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DYNAMICS OF THE ADSORPTION OF GELATIN ONTO ALUMINA

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ABSTRACT

The kinetic behavior of the adsorption of gelatin at a water–alumina interface has been studied at room temperature (25°C). All the adsorption experiments were carried out at constant pH (3.2), and the kinetic course of adsorption was followed by estimating the residual concentration of gelatin in bulk of its aqueous solution by a colorimetric method. For the evaluation of various adsorption and kinetic parameters, a new kinetic scheme has been proposed, and parameters like adsorption coefficient, surface coverage (θ), and the rate constants for adsorption and desorption have been calculated. The adsorption process has also been found to be affected by the variation in pH of the adsorption medium and the presence of low molecular weight inorganic salts.

INTRODUCTION

The adsorption behavior of polymers onto inorganic particles is of great practical significance as it affects the characteristics of composite materials in various ways; for instance, the reinforcing effect in particulate-filled rubber and plastics and the dispersibility of particles in paints. In the case when the adsorbing polymer is a biological macromolecule like a protein, the situation becomes much more important as it leads to a number of unusual significant biological applications. These include food processing, where surfaces tend to become fouled by the deposited biofilm, biotechnology applications requiring mass culturing of cells on surfaces with an intervening protein "glue," new delivery methods for protein drugs (e.g., insulin, human growth, hormone, tissue plasminogens activators) in which the proteins are in contact with the polymeric materials, and implant situations of all kinds such as dental opthalmologic, orthopedic, and cardiovascular. Besides these applications, the adsorption phenomenon covers a wide spectrum of applications in engineering and technology [1-4]. In spite of the fact that a great deal of work has been done in the field of polymer adsorption, much fewer investigations have been carried out for studying the dynamic aspects of the adsorption process [5-7]. The kinetics of protein adsorption is a fascinating and complex process that is known to have great impact [8]. In general, the rate of adsorption of a polymer onto a solid surface is determined mainly by two processes: (i) diffusion of matter from the bulk toward the interface, and (ii) attachment of macromolecules to the surface sites. Since the diffusion coefficient in protein molecules is rather small, it appears that the attachment of molecules to the surface should decide the kinetic fate of the adsorption process. Although reconformation of protein molecules also plays a major role in evaluating the adsorption parameter, like the thickness of the adsorbed layer, it is expected to be very rapid and, therefore, of not much significance for the kinetics of adsorption. Also, in the case of rigid protein molecules the reconformation may not be occurring to an adequate extent to affect the adsorption dynamics.

Thus, because of the need for a better understanding of adsorption dynamics, the present communication studies the kinetic aspects of the adsorption of gelatin, a fibrous protein of wide application value in pharmaceuticals, food, and technology [9-11], onto the surface of alumina, a well-known separative inorganic adsorbent of great potential significance. It also evaluates the kinetic and adsorption parameters of the adsorption process by following a previously developed simple mathematical approach [12].

EXPERIMENTAL

Materials

Gelatin in the yellowish amorphous granular form was supplied by BDH (Pule, England) and used without further purification. The adsorbent chosen was alumina obtained from E. Merck (Darmstadt, Germany) and was used as received. Other chemicals used in the experiments were also of guaranteed reagent grade. All solutions were prepared in bidistilled water, and fresh solutions of gelatin were prepared for each run.

Method of Adsorption

The adsorption experiment was carried out in the same manner as described in our other communications [12-14]. To a known volume of aqueous solution of gelatin (50 mL), maintained at a constant pH of 3.2, a fixed amount of solid alumina powder (0.4 g) was added. The suspension was constantly agitated by a magnetic stirrer for 2 hours, a time found to be sufficient for equilibration of the mixture. After equilibrium had been attained, the alumina was removed by centrifuging the solution at 1500 rpm for a given time. The amount of gelatin adsorbed was determined by measuring the absorbance of gelatin biurate complex solution in a digital colorimeter (Systronics, India) by following a method described in the literature [15].

Kinetics of Adsorption

In order to follow the kinetic course of the adsorption process, an adsorption experiment was performed with a definite concentration of gelatin (0.4 g/dL). Several aliquots of the suspension were withdrawn and then centrifuged to give a clear supernatent solution of gelatin in which the amount of residual gelatin was determined colorimetrically as described above.

pH Measurements

The pH of the adsorption medium was measured by a digital pH meter (Systronics, India). Variation in the pH of the solution was accomplished by adding a definite volume of 0.2 M NaOH solution to an aqueous gelatin solution. Also, the pH of the solution was checked before and after each adsorption experiment.

Molecular Weight Determination

The molecular weight of gelatin was determined by viscosity measurements as reported in the literature [16]. For this purpose an Ostwald-type viscometer was used, and the resulting molecular weight (viscosity average) was calculated to be 35,000. In all adsorption experiments the observations were replicated, and the results were found to be within experimental error.

RESULTS AND DISCUSSION

Since the present investigation aimed mainly at studying the dynamic adsorption of gelatin onto alumina, it is worthwhile to give an account of the kinetic scheme that was adopted for evaluating the adsorption and kinetic parameters of the adsorption process. Although the scheme has appeared recently [12], it will be summarized here. The scheme is applicable for the time period before the rate of adsorption is almost constant.

Case I

In most adsorption studies, the time required for equilibrium is quite long (in some cases several days). Therefore, as an approximation, the rate of adsorption may be considered constant for an appreciable time period. According to Langmuir's adsorption isotherms equation, the rate of adsorption (R_{ad}) is given by

$$R_{ad} = k_1C(1 - \theta) - k_2\theta \tag{1}$$

where k_1, k_2, C, and θ have their usual significance as described in other communications [12, 13]. Upon differentiating Eq. (1) with respect to time and on subsequent intergration, we obtain

$$\theta = \frac{(C_0 - C)}{(C_0 + k)} \tag{2}$$

where C_0 = initial concentration of the polymer solution, C = the residual concentration of polymer in solution after a definite time interval, k is a constant (= k_2/k_1), and θ = surface coverage. Obviously the value of θ can easily be calculated at various time intervals if the adsorption coefficient (k_1/k_2) is known. This quantity is determined with the help of Langmuir's adsorption isotherms equation:

$$\frac{C_e}{m} = \frac{C_e}{k'} + \left(\frac{k_1}{k_2}\right)\frac{1}{k'} \tag{3}$$

where C_e = equilibrium concentration of the polymer solution, k' = a constant, and m = amount of polymer adsorbed (in mg/g).

Case II

Evaluation of Rate Constants k_1 and k_2

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

$$R_{ad} = -\frac{dc}{dt} = k_1 C(1 - \theta) \tag{4}$$

where the rate of adsorption has been taken as $-dc/dt$. Again, for the constant rate region, on differentiating Eq. (4) with respect to time and on further integration, we get

$$\theta = 1 - \frac{C}{C_0} \tag{5}$$

Equation (5) gives the values of θ at different time intervals when no desorption occurs.

Again,

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

or

$$-\frac{dc}{dt} = k_1 \frac{C^2}{C_0} \qquad [\text{since } (1 - \theta) = C/C_0]$$

or

$$-\frac{dc}{C^2} = \frac{k_1}{C_0} dt$$

On integrating the above equation, we get

$$\frac{1}{C} = \frac{k_1}{C_0} t + \frac{1}{C_0} \tag{6}$$

Clearly, a plot of $1/c$ versus t should yield a straight line, from the slope of which k_1 may be calculated. Once k_1 is known, the value of k_2 may also be calculated since k_1/k_2 has already been calculated. The experimental data shall be treated to prove the validity of the above scheme.

(*i*) *Adsorption Isotherms.* In adsorption studies the first information on the adsorption characteristics of a given adsorbate–adsorbent system is commonly offered by the shape of the adsorption isotherms because they not only describe a quantitative correlation between the amount adsorbed and the supernatent solution concentration, but they also provide an idea about the way the polymer adsorbs [17]. The most common method of obtaining an adsorption isotherm is to determine the amount of polymer adsorbed with various equilibrium concentrations of polymer solution. The adsorption isotherm thus obtained in the present investigation is shown in Fig. 1 where the amount of gelatin adsorbed (in mg/g) has been plotted against the equilibrium concentration of the protein solution (in mol/L). The observed isotherm resembles those reported by other workers [18] in that it shows an initial rise to a plateau value. It is also clear from the shape of the adsorption isotherm that it belongs to the L2 isotherm category [17], which is indicative of the common or Langmuir type of adsorption. L2 adsorption isotherms are often encountered when the adsorbate has a strong intermolecular attraction for the surface of the adsorbent. The observed L2 shape in the present case clearly implies that gelatin molecules must be strongly attached to the alumina surface. Since the adsorption was carried out at pH 3.2, which is well below the isoelectric

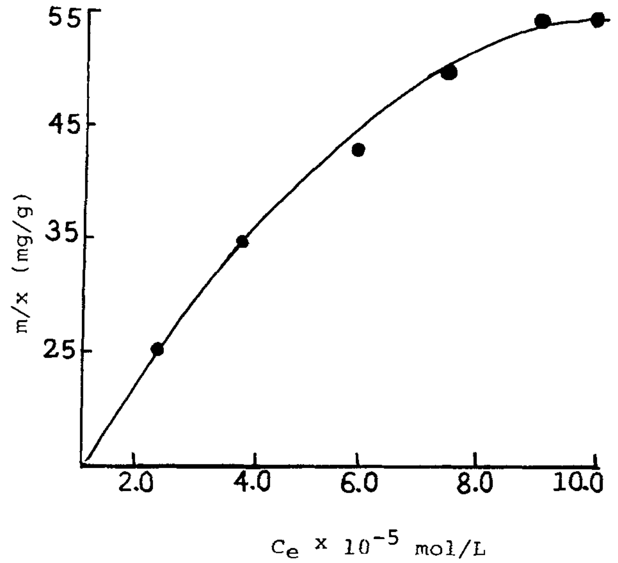

FIG. 1. Amount of gelatin adsorbed (in mg/g) versus the equilibrium concentration (C_e).

point of gelatin (4.85), it is quite obvious that the molecules of gelatin bear a net positive charge and, therefore, their interaction with the negatively charged alumina particles should lead to greater adsorption.

To evaluate the adsorption coefficient k ($= k_1/k_2$), a plot of C_e/m versus C_e is required as demanded by Eq. (3). From the intercept and slope of the straight line obtained, the value of k is calculated. In the present study the plot is shown in Fig. 2, and the value of the adsorption coefficient k is found to be 1.25×10^4 $L \cdot mol^{-1}$. Such a large value of k justifies the strong affinity of gelatin molecules for adsorption onto alumina.

Figure 3, where the amount of the adsorbed gelatin has been plotted against the time period of adsorption, describes the progress of the adsorption process. It is clear from the figure that the rate of adsorption is almost constant up to 60 minutes and attains a steady value near 90 minutes. Since the initial portion of the plot is quite linear for an appreciable time period, it is worthwhile to apply the proposed kinetic scheme to the present investigation.

(*ii*) *Surface Coverage* (θ). The fraction of the surface occupied by the adsorbing polymer is commonly termed "surface coverage" (θ). It is a significant adsorption parameter because it also quantitatively describes the adsorption process. The values of θ at different time intervals have been calculated from Eq. (2), and they are summarized in Table 1. The results show that θ increases with time, and this increase in θ also indicates how progressively the adsorption sites are being occupied by protein molecules. This type of behavior is also expected because as

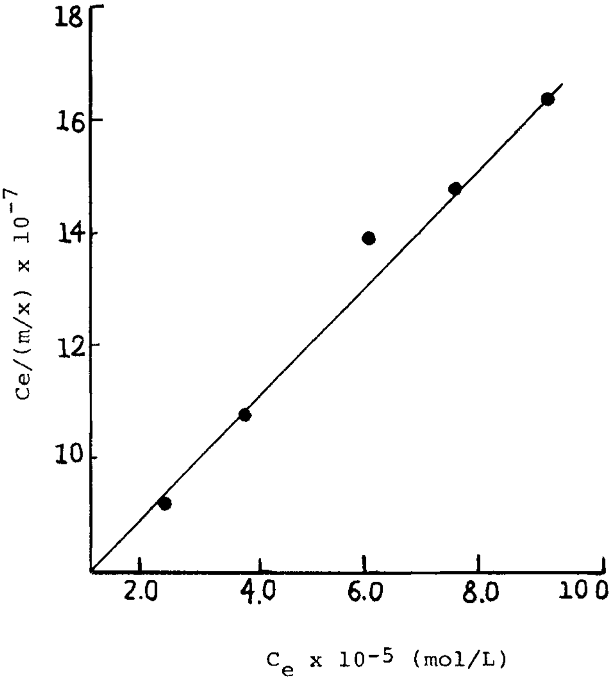

FIG. 2. Plot of $C_e/(m/x)$ versus equilibrium concentration C_e.

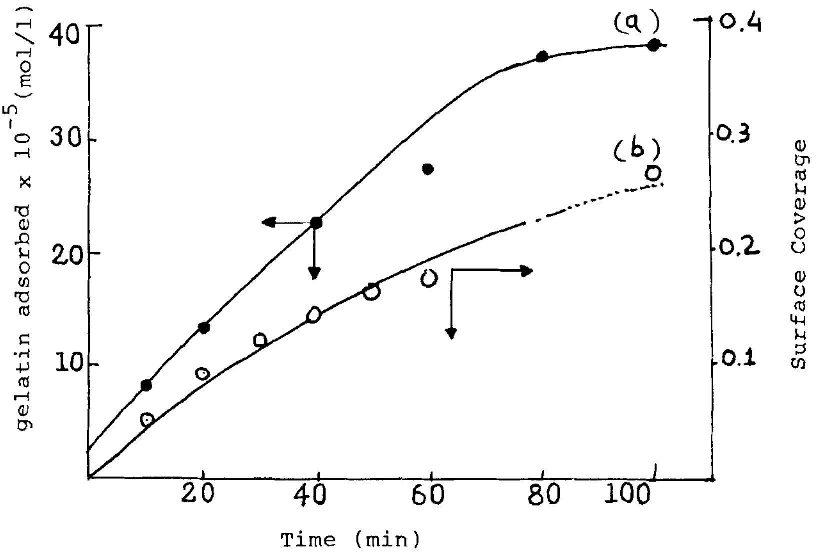

FIG. 3. Amount of gelatin adsorbed (in mg) versus time for fixed [gelatin] = 8.57 × 10^{-6} mol/L. [alumina] = 0.5 g, temperature = 25°C.

time passes, more and more surface sites are accommodated by the gelatin molecules. A similar type of result has been obtained by other workers [19].

One more interesting point is that at equilibrium, θ may be calculated by Langmuir's equation:

$$\theta_{eq} = \frac{KC_{eq}}{KC_{eq}+1} \tag{7}$$

In the present case, θ_{eq} is 0.37. By comparing the θ values calculated from Eq. (2) for the constant rate region with that obtained from Eq. (7), it is obvious that all θ

TABLE 1. Variation of Surface Coverage (θ) with Time for the Adsorption Experiment at [Gelatin] = 8.57 × 10^{-5} mol/L

Time, minutes	Surface coverage (θ)
10	0.05
20	0.09
30	0.12
40	0.14
50	0.16
60	0.17
100	0.37[a]

[a] Calculated from Eq. (7). The other values were calculated from Eq. (2).

values are in good increasing order. This evidence also supports the kinetic scheme proposed by the author.

(*iii*) *Evaluation of Rate Constants.* At present, the reversible nature of proteins adsorption is well confirmed. It would be easier to compare the relative dominating natures of the adsorption and desorption processes quantitatively if the numerical values of the rate constants were known. Fortunately, this can be readily achieved by means of Eq. (6), which implies that a plot of $1/c$ versus t should yield a straight line, and the value of k_1 may be calculated from the slope of this line. A plot so drawn is shown in Fig. 4, and the value of k_1 has been calculated to be $1.71 \times 10^{-4}\ \mathrm{s}^{-1}$. Once the value of k_1 is known it is easy to calculate k_2 from K ($= k_1/k_2$), and the value in the present case is 1.37×10^{-8} mol/L·s^{-1}. It is clear from the larger value of k_1 compared to k_2 that the process of adsorption is highly favored above that of desorption, and equilibrium must be reached at the extreme right of the process. The superiority of this method for evaluating k_1 and k_2 lies in the fact that no complicated mathematical computations (such as in the Runge-Kutta method or Marquardt's optimization routine [20]) are required, and only a simple linear plot will serve the purpose as well.

Factors Affecting Adsorption

(*i*) *pH Effect.* A variation in pH of a protein solution also causes a significant change in its adsorption patterns. This is due to the simple fact that a change in pH of a polyelectrolyte solution not only affects the charge density of the macromolecular coil but also results in a change in the dimensions of a macromolecule in

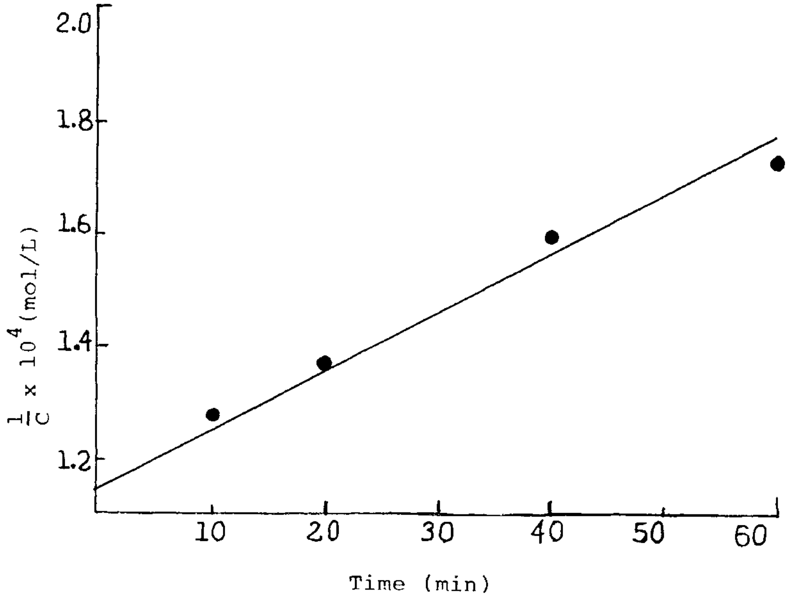

FIG. 4. Plot of $1/C$ versus time t for the evaluation of k_1.

solution. Both of these factors lead to a considerable change in the amount of polymer adsorbed.

The effect of pH variation on the plateau adsorption of gelatin is shown in Fig. 5. It is clear from the figure that upon varying the pH of the gelatin solution in the 3.2 to 8.8 range, the plateau adsorption initially rises to a certain pH value, called the isoelectric point of gelatin, and then decreases. The observed dependence of the adsorption of gelatin may be explained as follows.

Since the adsorption experiment was carried out at pH 3.2, the gelatin molecules in the solution possess a net positive charge because pH 3.2 lies on the acidic side of the isoelectric point (4.85). When a solution of 0.2 M NaOH is added to the solution in order to raise the pH, the added alkali causes ionization of the —COOH groups lying on the gelatin molecules and thus reduces the net positive charge by generating negative charged centers (COO^-) on the macromolecule. At this stage both positive and negative charged centers exist on the macromolecule, and this leads to a contraction in the dimensions of the macromolecule due to electrostatic intramolecular attraction. Obviously the decreased dimensions of gelatin molecules result in an increase in the adsorbed mass since the number of gelatin molecules reached per unit active site on the adsorbent surface will increase. This increase in adsorption continues until the isoelectric point of gelatin, 4.85, is reached, at which point the gelatin molecules become electrically neutral because the positive and negative charges are equal. At this pH the dimensions of gelatin molecules become minimum, and therefore the adsorption rises to the maximum. With a further increase of the solution pH, the gelatin molecules acquire a net negative charge, and this results in an expansion of the macromolecular dimensions, leading to a decrease in the amount adsorbed. The elongation of gelatin molecules due to the addition of

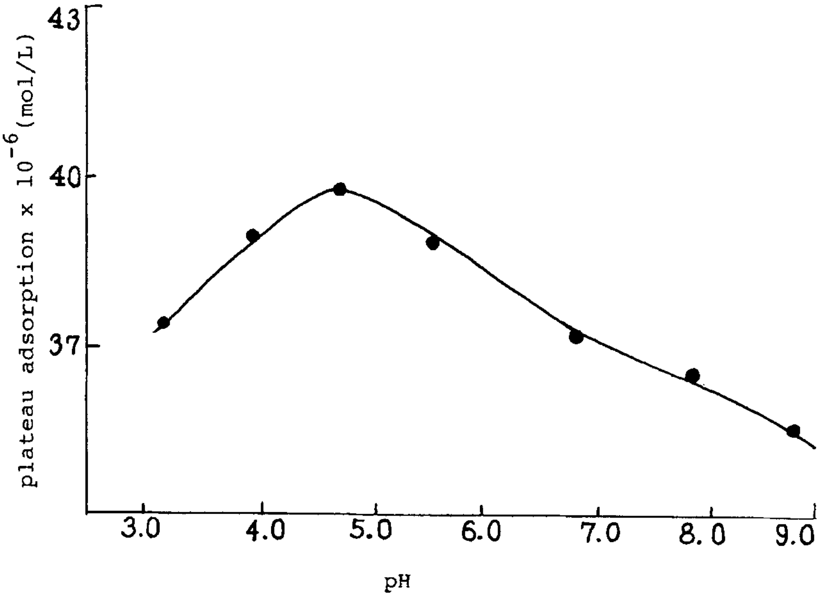

FIG. 5. Effect of variation of pH of gelatin solution on the plateau adsorption.

OH^- ions is also evidenced by an increase in the reduced viscosity of the solution, as shown in Table 2. A similar type of result has been obtained by other workers [21-23].

(*ii*) *Salt Effect.* The behavior of low molecular weight electrolytes is of prime importance in polyelectrolyte adsorption studies because their presence in the solution significantly affects the adsorption characteristics of a polymer. This is due to the simple fact that the addition of low molecular weight ionic compounds causes a change in the dimensions of a polymer molecule in solution, which ultimately affects the amount adsorbed and other related parameters. In the present study the effect of the addition of salts on the plateau adsorption has been investigated by adding sodium salts of chloride and sulfate ions to the adsorption medium at pH 3.2. The results, summarized in Fig. 6, clearly indicate an increase in the amount adsorbed when the two salts are to the adsorption medium in the 0.02 to 0.10 mol/L concentration range. This figure also reveals that in the studied range of salts concentrations the addition of sulfate ions results in a greater increase in plateau adsorption than does that of monovalent chloride ions. This increase may be explained as follows.

1. The increase in plateau adsorption upon the addition of salts may be viewed as due to a decrease in the dimensions of any polymer molecule in solution. This results from the poor solvent quantity of the medium as stated by Eisenberg and King [24]. It is quite obvious that a smaller radii of gyration will allow a greater number of gelatin molecules to occupy the surface sites and, therefore, the adsorption will increase.
2. Added mobile ions may also screen the electrostatic charges on the macromolecule, thus changing the conformation of the polymer molecule. This screening of charges results in a contraction of the macromolecular dimensions in the solution, which subsequently favors increased adsorption. It is also clear that sulfate ions, due to their greater charge, will cause much more screening of the electrostatic charges and, therefore, a comparatively larger increase in plateau adsorption is observed.

TABLE 2. Increase in the Reduced Viscosity (η_{red}) of a Gelatin Solution (8.5×10^{-5} mol/L) with an Increase in the pH of the Medium

pH of the gelatin solution (8.57×10^{-5} mol/L)	η_{red} (reduced viscosity of the solution) $\times 10^2$
4.0	66.5
4.5	62.5
5.0	91.5
6.0	108.2
7.6	120.0
8.4	133.7

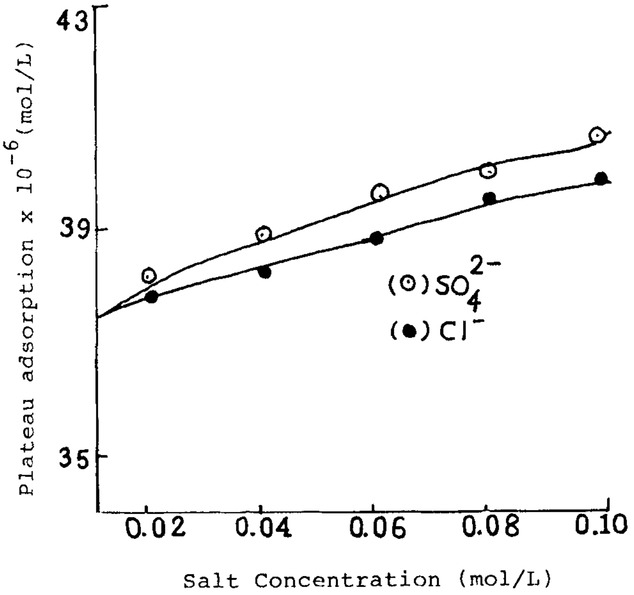

FIG. 6. Effect of addition of salts on the plateau adsorption of gelatin at an equilibrium concentration of 7.42×10^{-5} mol/L.

The results obtained are in good agreement with theoretical predictions [25] and have been reported by other workers [26, 27].

CONCLUSIONS

On the acidic side of the isoelectric point of gelatin, the stronger interaction between the oppositely charged gelatin molecules and the alumina particles results in greater adsorption of the former onto the surfaces of the latter. The rate of the adsorption process is almost linear up to 60 minutes and attains an equilibrium value within 100 minutes. The extent of adsorption is quite sensitive to any variation in the pH of the solution, and it shows a maximum near the isoelectric point of gelatin. Adsorption also increases with the addition of inorganic salts, and it varies directly with the valency of the added anions.

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