

Electrochemical experiments in space

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MS received 29 March 1982

Abstract. The probable effects of rarefied atmosphere and near-zero gravity conditions that prevail in space, in relation to electrochemical experiments, are briefly discussed. The various space electrophoresis experiments are reviewed and discussed. Some possible additional electrochemical experiments are suggested.

1. Introduction

Space environment is characterised by the absence of atmosphere and a near-zero gravity condition (the so-called micro-gravity). In the case of molten salt electrochemical systems, the lack of atmosphere could be an advantage since the molten salt and the products of electrolysis will not have any interaction with atmosphere. Aqueous and non-aqueous electrochemical systems will pose problems in such rarefied atmospheres due to the volatilisation of high vapour pressure solvent which will demand closed circuit. Apart from these experimental problems, no significant effect is likely to arise from the lack of atmosphere in space.

The near zero gravity condition can have significant effect on electrochemical experiments. By and large electrochemical systems are governed by Nernst equation, Faraday's laws of electrolysis, and rate law. The constants occurring in these laws are not influenced by G . The rate is however dependent upon mass transfer which can under certain circumstances be influenced by G .

The most important effects of near-zero gravity from the point of view of an electrochemist is as follows :

- (i) almost zero convection current due to density gradient.
- (ii) absence of sedimentation of particles.

These effects lead to a better electrophoretic separation in space as compared to 1 G condition. We shall briefly review here the electrophoresis experiments in space. We shall also attempt at suggesting certain other interesting electrochemical experiments that can be done in space and briefly dwell on the utility of such experiments.

2. Electrophoresis

In biological research there is always a necessity of separating a single type of cell from a mixture and also isolating specific macromolecules from biological fluids which contain several types of them. Several of the separation technique is not well suited for the task of cell separation since they damage them (Ramaseshan 1978). Electrophoresis is a well-established electrochemical separation technique for the type of materials referred to above.

Electrophoresis is the electrokinetic method that physically separates charged particles in an aqueous medium under the influence of an electric field. Many different types of electrophoresis have been developed since Picton and Linder introduced the moving boundary technique which was made into an acceptable practical method for separation by Tiselius by developing a substantially improved version of the apparatus (Picton and Linder 1892 ; Tiselius 1937). This subject has been reviewed extensively (Moore 1960 ; Tiselius 1968).

In moving boundary electrophoresis, the sample is introduced into a stationary medium (buffer) in which two electrodes are placed. On applying a field, the charged species migrate to the oppositely charged electrode at different rates (governed by charge and mass of particle) and separate into zones. This technique is frequently referred, in space literature as free zone electrophoresis.

Isotachophoresis and isoelectric focussing can be regarded as interesting modifications of free zone electrophoresis and are briefly described below.

Isotachophoresis (from the Greek meaning 'equal speed') consists of placing a mixture of charged particles (sample) of the same sign (co-ions) in a column, containing in addition two electrolytes, one of which has co-ions more mobile than any sample co-ions, while the other electrolyte has co-ions less mobile than any sample co-ion, the entire electrolyte having a common counter-ion. Upon applying a constant d.c. current, the sample co-ions initially move at different velocities until a steady state is reached in which the sample ions separate into continuous zones with sharp interfaces in order of their mobilities. The zones, thereafter, migrate at the same velocities and adjust themselves into compartments of various lengths, concentrations and conductivities such that the product of the co-ion mobility and the field gradient is the same within each zone. The polarity of the electric field must be such that the leading ion migrates towards the electrode that is placed on the same side of the sample as the leading electrolyte.

In isoelectric focussing the charged particles of the sample is made to migrate under an electrical field in an electrolyte medium having a pH gradient. The charged particle (of sample) becomes neutral when it reaches the pH that represents its isoelectric point and becomes stationary. Thus the sample is separated into species of equal isoelectric point.

The different types of electrophoresis described above are useful for the qualitative analysis but are of marginal value as preparative techniques since their through-put is very poor. Flow electrophoresis or continuous flow electrophoresis is well suited for preparative purposes. In this method the buffer solution is made to flow. The sample is continuously fed into the flowing liquids (figure 1a). An electric field is applied perpendicular to the flow direction. The sample undergoes

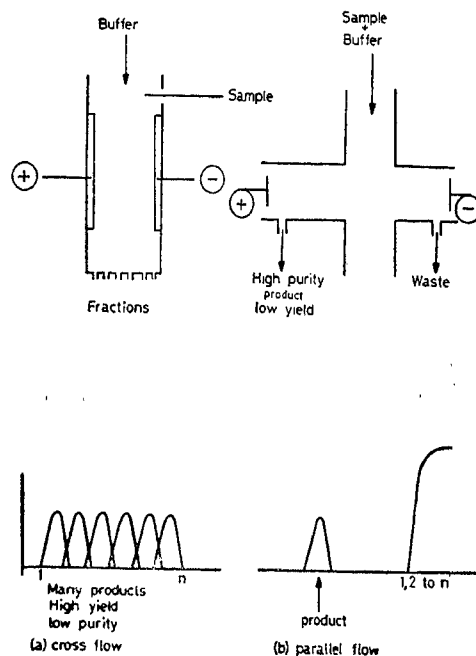


Figure 1. Modes of continuous flow electrophoresis.

separation during the residence time of the sample. By employing tapping ports, many products can be collected at high yield and low purity. If the electric field is applied parallel to the flow as in figure 1b then one of the products can be recovered at high purity, the yield however will be low.

3. Free zone electrophoresis and isotachopheresis experiments in space

Electrophoresis in a free fluid was first demonstrated in space during the Apollo 14 mission and was followed in the Apollo 16 mission (Snyder *et al* 1973) and in ASTP experiment MA-011. The Apollo 16 electrophoresis demonstration was performed using two different sizes of polystyrene latex particles. The results failed to yield much more than the proof that electrophoretic separation under micro-gravity can be achieved without sedimentation of particles.

The ASTP experiment MA-011 aimed at the electrophoretic separation of human lymphocytes, aldehyde fixed red blood cells and human kidney cells. Equipment problems during the attempted runs of lymphocytes prevented the acquisition of data that could have proved whether it is possible to obtain pure fractions of lymphocytes from heterogeneous cell populations.

Rabbit, human and horse red cells were partially resolved. The mean mobilities at the nearest neighbour populations (in this case) were separated by about $0.4 \mu\text{m S}^{-1} \text{V}^{-1}$. Therefore successful separation is not trivial.

Human foetal kidney cells produce the enzyme urokinase (UK) which is able to accomplish blood clot lysis and hence the interest in its commercial production for therapeutic purposes. Unfortunately only 5% cells in the cortex of the kidney produce UK (Bermic and Kwaan 1969). If these UK producing cells could be isolated and subcultured a 20 fold increase in production could probably be achieved. The kidney cell separation in ASTP experiment MA-011 was most encouraging. One of the separated band of cells on reculturing produced predominantly UK. The other band of cells on reculturing gave human granulocyte stimulating hormone as the prime product. This finding shows that the UK producing cells could be successfully separated in space, returned and cultured, thereby showing the possibility of using space electrophoresis for the commercial production of UK.

The isotachophoresis conducted in ASTP experiment MA-011, though demonstrated the remarkable sharpness of isotachophoretic boundaries was of limited value since equipment problems limited the value of the results. The potential application of this method in microgravity environment has been reviewed by Bier *et al* (1975). But the potentialities still remain unexplored.

4. Continuous flow electrophoresis experiments in space

The configuration for continuous flow electrophoresis is a rectangular parallelepiped with height, h , large relative to the width, w , and the depth d . The ratio d/w is also small. The electrode of length l is located on the end walls such that w represents the interelectrode distance. In this set-up the product form bands, parallel to the long axis. The occurrence of natural convection is detrimental because it results in a mixing of the fluid.

Two modes of natural convection can be distinguished : (i) conventional convection, (ii) unstable convection. These can either occur separately or together in a given configuration. Conventional convection is generated by a density gradient that is normal to the gravitational vector. This therefore results when the wall temperature and fluid temperature are different due to joule heating and wall cooling. Unstable convection can occur when the density gradient is parallel to but opposed to gravity vector. In this case, unlike conventional convection, the onset of motion is not immediate but starts when a critical temperature (density) gradient is exceeded. Once it starts it causes a lot more of mixing. The temperature gradient for this case is vertical, *i.e.*, the one that occurs when the fluid is passed down. Ostrach has presented a detailed analyses of both the types of convection (Ostrach 1976). These convectational disturbances are minimal if the interelectrode distance (gap) is small. But that affects the through-put. Thus through-put and resolution are opposed to each other under 1G condition. However, under microgravity condition, greater through-put can be achieved without sacrificing resolution by increasing the gap, since convection is virtually absent. Hence space environment offers specific advantage for preparative electrophoresis.

Continuous flow electrophoresis was attempted in ASTP experiment MA-014. A lot of experimental difficulties like long sample rest periods, absolute sealing of the fluid loops, resuspension of the sample in the absence of gravity and sepa-

ration and absorption of the hydrogen produced during electrophoresis were met with and were solved. The unsatisfactory working of the optical system imposed a limitation on the extent of availability of result. Rat bone marrow, rat spleen cells, rabbit and human erythrocytes and lymph node of rat were subjected to electrophoresis. The results in spite of the malfunctioning of the optical system show high resolution capability. The through-put was 7 cm³/hr whereas comparable ground equipment would have a through-put of 1.2 cm³/hr.

5. Discussion on the space electrophoresis experiments

Reviewing the results of batch type electrophoresis and continuous flow electrophoresis carried out in space, one finds that the runs yielded only partial qualitative results due to sample equipment and retrieval failures. It is probable that more significant results could have been obtained had a more fruitful and less ambitious course been followed in the planning of the experiments; no two runs were performed to separate the same initial mixture; no two flights carried exactly the same equipment. In spite of all these limitations the space electrophoresis experiments have established (1) good resolution could be achieved; (2) higher through-put could be obtained. With the exception of kidney cell separation, the space electrophoresis experiments have not shown it to be phenomenally different from that performed under 1G. This merits a detailed examination. Perhaps it is worthwhile to try out the suggestions of Ostrach to improve the through-put of 1G continuous flow electrolysis and compare it with space data.

6. Other electrochemical experiments that might be possible

6.1. Preparation of electrocomposites

Electroplating from plating baths containing suspended solids results in incorporation of the suspended solid (conducting or non-conducting) into the deposit. For example if Al₂O₃ were to be suspended in nickel plating bath and plated then the nickel plate contains a dispersion of Al₂O₃. In other words the suspension electrolysis has resulted in a composite of Ni + Al₂O₃. Since this composite has been produced by electrolysis, it is referred to as electrocomposite. Such composites can be tailored for improved wear resistance, abrasion resistance, for self lubrication or for cutting tool application.

The mechanism of 'Code position' of the suspended solid is little understood. Several theories like electrophoretic deposition, adsorption, etc., have been proposed. The experiments (Rajagopalan and Indira Rajagopalan) done by us in NAL makes us postulate the following hypothesis:

The suspended particles (Al₂O₃, SiC, WC, etc.) adsorb the metal ions say nickel ions. The particles are kept suspended by agitation. The particles of suspended solid moving within the liquid can hit the cathode. Some of them will bounce. A few can come to rest at the cathode surface because their kinetic energy is just equal to the energy absorbed by the metal on impact. Such particles would

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Possible studies on adhesion in space

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MS received 17 June 1980

Abstract. This paper reviews possible experiments on adhesion that can be carried out in a space lab environment. After introducing the basic concepts of adhesion physics, the proposed European experiment on surface energy measurement by dynamic methods in space environment is discussed and reviewed. It is concluded that as of now more studies on adhesion in terrestrial environment are desirable than space experiments.

Keywords. Adhesion; surface energy; space experiments.

“There are agents in Nature able to make particles of joint stick together by very strong attractions, and it is the business of experimental philosophy to find them out”

—Newton

1. Introduction

This paper will deal with possible studies pertaining to adhesion which can be carried out in *Spacelab*-like environment. Our concern will be mainly with the basic aspects of the phenomenon of adhesion, and related questions pertaining to surface physics. However, it may be pertinent to begin with a brief discussion of how adhesives are used in space technology. This will provide, though perhaps tenuously, some justification for engaging in basic studies!

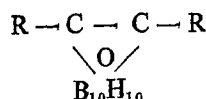
2. Adhesives in space technology

The ASTM Bulletin defines adhesion as “the state in which two surfaces are held together by interfacial forces”. An adhesive is a material that binds two surfaces by surface attachment.

For many years, adhesives had limited use in aircraft and spacecraft. The *Apollo* spacecraft was the first large airborne vehicle in which adhesives were utilised throughout most of the load-bearing structure. In the initial stages, there were many problems. Most of the bonds had to be scrapped or reworked due to voids caused by volatile matter escaping during the cure of adhesives. This led to a programme for developing stable, high-temperature adhesives, free from volatile formation.

The basic strategy was to try and introduce a stabilising linkage in the main chain of the epoxy monomer (Spiker and Barnes 1970). The chemical group

selected for this purpose was carborane $C_2B_{10}H_{12}$. The carbon and the boron atoms in carborane are arranged in an icosahedral array, and three isomers, ortho, meta and para, are possible, depending on the location of the carbon atoms. In orthocarborane, the two carbon atoms are adjacent to each other, and have a strong electron-withdrawing characteristic. Consequently, when this unit is bonded to other groups, the chemistry of these other groups is strongly affected. The structure of the substituted carborane is represented by



where R belongs to the epoxy. The monomer properties are substantially altered by bonding to carborane, and overall improved stability results. Incidentally we see here basic science in action to solve a practical problem.

3. Surface energy

We now address ourselves to the subject proper, and begin with a consideration of a crucial quantity, namely, the specific surface free energy. Denoted by γ , it is often abbreviated simply as surface energy. It is defined as the isothermal reversible work required for creating 1 cm^2 of a new surface. We can, for example, visualise this surface to be produced by applying a tension on a long prism with a square cross-section, and having a 1 cm edge. Further, the breaking is assumed to be done in a perfect vacuum. Since an energy γ is associated with each of the two surfaces created, it is evident by a converse argument that, if the solid could be restored to its original condition by a perfect adhesion of the two surfaces, the energy gained would be 2γ .

Observe that γ is essentially a macroscopic quantity. Though a tensor, we shall treat it here as a scalar. It is a convenient measure of surface properties, and fingerprints the latter the same way the yield stress, for example, gives a comprehensive feel for the mechanical properties of materials.

The calculation of γ from first principles has attracted considerable attention especially for atoms interacting *via* dispersion forces. We remind ourselves that such forces are operative mainly for closed-shell atoms.

The physical origin of these forces is schematically illustrated in figure 1. Here it is assumed that the interaction is instantaneous, *i.e.*, there is no delay in the inducing of a dipole moment on atom 2 due to a fluctuation in atom 1. Clearly this is not valid, especially for large r , since signals cannot travel faster than the velocity of light c . Retardation effects thus set in for large separations, and must be allowed for.

The force we have been considering so far is that between isolated atoms. As far as adhesion is concerned, we need to know something about forces between bodies with surfaces. These forces can be calculated by superposing the forces between all distinct pairs of atoms, one each in the two bodies. Table 1 (Israelachivili and Tabor 1972) gives a feel for such forces for different geometries.