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### Separations Using Aphrons

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## SEPARATIONS USING APHRONS

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### INTRODUCTION

The recent development of two novel colloidal systems has opened up new avenues for separation techniques, some very powerful. On the surface the two systems appear very different, but they both have one common feature, namely they have one phase, either liquid or gas, in a very finely comminuted form, surrounded by an aqueous soapy shell. Phases in this encapsulated form have been named aphrons because they are similar to the units from which foams are constructed. An example of a giant gas aphron is a free-floating soap bubble. A typical polyederschaum foam is comprised of an aggregate of giant gas aphrons or bubbles separated by a thin aqueous lamella, with the bubbles so congested that each unit is distorted into a polyhedron. The wetter kugelschaum foams simply comprise a very large number of spherical aphrons. The essential difference is simply one of crowding. When

the encapsulated soap bubbles are of colloidal dimensions, usually between 25 to 100 microns in diameter, the system is called colloidal gas aphrons, or CGA. Similar structures exist in which the internal core within the soapy film is a liquid which is immiscible with water. These could be known as colloidal liquid aphrons, or CLA. They are the units for a type of biliquid foam, Sebba<sup>1</sup>, in which water is the continuous phase, and which has been called a polyaphron; Sebba<sup>2</sup>. Polyaphrons can be made which contain up to 96% by volume of aphrons, which are micron or sub-micron in size and which are dispersed in 4% of water. If properly prepared these are stable enough to be stored for years without deterioration. Both these systems, either on their own, or in combination have remarkable capabilities in separation techniques.

#### 1. Colloidal Gas Aphrons, (CGA's)

These were first proposed in Sebba<sup>3</sup>, under the name microfoams. Subsequent experience with them has suggested that the present name is more appropriate. For several years, they were produced, as originally proposed, by the very rapid flow of a  $10^{-3}$ M aqueous solution of a surfactant through a venturi throat where entry of gas was permitted through an extremely narrow channel, usually under slight pressure. By recycling several times it is possible to incorporate up to 65% of gas in the water, with gas aphrons about 25 microns upwards in diameter. Gas aphrons less than 25 microns in diameter are transient and soon disappear because of the excess pressure inside them. This pressure is inversely proportional to the diameter so the smaller

aphrons lose their gas to the larger by diffusion. As the aphrons are still spherical and do not coalesce, the system flows very easily and can be pumped to the place of utilisation. The disadvantage of the venturi method is that it requires a powerful circulating pump as well as the need for recycling. This introduces problems for scale up.

An improved method which is simpler in design has recently been perfected; Sebba<sup>4</sup>. It involves a horizontal disc which rotates very rapidly (above 4000 rpm) and is positioned about two centimeters below the surface of the surfactant solution. The disc is mounted between two vertical baffles which extend well above the surface of the solution. Such a device will make three liters of CGA in a few seconds and could easily be scaled-up for large scale production, at a cost estimated to be less than 1 KWH of electricity for 10000 liters of CGA. A full account of the properties of CGA will be found in Sebba<sup>5</sup>.

CGA's can be used for separations in the following categories:-

- (a) Stripping of dissolved gases from water.
  - (b) Removing finely dispersed oils from water.
  - (c) Ion and precipitate flotation.
  - (d) Removal of finely divided suspensions of solids from water.
  - (e) Removal of ash forming materials from coal.
  - (f) Bubble-entrained floc flotation.
  - (g) Detergency.
  - (h) Removal of oil from sands.
  - (i) Flotation of microorganisms such as algae and bacteria.
- (a) Stripping of dissolved gases from water by use of CGA.

Because of the large area of interface between the gas bubbles and the water, transfer of gas from water to the bubble will be very rapid. One liter of CGA containing 60% of air, in bubbles 24 microns in diameter, will expose an area of  $150 \text{ m}^2$  of interface to the water. Although there has not yet been any experimental work to establish that stripping of dissolved gases from the water would be facilitated by the use of CGA, it is reasonable to suppose that equilibrium between the bubble and any dissolved gases would soon be established. Bubbles of diameter 30 microns will rise at about 0.09 cm/sec. This means that in a column of 50 cm in height, the contact time of each bubble introduced at the bottom of the column would be about 9 minutes, more than enough to establish equilibrium. However most of the bubbles will rise much faster than this. This is because there will always be some larger bubbles and the smaller bubbles tend to adhere to them and are thus buoyed up more rapidly. There is another factor which would promote efficient stripping. This is dealt with more fully in an analogous situation in the discussion on predispersed solvent extraction. Briefly, the relevant equilibrium is that prevailing just before the bubble moves through the surface to form a conventional foam. There is thus a procession of bubbles, each stripping from a slightly more dilute solution. The effect of this is that the efficiency of extraction depends upon an exponential relationship, with the number of gas aaphrons in the exponent. This is very large so that stripping should be very effective.

The converse may also be possible, namely dissolving contaminating gases out of air which has been made into a CGA, gases such as sulfur dioxide from smoke stacks.

## (b) Removal of finely dispersed oils from water.

Because CGA bubbles are encapsulated in a soap film, there will be a distinct surface between the outside of the bubble and the water. This surface will be slightly hydrophobic because of the surfactant in the soap film which will be orientated hydrophobic end outward. Oil droplets will tend to attach to this surface. If they have some surfactant dissolved in them, as is highly probable, these droplets will tend to spread at the interface, just as an oil slick will spread at a water-air interface. As the area of a bubble is limited, the spreading will be resisted by the surface pressure produced by the surfactant which is present in the bubble shell. The oil shows up under the microscope as tiny cusp-like droplets which sometimes completely surround the bubble. They are in general much smaller than the bubbles, so each bubble can transport perhaps hundreds of such oil droplets. They are then buoyed to the surface by the CGA bubbles. Often, but not always, once they break through the water-air interface, the bubbles are destabilised by the oil so that they break, the oil coalesces and there is very little foam built up. Should a foam build up, it eventually breaks, the oil droplets coalesce and a layer of the oil on the surface of the water is produced.

As an illustration of this capability, it was tried on the effluent from the tar-sands extraction plant in Alberta. This has a suspension of finely divided oil droplets which are very difficult to remove and give rise to a serious environmental problem. A sample of such effluent responded well to introduction of a CGA, the oil being floated to the surface by the gas aphrons.

Oils such as nitrobenzene, and limonene were also

removed from water in this way. It should be noted that no collector is needed for such flotation, the spreading pressure of the oil being enough to promote adherence to the bubble. There will, of course, always be some surfactant which is necessary for the production of the CGA.

(c). Ion and precipitate flotation.

These both depend upon the use of very small bubbles for the upward buoying process. CGA bubbles can be used for this purpose with the added advantage that they can be accurately metered. Ciriello, Barnett, and DeLuise<sup>6</sup> have demonstrated the use of CGA for removal of chromium, nickel and zinc from electroplating effluents. Shea and Barnett<sup>7</sup> have shown that dyes can be removed from effluents by ion flotation using CGA.

(d) Removal of finely divided solids from water.

The effectiveness of this is probably due to the fact that finely divided solids can get in between the outer surface of the gas bubble and the water in which it is immersed. The outer surface of a bubble is elastic and fine particles tend to stick in it and are thereby buoyed to the surface. Unlike ion and precipitate flotation which depend upon the attraction of opposite charges, this type of flotation does not have any charge relationship, and therefore uncharged particles can be floated by CGA made using surfactants carrying any charge, or even non-ionic surfactants. Barnett and Lin<sup>8</sup> have shown that the debris floating in fish culture ponds can be effectively removed by floating with CGA. Barnett has also successfully floated finely dispersed cellulose using a phrons.

(e) Removal of ash forming materials from coal.

In order to remove the ash forming materials from

coal it is necessary to crush the coal very finely in order to liberate the inorganic minerals. Separation of the coal from these particles which are often of colloidal dimensions becomes a difficult problem. Because CGA is exceptionally good for flotation of very small particles that cannot be floated by conventional flotation it has proved useful here. Yoon and his co-workers<sup>9</sup> have shown the possibilities in this connection. The process is a combination of agglomeration and flotation. A small amount of kerosine is added to a slurry of the finely crushed coal and an anionic CGA is introduced. Being anionic the bubbles repel the negatively charged clays and other minerals, but the coal, being wetted by the kerosine, adheres to the bubbles and is floated. By repeating the process a second time, significant clean-up of the coal has been achieved.

(f) Bubble-entrained floc flotation.

This is the name given to the process in which, instead of the solid adhering to the outside of the bubble, the solid is flocculated in such a way that the bubbles are entrained in the floc, thus making it buoyant; Auten and Sebba<sup>10</sup>. This shows promise on the industrial scale for separation of flocs as it eliminates the need for expensive filtration procedures which are sometimes very slow where gelatinous flocs are concerned. It has been successfully demonstrated on a bench scale for the flotation of the colloidal clays from the Florida phosphate slimes. These are very fine suspensions obtained in the washing of the phosphate ore prior to conventional flotation. The nature is such that they do not settle completely even on standing for several years. If suitable flocculants such as aluminum sulfate, after pH adjustment, or cationic starches or

other polyelectrolytes, are added, followed by addition of CGA made with an anionic surfactant, the clays are flocculated entraining the fine bubbles and are thereby buoyed to the surface, where they are retained in the froth. Because of the large surface area introduced by the bubbles such a froth dries in the air in a day or so, producing a fine powder of dried clay. The flocculating agent can be introduced in the CGA itself, the bubbles apparently nucleating the floc. For example, a CGA made of a mixture of cationic dodecylamine chloride (0.1 g/l) and non-ionic tergitol, 15-S-9 (0.25 g/l), will flocculate and float the clays, yet leave the considerable amount of finely divided phosphate rock, still present in the wash water slimes as an unfloated sediment. This demonstrates that given the correct conditions, bubble-entrained floc flotation can be made selective; Alexander, de Moor and Sebba,<sup>11</sup>.

The encouraging results with the Florida phosphate slimes suggests an even broader application. Because of the rapid depletion of the higher grade ores of minerals, it is imperative that methods be developed for extracting values from lower grade deposits. This will necessitate crushing to smaller sizes in order to liberate the desired minerals. This means that the powder will be so fine that conventional flotation methods can no longer be used. However, bubble-entrained floc flotation offers possibilities in this area as particles of colloidal size can be floated. What is necessary is that a selective flocculant be found which would promote a floc surrounding the bubbles, but leave the gangue unfloated.

Another application of bubble-entrained floc flotation which is being tested on a pilot plant scale at York, Pennsylvania, under a contract awarded by the

Department of Interior, is the clean-up of the effluent water from an industrial laundry. This black, murky water contains lint, soot, oil, and finely divided metallic particles. After addition of aluminum sulphate and adjustment of pH, two floatations with an anionic CGA produces a clear white water which could be reused.

(g) Detergency.

Although detergency is not usually looked upon as a separation process, the first stage, namely the removal of the soil from the substrate, is really a separation process involving the separation of liquid or solid soils from a solid substrate. CGA's have proved to be very effective for the removal of oily soils from solids, and, indeed, for several years now, CGA's have been used for cleaning oily glassware. Presumably, the imbalance of forces at the solid-oil-water-gas contact point involves the loosening of the oil with penetration of the surfactant solution between it and the solid. The oil, having been separated from the solid, attaches to the soap film surrounding the gas aphon and is then removed from the vicinity of the solid surface to which it does not return. The efficiency is much improved if the removal is assisted by use of a test-tube brush. Only a small volume of CGA is needed, but if the grease is very sticky a second treatment may be desirable. After the wash, the glass vessel is entirely free of oil and completely wettable by water.

(h) Removal of oils from sand.

This is very similar to detergency, except that the use of the test-tube brush is no longer possible. It has been found that if a CGA is passed through a bed of sand wetted by oil or gasoline, the advancing front

of the CGA carries with it the oil which it has removed from the sand; Michelsen, and Wallis<sup>12</sup>. There is potential application for this in clean-up of hazardous waste spills, such as oil or gasoline. It is also possible that this could be applied to tertiary oil recovery.

(i) Flotation of microorganisms such as algae and bacteria.

As very many organisms carry a negative charge on the surface, it is not surprising that a cationic CGA will attract the organism to the surface of the bubbles. The speed with which algae can be floated is very dramatic. If, to a suspension of algae in water so dilute that the green colour is barely observable, a cationic CGA made with dodecyltrimethylammonium chloride is added, within a few seconds a markedly green froth will be observed on the surface. This is a concentrate of the algae. This should be removed by skimming fairly quickly as sometimes there is a tendency, as the bubbles burst, for the algae to fall back into the water. One of the problems of run-off of nitrates and phosphates into natural bodies of water is the excessive growth of algae. These are very difficult to remove and the current method of dealing with this eutrophication problem is to kill the algae. However this does not solve the problem as the nutrients still remain. If the harvesting problem can be solved, as seems possible with CGA, then the nutrients are removed with the algae and the growth rate can be kept under control. Furthermore the harvested algae can be used as food for cattle, or as fertilizer. Other microorganisms could be collected in the same way; Honeycutt, Wallis and Sebba<sup>13</sup>. Many algae, bacteria and fungi manufacture useful chemicals which are retained in

their cells, but use cannot be made of this because of the difficulty of harvesting the microorganisms, i.e. separating them from the mother solution. Harvesting by flotation with CGA is so quick and efficient that there are new possibilities opened up for large scale microbiological production of chemicals.

## 2. Colloidal Liquid Aphrons and Polyaphrons.

Colloidal liquid aphrons, (CLA), differ from CGA in that, instead of gas in the hole, there is a liquid that is not soluble in the water, which is the continuous phase. The liquid aphrons can be much smaller than CGA bubbles, often sub-micron in diameter. In producing CLA often it is desirable to have some oil-soluble surfactant dissolved in the oil phase, and the size of the aphrons is determined by the concentration of surfactant; the higher the concentration, the smaller the aphrons. Like the bubbles in a CGA, the oil globules are encapsulated in a thin soapy film. This is the reason that concentrated CLA's, known as polyaphrons have some of the properties of foams, and are, in fact, biliquid foams of the type that have a continuous aqueous phase as the lamella, Sebba<sup>14</sup>. The methods of preparation of polyaphrons and some of their properties are fully described in Sebba<sup>2</sup>.

Polyaphrons containing as much as 96% of oil phase dispersed in 4% of water are easily prepared and can be stored for years without significant breakdown. Although they are thermodynamically unstable, it would seem that the encapsulating soapy film provides an energy barrier large enough to prevent spontaneous coalescence. It is convenient to describe polyaphrons in terms of the phase volume ratio, (PVR), which is the ratio of volume of oil phase to that of the continuous

aqueous phase. They are particularly useful in separations because of the very large interfacial area exposed. For example, one liter of polyaphron, PVR 9, with the diameter of aphrons averaging 2 microns, would have an interface between oil and water of  $2,700 \text{ m}^2$ . Such a large interface facilitates mass transfer across the interface.

There are several methods of separation being developed using polyaphrons. These methods include:-

- (j) Predispersed solvent extraction.
- (k) Separation of bitumen from tar and oil sands.
- (l) Detergency

(j) Predispersed Solvent Extraction.

Predispersed solvent extraction is a new method for separating solutes from aqueous solution by solvent extraction and one which has shown promise for extraction from extremely dilute solution very efficiently and very quickly. There are two unusual factors which contribute to this; there is no need for a mixing-settling stage, and the ratio of extracting solvent to pregnant solution can be very low, of order of one to a thousand or even lower. Mixer-settlers can be expensive, and for very dilute pregnant solutions the power costs can be significantly high and wasteful. The reason for this operation is the necessity for comminuting the phases in order to achieve a large interface between the pregnant and the solution in order to facilitate mass transfer. But there is really no need to comminute both phases. In fact, all that is necessary is to comminute one phase and clearly that would be the minor phase, namely the solvent. This can be achieved by converting the solvent into a polyaphron, which can be stored until it is to used. As

water is the continuous phase when a polyaphron is added to water it immediately breaks up into individual aphrons. In practice a fifty-fold dilution, prior to addition to the pregnant solution, has proved to be suitable.

Although the solvent is usually lighter than water and would be expected to rise to the surface under the influence of gravity, this is usually very slow because of the small size of the aphrons. Therefore, an essential feature of the new technique is the buoying of the aphrons to the surface by flotation using CGA. The microscopic liquid core aphrons adhere to the CGA bubbles, which being considerably larger than the solvent aphrons, have correspondingly more buoyancy. Thus they rise to the surface, very quickly, carrying the solvent with them. An essential step in this solvent extraction procedure is that after the diluted polyaphron has been added to the pregnant solution, an appropriate quantity of CGA is pumped into the cell, and left to stand for a few minutes, after which time the solvent will be found at the surface, having stripped the pregnant solution of the solute to be removed.

Predispersed solvent extraction can be achieved with very simple equipment, viz. a column that has a capacity about double the volume of the pregnant solution; entry points for the pregnant solution, the diluted polyaphrons, and the CGA; and a stopcock at the bottom of the column so that the raffinate can be run off and separated from the loaded solvent. A sketch of a laboratory cell is shown in figure 1. Presumably this could be modified very simply so as to operate as a continuous cell if the quantity of pregnant solution justifies this.

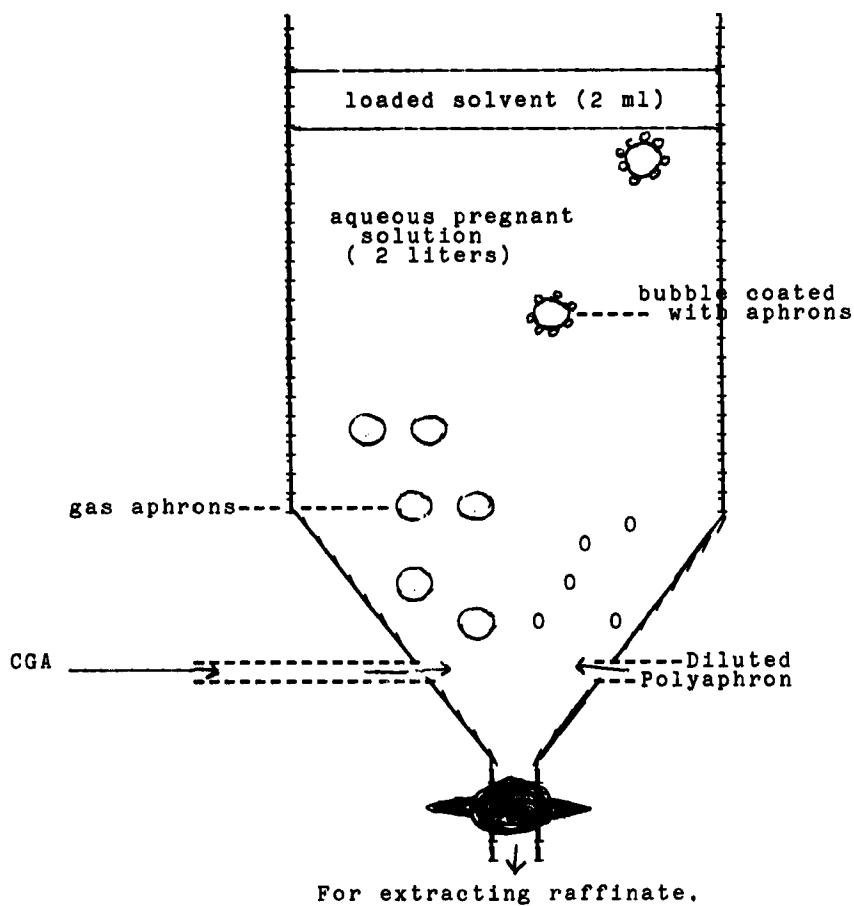
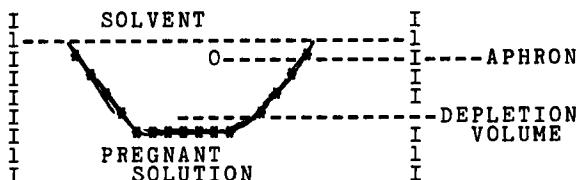


FIGURE 1

There is a very important difference between the theory of conventional solvent extraction and that of predispersed solvent extraction. Both depend, of course, on a favourable distribution coefficient of the solute between solvent and water. This will be referred to as the extraction coefficient,  $E$ . However in a mixing settling extraction, transfer from the

solution to the solvent will cease as soon as the equilibrium is established, so there is a limit to the amount of extraction at each stage. On the other hand, in predispersed solvent extraction the equilibrium is between each aphron and the pregnant solution at the point when the aphron is just about to leave the solution and enter the surface, effectively removing it from the equilibrium. Each aphron therefore leaves a portion of the solution which is slightly depleted in solute. Clearly each aphron cannot be in equilibrium with the total volume of pregnant solution, so it is convenient to define a Depletion Volume, which is that volume of pregnant solution with which the aphron has time to establish equilibrium just prior to leaving it, as sketched below.



The depletion volume would, of course, be dependent upon factors such as temperature, diffusion coefficient, and concentration, and would be an extremely small volume. However there are an enormous number of aphrons all following one another with each extracting irreversibly a small amount of solute. The net effect is that extraction in this way can be virtually complete, as the following derivation shows. A useful analogy is the case of washing a precipitate, where it is more efficient to wash a few times, having the wash liquid divided into small volumes, than once with the full amount.

Let volume of pregnant solution be  $V_T \text{ cm}^3$  which is stripped by a succession of  $N$  aaphrons, each of which has volume  $v \text{ cm}^2$ .

Let volume of solvent be  $V_S \text{ cm}^3 = f \cdot V_T$ , where  $f$  is ratio of volume of total solvent to volume of pregnant solution.

$$\text{Then } N \cdot v = V_S = f \cdot V_T.$$

Each aaphron prior to bursting through the surface of the solution is presumed to be in equilibrium with a limiting volume of the pregnant solution, the depletion volume,  $V_D$ .

Let initial number of moles of solute in volume  $V_D$  be "a".

If  $x_1$  moles of solute are left after extraction by aaphron 1, then amount extracted is  $a - x_1$  moles.

Let extraction coefficient  $E = C_S / C_W$ , where  $C_S$  is molar concentration of solute in solvent, and  $C_W$  is molar concentration of solute in pregnant solution.

$$\text{Then } C_S = (a - x_1) / v \text{ and } C_W = x_1 / V_D.$$

$$E = (a - x_1) / v \div x_1 / V_D = (a - x_1) \cdot V_D / x_1 v$$

$$\text{so } x_1 = V_D / (E \cdot v + V_D) \cdot a$$

After extraction by aaphron 2,  $x_2$  is left, and amount extracted is  $(x_1 - x_2)$ .

$$\text{Then } C_S = (x_1 - x_2) / v, \text{ and } C_W = x_2 / V_D$$

$$\text{and } E = C_S / C_W = (x_1 - x_2) / v \div x_2 / V_D.$$

$$\text{whence } x_2 = x_1 \cdot V_D / (E \cdot v + V_D)$$

$$= [V_D / (E \cdot v + V_D)]^2 \cdot a$$

After extraction by aaphron  $n$ ,

$$x_n = [V_D / (E \cdot v + V_D)]^n \cdot a$$

$$\text{or } x_n / a = p^n \text{ where } p = V_D / (E \cdot v + V_D).$$

It is the exponent " $n$ " which makes this form of solvent extraction so efficient. If " $f$ " is ratio of

total volume of solvent to total volume of pregnant,

$$n=f \cdot V_D/v.$$

If the aphon is delayed at interface for 0.5 secs. and diffusivity is  $10^{-5} \text{ cm}^2/\text{sec}$ , then  $V_D$  is approximately  $400 \mu\text{m}^3$

Assume  $f=0.3$  and  $v=1.0 \mu\text{m}^3$ , then  $n=120$ . Then if  $E=10$ ,  $x_n/a = 0.052$ , whereas for a single conventional extraction it would be 0.25.

On the other hand, if  $E=100$ , then  $x_n/a$  would be  $2.3 \times 10^{-12}$ , whereas for a single conventional extraction it would be 0.032.

There are two factors which determine the efficiency of the extraction. One is the value of "p" which must be as small a fraction as possible. Thus the larger the value of  $E$ , the extraction coefficient, the smaller "p" will be. Secondly the value of "n", the exponent, must be as large as possible. This would be determined by the ratio of volume of extracting solvent to the volume of the pregnant solution, "f", and by the size of the aphrons. The smaller the aphrons are, the larger "n" would be. As the aphrons are removed by flotation, a reduction in the size of the aphrons does not pose a problem unless they are made so small that they are virtually solubilised. Another way to ensure a large value for "n" would be to increase the value of the depletion volume. This could, perhaps be achieved by raising the temperature, thus raising the diffusion coefficient, but this has not yet been tried experimentally. It must be made clear that the above equations have not yet been tested quantitatively.

One potential problem that could prove troublesome is the amount of foam produced by the rising gas aphrons. An oil phase in the foam lamella often stabilises a foam, whereas ideally what is required is that the foam should break as quickly as possible once the bubbles have reached the surface. The problem can

often be avoided by a judicious choice of surfactant for the CGA, taking advantage of the contrafoam phenomenon as reported by Sebba<sup>15</sup>. This is the fact that a foam can often be broken by contacting it with a foam of opposite charge. If, for example, the polyaphron had been made using an anionic surfactant for the encapsulating soapy film, then the CGA that is to be used in the flotation stage should be made with a cationic surfactant. In this way the amount of foam is minimal provided no more CGA is used than is necessary for complete flotation.

As an example of the power of this technique, an oil-soluble dye, waxoline blue, was dispersed in water by dissolving it in alcohol and then adding it to two litres of water to produce a concentration of 2 parts per billion. At that concentration the dye behaved as though it was dissolved. The solution was placed in the cell. 1 ml of a kerosine polyaphron of PVR 20 was diluted fifty fold in water and then added to the pregnant solution. The polyaphron had been made using a solution of sodium dodecyl benzene sulphonate at a concentration of 4g per litre. As this was an anionic surfactant, the CGA was made using the cationic surfactant dodecyltrimethylammonium chloride at a concentration of 0.5g per litre. About 200 ml of CGA was introduced slowly into the pregnant solution, and within about a minute a layer of kerosine, coloured by the dye, collected above the solution. In this case, of course, the Extraction Coefficient must have been very high as the dye was an oil-soluble dye. Nevertheless, the speed and effectiveness of extraction at that low concentration is very encouraging. There is no reason why extraction could not be effected from even more dilute solutions in this way. It would seem that this method could be developed for extraction of hazardous

organic solutes from aqueous effluents, even if very dilute, before discharge into streams.

Copper has been extracted from a solution of copper sulphate ( $10^{-4}M$ ), using a 10% solution of a liquid ion exchanger, LIX-64N, an alpha-hydroxyoxime, in kerosine made up as a polyaphron with sodium dodecylbenzenesulphonate as the surfactant. In this case again the CGA was cationic so there was not any appreciable foam. The extraction in one pass was so effective that copper was undetectable in the raffinate. The procedure was based upon an earlier development, using more concentrated solutions, by Aggarwal <sup>16</sup>.

Uranium, as the complexed anion, has been concentrated from a solution of uranyl acetate, ( $5 \times 10^{-5}M$ ), using a polyaphron made up of 10% dodecylamine in kerosine, the surfactant in this case being cationic dodecyltrimethylammonium chloride. For that reason the CGA was made anionic, the surfactant being sodium dodecylbenzenesulphonate (0.3g per litre). Uranium at a similar concentration has also been extracted using a polyaphron made of tributyl phosphate dissolved in kerosine.

There have been cases where the raffinate has been slightly turbid. This is probably due to some solubilisation of the oil phase, although it does not seem to diminish the efficiency of the extraction. Should this be an undesirable feature, it can be easily remedied by adding a very small quantity of aluminium sulphate solution to the raffinate to produce a concentration of about 0.0001M, adjusting the pH to 5.5 and then introducing about 100ml of a CGA made of sodium dodecylbenzenesulphonate. An aluminium soap quickly floats to the surface containing all the suspended material leaving a perfectly clear solution.

This technique shows promise, not only for removal of traces of undesirable materials, organic as well as inorganic, from aqueous solution, but it might well also be used as a preliminary concentration technique in analytical chemistry, because it is so quick and simple.

(k) Separation of bitumen from tar and oil sands.

There is a very large quantity of hydrocarbon reserves tied up in tar and oil sands, but as yet there is no truly economic method for separating the organic material from the sand. One method being applied on an industrial scale is that in Alberta, which uses steam to reduce the viscosity of the oil, but that method only applies when the sand already has a thin film of water which separates it from the oil. Another possible method uses kerosine to liquefy the bitumen, but it is difficult to separate the kerosine solution from the sand. It has been found in the laboratory that polyaphrons made of kerosine have a good potential for achieving this separation. All that is necessary is to triturate the tar sand, previously broken up into fragments about the size of small nuts, with a polyaphron of PVR about 10. The aphrons break, the kerosine dissolves the bitumen, and the aqueous surfactant solution coats the mineral material, so that on dilution with a small quantity of water, the kerosine and oil float to the surface. There is a layer of water which may contain some suspended clay, and the sand, practically free of oil, sinks to the bottom of the vessel. A second trituration produces sand completely free of oil. This method applies equally well to tar sands which do not have a water layer round the sand. The water can be clarified from the clay by a bubble-entrained floc flotation using aluminum sulfate

as the flocculating agent. It is presumed that the very small size of the aphrons permits the water to get between the bitumen and the sand, wetting the sand because of the detergent that is there, and in this way providing an improvement on kerosine on its own.

A similar process could be developed for the large quantities of viscous oil deposits which are not recoverable with existing technology.

#### (1) Detergency.

The same principles that make polyaphrons suitable for removing bitumen from tar sands apply to give them special advantages in some forms of detergency. In this respect they resemble CGA's, and, like CGA's, they can be used for removing oil from glassware. All that is needed is to rub some kerosine polyaphron on the oily glass, and then rinse with water, when a completely water wettable glass surface will be produced. Similarly, polyaphrons, made of solvents suitable for cleaning textiles, can be used for removing stains from fabrics. Kerosine polyaphrons are particularly useful for removing tar from metals, leather or fabrics. They could also be used for degreasing metals in repair shops or factories. The special advantage is that, because of the thixotropic character of polyaphrons, they do not spread easily, so much smaller quantities can be used.

#### CONCLUSIONS.

CGA's and polyaphrons are still very new and there are possibly many other methods for separation that have not been mentioned in this paper. For example, it is possible that biomembranes are constructed of a monolayer of CLA's to produce one of the most efficient

separating processes. If we could develop similar structures using liquid aphrons, we might be able to produce equally efficient synthetic membranes.

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