**Separation Science and Technology**
Publication details, including instructions for authors and subscription information:
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**To cite this Article** Matis, K. A. , Stalidis, G. A. and Zoumboulis, A. I.(1988) 'Flotation of Germanium from Dilute Solutions', Separation Science and Technology, 23: 4, 347 — 362

**To link to this Article: DOI:** 10.1080/01496398808060709

**URL:** http://dx.doi.org/10.1080/01496398808060709

SEPARATION SCIENCE AND TECHNOLOGY, **23**(4 & 5), pp. 347-362, 1988

# Flotation of Germanium from Dilute Solutions

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### Abstract

In laboratory experiments, ion flotation was found effective as a concentration method for germanium from dilute aqueous solutions. Removals over 90% were obtained at neutral pH conditions and stoichiometric addition of the flotation reagents, these being pyrogallol as activator for complex formation and laurylamine as cationic surfactant. Parameters investigated were initial and residual concentration, gas flow rate, pH of the solution, ionic strength, type of salts added, laurylamine concentration, retention time, ethanol addition, and surface tension on the germanium recovery.

## INTRODUCTION

Germanium is known to be a scattered element occurring in traces in other ores, mainly mixed sulfides and coal. Concentration and separation of germanium from aqueous solutions are of technological significance (*1*). The available methods (solvent extraction, distillation, ion exchange, etc.) suffer from a number of disadvantages such as consumption of costly reagents and energy, and laborious and lengthy operations (as in settling, filtration, and dewatering of slimes). Precipitation of germanium by tannin substances (one of the industrial methods) also presents the unfavorable effect of tannin on zinc electrolysis in a hydrometallurgical plant (*2*). Known characteristics of ion flotation are its effectiveness, simplicity, relative cheapness, and fast treatment of large volumes containing low concentrations (*3*, *4*).

The first information on the (theoretical) possibility of germanium ion flotation removal from solutions, as $GeCl_6^{2-}$ by cationic surfactants, was due to Sebba (*4*). Knowledge of the chemistry of germanium(IV) in aqueous solutions, its speciation, and complex formation (*5*, *6*) are requisites for the development of a suitable separation method. This readily explains, for example, why germanium in the form of metagermanic acid, $H_2GeO_3$, cannot be floated by a surfactant alone (*7*), but also requires an effective activator.

Complex compounds of germanium with oxygen-containing organic molecules and, in particular, with hydroxy acids have attracted attention, specifically in the USSR (*8–10*). The reaction of phenylfluorone (2,3,7-trihydroxy-9-phenol-6-fluorone) with germanium constitutes the basis of the main analytical method for the element (*11*). The complexes of germanium with pyrogallol and catechol as activators were tried successfully by Gol'man and coworkers for flotation by laurylamine and cetyl-trimethylammonium bromide (*12*).

The germanium/pyrogallol/laurylamine system was selected for further research on the mechanism of ion flotation of the metal after preliminary experiments (*13*) for the following reasons. The reagents used were common and cheap, the method succeeded in obtaining nearly complete removal from dilute aqueous solutions, and it was promising for the selective separation of germanium from other metal ions with which it coexists in leach or spent solutions. The latter is the possible application of this work. The various parameters affecting ion flotation were investigated.

The flotation of germanium ion was effective in keeping values of [Ge]:[pyrogallol]:[laurylamine] equal to 1:3:2 (as mol/L). Pyrogallol is known (*6*) to form a strong complex acid with germanium in dilute solutions of composition $[H_2Ge]P_3$ (where P stands for pyrogallol). This acid dissociates as $GeP_3^{2-}$ anions, and it was floated by such cationic surfactants or collectors as amines.

## EXPERIMENTAL

The laboratory flotation apparatus used was a typical dispersed-air system, consisting of a nitrogen cylinder connected to the flotation cell through a gas humidifier, a filter, an open mercury U-tube manometer, a rotameter, and a low flow-rate controller. The cell, which had an approximate total volume of 120 $cm^3$, was made from a Schott D4 fritted funnel (porosity 10–16 μm), glass blown to a piece of tubing having the same diameter of 34 mm. The calculated (*7*) bubble size was of the order of 0.8 mm. Special arrangement was also provided for the collection of foam (concentrate) and for sampling.

## RESULTS AND DISCUSSION

### Feed Concentration

An important parameter of ion flotation in a continuous flow operation is the feed concentration of the metal ion to be removed, which in a batchwise system, as in the present work, is preferably referred to as the initial cell concentration. The process is most efficiently applied when the concentration of colligend is in the range of $10^{-5}$ to $10^{-3}$ *M*, according to Pinfold (*14*).

In the experiments the pH value was that of the solution (deionized water) as prepared, approximately 7. A constant amount (0.5%) of ethanol was added. Higher flotation recoveries were obtained at germanium initial concentrations of $1\text{-}2 \times 10^{-4}$ *M* with a stoichiometric ratio of reagents. It is noted that pyrogallol is sensitive to oxidation.

Above the optimum values the quantity of the product formed was inconveniently large, while below the optimum values the amount of surfactant present was insufficient to form a supporting foam, and flotation was incomplete. It is also interesting to plot these results as a function of the germanium remaining in the solution after the operation, representing that actually lost, as shown in Fig. 1. An apparent increase was seen with the initial concentration of germanium.

A potential application of the process is its use in analytical chemistry as a preconcentration step for recovering metals from natural waters, seawater, and industrial effluents. Quantitative recoveries of ion flotation at optimum conditions make it possible for it to be applied even in the ppb range.

In the experiments, 10% excesses of reagents were applied throughout, unless otherwise stated. A flotation retention time of 300 s was found to be optimum. No conditioning or any pretreatment was needed as with other techniques; for example, froth flotation or adsorbing colloid flotation. Because the reagents were in the form of solutions, their mixing was easily achieved by the bubbles passing through the column.

Elemental analysis of the sublate showed 3.28% N, 61.34% C, and 8.68% H, which deviates slightly from that theoretically calculated for a product of $L_2GeP_3$ (where L stands for the cation of laurylamine), relating to a substance of molecular type $C_{42}H_{68}N_2O_9Ge$.

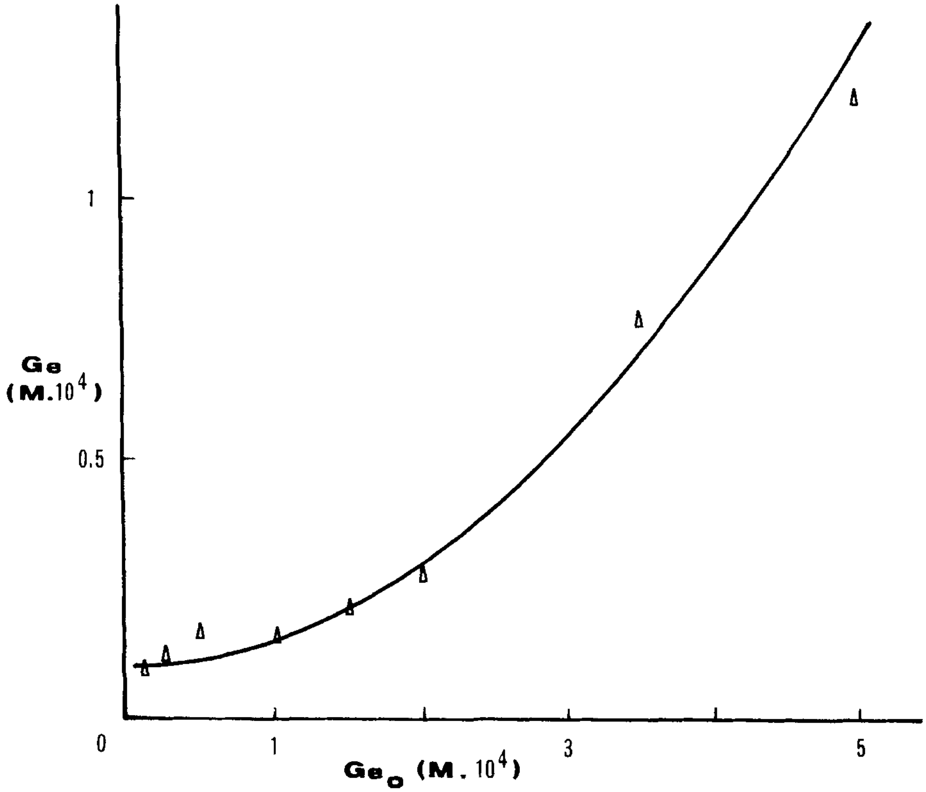

FIG. 1. Effect of germanium initial concentration on the amount of germanium remaining in solution after flotation ([Ge]:[pyrogallol]:[amine] = 1:3:2 mole:mole, pH about 7, gas flow rate 3.33 $cm^3/s$, retention time 300 s, ethanol 0.5% v/v).

## Gas Flow Rate

Investigations were performed on ion flotation using either low or high gas flow rates (*14*). In our case, flotation recoveries become more rapid on increasing the gas (nitrogen) flow and hence decreasing the flotation retention time, but only up to a certain maximum flow rate. The former is, among others, determined from the available equipment (such as the blower, rotameter, etc.) and the undesirable disturbance of the foam layer which, if severe, would lead to the return of floated particles to the solution.

The removal of metals in ion flotation is based on their preferential distribution between the gas-liquid interphase and the liquid phase. As a result, the larger the interphase, the better is the flotation obtained. This can be facilitated, for instance, by choosing a diffuser of finer porosity. Different fritted glasses in the cell were tested (*13*), and an increase in porosity gave better flotation results. However, there are flotation techniques, such as dissolved air and electrolytic flotation, which are known to generate gas bubbles less than 100 μm in diameter (*15*).

A 3.33 $cm^3/s$ flow rate was usually applied in the experiments, with a pressure difference, measured on the manometer, of about 26.6 $kN/m^2$. The ratio of gas flow rate over the initial cell concentration represents the gas/liquid interphase available for flotation. Figure 2 shows the effect of this parameter on the remaining germanium. Note that constant values were obtained from a flow rate of approximately 3.33 $cm^3/s$.

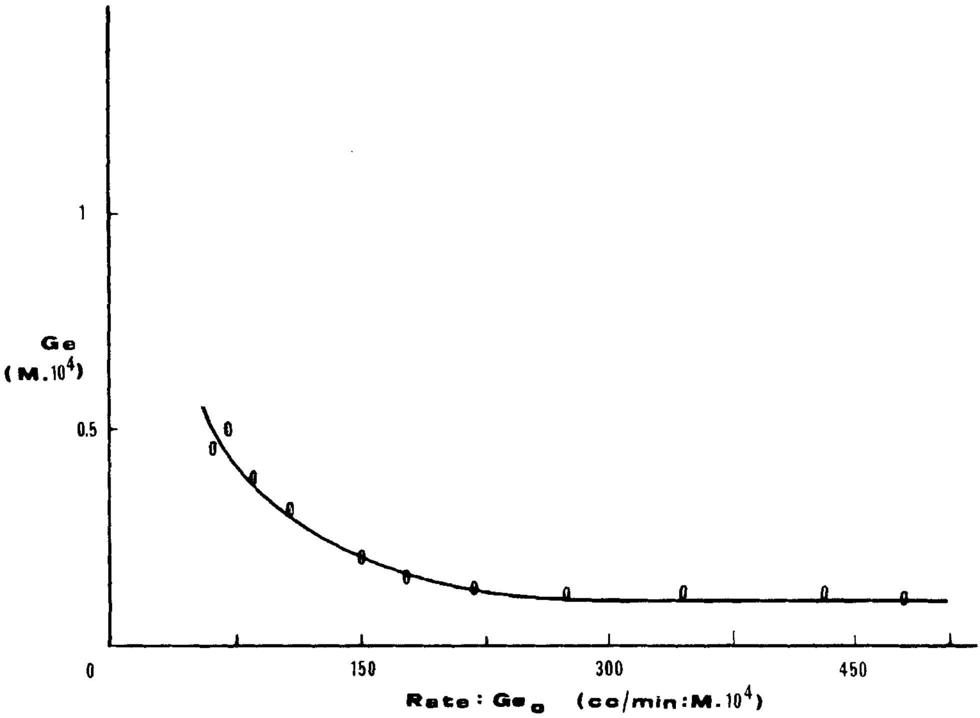

FIG. 2. Concentration of germanium remaining in solution after flotation when the ratio of gas flow rate/initial concentration is increased (where $[Ge]_0$ $1 \times 10^{-4}$ *M*, pH about 7, [pyrogallol] $3.3 \times 10^{-4}$ *M*, [dodecylamine] $2.2 \times 10^{-4}$ *M*, retention time 300 s, ethanol 0.5% v/v).

## pH of the Solution

This is the parameter studied by almost all investigators (*3*). The experimental results in this case are presented in Fig. 3; they show the best flotation at a pH value of approximately 7. Solutions of 0.1 *M* NaOH or HCl were used for the pH variations. The process is particularly susceptible to this parameter, so its control is of considerable importance, as is also often the case with conventional froth flotation of minerals.

Similar results on the pH effect were also obtained for the adsorbing colloid flotation of arsenic (*16*). Therefore, knowledge of how pH affects each system is a prerequisite for successful flotation. On adjusting the pH to extreme values, the process may be suppressed due to increased ionic strength.

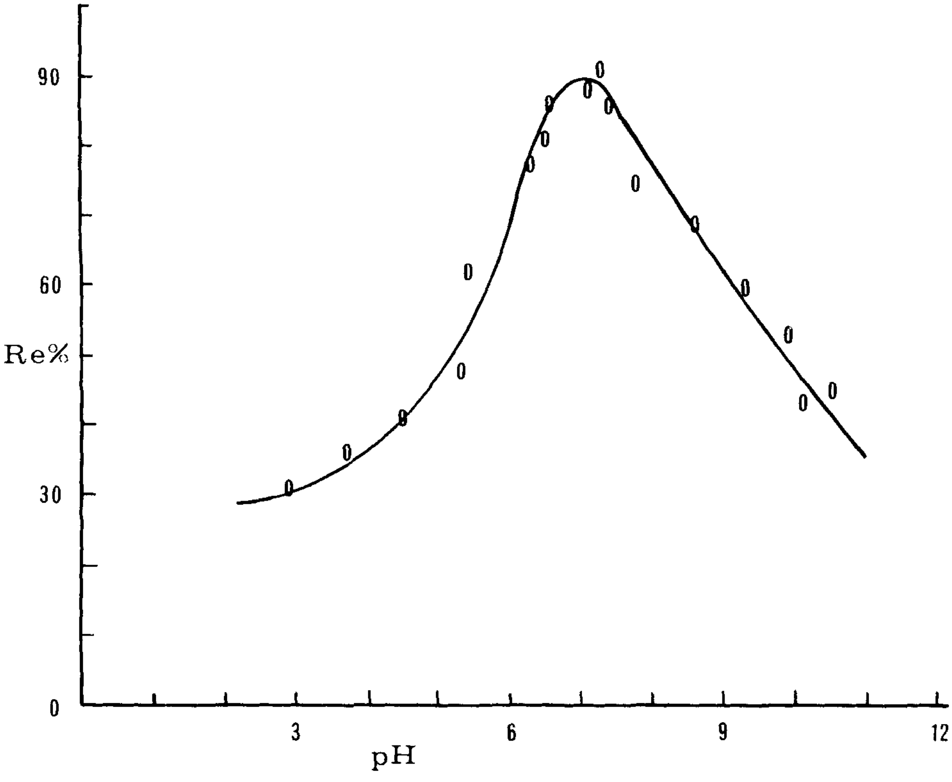

FIG. 3. Effect of the pH value of solution on flotation recovery of germanium (where $[Ge]_0$ $1 \times 10^{-4}$ *M*, [pyrogallol] $3.3 \times 10^{-4}$ *M*, [dodecylamine] $2.2 \times 10^{-4}$ *M*, pH about 7, retention time 300 s, ethanol 0.5% v/v).

## Ionic Strength

It is generally agreed *(14)* that the presence of neutral salts decreases the efficiency of ion flotation and that this arises because of competition for surfactants between the colligends and the added ions. Ions of a charge opposite to that of a surfactant have, as expected, the most influence.

In ion flotation of chromium *(17)*, also using laurylamine, it was found that interference was more marked in the presence of $PO_4^{3-}$ ions than of $SO_4^{2-}$ ions than of $Cl^-$ ions. Exactly the same influence was obtained for germanium, as shown in Fig. 4.

For these serious reductions in recoveries at quite high values of the ionic strength, three possible reasons were given: (a) the attachment of the surfactant was less secure because the zeta potential is reduced by increased ionic strength; (b) flotation of the surfactant was more rapid,

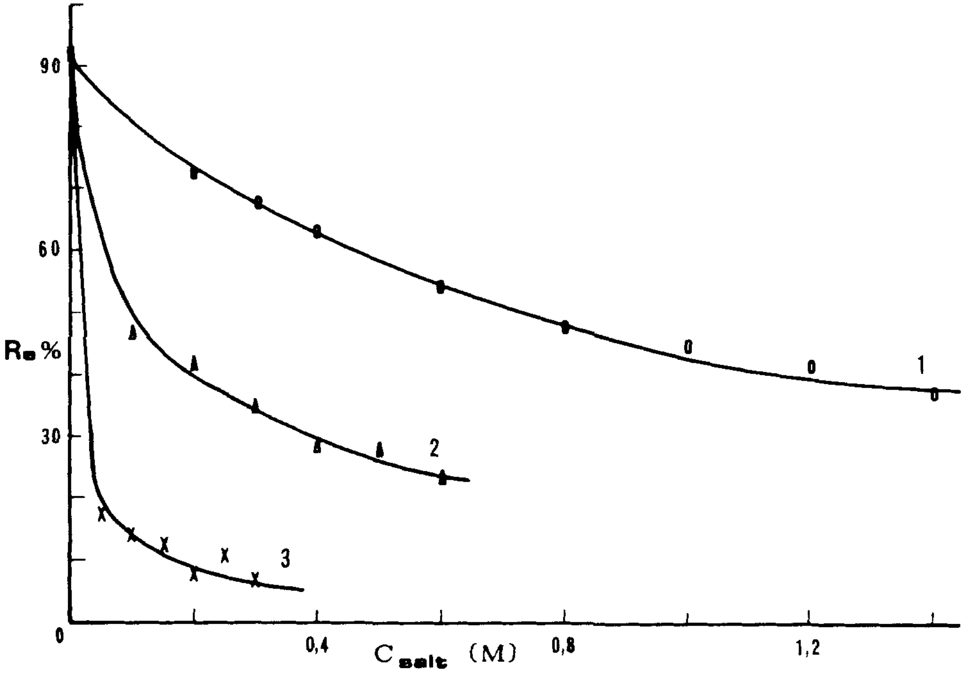

FIG. 4. Decrease of germanium recovery with the addition of increasing amounts of foreign salts as 1) $NH_4Cl$, 2) $(NH_4)_2SO_4$, and 3) $(NH_4)_3PO_4$ (where $[Ge]_0$ $1 \times 10^{-4}$ *M*, [pyrogallol] $3.3 \times 10^{-4}$ *M*, [dodecylamine] $2.2 \times 10^{-4}$ *M*, retention time 300 s, ethanol 0.5% v/v).

probably due to reduction in repulsions between bubbles; and (c) bubbles were more susceptible to rupture, and drainage from them was more rapid.

However, the addition of salts in order to increase the ionic strength of the solution changed the pH value due to their hydrolysis, possibly moving it outside the optimum range. Therefore the decreased recoveries were partly due to the changed pH value and not to the ionic strength. Some additional tests with corrected pH values confirmed the above explanation, as shown in Table 1, where the "new" recoveries at optimum pH were always greater compared with the initial ones (of Fig. 4), but still not quite satisfactory.

Another effort was increasing the added surfactant concentration and thus counteracting the negative effects of the foreign anions present in the solution, as shown in Fig. 5. The results again showed improved recoveries. In these experiments the amount of activator (pyrogallol) was kept constant because it was not expected to have an influence. In fact, the addition of even double the amount of pyrogallol normally used, at a constant amount of amine, had only a minor effect on germanium recovery. The ageing of solutions was also studied, but no significant differences were observed in flotation after a day.

Finally, two types of surfactant solutions were tested, aqueous and alcoholic. The results presented as Fig. 6 show increased recovery of germanium with the latter due mainly to greater dissolution of laurylamine in ethanol, as explained in more detail in the following section.

## Surfactant

The addition of surfactant can be made in one dose at the commencement of the process or through a number of small additions at various

TABLE 1

Effect of pH Correction on Germanium Recovery at Increased Ionic Strength

| I = 0.3 *M*, addition of | pH variation | | *R*% (comparison) | |
|---|---|---|---|---|
| | From | To | Initial | New |
| $NH_4Cl$ | 5.8 | 7.1 | 68 | 87 |
| $(NH_4)_2SO_4$ | 6.0 | 7.0 | 47 | 54.3 |
| $(NH_4)_3PO_4$ | 9.5 | 7.2 | 18 | 37.8 |

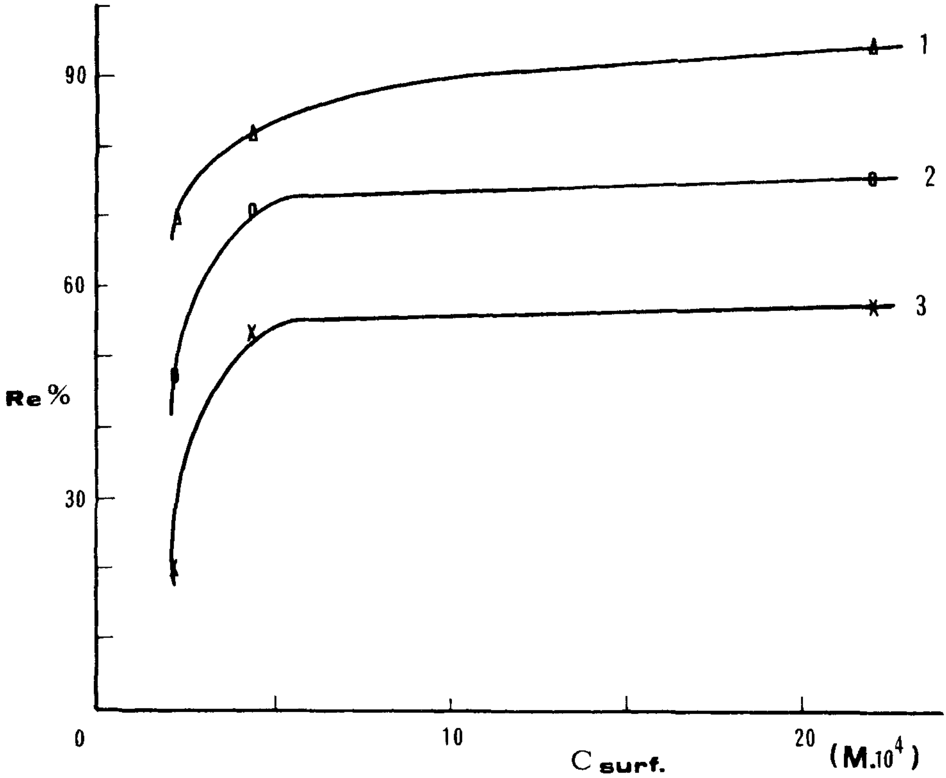

FIG. 5. Effect of surfactant (laurylamine) concentration on recovery, having an increased ionic strength of 0.3 *M*, adding 1) $NH_4Cl$, 2) $(NH_4)_2SO_4$, and 3) $(NH_4)_3PO_4$ (where $[Ge]_0$ $1 \times 10^{-4}$ *M*, [pyrogallol] $3.3 \times 10^{-4}$ *M*, retention time 300 s, ethanol 0.5% v/v).

intervals thereafter. No difference in removals was achieved by the two methods.

The amount of surfactant added must be controlled with some care, having in mind the extra operating costs of the excess surfactant added, and also the fact that the extent of foaming usually depends on the surfactant concentration. The results are given in Fig. 7. A significant negative influence of surfactant excess was noticed. It could be attributed to competition between the species and the surfactant ions for places on the bubble surface.

This influence was counteracted by increasing the retention time, giving again high germanium recoveries. The concentration limit of surfactant, considered as that producing at least 95% flotation, was found

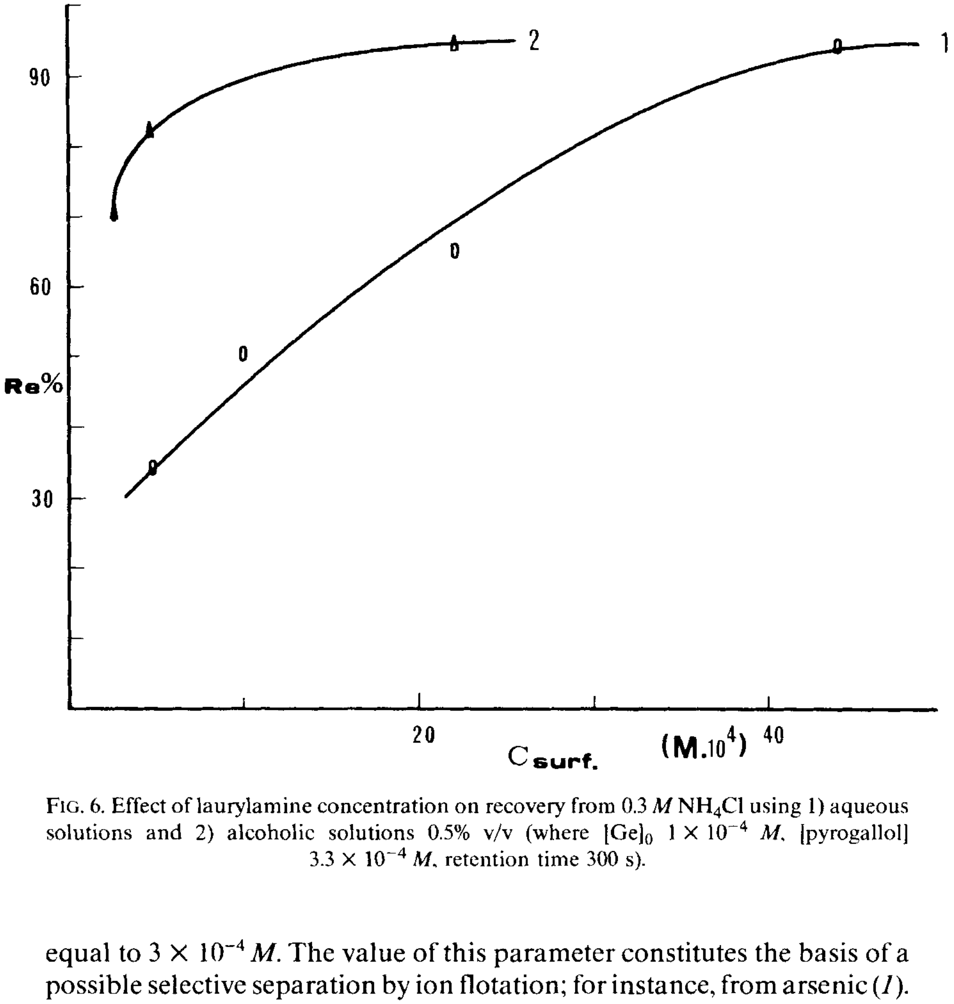

FIG. 6. Effect of laurylamine concentration on recovery from 0.3 $M$ $NH_4Cl$ using 1) aqueous solutions and 2) alcoholic solutions 0.5% v/v (where $[Ge]_0$ $1 \times 10^{-4}$ $M$, [pyrogallol] $3.3 \times 10^{-4}$ $M$, retention time 300 s).

equal to $3 \times 10^{-4}$ $M$. The value of this parameter constitutes the basis of a possible selective separation by ion flotation; for instance, from arsenic (*1*).

The type of surfactant was also examined; a number of primary aliphatic amines of varying hydrocarbon chain were tested in ethanolic solutions. The results are shown in Fig. 8. Higher germanium recovery was noticed with laurylamine (dodecylamine) at $2.2 \times 10^{-4}$ $M$.

The reasons for this behavior with increasing chain length were possibly the following: (a) the increase of hydrophobicity of amines, (b) the reduction in free surface energy (with the increasing chain length), (c) the reduction of amine solubility, and (d) the solution pH was kept at about 7 in all cases, which might not be optimum for the other surfactants. Hence, a medium length hydrocarbon chain was better.

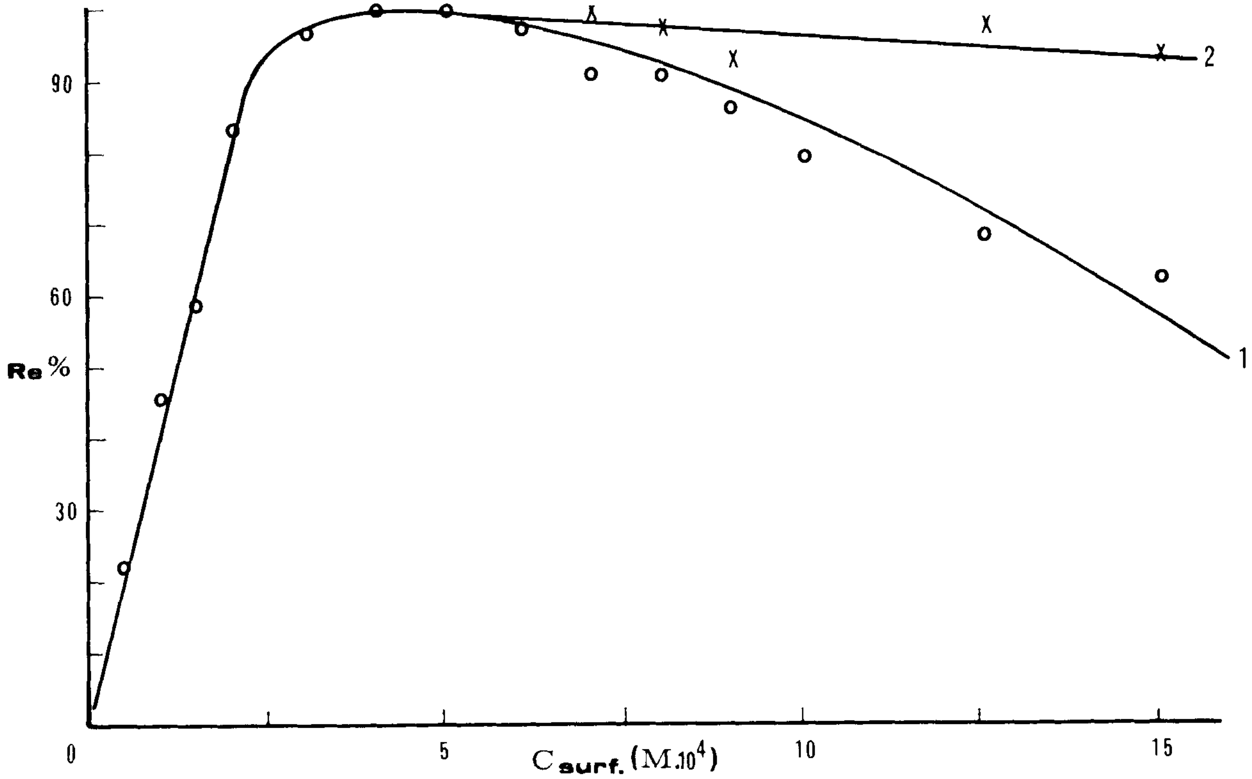

FIG. 7. Addition of an excess of laurylamine at optimum flotation conditions with retention times of 1) 300 s and 2) 600 s (where $[Ge]_0$ $1 \times 10^{-4}$ *M*, [pyrogallol] $3.3 \times 10^{-4}$ *M*, ethanol 0.5% v/v).

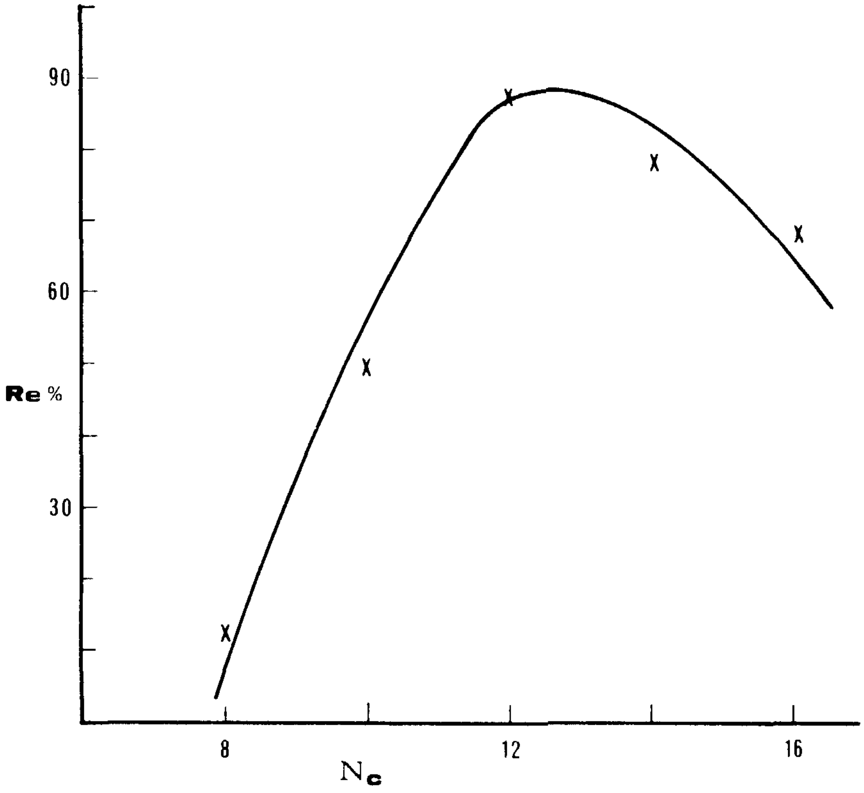

FIG. 8. Various aliphatic primary amines examined as surfactants; effect on flotation recovery of the number of carbon atoms contained in the surfactant (where $[Ge]_0$ 1 × $10^{-4}$ *M*, [pyrogallol] 3.3 × $10^{-4}$ *M*, [surfactant concentration] 2.2 × $10^{-4}$ *M*, retention time 300 s, ethanol 0.5% v/v).

Other reagents besides pyrogallol were then investigated as activators of germanium for ion flotation. In all cases the results were not promising.

## Frother

The surfactant is often added in the form of an ethanolic solution, which actually was first done in order to avoid the formation of micelles, but was later questioned (*14*) (the critical micelle concentration of laurylamine is 1.3 × $10^{-4}$ *M*). This procedure has been continued because many of the surfactants in use are not very soluble in water and it is convenient to maintain them in solution until they come in contact with the colligend.

Adding ethanol has the further advantage that the bubble sizes are smaller. Figure 9 shows the effect of the amount of ethanol added, where the surfactant concentration was kept constant. A decrease in germanium recovery was noticed with increased addition, depressing flotation; however, a small quantity was always added because it produced better results in comparison with aqueous solutions (Fig. 6).

The surface tension of the solution, measured with a Traube appararus, decreased as the ethanol concentration increased, as shown in Fig. 9; this has a significant effect in the present work. This decrease is mainly due to ethanol and not to the surfactant. A specific amount of ethanol produced

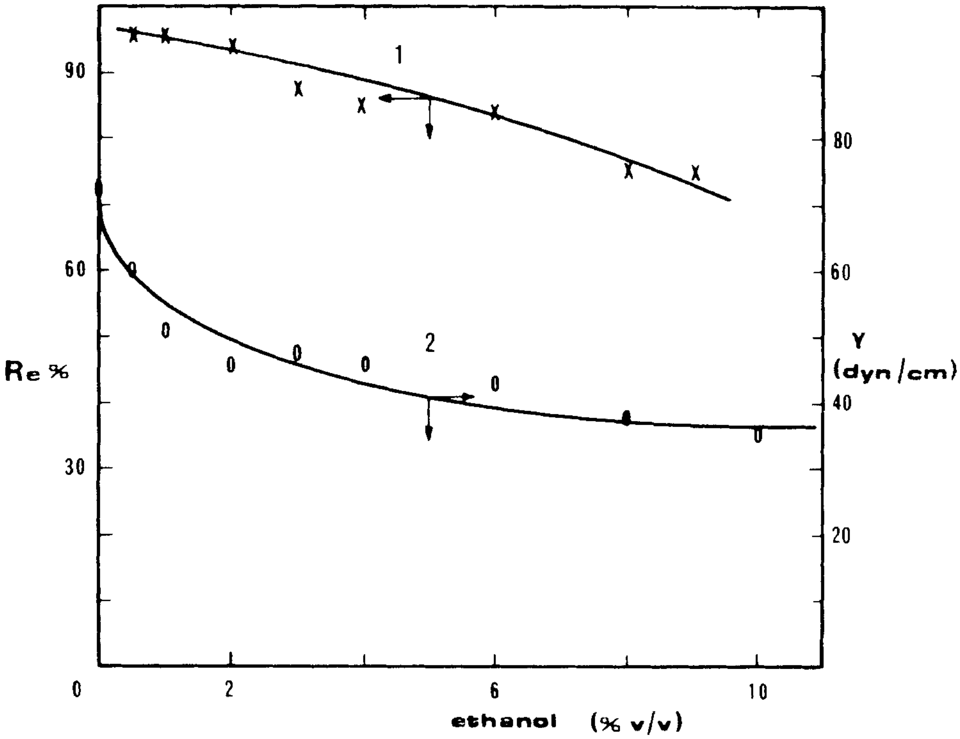

FIG. 9. Effect of ethanolic addition on 1) germanium recovery and 2) surface tension of solution (where $[Ge]_0$ $1 \times 10^{-4}$ *M*, [pyrogallol] $3.3 \times 10^{-4}$ *M*, [dodecylamine] $2.2 \times 10^{-4}$ *M*, retention time 300 s).

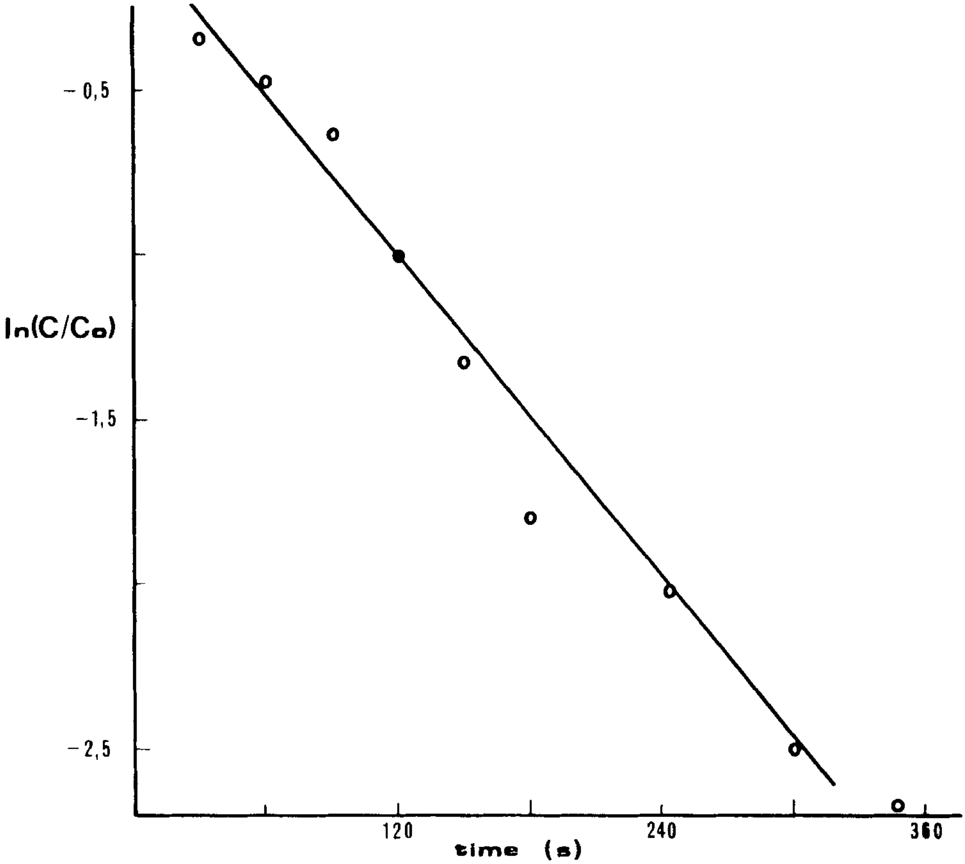

FIG. 10. Test of the first-order kinetic equation, $-dC/dt = kC$, with boundary conditions when $t = 0$, $C = C_0$ and $t = t$, $C = C$ (where $C$ stands for germanium concentration measured after the experiment and $t$ for flotation retention time). Conditions: $C_0$ $1 \times 10^{-4}$ $M$, [pyrogallol] $3.3 \times 10^{-4}$ $M$, [dodecylamine] $2.2 \times 10^{-4}$ $M$, ethanol 0.5% v/v.

the reduction, and additional ethanol did not have an appreciable effect. Tests carried out only with ethanol (and no surfactant) gave small recoveries.

Finally, the operation from the kinetic point of view and in the normal way was examined *(18)*. This could be a helpful tool for design calculations. In analogy with chemical reactions, the basic elementary reaction equations were tested, assuming that during the whole flotation procedure the order of the rate ($-dC/dt$) was not changed. The first-order kinetic equation was followed with quite good agreement obtained from a series of experiments with flotation time as a variable (Fig. 10). The flotation rate constant, $k$, easily calculated, was found to be 0.008 $s^{-1}$.

## CONCLUSIONS

Ion flotation was found promising for germanium removal by following the dispersed-air flotation technique on a bench scale and particularly for dilute aqueous solutions of $10^{-4}$ $M$ concentration. The effect of initial germanium concentration was examined. Pyrogallol as a ligand (flotation activator) and laurylamine as a surfactant were used, at specified pHs of the solution, both in stoichiometric amounts for a product collected in the foam with composition $L_2GeP_3$. The pH was an important parameter. A summary of the best conditions found are given in Table 2.

The surfactant was conveniently fed as an ethanolic solution, which decreased the surface tension of the system. Aqueous solutions were also examined, as well as the effects of the ageing of the solution. The significant parameters of the process were investigated and discussed. Other primary amines were tested.

The process was especially sensitive to the ionic strength of solution, studied extensively by the addition of ammonium salts. The relation found regarding the recovery decrease was $PO_4^{3-} > SO_4^{2-} > Cl^-$. A pH correction and the use of surfactant in excess in this case were observed to

TABLE 2
Laboratory Flotation Conditions and Results

| | |
|---|---|
| Tested volume | 100 $cm^3$ |
| Ge initial | $1 \times 10^{-4} M$ |
| Pyrogallol/Ge | Three times |
| Dodecylamine/Ge | Twice |
| + Reagents excess | 10% |
| Ethanol | 0.5% |
| pH | 7 |
| Stirring | No |
| Nitrogen flow rate | 3.33 $cm^3/s$ |
| Pressure difference | 26.6 $kN/m^2$ |
| Glass frit | $D_4$ |
| Retention time | 300 s |
| Ge recovery | >90% |
| Flotation rate | 1st order |

improve flotation. Agreement has been noticed of the obtained results with other flotation systems in the literature.

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*Received by editor January 26, 1987*
*Revised June 18, 1987*