+}
6	2	133	66.7	21	0.054	1267
12	2	189	94.5	26	0.064	1454
6	12	141	70.5	46	0.115	613

[a] Adsorption: initial $[Ga^{3+}]$ = 200 p.p.m.; initial $[Al^{3+}]$ = 40 000 p.p.m.; $[Ga^{3+}]/[Al^{3+}]$ = 1/200 (w/w); pH 1, room temp. Stripping: 0.1 M aqueous NaOH; 0.25 h, room temp. [b] C_{18}-Cup. = octadecylcupferron. [c] The concentrations of ions were determined by chelatometry. [d] ($[Ga^{3+}]$ in recovery solution/$[Al^{3+}]$ in recovery solution)/(initial$[Ga^{3+}]$/initial$[Al^{3+}]$).

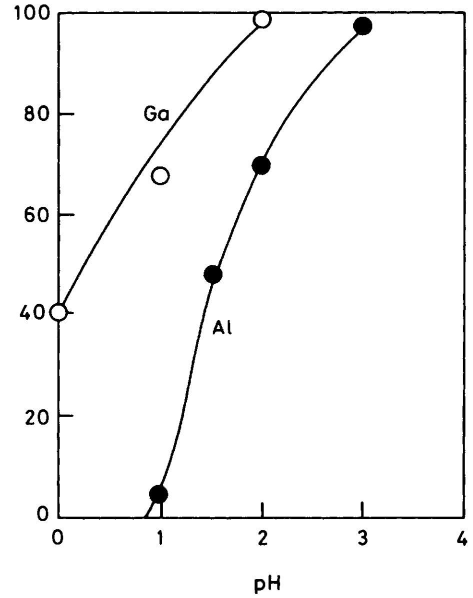

Figure 1. Effect of pH on the adsorption of Ga^{3+} and Al^{3+} by octadecylcupferron. $[Ga^{3+}] = [Al^{3+}]$ = 5mM; molar ratio of Ga^{3+} or Al^{3+} to octadecylcupferron = 1 : 3; adsorption time 8 h. Absorbed /% is defined as $\{([M]_o - [M]_r)/[M]_o\} \times 100$, where $[M]_o$ and $[M]_r$ are the concentration of metal ions in the initial and residual solutions, respectively.

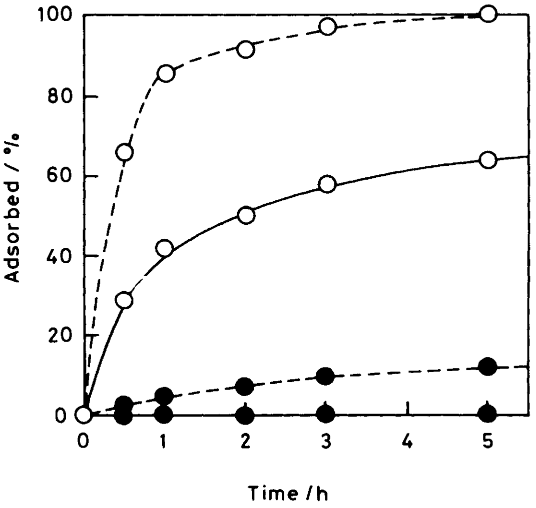

Figure 2. Dependence on time of the adsorption of the Ga^{3+}–Al^{3+} binary solution by octadecylcupferron. $[Ga^{3+}] = [Al^{3+}]$ = 5 mM; molar ratio $Ga^{3+} + Al^{3+}$ to octadecylcupferron = 1 : 3. ○, Ga^{3+}; ●, Al^{3+}; ——, pH 1; ----, pH 3.5.

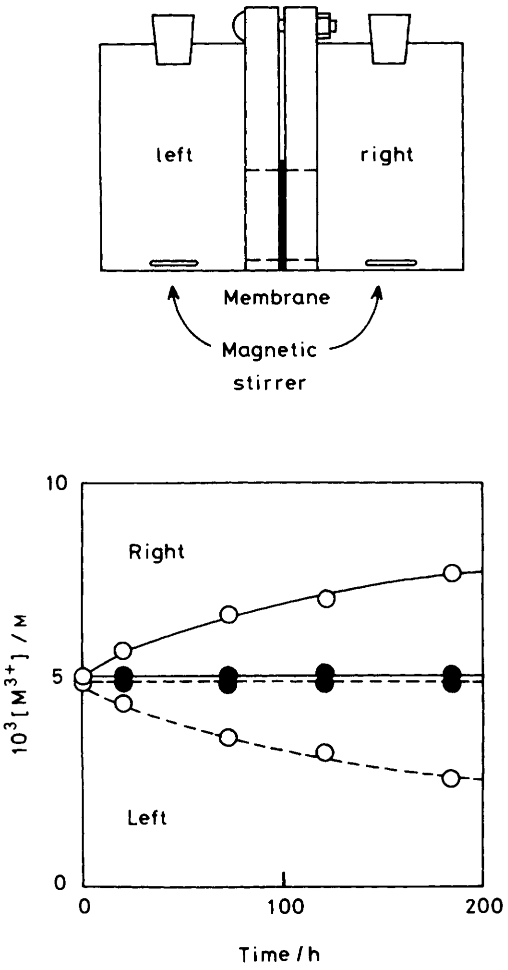

Figure 3. Dependence on time of the transport of the Ga^{3+}–Al^{3+} binary solution through the octadecylcupferron–polytetrafluoroethylene membrane. Initial conditions. $[Ga^{3+}] = [Al^{3+}]$ = 5 mM on each side; left, pH 1; right, pH 3.5; ○, Ga^{3+}; ●, Al^{3+}; ——, right; ----, left. A sketch of the transport cell is also shown.

particular pH. In Figure 2, the dependence on time of the adsorption of Ga^{3+} from a Ga^{3+}–Al^{3+} binary solution system by octadecylcupferron at low pH is shown; Ga^{3+} was selectively adsorbed. Octadecylcupferron has a high selectivity for Ga^{3+} adsorption even from a binary solution which contains only a small amount of Ga^{3+}. Gallium could be recovered even in the presence of a large amount of aluminium ($Ga^{3+} : Al^{3+}$, 1 : 200 w/w). This ratio is comparable to that for the circulating solution in an aluminium refinement process by the so-called Bayer method. Table 1 shows the recovery of gallium from gallium–aluminium solutions using octadecylcupferron. NaOH (0.1 M) was applied to remove gallium from the Ga^{3+}–octadecylcupferron adsorbate. The results show that increasing the amount of octadecylcupferron and reducing the time both increased the selectivity. Even in a solution which contained a large quantity of Al^{3+}, octadecylcupferron under acidic conditions chelated with Ga^{3+} selectively, and the chelated Ga^{3+} could easily be isolated using dilute aqueous alkali. In addition, gallium metal can be obtained by the usual electrolysis from the alkaline solution of Ga^{3+}.

Taking account of the characteristics of alkylcupferrons, the selective and active transport of Ga^{3+} through a membrane impregnated with a long-chain alkylated cupferron was studied. The microporous polytetrafluoroethylene membrane, Flourinert FHUP (Millipore Ltd.; 50 μm thickness, 85% porosity, 0.5 μm average pore size), was used. The octadecylcupferron-impregnated membrane was prepared by immersing Flourinert FHUP in a 0.1 wt% solution of octadecylcupferron in kerosene for 30 min with ultrasonication. The membrane was placed between the two chambers of the transport cell (Figure 3), each of which was equipped with a magnetic stirrer. The transport conditions were based on the above extraction data, and the transport was investigated with a Ga^{3+}–Al^{3+} binary solution. The dependence on time of the transport of Ga^{3+} through the membrane is shown in Figure 3. The concentration of Ga^{3+} on the right-hand side increased with time, with a corresponding decrease on the left-hand side. This suggests that active transport of Ga^{3+} caused by a counter flow of H^+ had occurred. There was little change in the concentration of Al^{3+}. Thus a selective and active transport of Ga^{3+} at low pH has been achieved.

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