The Development of the Adsorption Photometry of Cationic Dye by Using Transparent Granular Polymer Gel

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Abstract
A noble photometric method using a transparent polymer beads consisting of gelatinous poly(sodium acrylate) as an adsorbent was newly developed. Seven different cationic dyes were arbitrarily chosen as a colored species to establish the optimum conditions. It was confirmed that Beer’s law held between the absorbance of polymer beads and the concentration of cationic dye when 40 cm$^3$ of sample solution was equilibrated with 2.0 cm$^3$ of polymer gel by shaking for 60 min.

Key words: adsorption Photometry, transparent poly(sodium acrylate) beads, cationic dye

1 Introduction
In order to determine a trace amount of analyte in an aqueous solution spectrophotometrically, many methods, such as extraction photometry[1], application of long capillary[2], and ion-exchanger colorimetry[3,4], had been proposed. In the respect of operational convenience and the effect to environment, ion-exchanger colorimetry is considered to be most promising. However, ion-exchange resin itself is opaque and therefore the light-absorbing layer containing ion-exchange resin is limited to be short (1 mm length) in order to reduce blank absorbance. However, the blank absorbance still exceeds 1.0. Whereas, if the colored analyte in aqueous solution could be adsorbed to a small, soft and transparent beads, which can be handled just like liquid, it become possible to establish a new adsorption photometry without using any organic solvents.

From this point of view, the present study was undertaken by using a transparent poly(sodium acrylate) beads to confirm whether the Lambert-Beer’s law would be valid between absorbance of polymer beads adsorbing cationic dye and dye concentration. Seven cationic dyes were used as an analyte in this study because of the simplicity of assessment by avoiding the disagreement of optimum conditions between color development and adsorption. Various factors affecting on the absorbance such as pH, shaking time, type of dye and so on, were examined.
2 Experimental

2.1 Reagents and apparatus

A Nihonbunko model 560 double-beam spectrophotometer was used to obtain UV and visible absorption spectra with a 1 cm and/or 5 cm pathlength quartz cell. Since the arrangement of polymer gel beads in the optic cell is always random which brings about the various length of light absorption layer, the blank value of absorbance differed from each measurement. Then, in order to measure the absorbance correctly, the spectrophotometer having a computerized function correcting the baseline was helpful. A buffer solutions of 0.005 \( M \) (\( M = \text{mol dm}^{-3} \)) ammonium acetate- or 0.005 \( M \) sodium acetate-acetic acid and 0.005 \( M \) ammonium chloride-ammonia water were used to adjust pH in the range of 3-7 and 7-11, respectively. Seven cationic dyes were arbitrarily selected from three representative dye types, that is, 1-Methyl-4-(4-diethylaminophenylazo)pyridinium iodide (MDPP) from azo cationic, and Methylene Blue (MB) from thiazine derivatives, and Brilliant Green (BG), Ethyl Violet (EV), Malachite Green (MG), Pararosaniline (PR), and Crystal Violet (CV), from triphenylmethane dyes. These reagents were all of analytical grade and were used without further purification.

2.2 Preparation of polymer gel

Granular poly(sodium acrylate)(\( \sim 280 \ \mu \text{m} \)) was generously donated from Mitsubishi Kagaku Co. Ltd. and was swelled in aqueous solution containing Triton X-100 and potassium nitrate at 45°C for 4 days. By this treatment, a granular poly(sodium acrylate) swelled to form a transparent polymer beads with grain size of 1-3 mm. The absorbance of this gelatinous beads measured at 660 nm by using 5 cm long cell was around 0.005, and it means that this gel is perfectly transparent.

![Fig. 1 Effect of pH on the adsorption of dye on polymer gel.](image)

○: CV, △: MDPP, ◇: MB.

2.3 Concentration of cationic dye

Polymer beads (2.0 cm³) were sampled correctly by use of 2.5 cm³ plastic syringe, of which male lure portion was cut out to enlarge drawing hole. Aqueous solution (40 cm³) containing cationic dye and 2.0 cm³ of polymer beads were mixed in an extraction tube and were shacked moderately for 1 h. The polymer gel was filtered by use of domestic tealeaf-filter and was rinsed out the supernatant solution by dipping it in a beaker filled.
with distilled water, followed by being subjected to spectrophotometric determination by using 5 cm length cell.

3 Results and Discussion

3.1 Effect of pH

The effect of pH of aqueous dye solution on the adsorption to polymer beads was examined (Fig. 1). This polymer beads was stable against base until pH 12.5, but shrunk by decreasing pH below 4.0. The absorbances of dye absorbed on polymer beads were highest and/or constant in the pH range of 7.5-10.0 for MDPP, 6.2-8.2 for CV, and 7.1-8.7 for MB, respectively. When dye aqueous solution were shaken with polymer gel without using buffer solutions, the pH of supernatant solutions were settled in the optimum pH ranges in the almost all cases, so that buffer solution was not always necessary to adjust the pH for a neutral solution.

3.2 Effect of shaking time

Figure 2 shows the relationship between the shaking time and absorbance of polymer beads absorbing dye at pH 8.0. It took 30 min for MDPP, 45 min for CV, and 60 min for MB to attain the constant absorbance, respectively. The shaking time was set to 60 min in the following experiments.

3.3 Relationship between the absorbance of adsorbed dye and dye concentration

As can be seen from Table 1, good correlation coefficients for the relationship between the absorbance of polymer beads adsorbing dye and the dye concentration were obtained for all examined cationic monovalent dyes. Calibration sensitivity ratio was calculated by dividing the slope in the equation for the least-square line obtained with the relationship between the absorbance of polymer beads and dye concentration by that obtained with the relationship between the absorbance of dye solution and the dye concentration. The volume ratio of dye solution vs. polymer gel was 20, and optic cell used for the dye solution was 1 cm length while that for polymer beads was 5 cm length, therefore the value of calibration sensitivity ratio should be 100. The values of calibration sensitivity ratios were, however, mostly settled in the range of 20-40. Although the reason for this discrepancy is not still clear, the following factors may affect to the absorbance. That is, since the size of beads is relatively big compared to the cross section of incident beam, the dead volume which did not participate to light absorbing existed in the light path bring about the loss. Moreover, the used poly(sodium acrylate) gelatinous bead was a packed sphere but dye was adsorbed only on the surface of granule and did not permeate into the inside sphere, so that the actual light-absorbing layer was very thin and this might enlarge the depression of effectiveness. Repeatability was also examined with MB, MDPP, and CV, respectively. Taking into account the fact that the used poly(sodium acrylate) gelatinous beads were elliptic spheres of various sizes, it can be stated that the obtained coefficients of variation were reasonable. The determination of absorbance of polymer beads was always computer processed by subtracting the absorbance at the absorption maximum from the absorbance of baseline drawn through the both bases of the absorption maximum, since the arrangement of polymer gel beads in the optic cell is always random and this brings about the different background absorbance every time.

3.4 Adsorption mechanism

Other than the above 7 cationic dyes, Xylenol Orange as an anionic dye, tris(1,10-phenanthroline) iron(II) perchlorate as a neutral color species, and tris(1,10-phenanthroline)iron(II) as a divalent cationic color species were also subjected to the present adsorption photometry. The former two species were not adsorbed by the
Table 1  Relationship between absorbance of polymer gel and the concentration of dye solution

<table>
<thead>
<tr>
<th>Cationic dye</th>
<th>Equation for the least-squares line</th>
<th>Pearson correlation coefficient</th>
<th>Calibration sensitivity ratio</th>
<th>Coefficient of variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB</td>
<td>(0.173x + 0.006) ((0.25-2.5\times10^{-7} \text{M}))</td>
<td>0.9997</td>
<td>32.3</td>
<td>4.6</td>
</tr>
<tr>
<td>MDPP</td>
<td>(0.115x - 0.018) ((0.75-7.5\times10^{-7} \text{M}))</td>
<td>0.9981</td>
<td>22.1</td>
<td>4.5</td>
</tr>
<tr>
<td>EV</td>
<td>(0.151x + 0.001) ((0.75-5.0\times10^{-7} \text{M}))</td>
<td>0.9937</td>
<td>17.5</td>
<td>17.5</td>
</tr>
<tr>
<td>CV</td>
<td>(0.176x - 0.023) ((0.75-7.5\times10^{-7} \text{M}))</td>
<td>0.9982</td>
<td>27.2</td>
<td>7.5</td>
</tr>
<tr>
<td>PR</td>
<td>(0.148x - 0.049) ((0.50-10.0\times10^{-7} \text{M}))</td>
<td>0.9978</td>
<td>27.9</td>
<td>27.9</td>
</tr>
<tr>
<td>MG</td>
<td>(0.251x + 0.035) ((0.10-5.0\times10^{-7} \text{M}))</td>
<td>0.9981</td>
<td>20.4</td>
<td>20.4</td>
</tr>
<tr>
<td>BG</td>
<td>(0.258x + 0.034) ((0.50-2.5\times10^{-7} \text{M}))</td>
<td>0.9990</td>
<td>39.7</td>
<td>39.7</td>
</tr>
</tbody>
</table>

1) 40 cm³ of dye solution and 2 cm³ of polymer were equilibrated. 2) The values in the parenthesis indicate the useful concentration range. 3) Calibration sensitivity ratio was calculated by dividing the slope in the equation for the least-square line obtained with the relationship between the absorbance of dye concentration and polymer gel by that obtained with the relationship between the absorbance of dye solution and dye concentration. 4) 7 runs were carried out for \(5\times10^{-7} \text{M}\) dye solution.

In conclusion, it was confirmed that the Lambert-Beer's law was valid between the absorbance of beads absorbing dye and the concentration of dye solution, and therefore, the transparent poly(sodium acrylate) beads could be used as an adsorbent for the adsorption photometric determination of monovalent colored species.

References