Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Wang, Juh-Yaun , Chou, Kan-Sen and Lee, Chau-Jen(1998) 'Dead-End Flow Filtration of Solid Suspension in Polymer Fluid through an Active Kaolin Dynamic Membrane', Separation Science and Technology, 33: 16, 2513 — 2529

To link to this Article: DOI: 10.1080/01496399808545316

URL: http://dx.doi.org/10.1080/01496399808545316

SEPARATION SCIENCE AND TECHNOLOGY, 33(16), pp. 2513–2529, 1998

Dead-End Flow Filtration of Solid Suspension in Polymer Fluid through an Active Kaolin Dynamic Membrane

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ABSTRACT

In this study an active kaolin dynamic membrane formed on a SS-316 porous support was used to investigate the microfiltration of a solid suspension in polymer fluid. It was found that a homogeneous sodium acetate suspension in polymer can be completely removed by the active kaolin dynamic membrane to yield a very clear polymer product. The filtration rate as a function of operating temperature and pressure were experimentally determined. When the operating temperature was increased, the decreasing polymer viscosity resulted in an increase of filtration rate but was counteracted by the swelling effect of the membrane layer. Similarly, when the pressure was increased, the increase in driving force for filtration was counteracted by a simultaneous increase in particle packing. The filtration behavior of this dynamic membrane system was also simulated by the general blocking model $d^2t/dV^2 = k(dt/dV)^q$, where q was found to have negative values. Negative q values mean that our system reached a maximum blocking rate during the initial period of filtration and then decreased gradually. When the blocking rate became small enough, the system behaved like cake filtration. A satisfactory fit between experimental data and theoretical calculations was demonstrated.

Key Words. Microfiltration; Dynamic membrane; Polymer fluid; Active kaolin; Theoretical analysis

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INTRODUCTION

In a typical polymerization process, such as the manufacture of polyester, the synthesized polymer fluid may contain a solid suspension which affects both the color and the turbidity of product. Solid suspension dispersed in polymer mostly originates from the addition of catalyst for polymerization. The concentration of catalyst in the process is generally about 1700–3000 ppm (1). Several methods, such as filtration (2–5), adsorption by active charcoal (5, 6) or solvent extraction (5, 7, 8), can remove impurities from the polymer product. However, only adsorption by active charcoal can remove coloring impurities; it is ineffective in removing particulates. As for solvent extraction, most solvents remove some polymers along with salt impurities and therefore change the molecular weight distribution and reduce the yield of product. Filtration is by far the most effective method for removing impurities as a solid suspension and for decreasing the product's turbidity. Most of the patent literature we found (2–5) offered little in the way of detailed descriptions of filtration behaviors.

The dynamic membrane technique has been utilized for separations in various fields, e.g., textile dyeing wastewater (9, 10), desalination (11), apple juice concentration (12), sugar solution clarification (13), and proteins separation (14). The advantages of using dynamic membranes include "in-situ" formation and regeneration, reducing "downtime" in the operating apparatus, long support life, high permeating flux, mechanical stability, and durability at high temperature and under a wide range of pH (15–17). Active kaolin was selected in this work to form the dynamic membrane layer used for removing solid suspensions from a polymer fluid. Active kaolin is an inexpensive material which has the capability to remove coloring impurities through adsorption in addition to filtration of solid particles.

Researchers in membrane filtration are always concerned about the decline in filtration rate during operation. Various blocking mechanisms had been proposed (18, 19): complete blocking, standard blocking, intermediate blocking, and cake filtration (or boundary layer resistance). Numerous corresponding equations have also derived to describe the changes in flow rate versus time or filtrate volume for each situation. It is possible that the blocking of flow passages may change gradually from one mechanism to another as filtration progresses. The real situation will depend upon many parameters: particle size distribution versus pore size distribution of the filter medium, possible interactions between particles and the filter medium, operating pressure, shear stress on particles, solid concentration in solution, etc. It is a rather complex phenomenon. Researchers therefore usually choose only one model to describe their experimental results. However, it is not impossible that the experimental results could be simulated well by different models.

Type I: $0 \leq q \neq 1$

$$\frac{Adt}{dV} = \frac{\mu}{(-\Delta P)}\left(R_m^{1-q} + (1-q)k_I\frac{V}{A}\right)^{1/(1-q)} \tag{2}$$

where μ is the viscosity (g/s·cm), $(-\Delta P)$ is the pressure drop (dyne/cm^2), R_m is the resistance of the medium (cm^{-1}), k_I is the parameter of cake resistance, V is the volume of filtrate (cm^3), and A is the area of the medium (cm^2). The relation between k_I and k is

$$k_I = \left[\frac{(-\Delta P)}{\mu}\right]^{(1-q)} k \tag{3}$$

and k_I can be expressed in terms of α as follows:

$$k_I = c_s\alpha^{|1-q|} \tag{4}$$

where c_s is the concentration of filtrate (g/cm^3), α is the specific cake resistance ([cm$^{(1+q)}$·g^{-1}]$^{|1-q|}$). For example, when $q = 0$, we then have the cake filtration model:

$$\frac{Adt}{dV} = \frac{\mu}{(-\Delta P)}\left(R_m + c_s\alpha\frac{V}{A}\right) \tag{5}$$

If $q = 2$, we then have the complete blocking model as follows:

$$\frac{Adt}{dV} = \frac{\mu}{(-\Delta P)}\left(R_m^{-1} - c_s\alpha\frac{V}{A}\right)^{-1} \tag{6}$$

Type II: $q = 1$

$$\frac{Adt}{dV} = \frac{\mu R_m}{(-\Delta P)} e^{[(\mu c_s\alpha)/A(-\Delta P)(V/A)]} \tag{7}$$

This corresponds to the intermediate blocking model.

Decelerating Resistance, $q < 0$

The 11 equations offered by Luckert all have positive q values. However, when we plot (d^2t/dV^2) versus (dt/dV) (i.e., Eq. 1) from our filtration results of suspension in polymer fluid through a kaolin dynamic membrane, negative q values are observed. Bowen et al. (18) in their study of the steps of membrane blocking during protein microfiltration also observed conditions where q is negative (e.g., Fig. 7 in Ref. 18). After examining the above equations, we decided to extend the Type I equation to include the $q < 0$ situation, and to use it for fitting with our experimental results. The original data of dt/dV versus V were numerically differentiated to obtain (d^2t/dV^2) and then plotted against (*dt/dV*) to examine whether the q value is positive, zero, or negative. One of the working equations, e.g., Eq. (2) or (7), would then be chosen to determine the best fitted parameters of R_m, α, and q.

EXPERIMENTAL

Chemicals and Preparation of Polymer Fluid Containing Sodium Acetate

Sodium acetate (Riedel-de Haën, Germany) was selected as a model suspension solid and methanol (Riedel-de Haën, Germany) was used as the solvent to prepare the polymer fluid. The material chosen to form the dynamic membrane was active kaolin (Showa, Japan) which is insoluble in polymer and can adsorb impurities to decolorize the solution. Polyalkylene oxide (Dupont, Taiwan) containing units of four carbon atoms was chosen as our test polymer. It has a number-average molecular weight of 2000 ± 50 Da and a viscosity of 1650 ± 50 cP at 37°C.

A predetermined quantity of sodium acetate was first dissolved in 50 g deionized water and 500 g of test polymer was dissolved separately in 100 g methanol. The two solutions were then completely mixed at 50°C, after which water and methanol were removed by a vacuum evaporator (N-N type, Eyela, Japan). A crystal suspension of sodium acetate was uniformly formed in the polymer and was ready for subsequent microfiltration studies.

Analysis

The solution viscosity was obtained from a viscometer (DV-I, Brookfield, USA) with spindle LV-1. The shear stress and the shear rate were measured by a cone/plate viscometer (DV-II+, Brookfield, USA) with spindle CP-40. The particle size distributions of both active kaolin (dispersed in water) and sodium acetate (dispersed in polymer at around 30°C) were determined by laser particle analyzer (CIS-1, Galai, Israel). In theory, the pores in the dynamic membrane resulting from packing of active kaolin particles should be smaller than the particle size of sodium acetate to be effective for filtration. The surface of the SS-316 porous medium was observed by scanning electron microscope (S-2300, Hitachi, Japan).

Microfiltration Apparatus and Preparation of Dynamic Membrane Layer

The experimental apparatus is schematically shown in Fig. 1. Filtration was performed batchwise. The polymer solution containing a solid suspension was pumped via a syringe pump (Model 500D, ISCO, USA) and SS-316 tubing (ID 9 mm) into the filter module. This syringe pump was equipped with

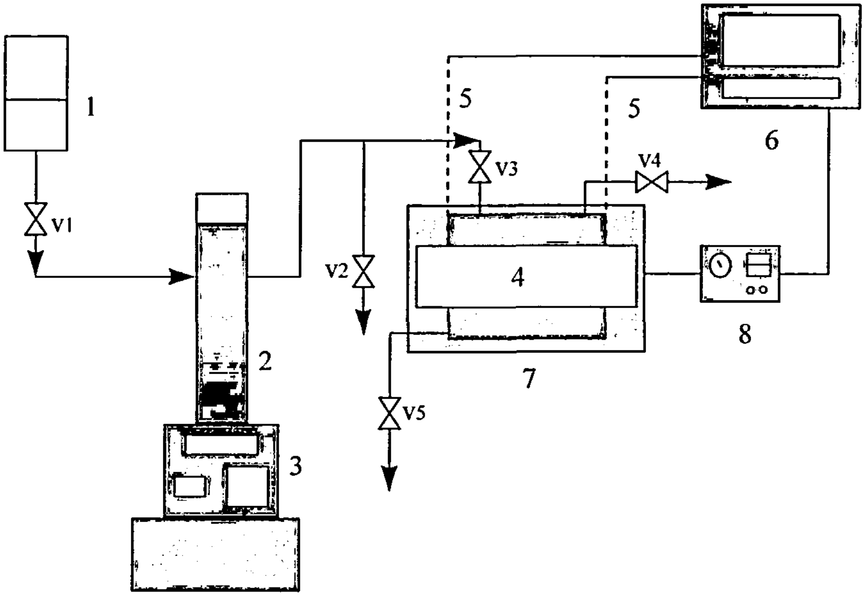

FIG. 1 Experimental apparatus: (1) sample vessel, (2) syringe pump, (3) pump controller, (4) filter modules, (5) thermocouple, (6) temperature indicator, (7) oven, (8) thermal controller, (v) valves.

a pressure controller for controlling the filtration pressures. It also provides us with data on time (t), total filtrate volume (V), and filtrate flow rate (dV/dt), from which the flow rate versus total filtrate volume data were used directly for further analysis. Values of d^2t/dV^2 were obtained by averaging the slopes of two adjacent data points as follows:

$$\frac{d^2t}{dV^2} = \frac{1}{2}\left[\frac{\left(\frac{dt}{dV}\right)_{i+1} - \left(\frac{dt}{dV}\right)_{i+1}}{V_{i+1} - V_i} + \frac{\left(\frac{dt}{dV}\right)_i - \left(\frac{dt}{dV}\right)_{i-1}}{V_i - V_{i-1}}\right] \tag{8}$$

At the start of each run we would wait 20 to 40 seconds until the system pressure reached the set point to record the first data. As a result, we observed a certain flow rate for $V = 0$ and $t = 0$. An oven and a temperature controller maintained a constant module temperature. Our system was designed to sustain up to 200°C and 250 atm as operating conditions. The SS-316 porous support (Mott, USA) has an effective diameter of 50 mm and a thickness of 5 mm. The estimated average pore size of this porous support from SEM (shown in Fig. 2) is about 4.7 μm. However, we can often find pores many times larger than the average size at the support surface. After each experiment the tubing system was cleaned by the pumping methanol and then dried with air, while the porous support was unmounted and washed thoroughly to restore its original characteristics.

Half a gram of active kaolin (as received) was stirred and mixed in 150 g polymer fluid, which was then passed through the porous support at 108°C and 100 atm. Particles of active kaolin plugged and accumulated at the surface of the support to produce a uniform dynamic membrane layer for subsequent filtration.

RESULTS AND DISCUSSION

Particle-Size Distribution and Pore Size

When particles of monosized spheres are arranged in a rhombic layer formation, there is a certain diameter ratio for a smaller sphere that can just pass through the triangular pore path formed by any three close-packed spheres. This ratio is termed the "critical ratio of entrance." In the tightest packing

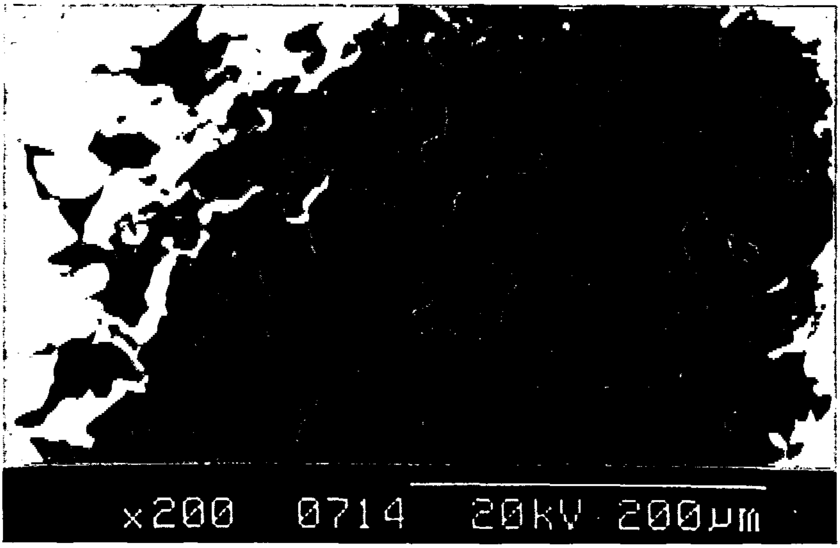

FIG. 2 SEM photograph of SS-316 porous support.

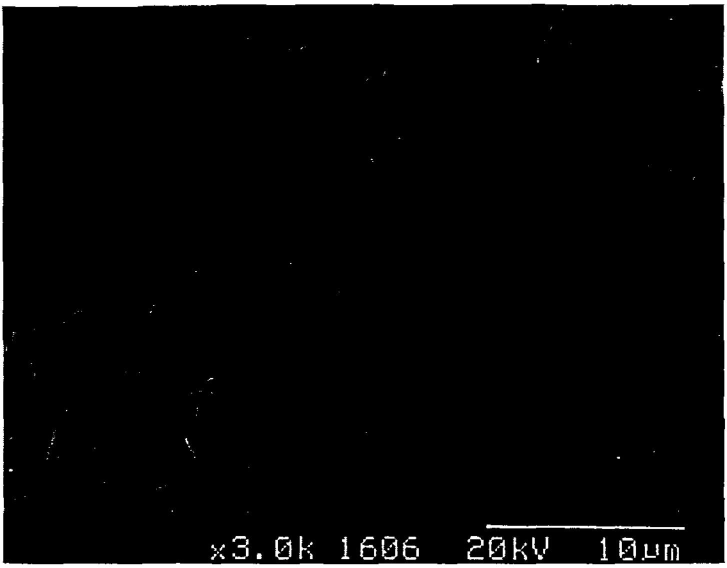

FIG. 5 SEM photograph of active kaolin dynamic membrane top view.

indicates a nonlinear relationship. In other words, the formation of this membrane layer does not follow the conventional basic cake filtration model.

The characteristic plot of (d^2t/dV^2) versus (dt/dV) for the formation of this active kaolin dynamic membrane is shown as Fig. 6(b). Clearly, the corresponding q value is negative for this filtration condition. This seems to suggest that the porous support was quickly plugged by kaolin particles at the start of the formation of this dynamic membrane layer. After that, the rate of increase in resistance, or blocking rate, gradually decreases while the total resistance (dt/dV) continues to increase. It maybe speculated that during this period some small-sized kaolin particles continue to penetrate into the dynamic membrane layer (causing an increase in specific cake resistance) or into the porous support (causing an increase in medium resistance). Nevertheless, this rate (d^2t/dV^2) will eventually approach zero, and the system will then behaved like cake filtration.

Next, we used Eq. (2) to best fit the experimental results and to estimate parameters of R_m, α, and q using the nonlinear regression technique. The respective numbers for these parameters are: $R_m = 2.47 \times 10^8$ cm^{-1}, $\alpha = 5.36 \times 10^9$ cm$^{-1.04}$·g$^{-2.43}$, and $q = -1.43$. The theoretical curve of dt/dV versus V based on this set of parameters is also plotted in Fig. 6(a) along with the experimental data. The fit is quite satisfactory.

Filtration of Polymer Suspension through Active Kaolin Dynamic Membrane

The filtration experiments were carried out with polymer fluid containing 1000 ppm sodium acetate suspensions under various temperature and pressure conditions. Measurement of the quality of polymer filtrate shows a clear product in terms of both turbidity and color. This demonstrates the capability of kaolin to remove coloring impurities. After each experiment the original white kaolin would become light gray in color.

Some representative results are shown in Fig. 7, where the inverse of the permeating rate is plotted against the filtrate volume. Corresponding characteristic curves (d^2t/dV^2 versus dt/dV) are shown in Fig. 8, again suggesting negative q values. Based on these figures, a number of features can be observed of this system. First, the rate of increase in resistance (or the blocking rate) rises rapidly at the start of filtration to a maximum value and then gradually declines asymptotically to some value close to zero. This is probably due to the very high pressure utilized in this work. When the filtration work was started, the coated kaolin membrane layer would be instantaneously compressed to a dense packing and therefore exhibited a very high blocking rate. After that, particles from the polymer suspension might still penetrate to some extent into the membrane layer while also accumulating into a cake at the same time. Finally, the blocking rate would become very small and the system would behaved like cake filtration.

Another feature noted is that the filtration resistance was higher under higher pressure. This fact demonstrates the compressibility of the kaolin membrane layer. As for the temperature effect, the resistance was higher at higher filtration temperatures (Fig. 7), but the rate of increase in resistance (blocking rate) was smaller at higher temperatures (Fig. 8). At high temperatures the viscosity of the polymer solution became smaller, e.g., from about 140 cP at 100°C to 33 cP at 167°C, which is beneficial for the filtration rate. Nevertheless, there is probably some swelling effect on kaolin particles which will make the membrane layer more compact and hence is detrimental to the filtration rate. Judging from the observed data, the swelling effect is more important than the viscosity effect in this case. Once the membrane layer is made more compact, it will be difficult for sodium acetate to penetrate. As a result, the blocking rate is rather small.

Next, Eq. (2) was used to best fit the experimental results (but only for the part after the maximum in d^2t/dV^2 vs dt/dV curves) and to estimate the parameters of R_m, α, and q using the nonlinear regression technique. Here R_m refers to the resistance offered by both the SS-316 support and the kaolin membrane layer. Relations between those parameters and the temperature and pressure are summarized and plotted in Figs. 9, 10, and 11. The predicted

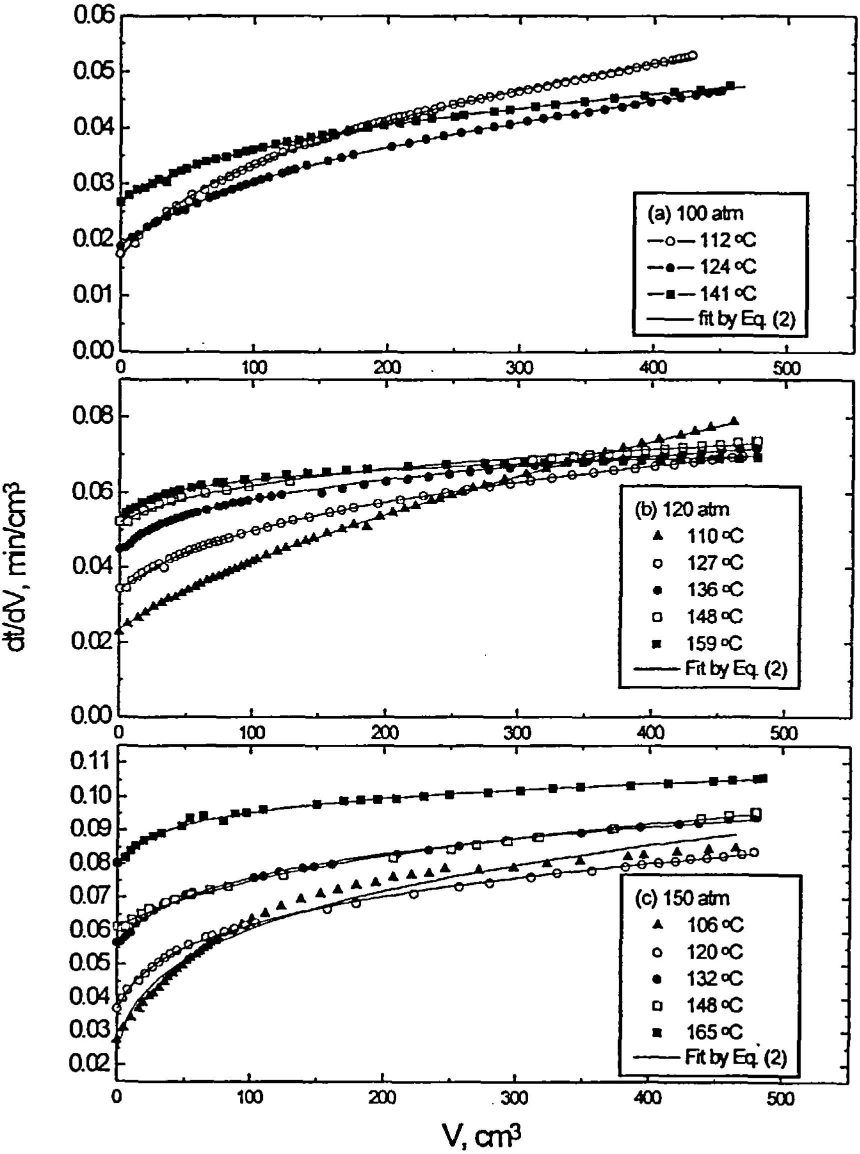

FIG. 7 Representative filtration results for polymer with 1000 ppm sodium acetate through active kaolin dynamic membrane at (a) 100 atm, (b) 120 atm, and (c) 150 atm.

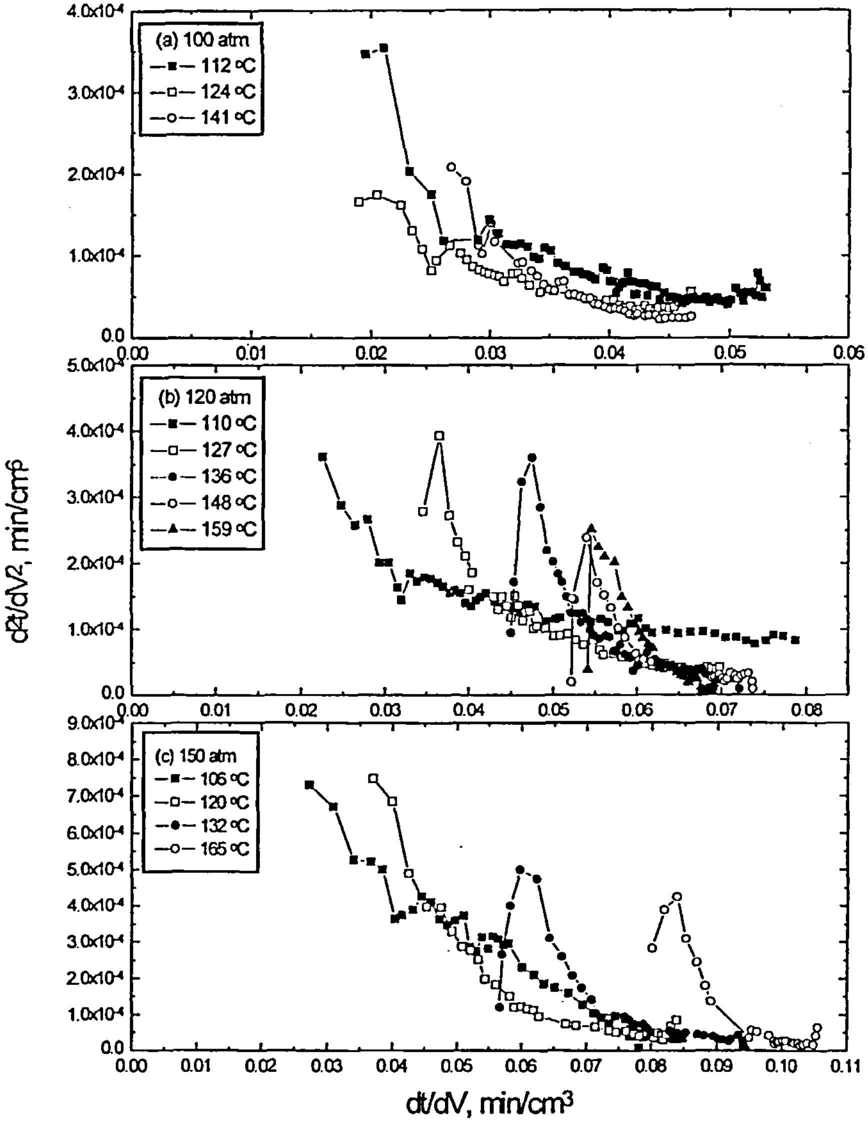

FIG. 8 Corresponding characteristic filtration curves for data shown in Fig. 7.

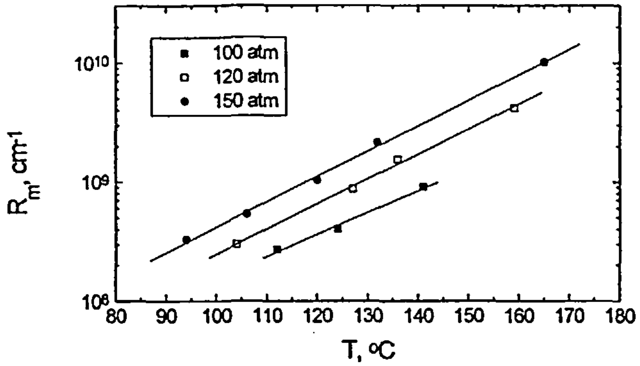

FIG. 9 Calculated R_m values as functions of temperature and pressure.

dt/dV versus V curves are also drawn in Fig. 7 to demonstrate the good fit to experimental results. For values of both R_m and α increase with both temperature and pressure in a similar manner, although the difference in α for 100 and 120 atm conditions is not significant. This suggests that the structure of the sodium acetate layer changes above 120 atm. As for q, its negative values show a decreasing trend in the blocking rate. The very high operating pressure quickly brought the system to a maximum blocking rate during the

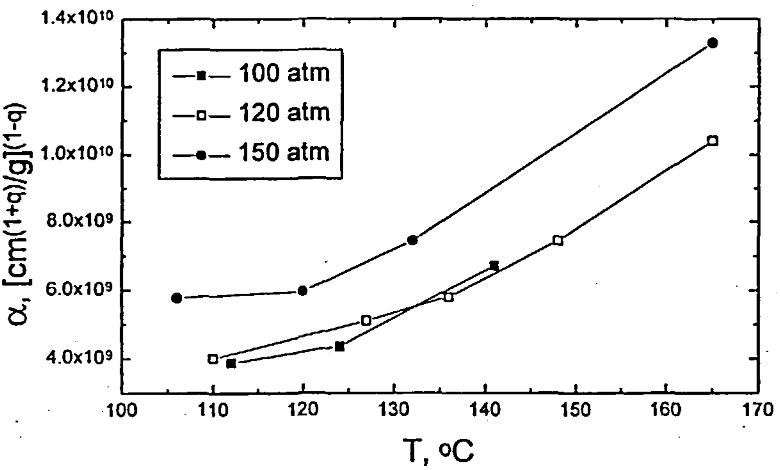

FIG. 10 Calculated specific cake resistance α as function of temperature and pressure.

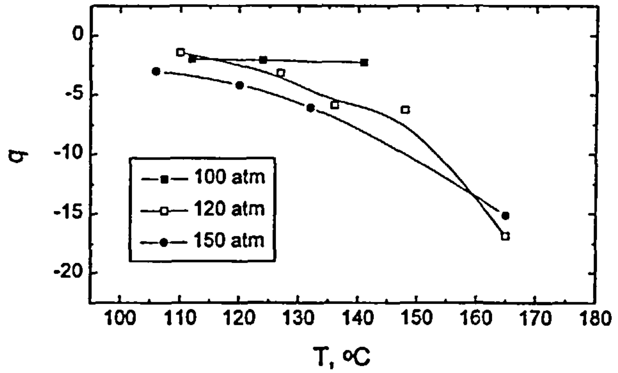

FIG. 11 Calculated q values as functions of temperature and pressure.

initial period of filtration. After that, the blocking rate continues to decrease to approach zero value. The system then behaves in the conventional cake filtration mode. The more negative the q value is, the faster this trend will be. A faster deceleration in blocking rate means that the membrane layer is more difficult to clog. Judging from the q values shown in Fig. 11, it occurred under high temperature and pressure conditions, suggesting that under these conditions the membrane layer is the most compact among all our experimental conditions.

CONCLUSION

Our experimental data demonstrated that solid particles such as sodium acetate in polymer can be completely removed by an active kaolin dynamic membrane. Due to its adsorptive nature, this kaolin layer is also effective in removing coloring impurities. In contrast to commercial membrane materials, this dynamic membrane system can be used at very high temperature and high pressure conditions. Other advantages of this dynamic membrane include high filtration rates and a slow decaying rate during filtration, as indicated by negative q values.

The filtration behavior can be satisfactorily fitted using the general blocking law models. Because of the very high operating pressure used for this system, the kaolin membrane layer was compressed at the start of a filtration operation to produce a maximum in the blocking rate, which then gradually declining asymptotically to a value close to zero. In other words, the system finally behaved in the cake filtration mode. Fitted parameters of R_m and α showed similar relations toward temperature and pressure. In general, both high pressure and high temperature resulted in the formation of closely packed membrane and cake layers. This type of structure produces a slower filtration rate, a higher resistance, and smaller blocking rates.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the National Science Council of the Republic of China through Grants NSC 85-2241-E-007-018 and 86-2214-E-007-012. They also thank the Process Development Division of Union Chemical Laboratories of Industrial Technology and Research Institute of ROC for help in the experimental set-up.

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Received by editor October 30, 1997
Revision received March 1998