Kinetics of Poly(acrylic acid) Adsorption at the Liquid–Glass Interface

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SYNOPSIS

The kinetic behavior of the adsorption of weak polyacid, namely, poly(acrylic acid) on a smooth glass surface has been studied at 30°C. For the evaluation of various adsorption parameters—the adsorption coefficient, surface coverage (θ), and thickness of the adsorbed layer—a new simple kinetic model has been proposed. The effect of the factors such as pH, electrolyte concentration, and molecular weight on adsorption behavior has been studied. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The adsorption of polymeric materials at the solid–liquid interface has been a phenomenon of prime importance in a number of technological and biological processes such as waste-water treatment, floatation separations, fine-particle recovery by selective flocculation, enhanced oil recovery, biological interplay between proteins, nucleic acids, plants, and animal membranes, etc.[1-4] To understand the behavior of macromolecules at the interface, much effort has been put into various experimental and theoretical techniques. Also, a number of reviews have appeared in the literature,[5,6] which present the adsorption phenomenon as a well-grown area of research. Apart from the good status of research in the adsorption field, not much satisfactory progress has been registered in the studies of kinetics of polymer adsorption, which is a prime factor in controlling the quantitative and conformational aspects of polymer adsorption.

Most kinetic studies done so far involve monitoring the change in the concentration of free polymer in solution.[7,8] Looking to the importance of kinetics in all areas of experimental research, a new simple mathematical approach has been developed, which not only provides information about the usual kinetic parameters but also enables one to evaluate various adsorption parameters such as the adsorption coefficient, surface coverage, and film thickness without the use of any intricate instrumental involvement. Although the kinetic scheme proposed has its own limitations, in the author's view, the method may be useful to researchers working with average facilities.

In the present communication, the kinetic behavior of adsorption of weak polyacid, namely, poly(acrylic acid), on a glass surface has been studied. The significance of the problem undertaken lies in the fact that, presently, the solids adsorbed or coated by polymers are finding increasing use as packing material in separate techniques like chromatography.[9-12] Looking to the utility of adsorbed solids in macromolecular separations, the present study has been carried out that involves studying the adsorption of poly(acrylic acid) onto glass balls with a kinetic approach.

EXPERIMENTAL

Materials

Poly(acrylic acid) (PAA) was supplied by the Jhonson Co. Ltd. (Bombay, India), in the form of 10% aqueous solution and was used without further purification. The molecular weight of unfractionated polymer was determined by viscosity measurements as reported elsewhere.[13] A portion of the polymer was fractionated by the method of Newman et al.[14]

using cyclohexane as the precipitant and viscosity-average molecular weights were determined viscometrically. All solutions used in the experiment were prepared in double-distilled water.

Adsorbent

To carry out the adsorption experiment, smooth-surfaced glass balls of known weights and dimensions were taken as adsorbents and used without any pretreatment. Although no method was used to characterize the smoothness of the surface, however, visual observation did not indicate the presence of any fracture on the surface of the glass balls.

Method

The method for conducting the adsorption experiment involves taking a known volume of PAA solution of definite concentrations in beakers containing glass balls as adsorbents. The solutions were constantly stirred with the help of a magnetic stirrer for several days. To determine the amount of adsorbed polymer at various time intervals, definite aliquots of the supernatant liquid (PAA solution) were withdrawn and the residual concentration of PAA in aliquots were determined by the titration method described in the literature.[15]

pH Measurements

For changing the pH of the PAA solution, HNO_3 was added to the medium and the resulting pH was noted using a digital pH meter (Systronics, India). The pH of the solution was noted before and after every adsorption experiment.

Film Thickness

For calculating the thickness of the adsorbed PAA film on the glass balls, it was assumed that the polymer was evenly adsorbed on the surface; the formula used to calculate the thickness was as follows:

Thickness (T)

$$= \frac{\text{Volume of the adsorbed polymer (in cm}^3)}{\text{Area covered by the adsorbed polymer (in cm}^2)}$$

The volume of the adsorbed polymer was calculated by dividing the weight of the adsorbed polymer (in g) by its density. For determining the density of the adsorbed film, again, a simplification is made that the density of the film is approximately the same as

in bulk solution and was determined by the method described elsewhere.[16]

The experimental results obtained were checked and found to be within the reproducible limits; however, an uncharacterized surface of the glass balls may give rise to somewhat different numerical values of the film thickness data. Here, it is worth mentioning that the present communication does not aim to give experimental data of the highest accuracy. The main objective is to provide a simple tool for a researcher to approach the kinetic aspects of adsorption phenomena.

RESULTS AND DISCUSSION

Prior to the discussion part of the results obtained, it is worthwhile to present the kinetic scheme of adsorption on which the work of the present communication is based. Although the scheme has appeared,[17] yet, in the author's view, it is essential to reproduce the scheme for the academic interest of the readers.

Case I

In most of the adsorption experiments, the time required to attain adsorption equilibrium is quite long (in some cases, several days) and, therefore, as an approximation, it may be supposed that for an appreciably longer period the rate of adsorption is almost constant. Now, according to Langmuir's adsorption isotherm equation, the rate of adsorption (Rad) is well given by

$$R_{ad} = k_1 c(1 - \theta) - k_2 \theta \qquad (1)$$

where k_1 and k_2 are the rate constants for adsorption and desorption, respectively; θ, the fraction of the surface covered due to the adsorbed polymer; and c, the concentration of polymer in solution (in g/dL). Now, on differentiating eq. (1) with time in the constant rate region, we get

$$0 = \frac{d}{dt} \{k_1 c(1 - \theta) - k_2 \theta\}$$

or

$$k_1(1 - \theta) \frac{dc}{dt} = (ck_1 + k_2) \frac{d\theta}{dt}$$

Since concentration of polymer in solution is falling off with time, a negative sign may be put with dc/dt. Now, the above equation becomes

$$k_1(1-\theta)\left(\frac{-dc}{dt}\right) = (ck_1 + k_2)\frac{d\theta}{dt}$$

or

$$\frac{dc}{(c+K)} = \frac{d\theta}{(1-\theta)}, \quad \text{where } K = \frac{k_2}{k_1} \quad (2)$$

Upon integrating eq. (2), we get

$$-\ln(c+K) = -\ln(1-\theta) + I \quad (3)$$

where I is an integration constant. Now, when $\theta = 0$, $c = c_0$ (initial concentration of polymer solution), then eq. (3) becomes

$$\theta = 1 - \frac{C+K}{C_0+K} \quad (4)$$

Thus, eq. (4) is the final equation that can yield corresponding values of θ at different values of c. To find the value of K ($=k_2/k_1$), we make use of Langmuir's adsorption isotherm equation according to which

$$\frac{Ce}{m} = \frac{Ce}{k} + \left(\frac{k_1}{k_2}\right)\cdot\frac{1}{k} \quad (5)$$

where Ce = equilibrium concentration of the polymer solution. m = amount of polymer adsorbed (in mg/g).

From eq. (5), it is clear that a plot between ce/m vs. Ce should yield a straight line and from the slope and intercept of which the value of k ($=k_2/k_1$) may be calculated. The only limitation of eq. (4) is that it is applicable to the time period up to which the rate of adsorption is constant.

Case II

Evaluation of Rate Constants k_1 and k_2

To calculate the rate constants for adsorption (k_1) and desorption (k_2), we may suppose that desorption is almost negligible in comparison to initial rate of adsorption. Now, for the rate of adsorption, we may write

$$R_{ad} = -\frac{dc}{dt} = k_1 c(1-\theta) \quad (6)$$

Here, the rate of adsorption has been taken as equal to $-dc/dt$ with the simplification that the fall in polymer concentration is due to adsorption only. Now, again, for the constant rate region, on differentiating eq. (6) with respect to time, we get

$$O = k_1(1-\theta)\frac{dc}{dt} - k_1 c\frac{d\theta}{dt}$$

or

$$k_1(1-\theta)\left(\frac{dc}{dt}\right) = k_1 c\frac{d\theta}{dt}$$

(since c is falling off with time) or

$$-\frac{dc}{c} = \left(\frac{d\theta}{1-\theta}\right) \quad (7)$$

Upon integrating eq. (7), we finally get

$$\theta = 1 - c/c_0 \quad (8)$$

From eq. (8), it is now possible to determine the surface coverage (θ) at different time intervals when no desorption is taking place. The θ values so obtained must be higher than those calculated from eq. (4) for a given time interval, because in the latter case [(eq. (4)], desorption was also considered.

Now, again,

$$R_{ad} = -\frac{dc}{dt} = k_1 c(1-\theta)$$

or

$$-\frac{dc}{dt} = k_1\frac{c^2}{c_0}$$

[since $(1-\theta) = c/c_0$) or

$$-\frac{dc}{c^2} = \frac{k_1}{c_0}dt \quad (9)$$

On integrating eq. (9), we get

$$\frac{1}{c} = \frac{k_1}{c_0}t + \frac{1}{c_0} \quad (10)$$

It is clear from eq. (10) that a plot between $1/c$ vs. t should yield a straight line from the slope of which

k_1 may be calculated. From cases I and II, the values of k_1/k_2 and k_1 are known and, therefore, k_2 may also be calculated.
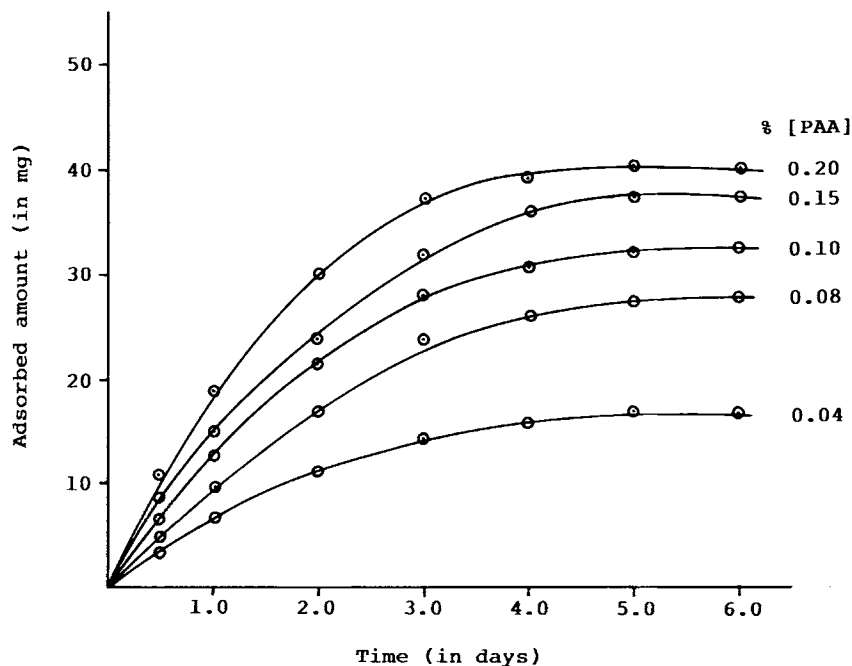
Treatment of Experimental Data

Now in the light of the experimental data obtained, validity of the above scheme would be proved.

Case I.

Adsorption Isotherm

Figure 1 shows the variation of adsorbed amount of PAA (in mg) with time (in days) for varying initial concentrations of the PAA solution in the range 0.04–0.20 g/dL. It is clear from Figure 1 that on increasing the initial concentration of the polymer solution the adsorbed amount m increases, and after a definite period, it attains an equilibrium value. It is also clear from the figure that the rate of adsorption is almost constant for an appreciable period when the adsorbed amount m/x (mg/g) is plotted against the equilibrium concentration (c_e). The isotherm so obtained is resembles well those reported by Ellerstein and Ullman,[18] showing an initial rise to a plateau that is a characteristic of Langmuir's adsorption isotherm (Fig. 2).

Calculation of Adsorption Coefficient (k_1/k_2)

To evaluate the value of adsorption coefficient K' ($=k_1/k_2$), which is an essential parameter for calculating surface coverage θ, a plot between $C_e/(m/x)$ is plotted against C_e values that according to Langmuir's adsorption equation should yield a straight line and from the intercept and slope of which the value of adsorption coefficient K may be calculated.

Figure 3 well describes the above fact, and the numerical value of the adsorption coefficient K has been calculated to be 16.66. Such a high value of the adsorption coefficient definitely supports the idea of negligible desorption in the present case.

Surface Coverage (θ)

The fraction of the surface occupied by the adsorbed polymer, termed surface coverage, at different time intervals may be calculated by eq. (4) after substituting the valve of K and C at different time intervals. For a given initial polymer concentration of 0.10 g/dL, the θ values at different time intervals are summarized in Table I. It is clear from the table that the surface coverage θ increases with time.

Film Thickness (T)

The thickness of the adsorbed film on a glass surface has been calculated by the method described in the

Figure 1   Variation of adsorbed amount of PAA with time for various initial PAA concentrations.
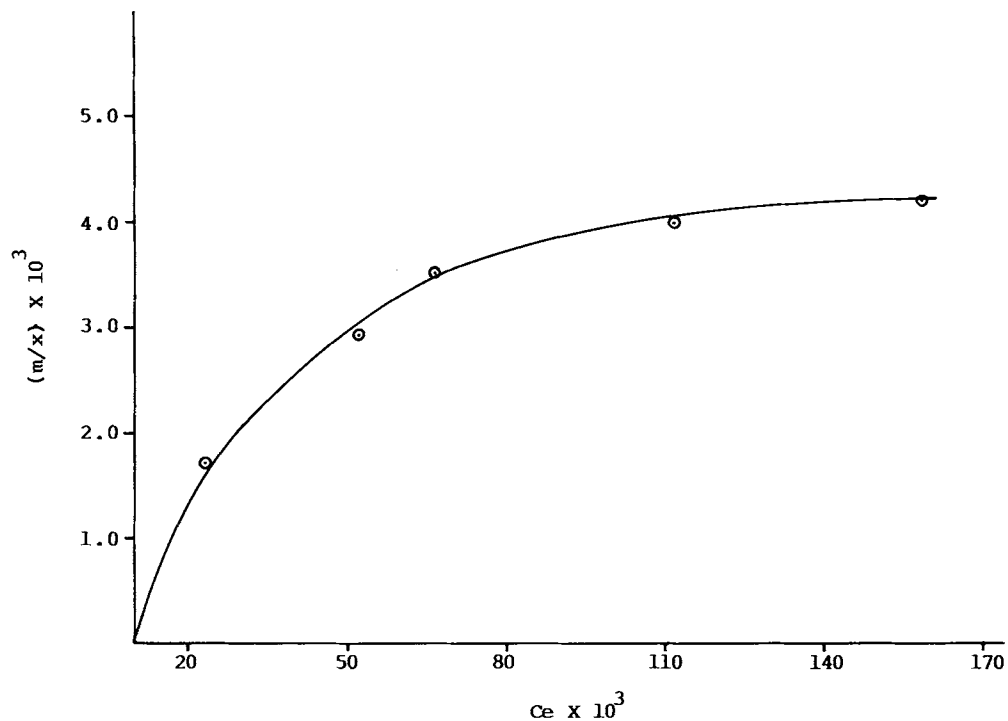
Figure 2   Adsorption isotherm drawn between m/x (adsorbed amount in mg/g) and equilibrium concentration C_e.

Experimental section. Table II gives the values of calculated film thickness at different time intervals for the given initial polymer concentration of 0.10 g/dL. It is quite evident from Table II that the film thickness T is almost constant at different time intervals. This constancy in film thickness also sup-

ports the idea of even adsorption of the polymer on a glass surface. Table II also describes the fact that the film thickness is also independent of the surface coverage θ. Our own observation finds support from the work done by others.[19] Although variation in film thickness with surface coverage has also been
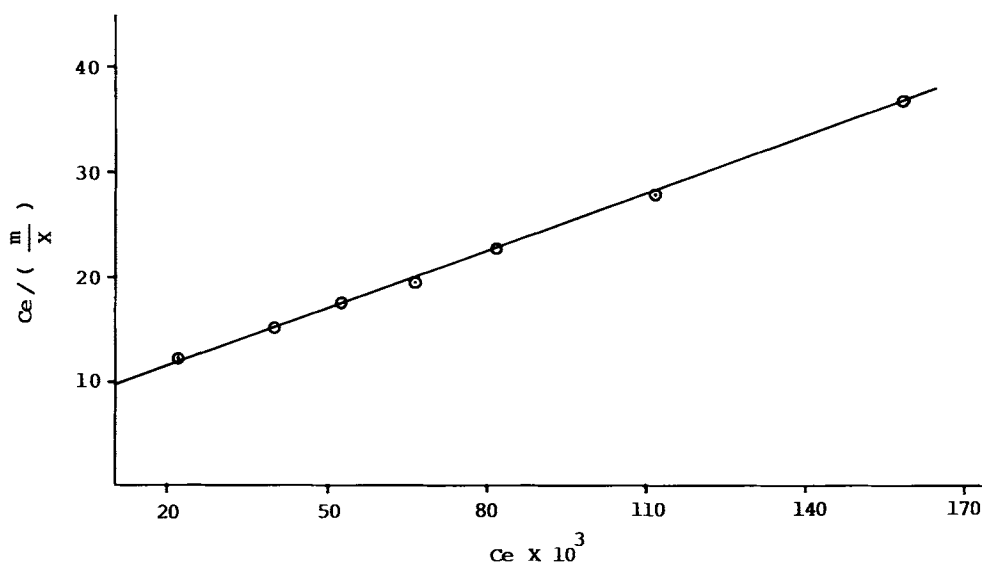
Figure 3   Plot drawn between $C_e/(m/x)$ and C_e for evaluation of adsorption coefficient K.

Table I   Values of Surface Coverage (θ) at Different Time Intervals for Adsorption of PAA (0.10 g/dL) on the Glass Surface at 30°C

Sample No.	Time (in Days)	$(c_0 - c) \times 10^3 = m$ (in g)	$\theta \times 10^2$
1	0.5	7.10	4.4
2	1.0	12.40	8.0
3	1.5	17.00	10.6
4	2.0	21.80	13.6
5	2.5	25.50	15.9
6	3.0	28.70	17.9

reported,[20] this observation, however, is absent in the present investigation.

Case II

Calculation of k_1 and k_2

For the evaluation of rate constants k_1 and k_2 for adsorption and desorption, respectively, eq. (10) would be helpful as it is clear from eq. (10) that a plot drawn between $1/c$ and time should be a straight line and from the slope of the line so obtained the valve of k_1 may be calculated. The plot so drawn is shown in Figure 4 and the value of k_1 has been calculated to be 1.54×10^{-5} s^{-1}. Also, from the knowledge of the values of K and k_1, one may easily calculate k_2, which, in the present case, has been found to be 9.0×10^{-7} s^{-1}.

Factors Affecting Adsorption

pH Effect

The pH of polyelectrolytes is an important parameter in studying their adsorption behavior at the

solid–liquid interface as it is directly related to the variation in charge density and, therefore, to the dimension of macromolecules within the solution. For studying the effect of pH of the medium on adsorption behavior, unfractionated PAA was used for the purpose and the pH of the medium was varied from 3.8 to 5.6. It is clear from Figure 5 that at low pH of the medium adsorption is more and it further decreases with increasing pH of the PAA solution. Also, the amount adsorbed is maximum at the pH value just around the pK_0 value of PAA where K_0 is the intrinsic dissociation constant of PAA. The value of pK_0 has been taken as 4.52 as given by Gregor et al.[21].

The decrease observed in adsorbed amount with increasing pH of the medium is due to the fact that at low pH of the medium the degree of ionization of PAA is quite low and, therefore, the polyelectrolyte molecule is in an almost protonated form. As pH of the medium is raised, the degree of ionization increases, which, consequently, results also in an increase in charge over the polyelectrolyte molecule. At high pH, when the macromolecule becomes highly charged, the inter- and intramolecular electrostatic repulsion oppose the accumulation of electrolyte

Table II   Values of Film Thickness (T) at Different Time Intervals for Adsorption of PAA (0.10 g/dL) on a Glass Surface at 30°C

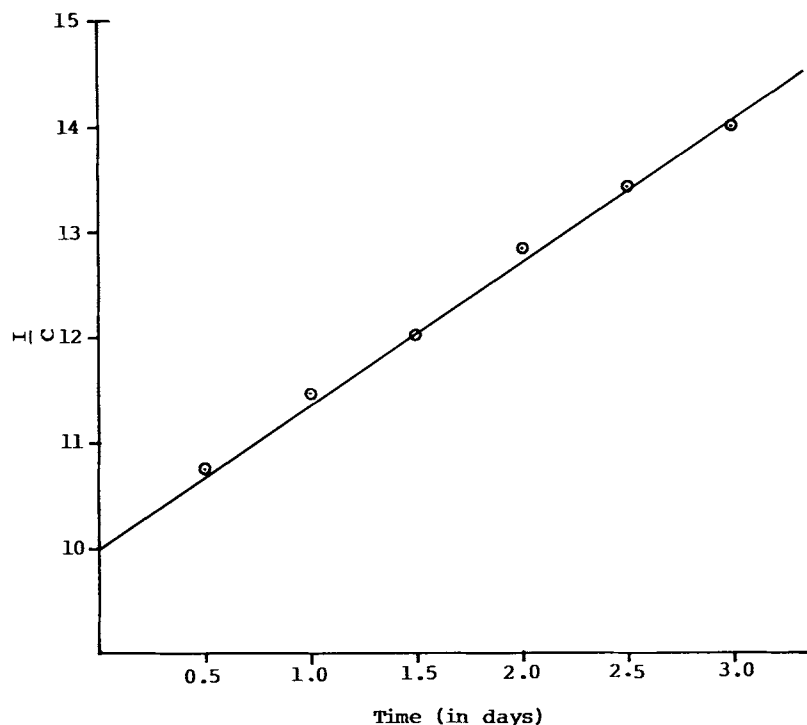| Sample No.	Time (in Days)	Adsorbed Amount m (g) $\times 10^3$	$\theta \times 10^2$	Thickness (T) (μm)
1	0.5	7.1	4.4	30
2	1.0	12.4	8.0	28
3	1.5	17.0	10.6	29
4	2.0	21.8	13.6	29
5	2.5	25.5	15.9	29
6	3.0	28.7	17.9	29

Figure 4   Plot drawn between $1/c$ and for evaluation of k_1 and k_2.

molecules at the interface and therefore the adsorbed amount decreases. Also, at higher pH, the increased charge points on the macromolecules cause greater repulsion among them, which results in an increased elongation of macromolecular dimension and, therefore, lower adsorption. The observed trends of isotherms are in good agreement with the theoretical predictions made by Bohmer et al.[22] In several investigations, an increase in the adsorbed amount has also been reported[23] with increasing pH; however, no such observation was found in the present work at any pH range.
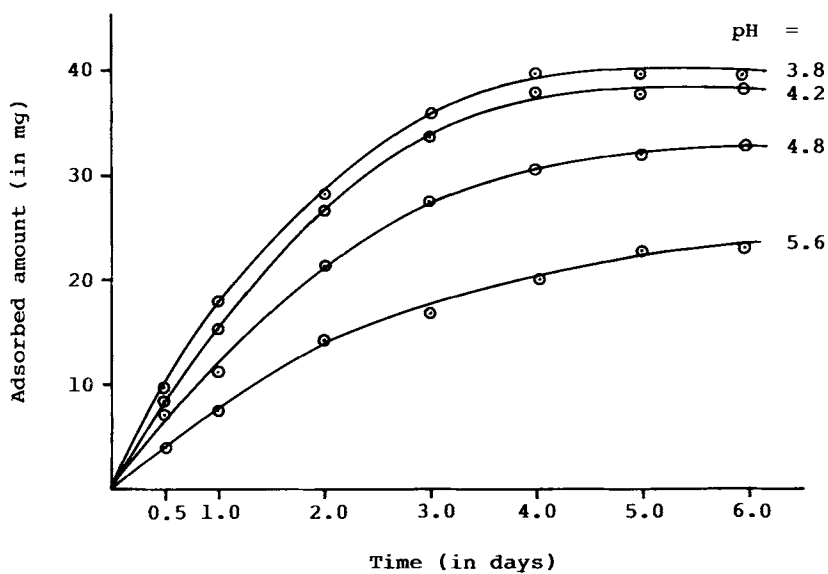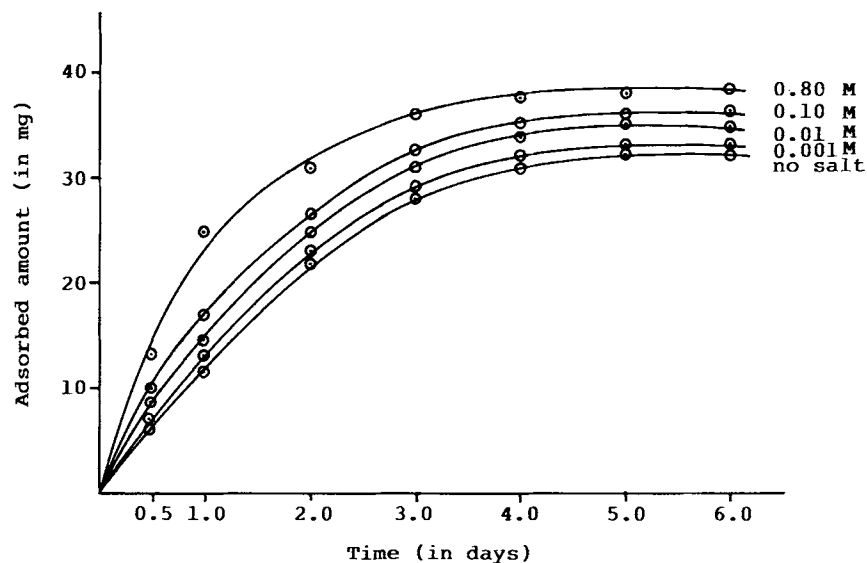

Figure 5   Plot showing the effect of pH on adsorption isotherms.

**Figure 6**   Plot showing the effect of salt concentration on adsorption isotherms.

Salt Effect

The effect of the addition of inorganic salts on the adsorption pattern has been studied by the addition of KNO_3 salt in the concentration range of 0.001 to 0.8 mol/L to the adsorption medium. The observed facts are well shown in Figure 6. It is clear from the figure that the adsorbed amount increases with increase in salt concentration in the studied range. The increase observed may be attributed to the fact that with increase in salt concentration the electrostatic repulsion acting along the macromolecule is screened, and as a result, the adsorbed amount increases. Another reason to observe the increase in

the adsorbed amount may also be the fact that increased ionic strength of the medium causes a decrease in solvent quality[24] and, therefore, the adsorption increases. The increased adsorption with increasing ionic strength of the medium has also been reported by many workers[25] and is in good agreement with the theoretical predictions.[22]

Molecular Weight Effect

The molecular weight of polymers is an important parameter as it largely affects many physical and mechanical properties of polymer. In the adsorption of polymers at the solid–liquid interface, molecular
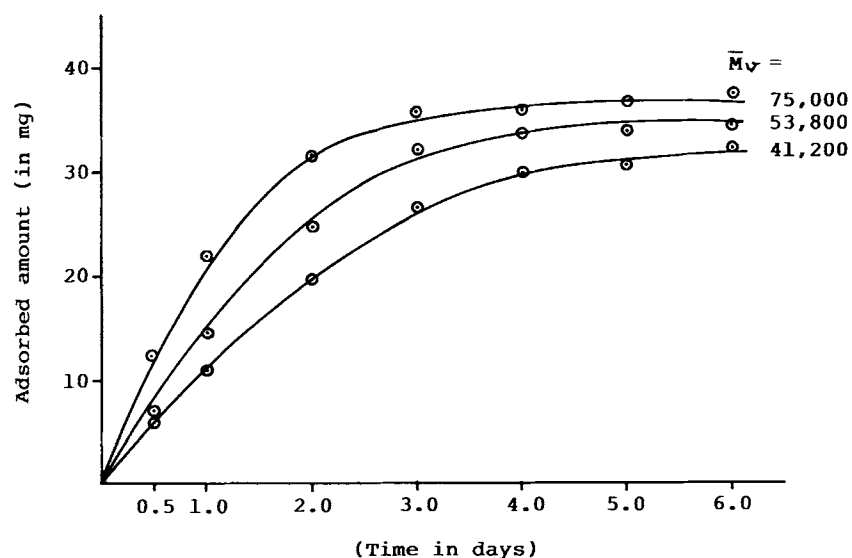
Figure 7   Effect of molecular weight of PAA on adsorption isotherms.

weight plays an important role as it provides some information about the conformation of the adsorbed polymer at the solid–liquid interface. If the polymer molecule is adsorbed at every polar group, i.e., the entire molecule lies on the surface in the form of "trains," then independence of adsorption on molecular weight should be expected. On the other hand, the adsorption of the polymer molecule at one end indicates the formation of "loops" at the interface and is directly affected by the molecular weight of the polymer.

In the present work, the effect of molecular weight of PAA on its adsorption has been studied using three samples of polymer of varying molecular weights. The effect of molecular weight on adsorption isotherms is shown in Figure 7. It is clear from the figure that increase in the molecular weight of the polymer results in an increased amount of adsorbed polymer. The observed fact is in good agreement with the theoretical predictions and has been widely reported by other workers.[26]

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