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Design of an Apparatus for Determining Isoelectric Point of Charge

by RA UL A. DEJU *and* ROSHAN B. BHAPPU

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Electrophoresis

When a potential difference is externally applied to a solution containing suspended particles, it causes a migration of the particles to the pole which carries a charge opposite to that of the particles. If they are small ions, the phenomenon is called *ionic conductance;* if they are large molecules, such as proteins, it is called *electrophoresis;* and if they are of colloidal size, it is called *cataphoresis*.

THE ELECTRICAL DOUBLE LAYER

Generally, a mineral particle in solution carries a charge on its surface. The charge at the surface plus the ions in solution near the surface, to maintain electroneutrality, constitute the electrical double layer around the mineral particle. The ions within the solid responsible for the surface charge are termed *potential determining ions*. The potential at the surface of the mineral is called the *phi potential (*Ψ_0*)*. Part of the ions near the surface of the mineral are anchored in a plane directly adjacent to the surface. These ions, which are said to be in the Stern plane, are strongly held to the surface by chemical as well as electrostatic forces. The potential at this plane is called *zeta potential* (ζ). The remaining ions are loosely held by electrostatic forces and constitute the diffuse layer of counter ions which extends well into the solution. Figure 1 is a representation of all these layers.

The zero point of charge for a solid in contact with a solution is determined by the concentration of potential determining ions in solution. At this critical concentration there is no net transfer of free charges, and the electrical double layer is absent.

$H+$ and OH^- are potential determining ions for quartz and some other minerals, but for many other minerals they do not act as such. If the zero charge is a function of $H+$ and OH^- concentration, then zero charge can be expressed in terms of pH. For example, Fuerstenau (1953) found the zero charge of quartz to be p H 3.70.

ZETA POTENTIAL

If a mineral particle is placed in an electric field, the particle will move in one direction and the diffuse layer of counter ions will move oppositely. The potential of the moving particle is called *zeta potential* and causes the diffuse layer to keep re-forming. Therefore, the particle continues to appear the same. The moving particle carries with it a very thin liquid film which contains the solvated ions in the Stern plane.

In general, zeta potential can be regarded as the potential difference in an otherwise practically uniform medium between a point some distance from the surface and a point on the plane of shear (fig. 1). If the applied potential is held constant, the relation between the velocity of the particles and the zeta potential is given by Henry's equation as shown by Adamson (1960):

$$\zeta = \frac{V \pi \eta}{E\, D\, g(k, r)},$$

where ζ is the zeta potential, V is the velocity of the particle, E is the applied potential, η is the viscosity of the solution, g(k, r) is a function of the reciprocal thickness of the double layer, D is the dielectric constant, and r is the radius of the particle. The velocity can be experimentally determined and ζ calculated from the equation as a function of g(k, r). Miaw (1957) found g(k, r) for quartz particles to be 0.180. For particles of tabular or cylindrical shape, he found g(k, r) to be 0.250.

There is a wide discrepancy in the values for ζ obtained by different experimenters. For example, Fuerstenau, using a streaming potential apparatus, found the zeta potential of quartz to be —7.00 x 10^{-2} volts in conductivity water. However, Gaudin and Sun (1946), using an electrophoretic technique, found it to be —3.60 x 10^{-2} volts in conductivity water. These discrepancies may be due to differences in the past histories of the minerals used.

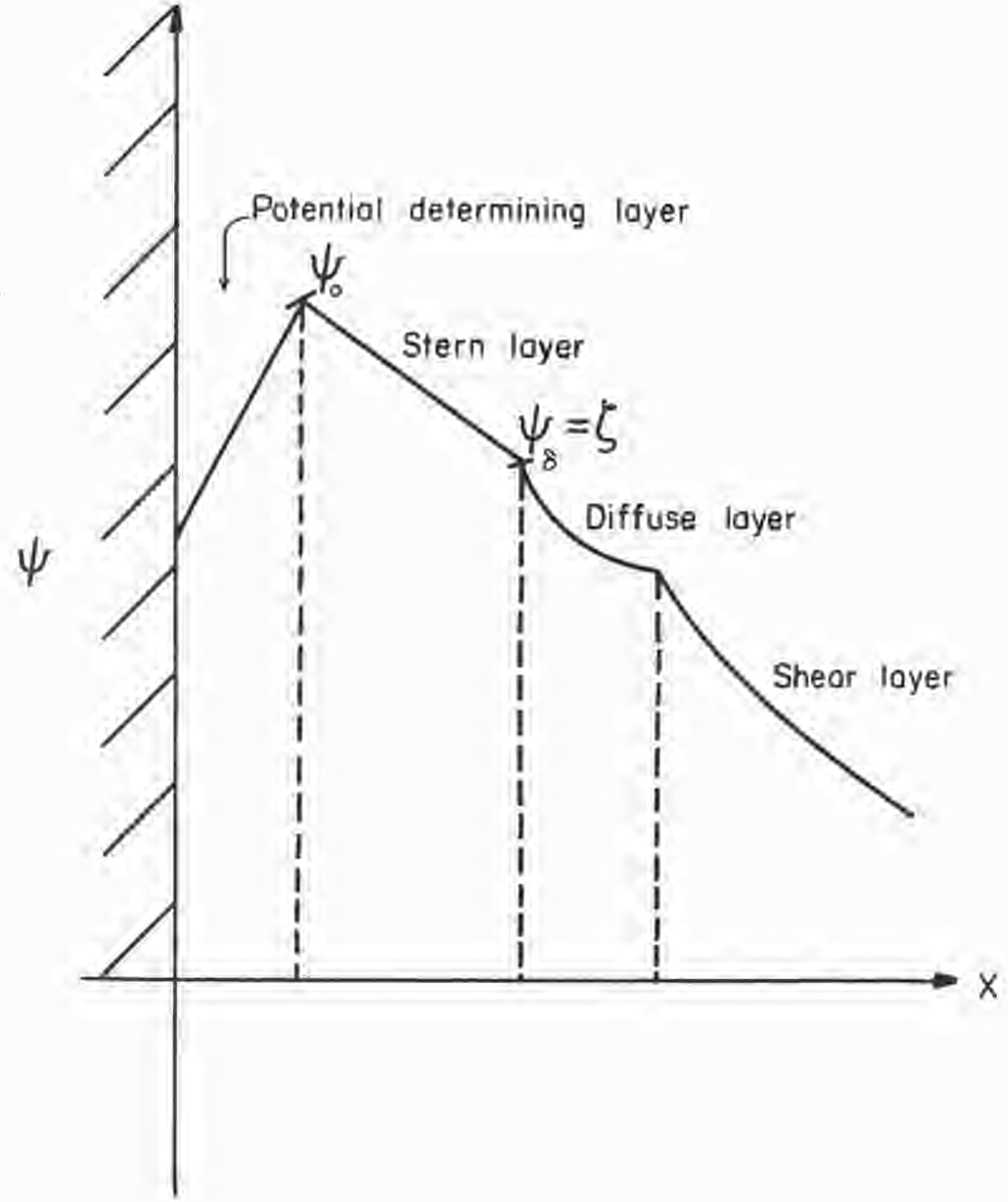


Figure 1
THE GENERAL VARIATION OF POTENTIAL WITH DISTANCE WHEN THE POTENTIAL DETERMINING LAYER IS DISTINCT FROM THE SOLID SURFACE

COMPLICATIONS IN THE THEORY OF ELECTROPHORETIC MOTION

There are, of course, a number of complications in the detailed theory of electrophoretic motion (Kruyt, 1952; Overbeek, 1959; Frumkin, 1946). The effective viscosity in the diffuse double layer is affected by the fact that the ions in it are also moving because of the field applied. This gives rise to *electrophoretic retardation.* Briefly, since the net charge in the fluid region of the double layer is opposite in sign to that of the surface, these ions on the whole move relative to the solution in a direction opposite to that of the surface. In turn, they entrain solvent with them (for example, through their hydration shells and ion atmospheres) so that there is a local motion of the medium opposing the motion of the charged particle or surface. Therefore, a more realistic value of the observed velocity must include a consideration of the local medium velocity, too.

There is also a relaxation effect in that, because of the motion of the particle, the double layer lags somewhat behind, and again the effect is one of retarding the motion of the particle. Another point is that the double layer region is a source of conductance and so is the surface of the particle itself. This last is difficult to evaluate, and for reliable zeta potential measurements, nonconducting surfaces or particles are necessary.

ZETA COEFFICIENT; APPLICATIONS TO FLOTATION

The term *zeta coefficient* is an expression coined to denote the difference between the magnitude of the zeta potential of a mineral suspended in solution A and that of the same mineral suspended in solution B, which consists of solution A and an additional chemical agent but is at the same pH.

It seems likely that the optimum pH values for the flotation of minerals with various collectors, activators, and depressants can be estimated by means of the zeta coefficient.

ZERO POINT OF CHARGE AND ELECTROPHORETIC MOBILITY

The zero point of charge of a mineral whose potential determining ions are H+ and OH^- is defined as the point on the pH scale at which the mineral possesses no surface charge and the adsorption of H+ and OH^- is nil. In the absence of specific adsorption of surface-active counter ions, electrokinetic measurements show a reversal in the sign of the zeta potential exactly at the zero point of charge. At this point, both the surface potential, [illegible] potential, ζ, are equal and zero.

By determining the electrophoretic mobility of fine mineral particles as a function of pH (see fig. 2 for quartz), the zero point charge of the mineral under study corresponds to the pH at which the mobility is zero. Electrophoretic studies were conducted in a special cell, shown in Figure 3. The cell and glassware were designed and built at the New Mexico Bureau of Mines; the projection apparatus was constructed by Rayoscope Corp.; and the power supply unit was built by Arthur H. Thomas Co. Results of measurements of the zero point of charge for quartz (3.70), microcline (2.40), beryl (3.00), and spodumene (2.6) using this cell are shown in Table 1.

A very important factor sometimes neglected in measurements of electrophoretic mobility is the effect of light. Strong, diffused daylight gives rise to convection currents inside the cell because of the heating effect of the sun's rays. It was shown by Whitney and Blake (1904) that suspended particles and not the glass itself are heated. In the setup described in the preceding paragraph and illustrated in Figures 3 and 4, the effect of light was minimized by introducing a heat filter and a colored filter.

SUMMARY

In the previous sections, the theory of electrophoresis is briefly outlined, and an apparatus which may be used for electrophoretic studies like the ones described is explained. The results obtained using this apparatus are in agreement with those obtained by other investigators.

Also explained is how to solve some of the complications which occur in the measurement of zero charge and zeta potential. It is believed at this point that the apparatus described in this paper allows rapid measurements of zeta potential, zero point of charge, electrophoretic mobility, and zeta coefficient.

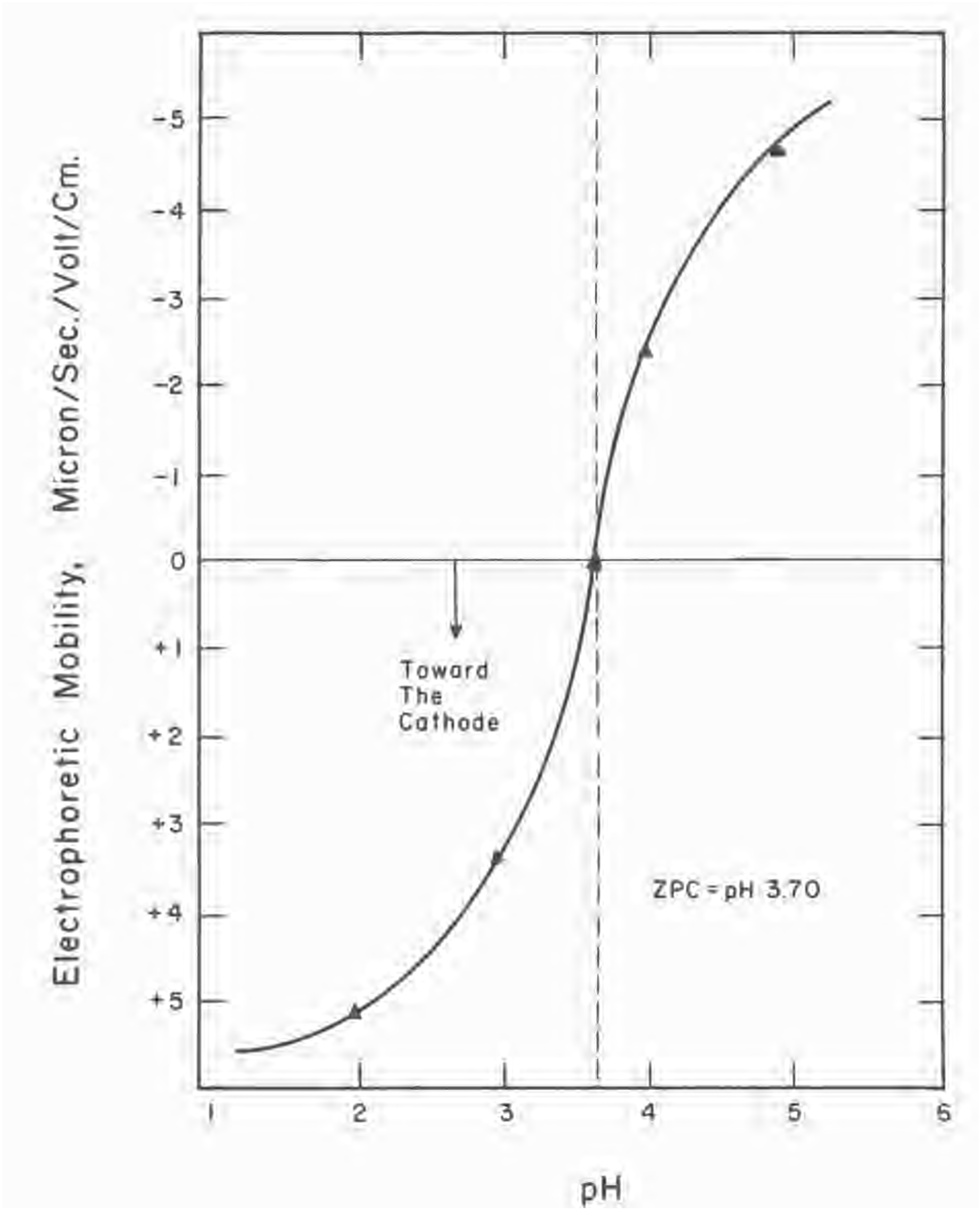


Figure 2
ELECTROPHORETIC MOBILITY OF QUARTZ

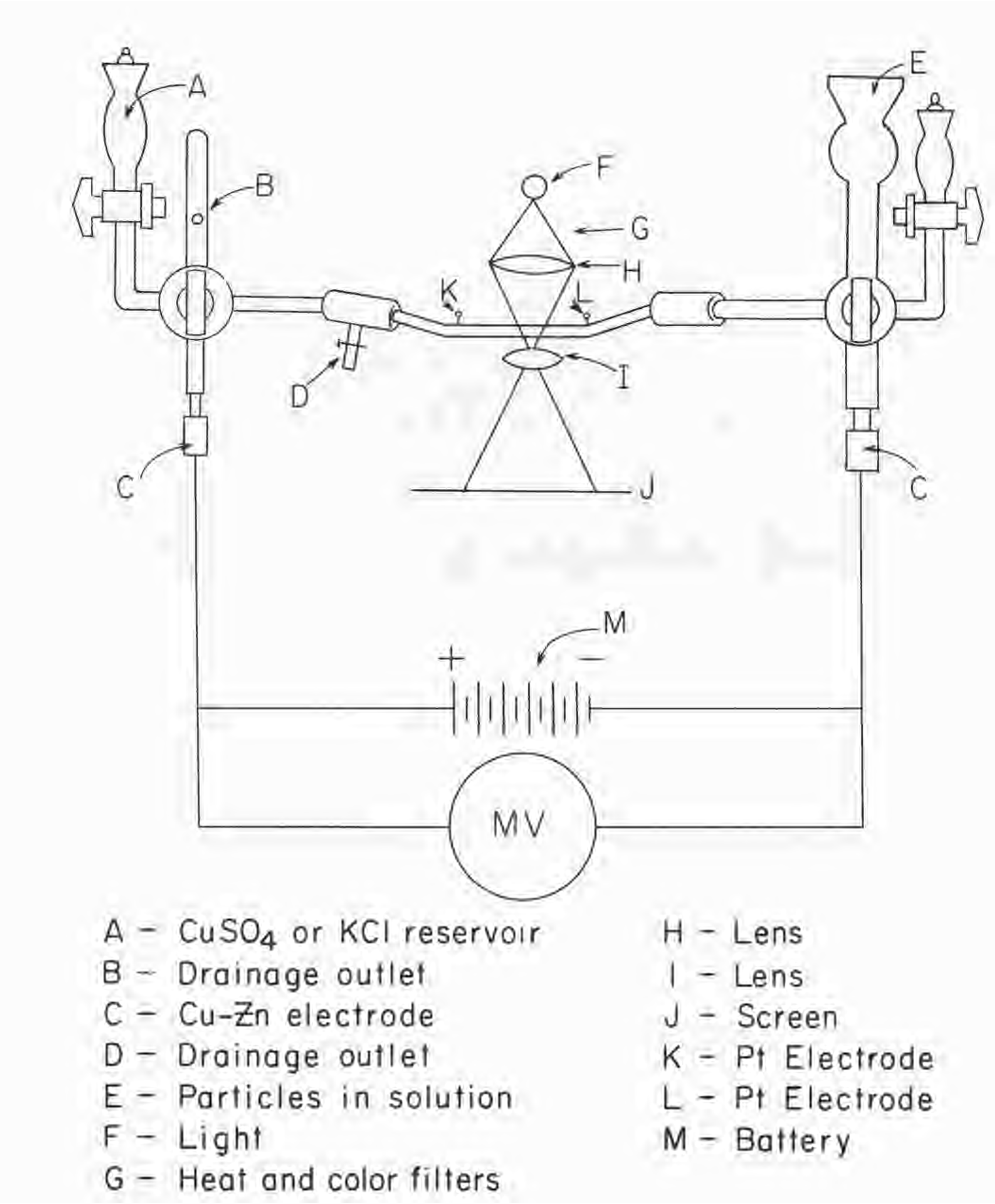
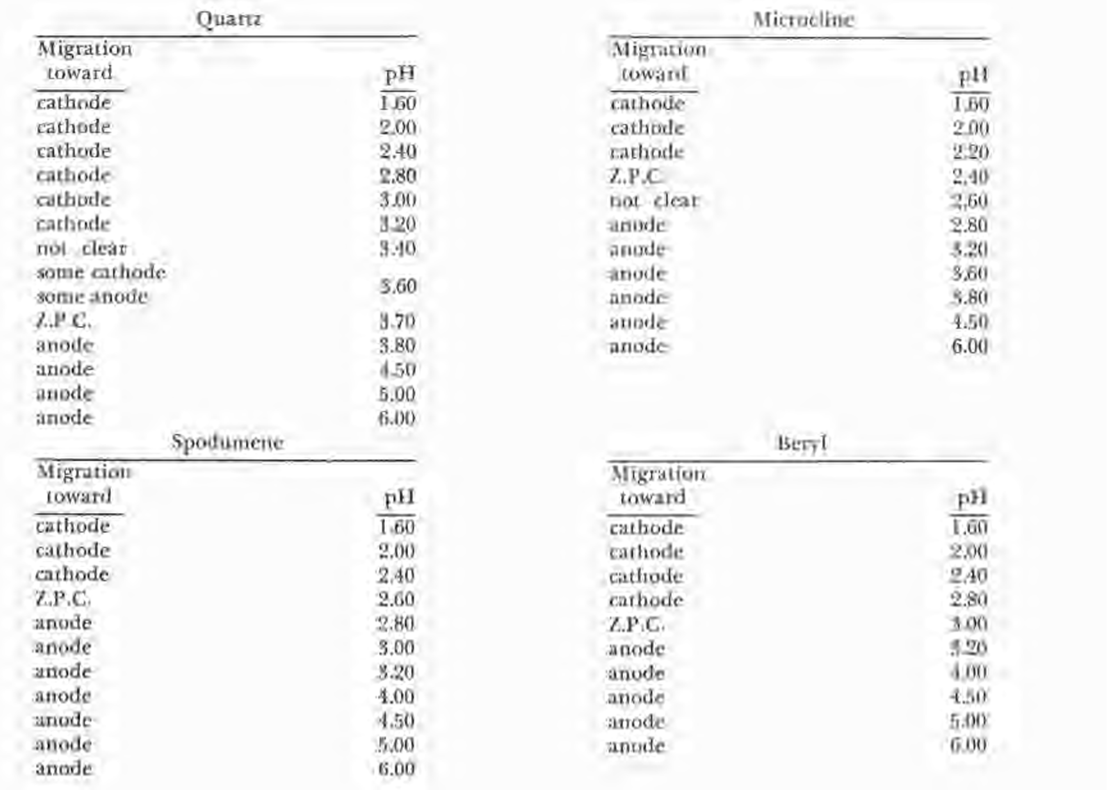


Figure 3

ELECTROPHORESIS APPARATUS DIAGRAM

Figure 4
Photograph of Electrophoresis Apparatus

TABLE 1. EXPERIMENTAL RESULTS OF ELECTROPHORESIS STUDIES



Quartz

Migration toward	pH
cathode	1.60
cathode	2.00
cathode	2.40
cathode	2.80
cathode	3.00
cathode	3.20
not clear	3.40
some cathode some anode	3.60
Z.P.C.	3.70
anode	3.80
anode	4.50
anode	5.00
anode	6.00

Microcline

Migration toward	pH
cathode	1.60
cathode	2.00
cathode	2.20
Z.P.C.	2,40
not clear	2,60
anode	2.80
anode	3.20
anode	3.60
anode	3.80
anode	4.50
anode	6.00

Spodumene

Migration toward	pH
cathode	1.60
cathode	2.00
cathode	2.40
Z.P.C.	2.60
anode	2.80
anode	3.00
anode	3.20
anode	4.00
anode	4.50
anode	5.00
anode	6.00

Beryl

Migration toward	pH
cathode	1.60
cathode	2.00
cathode	2.40
cathode	2.80
Z.P.C.	3.00
anode	3.20
anode	4.00
anode	4.50
anode	5.00
anode	6.00

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