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Ink diffusion in water

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Abstract

The diffusion of ink in water was investigated. Both stamp ink and Quink blue ink were chosen for the analysis. The displacement of the diffused ink front was measured at temperatures of 10–30 °C. The experimental data of the ink front were in good agreement with the theory of diffusion. The diffusion coefficients satisfy the Arrhenius plot, and the activation energy is smaller for the Quink blue ink than for the stamp ink. The mechanism of the ink diffusion is explained by the kinetics of viscous flow.

1. Introduction

Traditional oriental writing appeared more than 3000 years ago (Saito 1959, Thompson and Uchiyama 1960). It is considered a special kind of painting, slightly different from water colour painting (Small 1991). Guo and Kunii (1991) analysed the black ink diffusion based on a fibre mesh paper model, and later Lee (2001) modified Guo and Kunii's model by considering the characteristics of black ink, and incorporated with random (or regular) fibre mesh structured papers. Zhang et al (1999) also studied the ink diffusion using a 2D cellular automation model. Because of the sophisticated nature of the phenomenon, these researchers had to rely on the use of computer simulation. Although oriental writing is a beautiful art, it is difficult to make a mechanistic analysis and have a good understanding of the process. However, the popularity of using oriental writing has thus increasingly lessened. The tools of oriental writing consist of paper, brush, inkstick and inkstone which are often inconvenient to carry around. In the stage of improvement, the brush was modified to fountain pens, ballpoint pens etc, and both the inkstick and inkstone were discarded and replaced by an ink container. In order to further improve the ink printing process, it is necessary to have a clear understanding of its fundamentals, in particular, the mechanism of the ink diffusion in the printing medium, such as water, paper or a fabric. In this study, the diffusion of ink in water is analysed.

2. Theory

A drop of ink of radius a is put into a very shallow water bath of radius R maintained at a constant temperature, and R is much greater than a. The diffusion of ink in water follows the

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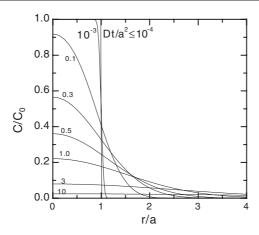


Figure 1. The concentration distribution at various times.

diffusion equation in the polar coordinate system as

$$D\left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r}\right) = \frac{\partial C}{\partial t} \tag{1}$$

where D and C are the diffusion coefficient of ink in water and ink concentration, respectively. Note that r and t are the radial coordinate and time. At the initial time the ink is distributed homogeneously inside water with the boundary of radius r = a. That is,

$$C(r \leqslant a, t = 0) = C_0 \tag{2a}$$

$$C(r > a, t = 0) = 0 (2b)$$

and the total mass of the ink is constant during the diffusion process. The solution of equation (1) can be obtained using the method of separation of variables as

$$C(r,t) = \frac{C_0}{2Dt} e^{\frac{-r^2}{4Dt}} \int_0^a e^{\frac{-r^2}{4Dt}} I_0\left(\frac{rr'}{2Dt}\right) r' dr'$$
 (3)

in which I_0 is the modified Bessel function of zeroth order. Figure 1 shows the concentration distribution at different normalized times Dt/a^2 . When $Dt/a^2 \le 10^{-4}$, the concentration is equal to C_0 for $r \le a$ and zero for r > a. The concentration gradient at the centre is zero because of the symmetry. The maximum concentration is always located at the centre. For a given time the concentration decreases with increasing r. The concentration level decreases monotonically with increasing time in the region $r \le a$.

3. Experimental details

Two kinds of ink, stamp ink and Quink blue ink, were obtained from the Liberty Company (Taipei, Taiwan) and the Parker Pen Company (Newhaven, England), respectively. A flat disc filled with water of 1 cm depth was placed in a thermostat water bath to maintain a constant temperature. The stamp ink was dropped into the centre of the flat disc. Then sequential pictures were taken periodically and the ink front was measured. The same procedure was repeated at different temperatures and with the Quink blue ink. We also used the Ubbelohde tube to measure the viscosity coefficients of the stamp ink and Quink blue ink. Both the ink (or water) and the Ubbelohde tube were immersed in a thermostat water bath that was maintained at 25 °C. The time was recorded when the ink passed through the upper and lower

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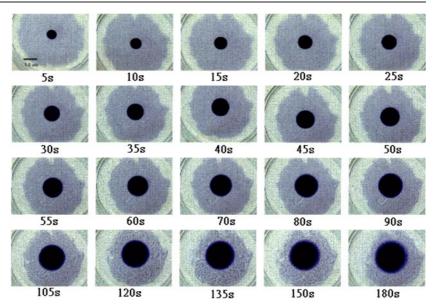


Figure 2. Sequential pictures of stamp ink diffusing in water.

scales of the Ubbelohde tube. The distance between the two scales is 4 cm. We also measured the densities of water and ink using an Ohaus digital balance.

4. Results and discussion

A series of sequential pictures of stamp ink diffusion at $21.3\,^{\circ}\text{C}$ are shown in figure 2. The ink front continues to move out with increasing time. The stamp ink fronts at different temperatures are plotted as a function of time in figure 3. These data are curve fitted with solid lines obtained from equation (3). The solid lines in figure 3 are the equi-concentration profiles where the concentration is equal to $0.999\,C_0$. The data at longer times deviate from the solid lines. This is because the solution, equation (3), was derived for an infinite medium, and the experimental ink fronts were measured in a disc of finite size. The effect of disc edge cannot be negligible when the time is long enough. The corresponding diffusion coefficients are shown in figure 4 by a solid line. It is found that the diffusion coefficients satisfy the Arrhenius equation and the corresponding activation energy is $75.2\,\text{kJ}\,\text{mol}^{-1}$. Similarly, the ink fronts of Quink blue ink at different temperatures are plotted as a function of time in figure 5. The diffusion coefficients of Quink blue ink are shown in figure 4 by a dashed line and satisfy the Arrhenius equation. The activation energy of Quink blue ink is $15.6\,\text{kJ}\,\text{mol}^{-1}$.

Comparing the stamp ink with the Quink blue ink, the activation energy is greater for the stamp ink than for the Quink blue ink. That is, the stamp ink is more difficult to diffuse in water than the Quink blue ink. This can be explained as follows. The viscosity coefficient of water at 25 °C is 0.89 cp (Weast 1980–1981). The total times, t, for water, stamp ink and Quink blue ink to move from the upper scale to the lower scale of the Ubbelohde tube are 927 s, 23 005 s and 1012 s, respectively. The densities, ρ , of water, stamp ink and Quink blue ink are 1 g cm⁻³, 1.004 g cm⁻³, and 1.193 g cm⁻³, respectively. The viscosity coefficient, η , of the ink can be obtained as

$$\eta = (t\rho/t_0\rho_0)\eta_0 \tag{4}$$

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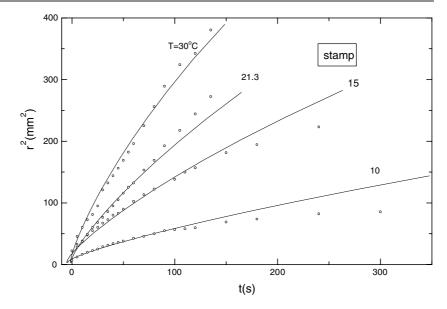


Figure 3. The stamp ink front as a function of time at various temperatures. The symbols and solid lines refer to experimental data and theoretical curves, respectively.

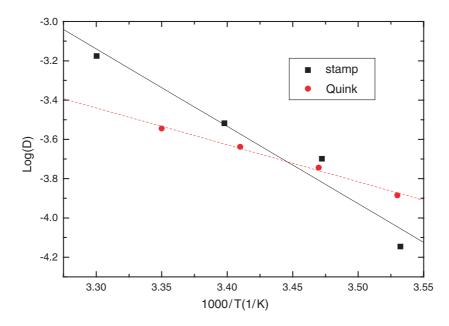


Figure 4. Arrhenius plot of diffusion coefficient versus reciprocal of temperature where the unit of diffusion coefficient is $\text{mm}^2 \, \text{s}^{-1}$. The solid and dashed lines refer to the stamp ink and Quink blue ink, respectively.

where the subscript 'o' denotes water. The viscosity coefficients of the stamp ink and Quink blue ink are 26.46 cp and 0.98 cp, respectively, using equation (4). That is, the viscosity coefficient is greater for the stamp ink than for the Quink blue ink. The viscosity coefficient

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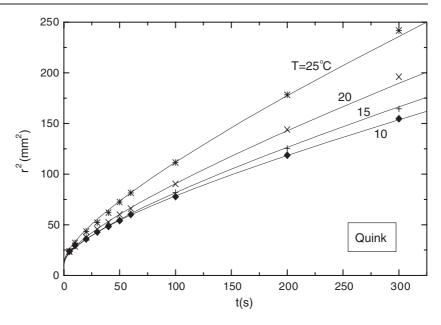


Figure 5. The Quink blue ink front as a function of time at various temperatures. The symbols and solid lines refer to experimental data and theoretical curves, respectively.

is inversely proportional to the mobility. According to the Einstein relation, the diffusion coefficient is equal to the product of mobility and kT where k and T are the Boltzmann constant and temperature in kelvin, respectively. Therefore, the ink with a higher viscosity coefficient is more difficult to diffuse than the ink with a lower viscosity coefficient. On the other hand, the activation energy is an energy barrier for an atom to overcome when it diffuses. This implies that the atom with a higher viscosity coefficient would result in higher activation energy. Note that both stamp ink and Quink blue ink are water soluble. The oil-based ink cannot diffuse in water.

In the present study the water depth is 1 cm so that the ink drop reaches the bottom of the disc very soon and the ink movement is dominated by the diffusion. When the water depth is larger than 5 cm, the ink motion is controlled by both the gravitational force and the diffusion. It is difficult to see that the ink diffuses in water following the Fickian equation. This is a very complicated phenomenon to be analysed by a simple mathematical model. Occasionally the ink front looks like an irregular star emanating from a circular shape due to surface tension.

5. Summary

Ink diffusion in water at different temperatures was investigated. Both stamp ink and Quink blue ink were analysed. The experimental data for the ink front were in excellent agreement with the diffusion model. The diffusion coefficients of both stamp ink and Quink blue ink satisfied the Arrhenius equation. The activation energies of stamp ink and Quink blue ink were determined to be 75.2 kJ mol⁻¹ and 15.6 kJ mol⁻¹, respectively. The measured viscosity coefficients of the stamp ink and Quink blue ink were 26.46 cp and 0.98 cp, respectively, which indicates that the ink with a smaller viscosity coefficient would result in a lower energy barrier for ink diffusion in water, as expected.

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