Adsorption of some quaternary onium salts on silica gel

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Abstract

The adsorption of quaternary onium salts such as hexadecyltrimethylammonium chloride, hexadecyltrimethylammonium bromide, benzyltrimethylammonium chloride and tetrabutylammonium bromide from aqueous solution, and of tricaprylylmethylammonium chloride (Aliquat® 336) and hexadecyltributyl phosphonium bromide from organic solution has been studied using silica as an adsorbent. The adsorption from the aqueous phase was found to be dependent on the pH of the medium, giving a type IV isotherm in acidic and alkaline solution. The adsorption from the aqueous phase in the medium pH region and from the organic phase appears to give a Langmuir-type isotherm. The equilibrium adsorption capacity and the adsorption rates in the aqueous phase were found to be higher than those observed for adsorption from the organic phase. The concentration–time profiles generated in an agitated slurry system indicate that in the case of aqueous phase adsorption in the middle pH range, external film diffusion controls the solute uptake initially and particle diffusion controls the solute uptake in the later stages, whereas for the organic phase adsorption, both film and surface diffusion seem to control the uptake.

Keywords: Adsorption; Silica gel; Quaternary onium salt

List of symbols

c	solute concentration
ΔC	change in solute concentration (mol cm^{-3})
C_0	initial solute concentration (mol cm^{-3})
C_e	equilibrium liquid phase concentration (mol cm^{-3})
$C_{s,t}$	surface liquid phase solute concentration at time t (mol cm^{-3})
C_t	solute concentration at any time t (mol cm^{-3})
d_p	particle size (cm)
D	particle phase diffusion coefficient $(\text{cm}^2\,\text{s}^{-1})$
k_f	external mass transfer coefficient (cm s^{-1})
K	Langmuir isotherm constant $(1\,\text{mmol}^{-1})$

q	solid phase solute concentration (mmol g^{-1})
q_m	Langmuir constant (mmol g^{-1})
q_s	equilibrium solid phase concentration (mol g^{-1})
q_t	concentration at time t (mol g^{-1})
r	radial distance (cm)
R	particle radius (cm)
S_s	surface area defined by Eq. (14)
t	time (s)
V	volume of solution (cm^3)
W	weight of solid adsorbent (g)
x	dimensionless radial distance (r/R)

Greek letters

ϵ_p	porosity of adsorbent particle
ρ_p	particle density (g cm^{-3})
τ	dimensionless time $(\tau = Dt/R^2)$

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1. Introduction

Various quaternary ammonium and phosphonium salts are known as phase transfer catalysts (PTC) for promoting reactions between non-electrolyte substrates dissolved in an organic phase and ionic reagents dissolved in an aqueous phase [1,2]. The use of PTC to promote reactions of industrial importance offers advantages such as mild reaction conditions, high reaction rate, high selectivity and byproduct suppression, etc. It is possible to exploit such reactions advantageously to extract toxic compounds such as phenolics from waste water [3,4]. However, the recovery of the PTC from either the aqueous phase or the organic phase is essential from economic considerations as well as from the environmental control point of view. In many cases, adsorption is considered to be an efficient separation method for the removal of solutes from solution. Silica gel is a good adsorbent for removing various organic compounds from an aqueous or an organic phase [5–11]. Excluding a single report on the removal of quaternary onium salts by filtration in a silica gel column [12], comprehensive investigations of the adsorption of such compounds have not been reported in the literature.

The present paper reports a study on the adsorption of some quarternary onium salts such as hexadecyltrimethylammonium chloride (HTMAC) and hexadecyltrimethylammonium bromide (HTMAB), tetrabutylammonium bromide (TEBAB) and benzyltrimethylammonium chloride (BTMAC) from the aqueous phase and tricaprylylmethylammonium chloride (Aliquat® 336) and hexadecyltributylphosphonium bromide (HTBPB) from the organic phase (toluene).

2. Experimental

2.1. Materials and methods

The quaternary ammonium and phosphonium salts were procured from Aldrich Chemical Company, Milwaake, WI, USA and had a purity greater than 99.5%. Toluene, used as the organic solvent, was obtained from BDH, India and was distilled before use. Other analytical reagents were obtained from E. Merck, Germany. The silica gel was supplied by BDH, India. It had a specific surface area of $380 \, m^2 \, g^{-1}$ (by BET N_2 adsorption), a 100–200 mesh size, a pore size of 75 Å, a porosity of 0.62, a density of $2.4 \, g \, cm^{-3}$ and a pore volume of $0.4–0.5 \, cm^3 \, g^{-1}$.

Batch adsorption experiments were conducted in a cylindrical glass vessel 8.5 cm in diameter and 11 cm in length. The liquid height was 5 cm and the liquid volume was $150 \, cm^3$ with a 3.0–3.5 g silica gel sample. The initial concentration of the onium salt taken was between 15 and 25 mmol l^{-1} at $30 \pm 0.5\,°C$. Mixing was provided by a stainless-steel six-bladed impeller while maintaining the stirring speed at around 550–600 rev min^{-1}. For the determination of adsorption equilibrium, both the amount of silica gel as well as the initial solute concentrations were varied. The mixing time in all experiments was maintained at 8–9 h, sufficient for equilibrium to be reached. The pH of the aqueous phase was regulated by using HCl and NaOH. After equilibrium was reached, the liquid fraction was filtered out, its volume noted and analysed for the onium salts via a procedure reported elsewhere [12]. The amount of quaternary salt (Q^+Y^-) in the organic solvent was determined by indirectly estimating the anion with 0.01 M $AgNO_3$ solution after thoroughly shaking the sample (volume, 5 ml) with 2 ml of a saturated aqueous solution of NaBr in order to completely convert the Q^+Y^- (PTC) to Q^+Br^-. The quaternary onium salt in the aqueous solvent was determined by directly estimating the anion Y^- in a 5 ml sample by titration with 0.01 M $AgNO_3$ (potentiometric titration in 50 ml of MeOH). An acidified ferric alum (5 M) solution was used as the indicator in both cases. The amount of quaternary onium salt in the liquid phase was cross-checked by evaporating the sample (20 ml) to dryness and taking the dry weight.

Since the concentration of adsorbate in the solid phase was necessarily higher than that in the bulk solution, the amount adsorbed, q (mol g^{-1}), was calculated according to

$$q = \frac{V\Delta C}{W} \tag{1}$$

where ΔC is the change in solute concentration (mol l^{-1}), V is the solution volume (l), and W is the weight of adsorbent (g).

3. Results and discussion

3.1. Adsorption from the aqueous phase

Silica gel is basically a macromolecular silicic acid having an irregular three-dimensional network of SiO$_4$ tetrahedra. There are surface hydroxyl groups (silanol groups) on the surface of the elementary macroparticles, coherent aggregates of which form the silica gel. A typical value of the surface hydroxyl group content is around 2.54 mmol g^{-1} [13]. The silanol group renders the silica gel surface weakly acidic, and the silacon bridges (Si–O–Si) on the surface are expected to be the possible adsorption sites for hydrogen bridge donors. The silica gel surface is positively charged and the state of the charge will be influenced by the pH value. Thus the pH and the presence of additional ions will affect the mechanism of adsorption of cationic quaternary onium salts in the aqueous phase. Typical values of the cross-sectional area of the onium salt molecules fall in the range 0.45–0.6 nm^2. The silica gel, having an average pore size of 75 Å has a pore cross-sectional area marginally higher than the area of the molecules. Thus it may be expected that adsorption takes place on the external surface as well as inside the pores.

Experimental isotherms for the adsorption of four different onium salts are shown in Fig. 1, which refers to the aqueous phase without the addition of HCl or NaOH for pH regulation. The effect of pH on the isotherm for two onium salts of different chain lengths is shown in Figs. 2 and 3. It may be noted that the values of the pH of the aqueous phases consisting of the onium salts alone fall in the range 5.5–0.62. From Figs. 2 and 3, it is apparent that the adsorption density and the shape of the isotherm depend on the pH of the aqueous phase. In the aqueous phase, the positive charge of the quaternary onium salts is unaffected by a pH change, i.e. the positive charge is retained either under acidic or alkaline conditions. Therefore, the

pH dependence of the adsorption should be attributed solely to the changes in the surface charge of the silica gel. The isotherm, particularly at high pH appears to be a type IV isotherm, exhibiting an S-shaped behaviour characteristic for the adsorption of an ionic surfactant on an oppositely charged surface [14,15]. There are three distinct adsorption zones. In the low concentration zone the cationic onium salts adsorb mainly due to ion exchange, particularly at high pH. This is followed by a zone where there is a marked increase in adsorption, probably resulting from the interaction of hydrophobic chains of the incoming surfactant ions with those of the adsorbed surfactant and with themselves. This interaction or aggregation of the hydrophobic group occurs at a concentration below the critical micellar concentration (CMC), the values of which for the onium salts studied lie between 3.5 and 4.5 mmol l^{-1} [16]. There is a zone of reduced adsorption assigned to hemimicelle formation or cooperative adsorption where the charge of the silica gel surface is eventually reversed, due to adsorption on the positively charged surface. The adsorption is complete when the surface is covered with a monolayer of the surfactant. This appears to occur near the CMC, since the adsorption involves a single ion rather than a micelle. Similar adsorption behaviour has been reported for sulfonate/alumina or mineral sand systems [15,17]. However, HTMAB is reported to adsorb onto a quartz surface by polar attraction forces, the forming monomolecular layer hydrophobic group being directed outwards [18]. HTMAC, on the other hand, was found to be adsorbed on a zeolite-A surface through a parallel process of ion-pair formation and ion exchange [19]. As shown in Fig. 2, the increase in adsorption intensity at high pH is specific for the silica gel surface. Since quaternary onium salts are positively charged, a reduction of the pH will reduce the adsorption. With an almost identical shape of isotherm, the adsorption density exhibits a systematic increase with increase of pH.

Fig. 1 indicates that an increase in chain length of the hydrophobic group of the onium salts increases the adsorption density. This may be attributed to the fact that the free energy decrease associated with the removal of the hydrophobic
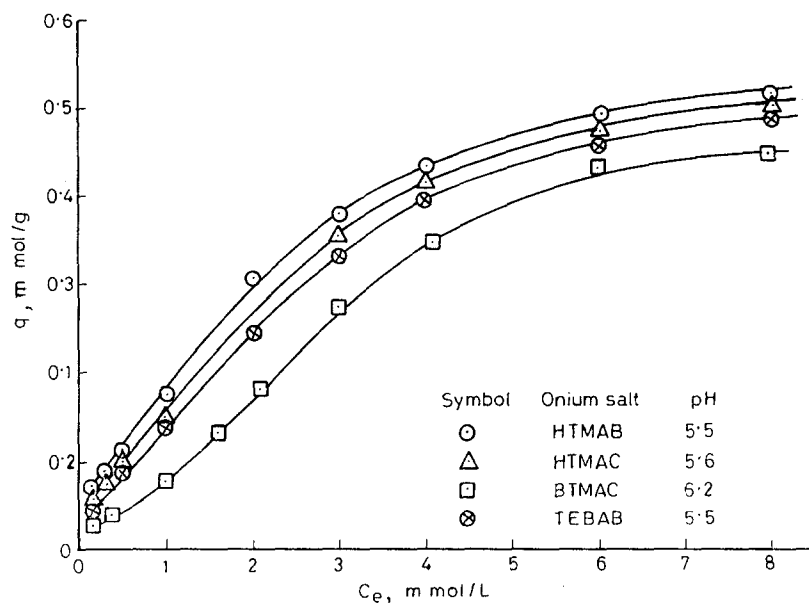
Fig. 1. Adsorption isotherms for various onium salts in the aqueous phase at 30°C.
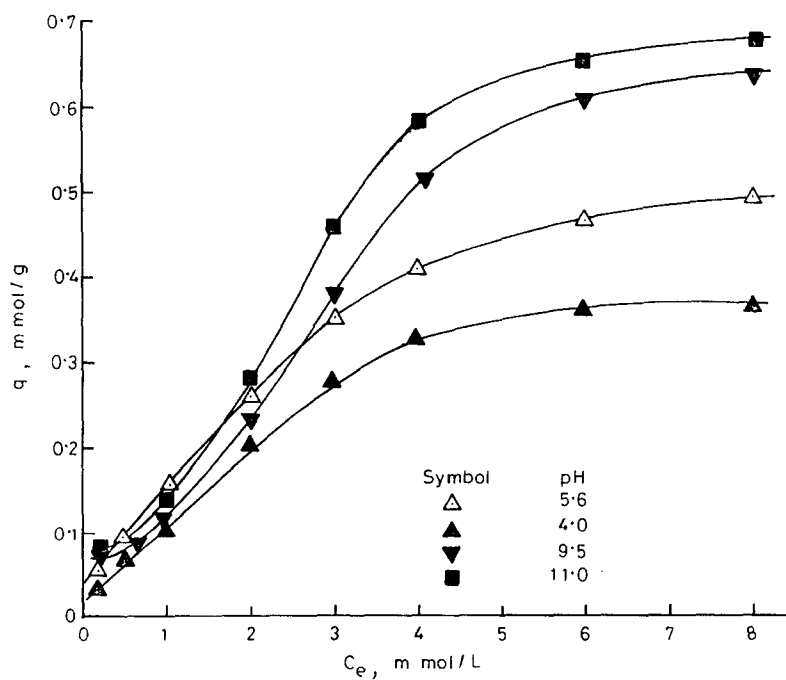

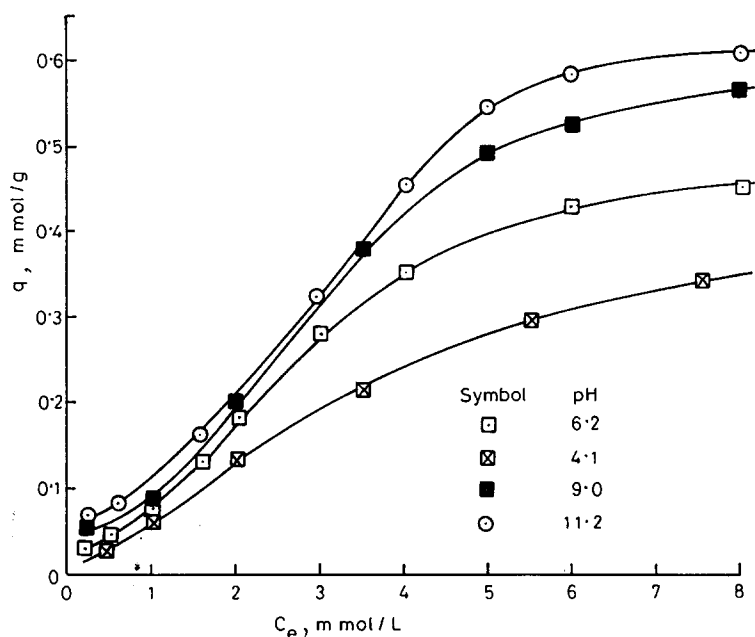Fig. 2. pH effect on isotherm for HTMAC in the aqueous phase at 30°C.

Fig. 3. pH effect on isotherm for BTMAC in the aqueous phase at 30°C.

chains from contact with the water and with the tendency to aggregate or adsorb via dispersion forces increases with the increase in the length of the chain. The increased adsorption at high pH does not appear, however, to be dependent on the chain length of the quaternary salt, as is evident from Fig. 2 which shows data for two onium salts of appreciably different chain lengths. The difference in adsorption density may also be explained by the different amounts of space required by the onium salts, which can be grouped according to their adsorption intensity in the order HTMAB > HTMAC > TEBAB > BTMAC. However, BTMAC exhibits an appreciably lower value of adsorption compared to the other three compounds, whose adsorption intensities differ from each other only marginally. In general, chain length and branching affect only the lateral interaction in the hemimicellar region of the isotherm [19]. This may be the reason for the observation of markedly different slopes of the isotherm in this region obtained for BTMAC. It may be expected that hemimicelle formation increases with increase of pH, resulting in an increase of slope of the isotherm.

3.2. Adsorption from the organic phase

The isotherm for the adsorption of both onium salts from the organic phase, shown in Fig. 4, indicates in general that the adsorption intensity is lower than that obtained for the adsorption of any of the onium salts from the aqueous phase, and the isotherm follows Langmuir-type behaviour. Regression analysis of the data was performed to evaluate the Langmuir constants K (1 mmol^{-1}) and q_m (mmol g^{-1}). The values of K and q_m were found to be 2.665 l mmol^{-1} and 1.82 l mmol^{-1} and 0.506 mmol g^{-1} and 0.66 mmol g^{-1} for Aliquat® 336 and HTBPB, respectively. A Langmuir isotherm analysis carried out according to the procedure suggested by Vermeulan et al. [20] indicates that the adsorption system is favourable. The observation of isotherm linearity given by Henry's law in the low concentration region is identical to that for the adsorption of various polar organic compounds onto silica gel [5,7,8]. The maximum adsorption intensities corresponding to monolayer coverage were 0.506 mmol g^{-1} and 0.66 mmol g^{-1} for Aliquat® 336 and HTBPB, respectively. A

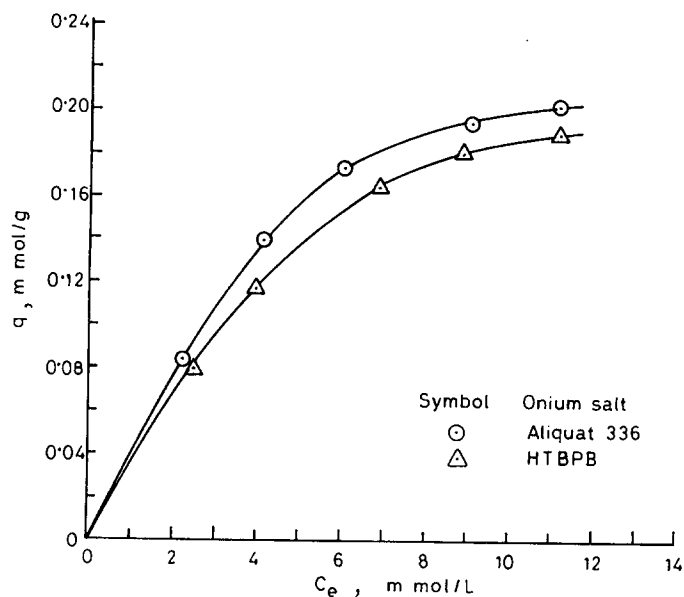Fig. 4. Adsorption isotherm for onium salts in organic phases at 30°C.

3.3. Batch uptake

monolayer of the salts contains approximately 3×10^{20} molecules. If the active sites that cause the adsorption are considered to be hydrated hydroxyl groups on the silica gel surface, this number seems to be lower than the total number of hydroxyl groups on the surface, i.e. 8.2×10^{20} obtained from thermogravimetric data [21]. We expect that competitive solvent adsorption may be the reason for such a discrepancy in the monolayer coverage of the onium salts. It is reported that a monolayer of benzene (adsorbed from heptane as solvent) contains approximately 5.4×10^{20} molecules and, assuming that this figure is applicable to toluene also, a monolayer coverage of both the adsorbed solvent and the onium salts can thus account for the total number of active sites on the silica gel surface.

Generally, the purpose of adsorption kinetics experiments is to determine the pore diffusion coefficient, which is required when designing industrial equipment. When determining pore diffusion coefficients from concentration–time data, it is necessary to consider the effects of external diffusion resistances as well as a possible deviation from ideal mixing. However, external diffusion coefficients determined from experiments in laboratory stirred-tank devices are of little practical significance as the performance of the column adsorber generally used in practice cannot be predicted from such data. However we feel that adsorption rate data generated in a well-mixed system, where external film mass transfer can be assumed to be negligible, can provide some insight into the adsorption mechanism.

Adsorption rate curves generated at a single initial solute concentration (C_0) of BTMAC and Aliquat® 336 and a constant mass of silica gel are shown in Fig. 5. It may be inferred that the time required to reach saturation is nearly 4–5 h and a relatively large saturation time is required for the adsorption of the salt from the organic phase.

The kinetics of solute transport from the solution (solvent–solute) phase to the surface of the adsorbent are controlled either by the film or by external diffusion, internal diffusion in the liquid-filled pores, pore surface diffusion (homogeneous particle diffusion) and adsorption on the particle surface, or the combined effect of more than one of these. In general, adsorption is a rapid process, not
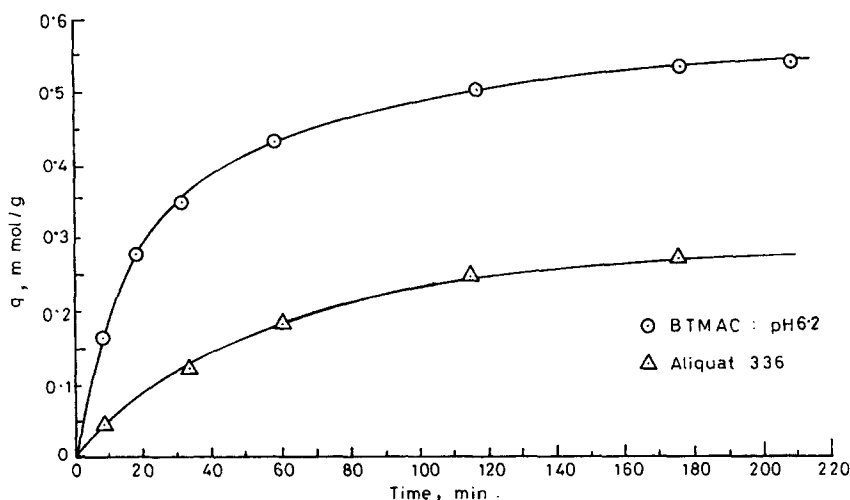
Fig. 5. Adsorption rate curves for BTMAC in the aqueous phase and Aliquat 336 in the organic phase. $\bigcirc$, BTMAC ($C_0 =$ 25 mmol l^{-1}; $W = 3.5$ g); $\triangle$, Aliquat® 336 ($C_0 = 20$ mmol l^{-1}; $W = 3.0$ g).

a rate-controlling step. The internal diffusion comprises pore and surface diffusion. Whether surface diffusion or pore diffusion (intraparticle) is the controlling mechanism depends to a large extent on the method by which the adsorbed particles are contacted with the solution. In a well-mixed system, the boundary layer or external resistance will be small and intraparticle diffusion will be the controlling mechanism. Since the silica gel particles used in our experiment were of reasonably small size, it is justifiable to assume negligible intraparticle diffusion resistance. The quaternary onium salts are of relatively large molecular size, and restricted mobility in solution may be expected.

Owing to the relatively large size of the molecules, associated with their complex solution behaviour, it is difficult to assign a tortuosity factor for the estimation of the pore diffusivity or to isolate the respective pore and surface diffusion components. In view of such considerations, a two-resistances model based on external mass transfer and particle surface diffusion, as reported by Mathew and Weber [22] and McKay and McConvey [23], has been used to generate a theoretical concentration–time decay curve. Although such a model usually holds good for homogeneous permeable, non-porous particles, the applicability of the model to adsorption on porous small particles was demonstrated by the above

workers. The equations describing the model are given below.

The rate of change of concentration of the solid phase is equated to the rate of mass transfer of the solute from the fluid phase through the film to obtain the equation

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = \frac{k_f}{V_p \rho_p (1 - \epsilon_p)} (C_t - C_{s,t}) \tag{2}$$

The average solid-phase concentration of the particles is obtained by averaging the point concentration over the volume of the particle

$$q_t = \frac{3}{R^3} \int_0^R q r^2 \, \mathrm{d}r \tag{3}$$

The Langmuir isotherm will be used to represent the equilibrium adsorption at the surface of the particle

$$q_s = \frac{(K q_m) C_s}{1 + K C_s} \tag{4}$$

The Langmuir isotherms for BTMAC and Aliquat® 336 will only be considered for the analysis. For a spherical particle, the variation of the solid-phase concentration in the radial direction is

given by

$$\frac{\partial q}{\partial t} = D\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right) \tag{5}$$

The material balance for the solute is given by

$$V\frac{\partial c}{\partial t} = -W\frac{\partial q}{\partial t} \tag{6}$$

Initial conditions

$$q(r, 0) = 0 \qquad C(0) = C_0 \tag{7}$$

Boundary conditions

$$q(R, t) = q_s(t) \qquad \frac{\partial q}{\partial t}(0, t) = 0 \tag{8}$$

Eq. (5) can be changed to dimensionless variables by use of the transformations $\tau = Dt/R^2$ and $x = r/R$. Change of variable with $U = xq$ and rearrangement give

$$\frac{\partial U}{\partial \tau} = \frac{\partial^2 U}{\partial x^2} \tag{9}$$

$$U(0, \tau) = 0 = U(x, 0) \quad \text{and} \quad U(k, \tau) = U_s(\tau) \tag{10}$$

$$\int_0^1 \frac{\partial U}{\partial \tau} x \, \mathrm{d}x = \frac{k_f R(C - C_s)}{1000\rho_p D(1 - \epsilon_p)} \tag{11}$$

$$q = 3 \int_0^1 Ux \, \mathrm{d}x \tag{12}$$

$$V\frac{\mathrm{d}C}{\mathrm{d}t} = -W\frac{\mathrm{d}q}{\mathrm{d}t} \tag{13}$$

The set of Eqs. (9)–(13) with Eq. (4) was solved by the finite difference technique illustrated by Mathew and Weber [22].

The value of the external mass transfer coefficient, k_f, was estimated by using an expression for the initial mass transfer rate (when all the mass transfer resistance is restricted to the external boundary layer and the surface concentration is assumed negligible)

$$k_f = -\frac{1}{S_s}\left[\frac{\mathrm{d}(C/C_0)}{\mathrm{d}t}\right]_{t=0} \tag{14}$$

where

$$S_s = \frac{6W}{d_p\rho_p(1 - \epsilon_p)} \tag{15}$$

The values of k_f thus obtained were 2.33×10^{-5} cm s^{-1} and 1.15×10^{-5} cm s^{-1} for BTMAC and Aliquat® 336, respectively. The values of the surface diffusion coefficient which predicted the concentration–time decay curves in agreement with the experimental data (Fig. 5) are 1.20×10^{-8} cm^2 s^{-1} and 0.96×10^{-8} cm^2 s^{-1} for BTMAC and Aliquat® 336, respectively. In fact, at a constant agitation rate, the values of k_f for both systems should be the same. The observed variation in the k_f values and the surface diffusivities are probably due to the different activities and molecular mobilities of the onium salts in the aqueous and the organic phases, and higher values for BTMAC may be attributed to ionic dissociation in the aqueous medium [24]. The results of a computation of the concentration vs. time profile using a single-resistance model ($D \to \infty$) are shown as the broken lines in Fig. 6. During the first 20 min, the single-resistance model fits the experimental data well for both systems, however the fit is better in the case of adsorption from the organic
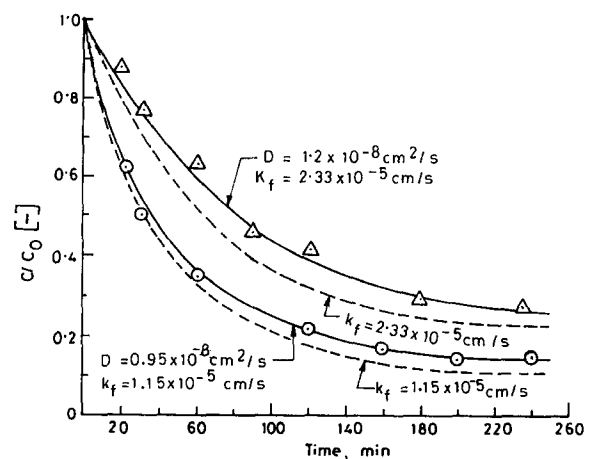

Fig. 6. Concentration–time decay curves for BTMAC in the aqueous phase and Aliquat® 336 in the organic phase. ○, BTMAC ($C_0 = 25$ mmol l^{-1}; $W = 3.5$ g); △, Aliquat-336 ($C_0 = 20$ mmol l^{-1}; $W = 3.0$ g). ---, theoretical curves of single-resistance model.

phase. Experimentally observed slower decay curves suggest an additional resistance which affects the rate of adsorption, particularly beyond the initial time period. The deviation of the theoretical concentration–time curve (single-resistance case) from the experimental data is more pronounced in the case of adsorption from the aqueous phase. This implies that the assumption of negligible surface diffusion resistance is more appropriate in the case of the adsorption from the organic phase. Such an effect was demonstrated by Mathew and Weber [22] for the adsorption of bromophenol on activated carbon. Lower values of both k_f and D for the solute in the organic phase infer that both external mass transfer and surface diffusion equally play a role over the period of the adsorption of the solute from the organic phase. In the case of adsorption from the aqueous phase, film diffusion controls the solute uptake rate initially, and particle diffusion controls the solute uptake in the latter stages. However, it is necessary to discover the role of surface diffusion at a very high agitation intensity. Indeed, if one is to make a quantitative study of the effect of internal diffusion it is better to eliminate the effects of external mass transfer [25] and carry out uptake studies at different initial solute concentrations and adsorbent loadings.

3.4. Preliminary desorption study

The percentages of adsorption from aqueous and organic solutions with an initial concentration of 20–30 mmol l^{-1} were found to be 75% and 88%, respectively. This concentration level is typical of that used in catalytic reactions studied earlier [3,4]. The amounts adsorbed at saturation are reasonably high. Desorption of Aliquat® 336 was attempted by the elution of the loaded adsorbent placed in a small glass packed section (0.01 × 0.02 m) with 0.1 l of methanol which was allowed to flow downward through the packed bed at a rate of about 1.0 cm^3 min^{-1}. The extent of desorption was found to be around 80%. The onium salt (BTMAC) adsorbed from the aqueous phase cold be as much as 90% desorbed by using 0.1 N H$_2$SO$_4$ under identical elution condition. Thus adsorptive recovery/separation of quaternary

onium salts from low-concentration feed solutions seems promising. However, further studies on the evaluation of breakthrough curves are required in order to suggest a suitable scheme for practical separations.

Acknowledgement

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