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Study on the swelling kinetics of superabsorbent using open circuit potential measurement

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Abstract

Open circuit potential measurement was used to trace the swelling kinetics of superabsorbent. The calibration curve and its fitting result showed the validity of the method in determining the concentration of chloride ion in aqueous solution. According to the regression analysis and theoretical derivation, the relationship between the open circuit potential change and the swelling ratio was obtained. Comparing with tea bag method, it was verified that open circuit potential measurement could be employed to trace the swelling kinetics of superabsorbent. The hysteresis effect of solute entering into superabsorbent and the overflow of soluble parts of hydrogel were also observed. Besides, we found that the entrance of solute and water were almost synchronal, and the concentration of solution absorbed by superabsorbent was lower than that of swelling medium. Moreover, the swelling model of superabsorbent in salting liquid was slightly modified.

Keywords: Superabsorbent; Swelling kinetics; Open circuit potential measurement; Hysteresis effect; Chloride ion-selective electrode

1. Introduction

Superabsorbent are lightly crosslinked polymer that can absorb and retain large amounts of aqueous solution, and the absorbed solution cannot be released even under certain load. Based on these fine performances, numerous works have been made on the swelling mechanism and the preparation of superabsorbent, since it was first reported by the US Department of Agriculture [1–5]. As one aspect, it is important to study the swelling kinetics of superabsorbent for uncovering swelling mechanism.

Some methods, such as natural filtration method, tea bag weight method, capillary method and picture analysis have been used to trace the swelling kinetics of superabsorbent [6–9]. But the interests of them only focused on the relationship between the properties of superabsorbent itself and the swelling time. So, no comprehensive knowledge was provided by these experiments. Heretofore, only two methods, calorimetrical analysis [8] and conductance method [10] have been used to trace the swelling kinetics by physicochemical changes in the swelling process. But the energy change of system is almost zero after a short-time exothermic process,

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so it is infeasible to trace the whole swelling process using calorimetrical analysis. The conductance method is limited due to its nonselective nature. Furthermore, the mole conductivity of the electrolyte aqueous solution was considered to be a constant, and it introduced error into the experimental results. Therefore, further work is needed for clarifying the swelling mechanism.

Ion-selective electrodes are relatively cost-effective, operation-simple and measurement range-wide. Besides, they are unaffected by sample colour or turbidity and sample is not destroyed in measurement. So they have been widely used in fields such as pollution monitoring, food processing, detergent manufacture, paper manufacture, in pharmaceuticals and so on [11–13]. Sodium ion-selective electrode has been used to determine superabsorbent polymers and their degree of neutralization [14]. However, it is rarely applied in study of swelling kinetics of superabsorbent.

Based on our previous works on superabsorbent [10,15–18], we use chloride ion-selective electrode to trace the swelling kinetics of superabsorbent by measuring the variation of open circuit potential in swelling medium. The calibration curve and its fitting result showed the validity of method in determining the concentration of chloride ion in aqueous solution. According to the regression analysis and theoretical derivation, the relationship between the open circuit potential change and the swelling ratio was obtained. Comparing with tea bag method, the reliability of open circuit potential measurement in tracing swelling kinetics of superabsorbent was verified. The hysteresis effect of solute entering into hydrogel and the overflow of soluble parts of superabsorbent were also observed.

2. Theoretical backgrounds

2.1. The principle of thermodynamics

According to the viewpoint of thermodynamics, if the difference of chemical potential between hydrogel and swelling medium is larger than zero ($\mu > 0$), the hydrogel will swell until $\mu = 0$; while $\mu < 0$, the hydrogel will deswell till $\mu = 0$. Considering the mixing, elastic and the osmotic pressure of ion contributions to the hydrogel free energy, Flory [19] drew the relationship between the equilibrium swelling ratio of the superabsorbent and the influencing factors as shown in Eq. (1):

$$Q_{\mathrm{eq}}^{5/3} = \left[\left(\frac{i}{2 \cdot V_u I^{1/2}}\right)^2 + \left(\frac{1}{2} - \chi_1\right) \Big/ V_1\right] \Big/ (V_e/V_0) \tag{1}$$

where, Q_{eq} is the equilibrium swelling ratio. i, V_{u} and I denote the charge number that fixed on the hydrogel molecular chains, the mole volume of structural repeat units and the ion strength of swelling medium. χ_1 and V_1 are the Flory interaction parameter and the mole volume of solvent. V_{e} and V_0 denote the number of effective subchains in network and the total volume of swollen hydrogel. i/Vu is defined as the charge density that fixed on the hydrogel molecular chains and V_{e}/V_0 is defined as the crosslinking degree of hydrogel. The first term on the right-hand side of Eq. (1) represents the osmotic pressure, the second term the hydrophilic ability of function groups.

From Eq. (1) it is apparent that the charge density and the ion strength of swelling medium will influence the swelling ratio of superabsorbent. In the swelling process, the hydrophilic groups on the polymer chains will dissociate. The counterions will move freely only in hydrogel according to the electronic neutrality principle. So, the osmotic pressure between hydrogel and the external solution will make the external solution enter into hydrogel, and the repulsive force among the polyanion also will accelerate spread of polymer network until the swelling equilibrium reaches. At the same time, the chemical potential of solute both in hydrogel and the external solution tend to be equilibrium. Thus, the concentration of solute in external solution will change with the swelling of superabsorbent. So the open circuit potential will change in the swelling process. And it is possible to study the swelling kinetics of superabsorbent by the open circuit potential measurement.

2.2. The principle of the open circuit potential measurement

Ion-selective electrodes (ISE) work on the basic principle of the galvanic cell (Meyerhoff and Opdycke), and the basic formula is given as follows [20]:

$$E = E_{\mathrm{ise}} - E_{\mathrm{ref}} \tag{2}$$

where, E, E_{ise} and E_{ref} denote the potential for the cell, the ISE and the reference electrode.