LIQUID LIMIT AND DYE ADSORPTION

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ABSTRACT

Cation exchange capacity (c.e.c.) determined by methylene blue can be regarded as a useful soil mechanical test in its own right. When a large number of liquid limit (LL) tests have to be done to determine variation in clays of the same general type, as on an engineering site, economy of operation could be achieved by carrying out many c.e.c. tests and few LL tests. It is only when comparing clays of widely different types that correlation is poor.

INTRODUCTION

In 1951 Robertson and Ward proposed a method of estimating the cation exchange capacity of clays by the chemisorption of methylene blue. Brief details of the method are as follows:—

3 g (or for kaolins 1 g) of methylene blue of known purity are dissolved in water to make one litre of stock solution. Suitable weights of clay are put into glass-stopped bottles, 25 ml of dye solution added by pipette, and the mixture shaken for 20 minutes. Six tests are usually done at the same time. The suspension is then filtered through a 15 cm Whatman's No. 4 filter-paper into a boiling-tube; the first light coloured runnings are rejected and the remaining filtrate shaken before estimating its dye content by matching with stock solution diluted to known amounts. For most practical purposes it is sufficient to estimate the water of hydration of the dye by drying at 105°C to constant weight.

The weight of dry clay required for this test was that which, after the adsorption under specified conditions had taken place, left in the filtrate between 0.5 and 15% of the original dye (called "excess dye"), the clay having adsorbed the remainder. The cation exchange capacity in milliequivalents per 100 g of dry clay was worked out in the following manner:—

\[
\text{Equivalent weight of dye} \times \frac{100}{1000} \times \frac{\text{Volume of dye used in ml}}{\text{dry weight of clay}}
\]

Example: Fuller's earth, YB 20.

<table>
<thead>
<tr>
<th>Percentage of dye initially</th>
<th>Percentage of dye in filtrate</th>
<th>Moisture content of dye</th>
<th>Purity of dye taken as</th>
<th>Milliequivalents of dye (anhydrous)</th>
<th>Volume of dye solution used</th>
<th>Weight of clay (moist)</th>
<th>Moisture content of clay</th>
<th>Dry weight of clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>0.01</td>
<td>20.6%</td>
<td>79.4%</td>
<td>0.3199</td>
<td>25 ml</td>
<td>0.301 g</td>
<td>10.9%</td>
<td>0.301 × 0.891 g</td>
</tr>
</tbody>
</table>
The c.e.c. therefore is:

\[
\frac{0.29 \times 79.4}{0.3199 \times 4 \times 0.301 \times 0.891} = 67.1 \text{ milliequivalents/100 g}
\]

In these previous studies it was established that 20 minutes was a reasonable time of shaking for the test; that temperature had little effect on the result (between 16°C and 75°C); and that the stock solution could be between 0.3% and 0.1% in strength without affecting the result.

Nevertheless it was felt that it would be possible to increase the accuracy of the determination by choosing the endpoint more rationally hence several series of tests were made with a range of weights of clay (Fig. 1). With 0.1% dye solution, the curve inflects rather sharply when there remains 6 to 8% of the dye in the filtrate. For the purpose of future work, we recommend an endpoint at 7.5% of excess dye, or when the filtrate has a concentration of 0.0075%.

With 0.3% dye solution (Fig. 2) an endpoint at 1.7% excess dye was chosen for the present research, but the large number of graphs obtained suggest that 2.5% would represent more accurately the point of inflexion. In this case the endpoint occurs when the filtrate has the same concentration as when the weaker dye solution was used.

Measurement of van der Waals adsorption has been made from these graphs. When twice the amount of dye required to satisfy the c.e.c. is present, the clays adsorb a further amount of dye by physical
forces; this amount can be expressed as a percentage of the c.e.c., thus:

Kaolinite, Pugu D, 13%; Kaolinite, Pugu K, 5%; Calcium montmorillonite, YB 20, 10%. These figures show how important it is to conduct the dye adsorption test so that physically adsorbed dye is practically absent.

If the physically adsorbed dye thus measured is in proportion to the specific surface of the clays, we can calculate the specific surface of the other clays by scaling to Pugu D = 44.9 m²/g, a previously measured value (Robertson et al., 1954). Thus Pugu K calculated 13.2 m²/g, measured 15.3 m²/g; YB 20 calculated 429 m²/g. The value for the calcium montmorillonite is clearly of the right order since this clay contains 20 to 25% of impurities.

In their previous paper Robertson and Ward (1951) recommended that swelling clays should be soaked overnight in water before the dye test. Vermiculite gives a high c.e.c. only if pretreated with lithium chloride. All clays should be ground to pass a 100-mesh B.S. sieve before the test.

**End-point Determination**

In the present work 59 samples have been subjected to methylene blue as well as to standard soil mechanics tests. A typical graph drawn for the purpose of determining the end-point, in this case with an excess dye at 1.7%, is shown in Fig. 3. There are enough points here to show the sharp inflexion when the dye is nearly exhausted; and the van der Waals “bulge” of one clay is about 6.5% when the amount of dye used is twice the c.e.c. With the exception of the Buckland Pit samples, collected by the senior author, all samples tested came from borings made by Messrs Soil Mechanics Limited in the course of normal site investigations.

**Comparisons**

**A. With other methods of measuring c.e.c.** We have not been able to make an exhaustive comparison of the new methylene blue test with other methods of measuring c.e.c. We have however compared a number of methylene blue results with those obtained by titration of electrodialysed clays with sodium, calcium and barium hydroxides to pH 7 and to the point of inflexion, and by the ammonium method. These methods vary so much among themselves that it is difficult to determine the status of the methylene blue test; but in comparison with the ammonium method alone, methylene blue is believed to give
comparable results for smectites, illites, and lithium-treated vermiculites, and slightly low results with kandites when hydrogen ions are present. It does not measure the full c.e.c. of peat, zeolites, glauconite, the impurities of diatomite, or, as Krishnamoorthy and Desai (1955) have shown, organic ion-exchangers. Methylene blue however gives about twice the ammonium value for Vallecas sepiolite, though in this case the calculated value agrees with methylene blue.

B. Methylene blue adsorption and plasticity limits. Samson and Gaskin in 1951 published the Atterberg plasticity index, that is the difference between the liquid and the plastic limits, and the methylene blue adsorption of a large number of kaolinitic clays from South Australia. The correlation coefficient between the two measurements was 0·36. The correlation coefficient of all 59 of our samples with liquid limit (Fig. 4) is 0·48 and with plastic limit is 0·40. The figure shows the whole population of results. The degree of correlation however is found to be very much higher when samples from limited areas are examined. Thus 12 samples from the Thames Alluvium at the Isle of Grain gave a correlation coefficient against liquid limit of 0·89 and against plastic limit of 0·61. A series of samples from Marchwood, known not to be homogeneous, i.e., of one geological age, gave 0·52 for both liquid and plastic limits. It is interesting that 25 very miscellaneous samples gave figures of 0·70
and 0.65 respectively for liquid and plastic limits. This rather consistent collection of samples, many of them foreign, contains very few Quaternary samples.

C. Methylene blue adsorption and plastic limit. Statistical examination shows that the correlation between methylene blue adsorption and plastic limit is not quite so good as with liquid limit. Fig. 5 shows the whole population. The reason why three points are so remarkably aberrant is unknown. Plastic limit is, however, a comparatively quick, though skilful, test and requires no substitution.

![Fig. 5—Plastic limit compared with methylene blue adsorption of all samples.](image1)

![Fig. 6—Liquid and plastic limits of Isle of Grain (Thames Alluvium) samples compared with methylene blue adsorption. (xx Pipe clay, Poole Harbour).](image2)

**INDIVIDUAL SAMPLES**

A. Isle of Grain. Fig. 6 shows the results obtained from twelve samples of Thames Alluvium. The best line drawn by eye—since the regression line is too much affected by the three aberrant values—shows a liquid limit of 14 when methylene blue adsorption is nil; or a plastic limit of 13. These values are what one would expect of a fine silt, containing no clay. (It is of passing interest that a pipe clay from Poole Harbour fits this graph as well).

The clay content of these 12 samples was measured (a) after removal of organic matter and (b) after further treatment with hydrochloric acid. The clay was apparently not very easy to disperse so the higher value obtained by the two methods was taken. The methylene blue
c.e.c. of the clay fraction averaged 13.5 milliequivalents/100 g and ranged from 7.3 to 22.2. It is clear that the clay mineral composition is not varying much in quality here, but varies mainly in quantity in the soil samples. Methylene blue therefore gives a trustworthy indication of liquid limit.

B. Buckland Pit. Three samples taken from Buckland Pit give almost perfect correlation with liquid limit (Fig. 7); the statistician will not comment on so small a population, but we can at least show the graph. There are not enough figures to let us know if the best line really should pass so close to the origin. If soils contain no sand or silt particles, the line might be expected to pass through the origin.

![Fig. 7](image1.png)  
**Fig. 7**—Liquid limit of Buckland pit (Cretaceous) samples compared with methylene blue adsorption.

![Fig. 8](image2.png)  
**Fig. 8**—Liquid limit and methylene blue adsorption of Marchwood samples (glaucnitic samples marked G).

C. Marchwood Power Station, Southampton Water: Of nineteen samples taken from this site, fourteen were of Bracklesham sands and clays and five of River Test alluvium (Fig. 8). The alluvial samples are all well above the line and approach the line of the Thames alluvial samples from the Isle of Grain. Among the Bracklesham samples, four, glauconitic to the eye, fall below the line. Without these samples the correlation coefficient would be very high. The best line points to a liquid limit of 32 at methylene blue = 0 and a much lower slope than in the Isle of Grain samples.

CONCLUSIONS

We conclude that for a given engineering site methylene blue can be used as a convenient substitute for liquid limit provided the two methods are calibrated. Since the relationship varies with clays of
different geological types, methylene blue results should be kept in groups according to the geological age of the specimens. At least alluvium and drift should be kept separate from solid.

It follows that where the rocks show great variation, or where the site is very large, and a great many plasticity tests are needed, it would be economical to do many methylene blue tests and few liquid limit tests. At overseas sites methylene blue tests could be done in a field laboratory.

Up till now we have considered methylene blue as a partial and economic substitute for liquid limit tests; or as a reconnaissance or field test. But we should regard the measurement of cation exchange capacity as of value in its own right; it may be regarded as a fundamental rather than a secondary property of unconsolidated rocks. In soil stabilisation by chemical or electrical means, it would be useful to know the c.e.c. Moreover, in the practical examination of the weathering of rocks, c.e.c. can be very informative.

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REFERENCES

DISCUSSION
Dr R. M. S. Perrin asked how much organic matter needed to be present before interference occurred with the methylene blue adsorption test. In reply Robertson stated that 2-3% was an upper limit, for peat had almost the same exchange capacity as montmorillonite. Because of this, clays which were black or dark-brown to the naked eye were not tested.

Dr I. Havenaar asked how low an exchange capacity could be determined using the method and the length of time per test. Robertson in reply stated that the method was never used below 1 meq/100g (obtained using a kaolinite from Cornwall for which sample the same value was obtained as by the classical method). Approximately six tests could be carried out per hour.

Mr D. A. Holdridge drew attention to the fading of colour which occurred with methylene blue in daylight. Robertson in reply
agreed and said that it was for this reason that the solution should be made up at least once per week. Some further discussion on this subject ensued in which Mr G. P. Chambers pointed out that the glass of the bottle also adsorbed some of the dye. Robertson replied with his remark printed above, *viz.*, frequent new solutions and added further that after the first solution, a type of skin formed upon the glass and this protected the surface from further large adsorption.