

Adsorption of Tributyl Phosphate on Silica Gel[†]

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ABSTRACT: The adsorption behaviour of tributyl phosphate (TBP) on silica gel was studied. It was found that the adsorption isotherm shapes were complicated, being considered as S- and L-type isotherms according to the Giles classification. Adsorption itself was polymolecular and of a physical nature, the first adsorptive layer involving hydrogen bonding between the protons of surface silanol groups and the electron-donating oxygen atom of the adsorbate molecule. Subsequent adsorption layers were formed via van der Waals interaction. The free energy of adsorption of the system lay between -22.1 kJ/mol and -23.8 kJ/mol. The enthalpy change was negative and very small, i.e. -6.3 kJ/mol, while the entropy change was positive and in the range 53.9 J/(mol K) to 55.4 J/(mol K). The increase in entropy was explained in terms of the mobility of the TBP molecules in the adsorptive layer arising from their replacement on the silica gel surface by water molecules derived from the aqueous medium.

INTRODUCTION

The practice of extraction removal and separation of coloured metal ions is often faced with the problem of extractant losses (Treybal 1966; Vyatkin *et al.* 1990), the large losses of tributyl phosphate (TBP) during the extraction isolation of uranium from ore residues being one such example (Vdovenko 1960). A possible reason for this phenomenon could be adsorption of TBP on various components of ore residues present as impurities, e.g. silicon dioxide, kaolin, micas, ferric oxides, etc.

A solution to this problem is vital since such losses often complicate the operation of a given extraction process, with extractant recovery being very expensive and its presence in wet sludge sites leading to environmental pollution [the maximum allowable concentrations (MAC) of the most widespread extractants lie within the range 0.01–0.05 mg/l with $MAC_{TBP} = 0.01$ mg/l].

We present below the results of experiments undertaken with a view to establishing the basic conditions necessary for the adsorption of TBP on silica gel (silicon dioxide). The influence of pH and temperature on the adsorption process has been established and an attempt made to explain the mechanism of the adsorption process whose basic thermodynamic parameters have been calculated.

EXPERIMENTAL

The TBP employed in the studies was of 99% purity and obtained from Janssen Chimica, Geel, Belgium, while all other reagents employed were of analytical grade having been obtained from

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'Reakhim' (former USSR). The concentration of the aqueous solution of TBP employed, which contained 300 mg/l TBP, was close to saturation (Nikolotova and Kartashova 1978). Concentrated sulphuric acid was used to change the acidity of the solutions. Silica gel (type L 100/250, for chromatography) from Lachema with a specific surface area of 600–750 m²/g and an average pore diameter of 8 nm was used as the adsorbent.

The adsorption experiments were conducted as follows. A known amount (50–200 mg) of the adsorbent was placed in a 200 ml glass volumetric flask containing 100 ml of TBP solution, the flask closed with a ground glass stopper and shaken by means of an ABU-6C shaker for 40 min, initial studies having demonstrated that this time length was sufficient to achieve adsorption equilibrium. The volumetric flask and contents were then centrifuged for 20 min on a CLS-3 laboratory centrifuge at a speed of 5000 rev/min. After centrifugation, the solid residue was separated and placed in a second flask. The extent of adsorption was calculated from the difference between the TBP concentration of the initial solution and that present in the solution after centrifugation. Solution concentrations were determined colorimetrically using a standard procedure (Pan and Grebennikov 1976) involving measurement of their optical density after conversion of the residual phosphate ions into heteropoly phosphomolybdic acids. Such optical densities were measured using an LMP-72M laboratory photometer at a wavelength λ equal to 720 nm, the relative error of such measurements being $\pm 4\%$.

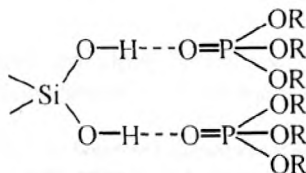
Desorption experiments of TBP from silica by the addition of water or sulphuric acid solutions were carried out as follows. The solid residue obtained from centrifugation was placed in a 200 ml glass volumetric flask fitted with a ground glass stopper, 100 ml of water or an aqueous solution of sulphuric acid added and the mixture shaken using the ABU-6C shaker. Desorption of TBP from the adsorbent surface occurred under these conditions with the concentration of TBP in the solution phase increasing with time. The solution was tested periodically for its TBP content using the standard procedure mentioned above. Shaking was terminated when the TBP concentration of the solution had reached a constant value.

All experiments, except those involving special cases as stipulated below, were conducted at 20°C.

RESULTS AND DISCUSSION

The results depicted in Figure 1 indicate that the adsorption isotherms for TBP on a silica gel surface were complicated. Using the Giles basis (Parfitt and Rochester 1986), they may be classified as being of the S (plots \circ , \blacktriangle and \blacksquare) and L type (plot \bullet), respectively. Such isotherm types demonstrate the polymolecular nature of the adsorption process.

If the functional groups associated with TBP are taken into account as well as the nature of a silica gel surface when immersed in an acidic medium (Ayler 1982), it is reasonable to assume that the first adsorptive layer is formed as a result of hydrogen bonding between the protons of the silanol groups on the adsorbent surface and the electron-donating oxygen atoms of the adsorbate molecule, i.e.



where R depicts a hydrocarbon radical ($-C_4H_9$).

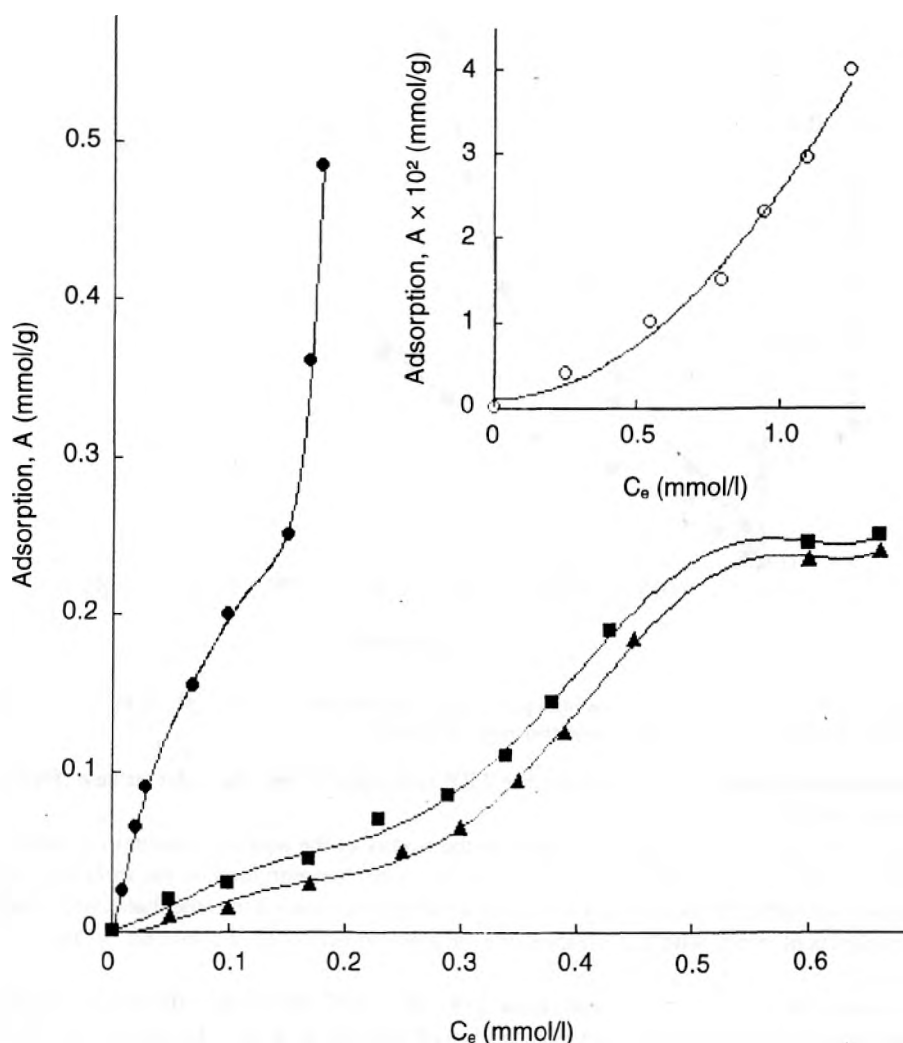


Figure 1. Adsorption isotherms for TBP on silica gel in the presence of various sulphuric acid concentrations. H_2SO_4 conc. (mol/l): \circ , 0.0; \blacktriangle , 1.0; \blacksquare , 3.0; \bullet , 6.0; C_e = equilibrium concentration of TBP (mmol/l)

The presence of an isolated (i.e. not connected by hydrogen bonding to each other) pair of hydroxy groups on a silica gel surface was demonstrated by IR spectroscopic studies of silica gel samples initially maintained in 6 M H_2SO_4 solution for 40 min and then dried in air to constant weight. Such IR spectra were obtained using the KBr pellet technique employing a model 833 Perkin-Elmer IR spectrophotometer over the wavelength range $4000\text{--}200\text{ cm}^{-1}$. The absorption band observed in the IR spectrum at 3660 cm^{-1} was associated with the valence vibrations of an isolated pair of --OH groups whose protons were separated by a distance $r_{\text{HH}} = 25\text{--}26\text{ nm}$ (Farrah and Pickering 1976). This band, together with another at $3400\text{--}3450\text{ cm}^{-1}$ typical for water molecules weakly coupled by hydrogen bonding to the surface silanol groups, formed an intensive broad band extending over the spectral range ca. $3400\text{--}3600\text{ cm}^{-1}$. Subsequent adsorptive layers were probably formed via van der Waals forces. Adsorption isotherms of type L and S suggest a

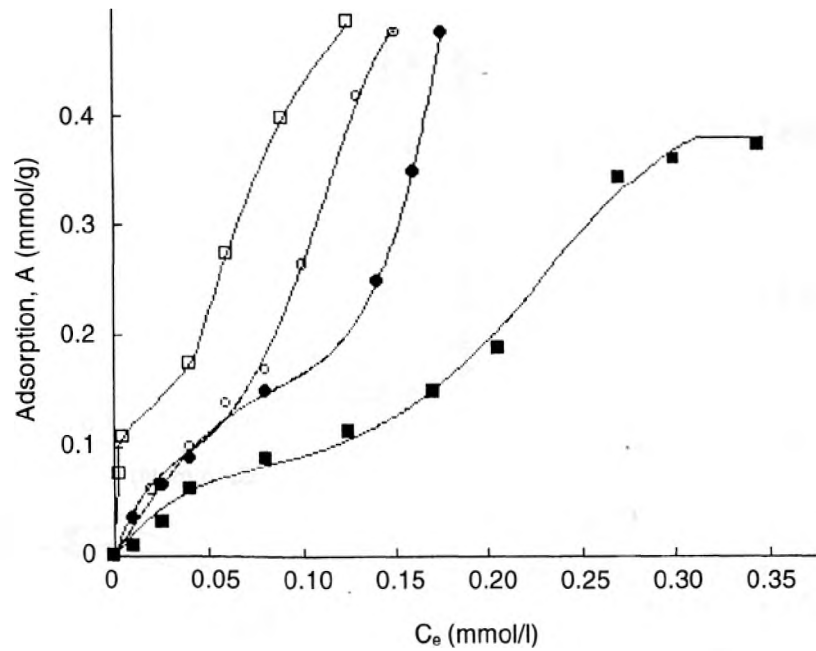


Figure 2. Adsorption isotherms for TBP on silica gel at various temperatures. Temp. (°C): ●, 20; ■, 30; ○, 40; □, 50; H₂SO₄ conc., 6.0 mol/l; C_e = equilibrium concentration of TBP (mmol/l)

poorly organised parallel orientation for the TBP molecules on the silica gel surface (Parfitt and Rochester 1986).

Figure 1 shows that adsorption increased as the acidity of the aqueous medium increased. This may be explained, on the one hand, by a decrease in water concentration on the surface as a result of competition with TBP molecules at the liquid–solid interface and, on the other hand, with ‘opening’ of the adsorbent pores with a corresponding increase in access of the internal surface to TBP molecules.

Increasing the solution temperature from 20°C up to 50°C had little influence on the type of adsorption isotherms generated (see Figure 2), with adsorption at first decreasing (at 30°C) and then increasing (40°C and 50°C). Such observations lead to the following conclusions: (1) the adsorption of TBP on silica gel is physical in character since the corresponding adsorption isotherms (S and L type) are generally characteristic of non-chemical types of adsorption (Parfitt and Rochester 1986); and (2) over the temperature range 40–50°C ‘opening’ of the pores and, as a consequence, an increase of the number of accessible active centres in the pores is well known (Frolov 1982), leading to more effective adsorption.

Over their initial stages, the data associated with the adsorption isotherms for TBP on silica gel may be approximated by the Langmuir adsorption isotherm equation (Frolov 1982):

$$\frac{C_e}{A} = \frac{1}{\beta \cdot A} + \frac{1}{A_m} \cdot C \quad (1)$$

where A is the adsorption corresponding to the equilibrium concentration C_e, A_m is the maximum (limiting) adsorption and β is a constant which may be linked with the adsorptive equilibrium constant by the equation (Zapolskiy *et al.* 2000):

TABLE 1. Thermodynamic Quantities Relating to the Adsorption of TBP on Silica Gel

Temp. (K)	A_{∞} (mmol/l)	$-\Delta G^0$ (kJ/mol)	$-\Delta H^0$ (kJ/mol)	ΔS^0 [J/(mol K)]
293	0.40	22.1	} 6.3	53.9
303	0.24	23.1		55.4
313	0.41	23.4		54.6
323	0.44	23.8		54.1

$$K = \gamma \cdot \beta \cdot \frac{S_s}{S_a} \tag{2}$$

where γ is the number of mol solvent in 1 kg of its own weight and S_s and S_a are the areas on the carrier surface occupied by adsorbate and solvent molecules, respectively.

Equations (1) and (2) enable the values of A_{∞} , β and K to be calculated and then through the use of the equations:

$$\Delta G^0 = -RT \ln K; \quad \Delta H^0 = RT \cdot \frac{d \ln K}{dT}; \quad \Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$$

the standard differential changes in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0), respectively, may be calculated.

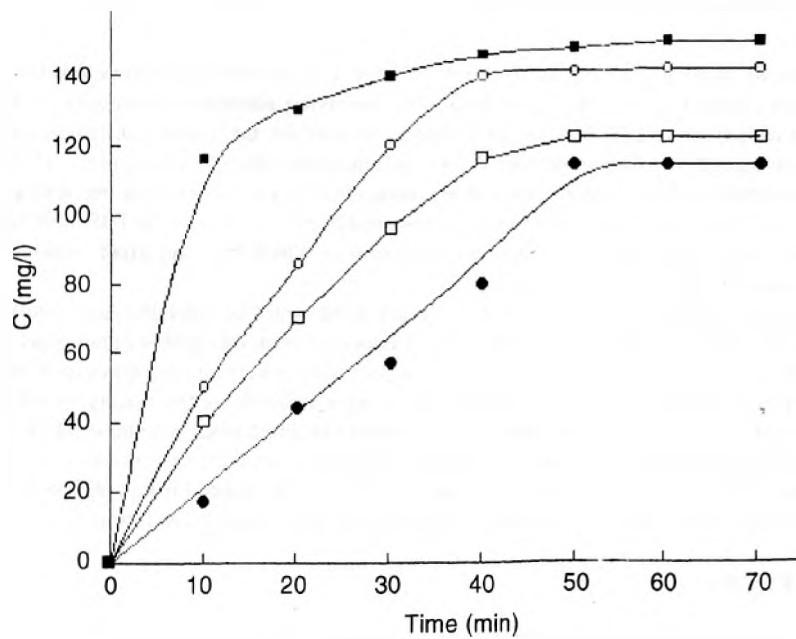


Figure 3. Kinetics of TBP desorption from silica gel by water (■) and by various concentrations of sulphuric acid: H_2SO_4 conc. (mol/l): ○, 1.0; □, 3.0; ●, 6.0.

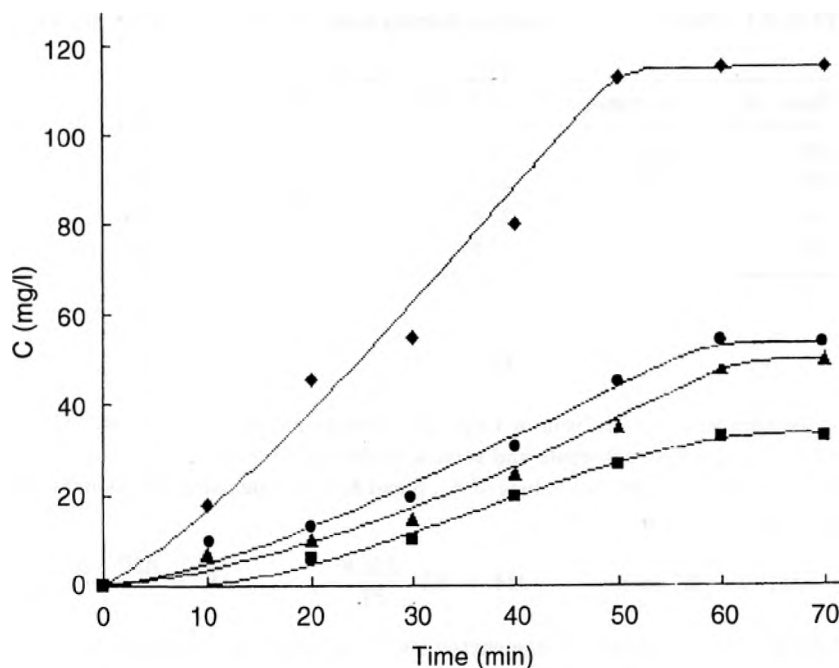


Figure 4. Kinetics of TBP desorption from silica gel at various temperatures in the presence of sulphuric acid: \blacklozenge , 20; \bullet , 30; \blacktriangle , 40; \blacksquare , 50; H_2SO_4 conc., 6.0 mol/l.

The results of such calculations are listed in Table 1, from which it follows that the standard differential changes in free energy of the system involving adsorptive interaction of TBP with silica gel were quite large (-22.1 to -23.8 kJ/mol). In contrast, the standard differential change in enthalpy was negative and quite small (-6.3 kJ/mol) indicating that the adsorption of TBP on silica gel was exothermic. The standard differential changes in entropy were positive and also quite large [53.9 to 55.4 J/(mol K)]. Such values may be explained by the mobility of the TBP molecules in the adsorptive layer, which must be related to the ease with which they can expel weakly adsorbed water molecules from the surface.

Desorption experiments of TBP from silica gel using water or sulphuric acid solutions have shown that, when adsorbed, TBP is not strongly associated with the surface of silica gel particles. As shown in Figures 3 and 4, time is an important factor for achieving the greatest possible degree of desorption, with desorption becoming increasingly difficult as the acidity of the aqueous medium and the temperature increased. This is readily explained when account is taken of the fact that desorption from pores becomes increasingly difficult under these circumstances. It should be noted that when washed from a silica gel surface TBP can be isolated from solution by flotation (Skrylev *et al.* 1999), added to the main extract and the total subjected to further processing.

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