## 187. *A Source of Error in Micro-cataphoretic Measurements with a Cylindrical-bore Cell.*

By Douglas C. Henry.

A micro-cataphoresis cell with a cylindrical bore and plane exterior faces has been recommended by Mattson (*J. Physical Chem.*, 1928, **32**, 1532; 1933, **37**, 223) and employed by a number of other workers. In order to make the necessary allowance for electrosmotic flow it is essential with this, as with all other closed micro-cataphoretic cells, to know with precision the level within the cell at which velocity measurements

are made, or alternatively to make all measurements in the zone of zero electrosmotic flow. For a cylindrical bore this zone is the annulus distant 0·707 × radius from the axis of the cell. Two methods are available for locating the level of observation; either the relative position of the cell and the horizontal illuminating beam is so adjusted that the desired level alone is illuminated, or the viewing objective is so set that the desired level alone is in focus. Either method, or a combination of both, is relatively simple in operation when a cell of rectangular cross-section is being used, but both involve some complication when a cell of the Mattson type is employed; in this type of cell the glass walls act as a plano-concave cylindrical lens separating air and experimental liquid which refracts both the illuminating and the viewing beam.

Buswell and Larson (*ibid.*, 1936, **40**, 833) have pointed out the difficulty which arises when the first method of locating the level is adopted; they show, in fact, that if it is desired to illuminate the level of zero electrosmotic flow, the illuminating beam must enter the cell, not 0·293 × $a$ but 0·377 × $a$ below the highest point of the cylindrical bore. Their figure further shows that the illuminated stratum within the liquid is not horizontal but tilted.

A similar, but more insidious, difficulty arises when it is attempted to locate the desired level by use of the fine focusing adjustment of the microscope. By the usual methods of geometrical optics it can be shown that the actual point of focus of the objective and the focus point of the same objective in air are related by the equation :

$$\frac{\mu_1}{p - \mu_1 k/\mu_2} = \frac{\mu_3}{q - k} + (\mu_2 - \mu_3)$$

where $\mu_1$, $\mu_2$, $\mu_3$ are respectively the refractive indices of air, of the cell material, and of the liquid; $ka$ is the thickness of glass between the plane top surface of the cell and the highest point of the cylindrical bore; $pa$ and $qa$ are respectively the distances below the same top surface and the positions of the focal points "in air" and in fact; $a$ is the radius of the cylindrical bore.

If, for an example, we consider a glass cell of 2 mm. internal diameter with a minimum wall thickness of 0·25 mm., $k = 0{\cdot}25$; if, further, we set $\mu_1 = 1{\cdot}000$, $\mu_2 = 1{\cdot}515$ (glass), and $\mu_3 = 1{\cdot}342$ (water), col. 2 in the following table gives the correct setting of the fine adjustment (arbitrarily taken as zero when focused on the top exterior surface) which will focus the objective at various levels within the liquid.

| Depth of actual focal point below top of bore = $(q - k)a$, mm. | Setting of fine adjustment (mm.). Correct. | Evaluated by linear interpolation. | Difference. |
|---|---|---|---|
| 0 (top of bore) | 0·165 | (0·165) | — |
| 0·2 | 0·310 | 0·283 | 0·027 |
| 0·293 (zero level) | 0·375 | 0·339 | 0·036 |
| 0·4 | 0·448 | 0·402 | 0·046 |
| 0·6 | 0·580 | 0·520 | 0·060 |
| 0·8 | 0·705 | 0·639 | 0·066 |
| 1·0 (axis) | 0·825 | 0·757 | 0·068 |
| 1·2 | 0·939 | 0·876 | 0·063 |
| 1·4 | 1·049 | 0·995 | 0·054 |
| 1·6 | 1·153 | 1·113 | 0·040 |
| 1·707 (zero level) | 1·207 | 1·176 | 0·031 |
| 1·8 | 1·254 | 1·231 | 0·023 |
| 2·0 (bottom of bore) | 1·350 | (1·350) | — |

When working with a cell of rectangular cross-section the usual (and correct) practice is to locate the desired level by linear interpolation between the fine adjustment readings corresponding to the top and to the bottom interior surface. Col. 3 of the table shows that this method is not permissible with the Mattson type of cell. If, for example, in the desire to obtain the upper zero level, the microscope were set by linear interpolation at 0·339, the actual point of focus would lie at 0·240 mm. below the top of the bore instead of 0·293 mm. as intended, an error of 0·053 mm.; a similar error of 0·062 mm. results from an attempt to locate the lower zero level by linear interpolation.

That this error, amounting to over 5% of the bore radius, is not immaterial is shown by the following considerations. The velocity ($w$) of flow at any distance $r$ from the axis

of the bore is given in terms of the electrosmotic velocity ($w_0$) at the wall by the equation

$$w/w_0 = 2r^2/a^2 - 1$$

whence

$$\partial w/\partial(r/a) = 4w_0 \times (r/a)$$

An error of 5% in the evaluation of $r/a$ therefore produces an error in the velocity measured amounting to $0{\cdot}20 \times w_0$. If the true cataphoretic velocity of the particle under observation happens to be of the same order as $w_0$ (it may easily be much less), a 20% error in its value will result.

Authors do not, in general, specify what steps they have taken to locate the desired levels of measurement; one would, however, imagine that if the complications described in this note had been appreciated, some reference to them would have been made. It therefore seems not unlikely that these considerations may have escaped notice, and that in consequence many of the published measurements obtained with the cylindrical-bore cell may be seriously in error.

THOMAS GRAHAM COLLOID RESEARCH LABORATORY,
THE UNIVERSITY OF MANCHESTER.

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