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A novel semi-automated apparatus to concentrate aqueous polymer solutions with a thermosensitive hydrogel

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Abstract

Construction and use of a novel, semi-automated apparatus for concentrating aqueous polymer solutions by means of a reversibly thermosensitive hydrogel are described. The gel was chemically crosslinked poly(*N*-isopropylacrylamide-co-acrylic acid), which has a lower critical swelling temperature (T_c) of 37°C, and the solute in the test solution was Dextran Blue (molecular weight 2×10^6 g mol^{-1}). The hydrogel is placed in a double-walled cell, which is maintained at a temperature below or above T_c by passage of water from external baths. Switching between the two temperatures is effected by solenoid valves. Test solution is transferred from a reservoir into the cell, the flow rate and hence mass of test solution being controlled by another solenoid valve. After swelling of hydrogel at the lower temperature the resultant, more concentrated test solution ('raffinate') is removed via a drainage stopcock and its concentration measured by VIS spectroscopy. The hydrogel is then deswollen by switching to the higher temperature mode, the water thereby expelled being removed via the drainage stopcock. A considerable level of automation of the apparatus is achieved by use of individual timers for each of the five solenoid valves. Separation factors and efficiencies of separation were evaluated and found to be dependent on (a) time of swelling; in some cases times were deliberately kept short and final equilibrium swelling was not reached, (b) concentration of test solution and (c) mass of test solution relative to that of the initial gel.

Keywords: Dextran blue; Separation process; Poly(*N*-isopropylacrylamide-co-acrylic acid)

1. Introduction

Chemically crosslinked thermosensitive hydrogels imbibe water at ambient temperatures but expel it on heating via the lower critical swelling temperature (T_c) [1–3]. Chemically crosslinked polymers of *N*-isopropylacrylamide (NIPA) are the most widely studied thermosensitive hydrogels [4]. Because the swellability of the PNIPA network is low, incorporation of comonomers that are acidic [1,2], basic [5] or salts [3] is often preferred. Attainment of increased swellability at ambient temperatures in these copolymer hydrogels is sometimes offset by either inconveniently high or completely absent values of T_c. Our previous studies [1–3] indicated that some of the comonomers were unsuitable and that an optimum balance between swellability and T_c was provided by P[NIPA-co-acrylic acid (AA)] xerogels of specific compositions of principal comonomers and of chemical crosslinker, *N*,*N*′-methylene bis-acrylamide (BIS).

Hydrogels have been proposed for use in the separation of vaccines [6], macromolecules [7–13], yeasts [14] and bacteria [15] from dilute aqueous solutions. This application of thermosensitive hydrogels to the separation of water from dilute solutions has the advantage that, after absorption of water, the swollen gel can be heated above T_c to expel the water and hence regenerate the xerogel for further use. Factors determining the feasibility of using hydrogels as separation devices include high swellability, a convenient value of T_c and size selectivity.

In previous studies on the concentrating of aqueous solutions by the swelling of a thermosensitive hydrogel the methodology has been simple, the absorbent gel being manually placed either directly into the test solution for mechanically strong hydrogels [7–15] or first into a sealable water permeable bag in the case of fragile hydrogels [16]. When swelling and hence separation is complete, the hydrogel or bag containing hydrogel is removed by lifting the hydrogel or bag containing hydrogel out of the resultant, concentrated test solution. In the procedure of Cussler et al. [8] the hydrogel is removed by raising a perforated stainless steel ladle on which the hydrogel rests. Though highly effective, these separation experiments are entirely manual

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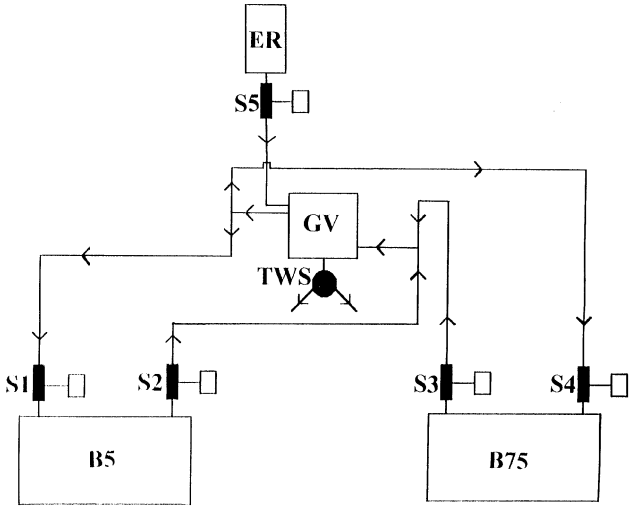

Fig. 1. A schematic diagram of the semi-automated apparatus. Explanation of the abbreviations is given in the text.

in operation and hence not especially suited to any potential industrial applications. Consequently, in the present study a semi-automated apparatus has been constructed and tested for the concentrating of a dilute aqueous solution of a high molecular weight polymer by swelling of a thermosensitive hydrogel. The purpose of this device is to illustrate the possibility of developing a more automated, and fully integrated, separation system obviating the need for all but the briefest of operator attention. In this way the suitability of such a system for industrial usage will be highlighted.

Furthermore, in previous studies [7–15] in order for the hydrogel to reach its equilibrium (or maximum) degree of swelling the time taken for the separation experiments has been long, typically in excess of 24 h. Clearly this lengthy period is inappropriate for industrial applications of this technology. Hence in the present study swelling times have been restricted to ≤4 h. Such times do not necessarily allow for full swelling equilibrium to be reached and indeed no attempt is made to characterise the partially swollen networks. Hence a balance is required between the imposed time of swelling and the resultant degree of swelling, the latter being a critical factor in the extent to which the test solution becomes more concentrated.

As far as the authors are aware, such a device has not been reported previously. As a model water-soluble polymer, dextran blue 2000 (DB) was selected due to the authors' prior, experience [12], its ready availability and ease of analysis in aqueous solution.

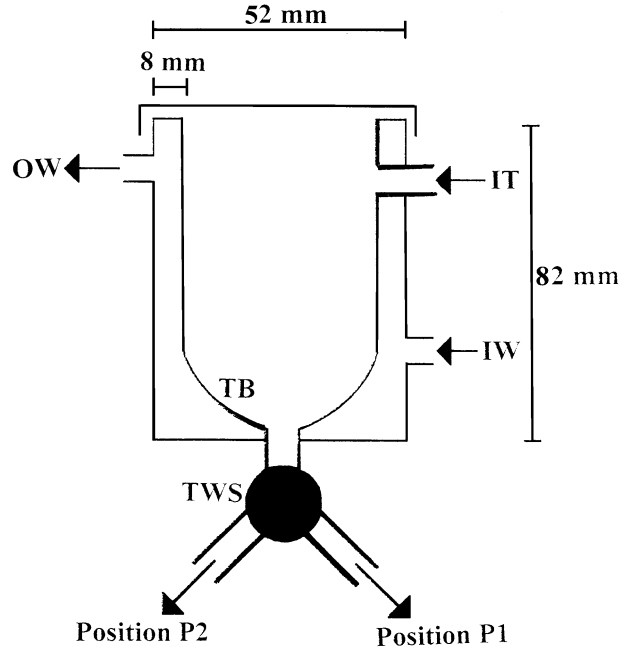

Fig. 2. Diagram of the double walled vessel GV. Explanation of the abbreviations is given in the text.

2. Experimental

2.1. Materials

The source of water, NIPA, AA, the initiator ammonium persulphate, the crosslinker BIS and the activator tetramethylethylene diamine were as given before, as was also the mode of purification of water, NIPA and AA [1]. DB was obtained from Amersham Pharmacia Biotech, St. Albans, UK. DB is produced from dextran, of nominal molar mass of ca. 2×10^6 g mol^{-1}, by attachment of a complex polycyclic chromophore to the polymer backbone. The scission of the chromophore from the dextran chain has been asserted not to occur in aq. solution [17]. Accurate adherence to the Beer-Lambert law was verified, the absorption coefficient at 620 nm in terms of the mass concentration of DB being 0.812 g^{-1} dm^3 cm^{-1}.

The UV/VIS measurements were performed with a Hewlett Packard HP8452A Diode Array Spectrophotometer. A quartz cell with a path length of 1 cm and a volume of ca. 1 ml was used. The spectrum over the range 190–820 nm was recorded in order to check that it did not change in form with concentration. Only the absorbance (A) at 620 nm was utilized in this study.

2.2. Synthesis of hydrogels

The gels were prepared in a mould by free radical crosslinking copolymerisation in aqueous solution at 25°C according to procedures given previously [1]. A single composition was used, the contents of AA and BIS being 10 and 0.25 mol% based on NIPA and total principal comonomers (NIPA + AA) in the feed, respectively. High fractional conversions (ca. 0.92) were obtained.

The hydrogels were prepared in the form of strips as determined by the mould geometry (50 mm × 15 mm × 3 mm). Preliminary experiments indicated that increasing the surface to volume ratio of the hydrogels employed here increases the rates of both the swelling and deswelling,

which is a highly desirable feature for a separation device. Therefore, prior to use in the separation apparatus, the hydrogels were swollen in water at ambient temperature for 24 h to facilitate cutting with a sharp scalpel into regular sized pieces (ca. 5 mm × 5 mm × 5 mm). Once cut, the hydrogel was dried at 47°C for 48 h and then to constant weight in a vacuum oven at 45°C for ca. 24 h. The mass of xerogel used in these experiments was 1 g.

2.3. The apparatus

A schematic diagram of the whole apparatus is given in Fig. 1. Fig. 2 is a more detailed diagram of the glass double walled vessel that contains the hydrogel and test solution. In Fig. 1 the key features are:

B5-water bath fitted with pump unit maintained at 5°C;
B75-water bath fitted with pump unit maintained at 75°C;
GV-double-walled glass vessel containing hydrogel with glass lid;
ER-elevated reservoir for test solution;
S1-solenoid valve and timer controlling flow of cooling water from GV;
S2-solenoid valve and timer controlling flow of cooling water to GV;
S3-solenoid valve and timer controlling flow of heating water to GV;
S4-solenoid valve and timer controlling flow of heating water from GV;
S5-solenoid valve and timer controlling flow of test solution into GV;
TWS-a two way stop-cock.

In Fig. 2, GV was specially constructed for this system. Its key features are: (1) inlet tube (IT), for the addition of test solution from ER to the hydrogel without opening the closed vessel, thus preventing unnecessary heat transfer; (2) the double wall, so that the temperature of GV and contents can be controlled (IW and OW are tubes for inlet and outlet of water, respectively); (3) a tapered bottom (TB) to the internal container facilitating drainage of the liquid from GV; (4) TWS fitted to the drainage tube facilitating the separation of the raffinate from hydrogel after swelling and of expelled water from deswollen gel after deswelling. GV has a total volume of ca. 75 ml and the following dimensions: external jacket of height 82 mm and width 52 mm, internal chamber of height 72 mm and width 36 mm, thickness of double wall 8 mm and angle of sloped bottom ca. 35°.

As an alternative to the use of the two thermostated water baths and GV (a rather large set of apparatus but one which could be scaled down easily in the future) consideration was accorded to the feasibility of using Peltier heaters to control the temperatures. These are electronic devices, which can either heat or cool their environment by the switching of the direction of their power supply. Although such devices can facilitate rapid changes of temperature, their practical application is complicated by the need for achieving excellent thermal conductivity between the Peltier unit and the sample, often accomplished by fabricating the sample holder from a material of high thermal conductivity such as anodised aluminium. The use of such Peltier units is further complicated by the requirements for expensive transformer and wiring systems. Accordingly, it was decided not to embark on a design involving Peltier heaters.

The solenoid valves, 2/2 way miniature solenoid valves with threaded port connections (RS components U.K.) and DIN plug timers (RS components U.K.) required a 24 V dc power supply. The construction and operation of the solenoids were such that they remained closed unless acted upon by the power supply. Programming of the timers was via built-in DIP switches and internal potentiometers. The timing range afforded by the timers was 0.5 s up to 10 h. In addition the timers could be programmed with on-delay, asymmetrical recycler pause/pulse start functions. The solenoid valves were connected to the water baths by silicone tubing (internal diameter 5 mm). Connection between the solenoid valves and tubing was made with screw-in half union connectors (RS components) and push-in nipples.

Cooling of the GV and contents was effected by opening S1 and S2, while S3 and S4 remain closed. The cooling period, i.e. the length of time during which S1 and S2 are open, was controlled by the appropriate timers. Heating of the GV was effected by the opening of S3 and S4, with S1 and S2 closed. Again the length of heating was controlled by the appropriate timers.

The addition of a known volume of test solution was made possible simply by calibrating the rate of flow of aq. DB test solution through S5 and setting the timer of S5 to a time, which allows that volume of test solution to flow through S5. The raffinate was removed from GV by opening the TWS to position P1 (Fig. 2). Preliminary experiments indicated that, in order to ensure complete removal of raffinate from GV, the stopcock TWS should remain open in position P1 for 3 min. Water was removed from GV after deswelling of the hydrogel by opening TWS to position P2. Again preliminary experiments indicated that, in order to ensure complete removal of water from GV, the stopcock TWS should remain open in position P2 for 3 min.

2.4. Separation experiments

The separation experiments followed a basic routine in which the initial step was the deswelling of a swollen hydrogel at an elevated temperature (75°C). Test solution was then introduced to the deswollen hydrogel and both were cooled to a lower temperature (10°C), at which the hydrogel swells in the test solution and the latter becomes more concentrated. A separation experiment is complete once swelling has occurred and the raffinate has been removed. It is emphasised that 'complete' refers to the experiment conducted for a preset selected time and not necessarily to ultimate possible (equilibrium) swelling.

Table 1
Experimental parameters for the separation experiments

Time at 10°C (h)	Time at 75°C (h)	Swelling ratio r[a]	Initial concentration of test solution (g dm^{-3})	Initial mass of test solution (g)
0.25	0.25	1.7	0.25	40
0.25	0.25	1.6	0.50	40
0.25	0.25	1.7	1.00	40
1	1	2.2	0.25	40
1	1	1.9	0.50	40
1	1	1.8	1.00	40
2	2	2.5	0.25	40
2	2	2.2	0.50	40
2	2	2.2	1.00	40
4	4	3.1	0.25	40
4	4	3.1	0.50	40
4	4	2.9	1.00	40
1	1	1.4	1.00	10
1	1	1.8	1.00	20
1	1	1.9	1.00	30
1	1	2.0	1.00	50

[a] This is the swelling ratio r as calculated from the masses of the deswollen gel and hydrogel prior to and after the concentrating of the test solution respectively.

Ideally one might expect the dry xerogel instead of a deswollen hydrogel to serve as the starting point for swelling in order to achieve maximum swelling and concentrating. However, the use of the xerogel has the disadvantage of a long period of time to reach significant degrees of swelling. In addition, the production of a dry xerogel between separation experiments would involve the removal of the hydrogel from GV followed by the time consuming process (ca. 48 h) of drying at elevated temperatures in both an oven and vacuum oven.

Because the gel was cut and dried to constant weight after synthesis (see above) a priming stage is required before any separation experiments can be carried out. The priming stage consists of placing the swollen gel (ca. 63 g) in the GV, the xerogel (1 g) having been swollen previously in water (1 dm^3) at 25°C for 24 h. The water baths were allowed to reach temperature (5°C and 75°C) and the DB test solution was placed in ER. Although the cooling water bath was thermostated at 5°C, the contents of GV were found to remain at a constant temperature of 10°C, the difference in the two temperatures being due to the slow flow of cooling water around the GV and the concurrent transfer of heat from the environment to the GV. The slow rate of flow of cooling water (50 ml min^{-1}) is believed to be due to the contraction of the brass fittings constituting the pathway of water through the solenoid valve; the flow of heating water at 75°C (100 ml min^{-1}) was similar to that of the rate of flow of water at ambient temperature (110 ml min^{-1}). However, because the constant temperature of the contents of GV was relatively low and therefore conducive to significant swelling, no alteration of the apparatus was required.

Prior to activation of the solenoid valves the timer for each solenoid valve was set to a predetermined time t, where t was 0.25, 1, 2 and 4 h. (Table 1). It should be noted that t represents both the deswelling time (heating) and swelling time (cooling), i.e. the same times were selected for deswelling and swelling. The equality of the two times has no especial significance and is purely a matter of convenience. Power was then switched on to the solenoids. Initially solenoids S3 and S4, and the TWS (in position P1) were opened for the time t. This procedure allowed the hydrogel to be heated and thus deswollen, and for the water associated with deswelling to be removed. After time t solenoids S3 and S4, and stop-cock TWS were closed and the deswollen hydrogel removed, lightly surface dried and weighed (m_{ds}). The hydrogel was then returned to the GV and solenoids S1 and S2 opened, resulting in the cooling of the GV and hydrogel. Test solution was added to GV by opening the solenoid S5 for a time that, in conjunction with the previously measured rate of flow of test solution through S5 into the GV (30 g min^{-1}), allows the mass of added test solution (m_t) to be known. The system was maintained at 10°C for the time t after which the raffinate was removed via drainage through stop-cock TWS in position P2, and the hydrogel removed, lightly surface dried and weighed (m_h). The process of removing and weighing the swollen and deswollen hydrogel was required only for the purpose of quantifying the parameters S and η described below and so during 'normal' usage these interrupting steps are not required. The system was then ready for further separation experiments.

The mass of raffinate (m_r) remaining after separation was calculated via Eq. (1)

$$m_r = (m_{ds} + m_t) - m_h. \quad (1)$$

A separation factor S, based purely on the increase in concentration of test solution, the mass of solute in it remaining constant, is expressible as change in concentration

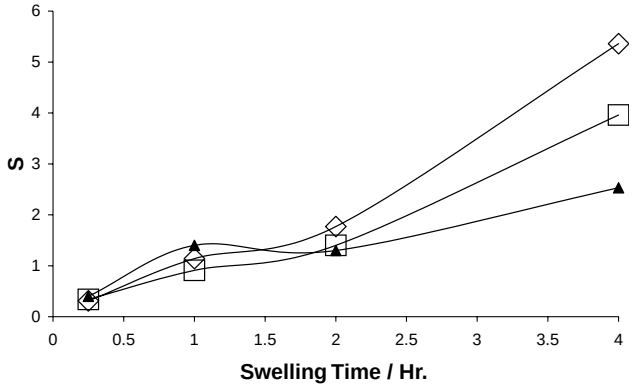

Fig. 3. Variation of separation factor S at 10°C with swelling time for aq. DB of initial concentrations C_0 (◇) 0.25, (□) 0.50 and (▲) 1.00 g dm^{-3}. Mass of intial test solution = 40 g.

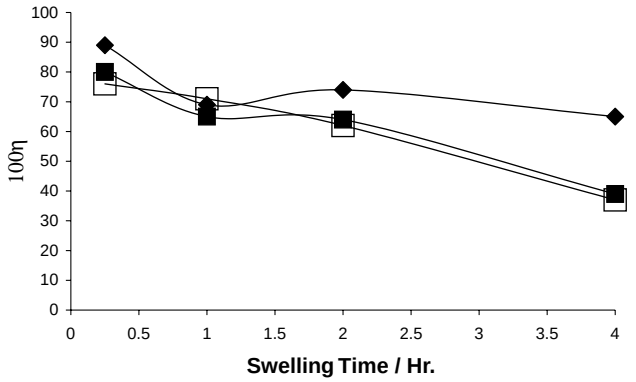

Fig. 4. Variation of efficiency of separation 100η at 10°C with swelling time for aq. DB of initial concentrations C_0 (◆) 0.25, (■) 0.50 and (□) 1.00 g dm^{-3}. Mass of intial test solution = 40 g.

relative to initial concentration, viz.

$$S = [(1/m_r) - (1/m_t)]/(1/m_t) \quad (2)$$

$$S = (m_t/m_r) - 1 \quad (3)$$

If no water passes into the xerogel, $S = 0$. However, when swelling does occur, there is no limiting maximum value attainable in principle for S.

Utilising both changes in concentration of test solution and mass of water imbibed by gel, one can define an efficiency factor of separation (η) as a fraction (or more usually as a percentage):

$$\eta = (C/C_0)/(C/C_0)^*. \quad (4)$$

In Eq. (4) no subscript appended to concentration C relates to raffinate and subscript — 0 relates to initial test solution. $(C/C_0)^*$ denotes the concentration ratio obtained assuming no change in mass of solute within test solution, i.e. transfer of pure water only from test solution into the gel. In practical terms the value of the numerator is measured as A/A_0, where A and A_0 are the absorbances at 620 nm of the raffinate and initial DB test solution respectively, and the denominator is measured as $(1/m_r)/(1/m_t)$.

The swelling ratio r of the hydrogel for each separation experiment was determined according to Eq. (5) where m_h and m_{ds} are the weights of swollen hydrogel and deswollen hydrogel, respectively. It should be noted that, in contrast to previous studies, [1–3,12,15,16] r is the ratio of the mass of the swollen gel to the mass of the deswollen hydrogel and not to that of the completely dry xerogel.

$$r = \frac{m_h}{m_{ds}}. \quad (5)$$

3. Results and discussion

Dilute aqueous solutions of DB were concentrated using this semi-automated system. The values of the separation factor S and the efficiency of separation factor η were found to be dependent on (i) the time allowed for swelling/separation to occur, (ii) the mass of test solution and (iii) the concentration of the test solution. The effect of these three parameters will be discussed separately.

3.1. Effect of swelling time

The values of S increased with time of swelling (Fig. 3). This is due to the increased swelling of the hydrogel resulting in a decrease in the mass of raffinate (m_r), i.e. in Eq. (3) m_r is decreased as swelling time increases. The values of η decreased with swelling time (Fig. 4), i.e. as the hydrogel becomes more swollen, the quantity of DB adsorbed onto the hydrogels increases probably due to the increase in the surface area of the hydrogel on swelling. The impenetrability to DB of the hydrogels employed in this study has been investigated previously [12]. It was demonstrated that the decrease in the value of η for this gel/solution system was due to the adsorption of DB onto the hydrogel surface.

3.2. Effect of mass of test solution

It was found that at any single swelling time the value of S decreases as the mass of test solution added to the GV increases (Fig. 5). This decrease is due to the increase in the mass of raffinate m_r remaining on swelling of the hydrogel (see Eq. (3)), i.e. the value of m_r increases with increasing mass of test solution.

For a single swelling time the efficiency η increases in value with increasing mass of test solution added to initially deswollen gel in GV (Fig. 5). The increase in η may be attributed to the reduced significance of adsorption of DB on the surface of the hydrogel, i.e. the mass of solute adsorbed becomes less as the initial mass of test solution increases. The argument for the influence of initial mass of test solution on η is based on the degree of swelling of the hydrogel being unaffected by the concentrating of the various initial masses of test solution (for fixed time t and

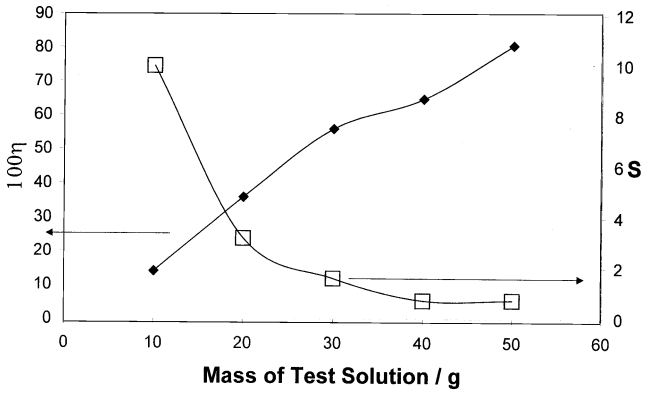

Fig. 5. Variation of (□) separation factor S and (◆) efficiency of separation 100η with mass of DB test solution of concentration 1.00 g dm^{-3} in the aqueous swelling medium. Data relate to swelling for 1 h at 10°C.

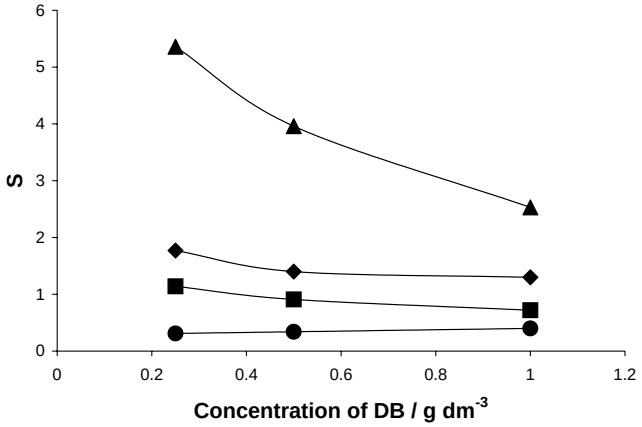

Fig. 6. Variation of separation factor S at 10°C with concentration of aq. DB test solution for swelling times of (●) 0.25, (■) 1, (◆) 2 and (▲) 4 h. Mass of intial test solution = 40 g.

initial concentration of test solution). This assumption is justified, because the value of swelling ratio r does not change significantly with initial mass of test solution (Table 1). On this supposition, swelling of a hydrogel to a value of r in a small mass of test solution is expected to produce a more concentrated raffinate than is produced on swelling of the hydrogel to the same value of r in a larger mass of initial test solution. Further, in a previous study [12] on the concentrating of DB by the same hydrogel as employed here, but with swelling reaching equilibrium, the present authors have shown that the adsorption of DB to the surface of the hydrogel increases with concentration of DB. In summary, reducing the initial mass of test solution results in a more concentrated raffinate, which in turn results in a greater mass of solute being adsorbed onto the hydrogel surface, and hence a smaller value of separation efficiency.

3.3. Effect of concentration of test solution

For the swelling times examined the value of S decreases as the concentration of the test solution increases due to the reduced swelling of the hydrogel in the presence of DB (Fig. 6). This decrease could be attributable in principle to several factors including (i) a reduction in the degree of ionisation of the AA groups due to the DB solution possessing a lower pH than that of water, (ii) a reduction in electrostatic repulsion between ionised AA groups due to the presence of a counterion such as sodium (a component of DB), (iii) the formation of hydrogel–solute complexes by the penetration of DB into the swelling hydrogel or (iv) differences in the chemical potential of pure water and the water in the DB solutions. The DB solutions were dilute, and exhibited values of pH and conductivity equal to those of water, and hence the effect of these two parameters on the swelling of the hydrogels can be discounted. Furthermore, the impenetrability of the hydrogel to these solute molecules has been demonstrated previously [12]; there is thus minimal possibility of hydrogel–solute complex formation. Therefore, the reduction in the swelling of hydrogels is due to chemical potential differences between water and the water in the test solutions. Similar effects have been observed for the swelling of poly(2-hydroxyethyl methacrylate) in aq. DB solutions [17] and of crosslinked polyacrylamide in aq. solutions of poly(ethylene oxide) [18,19].

It should be noted that the separation factor S is enhanced by both the longest swelling time and by use of the most dilute initial test solution.

For the swelling times examined the value of η decreases as the concentration of the test solution and time of swelling increase (Fig. 7). It has been indicated that the reduction in efficiency for the aq. DB system is likely to be associated with the adsorption of DB to the hydrogel, with the mass of solute adsorbed increasing with concentration of test solution. A further convincing demonstration of the role of solute adsorption in determining the separation efficiency of a solute/gel system has been provided by Okay and coworkers [9]. It was shown that coating PNIPA gel beads with solute bovine serum albumin (BSA) prior to separation

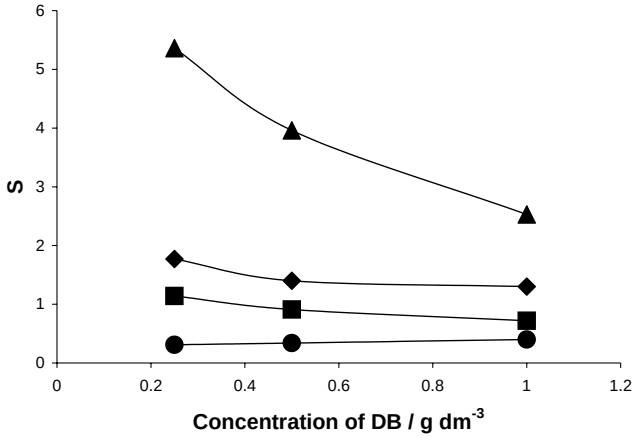

Fig. 7. Variation of efficiency of separation 100η at 10°C with concentration of aq. DB test solution for swelling times of (●) 0.25, (■) 1, (◆) 2 and (▲) 4 h. Mass of intial test solution = 40 g.

increased the value of η due to the fact that the possibility of adsorption during separation is thereby minimised, if the hydrogel surface is no longer free to participate in adsorption of BSA.

4. Conclusions

1. A semi-automated system for the concentrating of aqueous solutions of water soluble polymers via the swelling and subsequent deswelling of a thermosensitive P(NIPA-co-AA) hydrogel has been developed.
2. The value of the separation factor S and efficiency of separation η are influenced by (a) the time allowed for swelling/separation to occur, (b) the mass of test solution used in the separation experiments relative to the mass of deswollen gel and (c) the concentration of the test solution.
3. The relationship between η and the concentration of the aqueous DB test solution established in the present semi-automated apparatus confirms that obtained previously [12].
4. For DB as solute, the value of S increases as η decreases and hence a balance between enhancement of concentration and efficiency of separation is required for maximum performance of the semi-automated device.
5. The period allowed for swelling and deswelling of the hydrogel has a profound effect on the magnitudes of S and η. Increasing the times of swelling and deswelling increases the value of the separation factor S, which is highly desirable. However, not only does increasing the duration of swelling decrease the magnitude of η, it also decreases the value of the semi-automated system as an attractive practical device, i.e. due to the increased time required for a sample to be concentrated. Thus a balance must be found between the values of S and η and the duration of an experiment.
6. Slow swelling of completely dry xerogels has been attributed [20,21] to the initial slow diffusion of water into the outer glassy matrix layer. Accordingly, the procedure adopted here is perhaps atypical in the respect that the starting point for the swelling/separation was a deswollen (but not dry) gel. Swelling at times below equilibrium swelling time is normally employed to follow diffusion kinetics [22]. It has also been utilised [22], along with other procedures [23–25], to probe the subdivision of states of water within a hydrogel at different levels of water content. However, we believe that the comparatively short times involved in the present study are the first to be focused solely on concentrating solutions by reversibly thermosensitive hydrogels.
7. These experiments are a guide to the use of the semi-automated device described here. The values of S and η can be used to calculate the concentration of solute in the raffinate (C) without the need to weigh the hydrogel in its deswollen and swollen states, provided that the conditions such as time of swelling and deswelling are identical to those employed here.
8. In the concentrating of solutes other than DB or in the use of physical conditions different from those employed here it is suggested that a similar range of experiments be carried out in order to determine the values of S and η for that system. Again, once determined, these values can be used to calculate the concentration of solute in the raffinate without the need to weigh the hydrogel in its deswollen and swollen states.

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