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# Silica-gel-immobilized acetylacetone—some thermodynamic data in non-aqueous solvents ☆

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**Abstract**

Acetylacetone was covalently immobilized on silica gel to produce a new surface (Sil–ac), having 0.62 mmol of ligand attached per gram of silica, which was characterized by means of elemental analysis and physical measurements, before being submitted to calorimetric measurements. Thus, a suspension of this anchored surface in ethanol or acetone was calorimetrically titrated with divalent cations (Co, Ni, Cu, Zn, Cd, Hg). The resulting isotherms conformed to a modified Langmuir equation. After linearization of these isotherms, the enthalpies of cation/surface adsorption and the interfacial equilibrium constant, as well as the variation of free energies and entropies, were calculated. In acetone, adsorption of copper gives rise to an exothermic $\Delta H$ of $-93.38 \pm 0.94$ kJ mol$^{-1}$, while cobalt, $41.80 \pm 0.42$ kJ mol$^{-1}$, and zinc, $2.38 \pm 0.02$ kJ mol$^{-1}$, give an endothermic adsorption. In ethanol, the endothermic $\Delta H$ of $52.64 \pm 0.53$ kJ mol$^{-1}$ for zinc contrasts with the exothermic enthalpies of adsorption observed for other cations, especially for mercury, $-102.20 \pm 1.02$ kJ mol$^{-1}$ and nickel, $-137.70 \pm 1.38$ kJ mol$^{-1}$.

*Keywords:* Acetylacetone; Immobilization; Silica gel; Thermodynamic data

## 1. Introduction

Inorganic oxides such as silica gel have received great attention not only due to the surface reactivity [1, 2], but also due to the ability of immobilizing organic molecules

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onto it [3]. The interest in these new kinds of materials is reflected in applications such as chemically bonded stationary phases for chromatography [4], supports for catalysts [5], and uses in pre-concentration of sorbents [6, 7], ion exchange [8] or biotechnology [9].

The main procedure consists of immobilizing a precursor functional molecule onto the support, which normally occurs using a silylated agent containing a trialkoxysilyl group, which reacts with the silanol on the surface [7]. Subsequent reactions can expand the organic covalent chain or the side chains. In any case, the objective is to anchor desirable functional groups on the solid surface. The choice of the chemically bonded molecules is normally based on having chelating agents and on their ability to extract cations from aqueous or non-aqueous dilute solutions [3, 10, 11].

The most commonly anchored molecules contain nitrogen or oxygen, or a combination of both, as basic centres in the backbone chains [12, 13]. Depending on the syntherizing method, these chelating agents can bind cations in mono- or polydentate fashion, with nitrogen usually as part of the heterocyclic ring [14]. In this connection, the coordinative ability of amines in extracting cations from aqueous and non-aqueous solvents has been explored [15]. Other sorbents containing simple or complex molecules, like quinoline derivatives [16], imidazole [17] and aminopyridine derivatives [18] showed the efficiency of the cyclic nitrogen in adsorbing cations from non-aqueous solvents. For example, divalent cations dissolved in ethanol or acetone were easily extracted from these solutions by aminopyridine derivatives [13, 18] anchored on silica gel and the thermodynamic data for these equilibria were obtained. Urea and derivatives immobilized on silica have been studied recently. The results demonstrated a great tendency of these surfaces for adsorbing cations from non-aqueous solutions and the thermodynamic values for these free-energy-favourable equilibrium systems were calculated. These data showed that the integral heats of adsorption of cations to form a monolayer on urea-immobilized surface were larger in acetone than in ethanol [19].

The purpose of this publication is to report the calorimetric titration, with divalent cations, of a suspension of acetylacetone immobilized on silica gel. This surface was previously characterized by physical measurements. In this particular case, the property of bidentate oxygen atoms anchored on the surface in bonding cations from ethanol and acetone solutions was explored.

## 2. Experimental

Silica gel (Merck) with a particle size of 80–170 mesh, surface specific area of 503 $m^2 g^{-1}$ (determined by BET method) and 60 Å mean pore diameter was outgassed [19, 12] immediately before use in the immobilization. Acetylacetone was freshly distilled before use. Ethanol and acetone for calorimetric titration were dried and stored over appropriate dehydrating agents. 3-Aminepropyltriethoxysilane (Merck) was used without further purification. Solutions of divalent cations for calorimetric determinations were prepared from anhydrous salts [7, 13, 19].

The immobilized surface was prepared by reacting 3-aminepropyltriethoxysilane with the activated silica in xylene [13]. 3-bromoacetylacetone was added to a suspension of the aminated silica in ether [20] to produce the final surface.

The silanized surface ≡Sil–ac was characterized by elemental analysis, which gave an amount of 0.62 mmol of organic molecules per gram of silica attached to the surface [13, 18]. This agrees with the determination of basic centres through hydrochloric acid adsorption. The infrared spectrum obtained on discs [7] showed the presence of weak peaks in the 1662–1470 $cm^{-1}$ range, which correspond to CO and CC stretching frequencies [21]. The solid-state carbon NMR spectrum showed, in addition to other peaks in the 9–58 ppm range, a clear peak at 182.0 ppm attributed to a carbonyl group [19, 22], which indicated the presence of acetylacetone bonded on the surface.

An LKB 8700–2 isoperibolic precision calorimeter system was used in the calorimetric titrations [7, 13, 18]. In these experiments, anhydrous metal chlorides (Co, Ni, Cu, Zn, Cd, Hg) dissolved in ethanol or acetone, thermostated at 298.15 ± 0.02 K and protected from humidity, were incrementally added to an accurately weighted amount of ≡ Sil–ac (0.50 g) suspended in 90.0 $cm^3$ of the same solvent, under vigorous stirring. The heat of interaction of metal ion with the surface is outlined as

$$\equiv \text{Sil–ac.solvent} + \text{MCl}_2\text{.solvent} = \equiv \text{Sil–ac.MCl}_2\text{.solvent} + \text{solvent}; Q_1$$

To correct the effect of dilution during the titration, metal ion solutions were added to the solvent and also pure solvent was added to a surface suspension in the calorimetric vessel in order to determine the thermal dilution effects $Q_2$ and $Q_3$, respectively. The net heat of the chemical reaction was obtained by subtracting from $Q_1$ the thermal effects of dilution, i.e. $Q = Q_1 - (Q_2 + Q_3)$. The dilution value $Q_3$ is null, as observed before [13]. Hence, the variation in enthalpy ($\Delta H$) is determined through the expression $Q = n\Delta H$, where $n$ is the amount of solute adsorbed on the surface.

## 3. Results and discussion

The infrared and the solid-state carbon NMR spectra results are inequivocal evidence of the success of immobilization. This surface has an amount of 1.24 mmol of basic centres per gram of silica, which was determined through hydrochloric acid adsorption. These available groups chemisorb cations from dilute solutions.

However, the variation of chemisorption capacity shows a considerable influence of the solvent in the adsorption process, which takes place in heterogeneous medium [23]. This feature can be easily verified when the batch process is considered in the adsorption. The solvation of cations by solvents generates competition for the cations between the solvent and the basic centres of the immobilized molecule. In this case, both oxygen atoms of the pendant groups interact with cations in solution. The high polarity of water favours its interaction with the surface. Also the cations are highly solvated, which inhibits the interaction of cations with the surface. To avoid any competition, anhydrous conditions are desirable. Then, less polar solvents such as acetone have a lower interactive action with both cations and the basic centres of the support [7, 13, 18].

This interaction involving cations in acetone or ethanol with basic oxygenated centres of ≡ Sil–ac at the solution/support interface causes a variation in enthalpy. For illustration the results of a calorimetric titration of the suspension of the support with $ZnCl_2$ in ethanol are shown in Table 1. Fig. 1 shows a complete process of titration in which the dilution effect is included. The net curve obtained can be adjusted to a modified Langmuir equation, as observed before for other surfaces [24, 25]. The thermodynamic values for these interactions can be calculated by considering the enthalpy of adsorption and the concentration of the cations in equilibrium, as described by the equation

$$N/Q = 1/(K-1)Q_m + N/Q_m$$

where $Q$ is the integral enthalpy of adsorption (J $g^{-1}$), $N$ is the mole fraction of the metal ion in solution, $K$ is a proportionality factor that includes the equilibrium constant, and $Q_m$ is the integral heat of adsorption for a saturated monolayer of unit mass of the functionalized material.

After equilibrium has been reached with incremental additions of solute in the calorimetric titration, the unknown number of moles of the solute adsorbed per gram of solid $n$ can be determined. These values can be calculated by considering the adsorption isotherms obtained through a batch process [18, 19, 26].

The net heats adsorption of cations on support can be shown by the isotherm of $CuCl_2$. A plot of $N/Q$ against $N$ for sorption of cations provides $Q_m$ values from the slope of the straight line, as shown in Fig. 2. From this determination and the respective amount of adsorbate, $\Delta H$ values for these interactions can be calculated [19, 26]. A summary of these results is listed in Table 2.

Table 1
Calorimetric titration of 0.2027 g of ≡Sil–ac suspended in 90 $cm^3$ of ethanol with $ZnCl_2$ ($4.90 \times 10^{-3}$ mol $dm^{-3}$) at 298.15 K

| $V/cm^3$ | $\Sigma Q/J$ | $\Sigma Q/m/J\,g^{-1}$ | $\Sigma N \times 10^6$ | $\Sigma N/(\Sigma Q/m) \times 10^6/g\,J^{-1}$ |
|---|---|---|---|---|
| 1.00 | 0.20 | 0.987 | 2.025 | 2.051 |
| 2.04 | 0.38 | 1.875 | 4.110 | 2.192 |
| 3.05 | 0.53 | 2.570 | 6.123 | 2.390 |
| 4.07 | 0.66 | 3.208 | 8.141 | 2.538 |
| 5.09 | 0.76 | 3.701 | 10.147 | 2.742 |
| 6.11 | 0.84 | 4.071 | 12.137 | 2.981 |
| 7.14 | 0.90 | 4.441 | 14.110 | 3.177 |
| 8.14 | 0.95 | 4.690 | 16.073 | 3.427 |
| 9.16 | 0.98 | 4.811 | 17.990 | 3.738 |
| 10.17 | 1.01 | 4.934 | 19.922 | 4.037 |
| 11.17 | 1.04 | 5.058 | 21.828 | 4.320 |
| 12.17 | 1.07 | 5.181 | 23.708 | 4.580 |

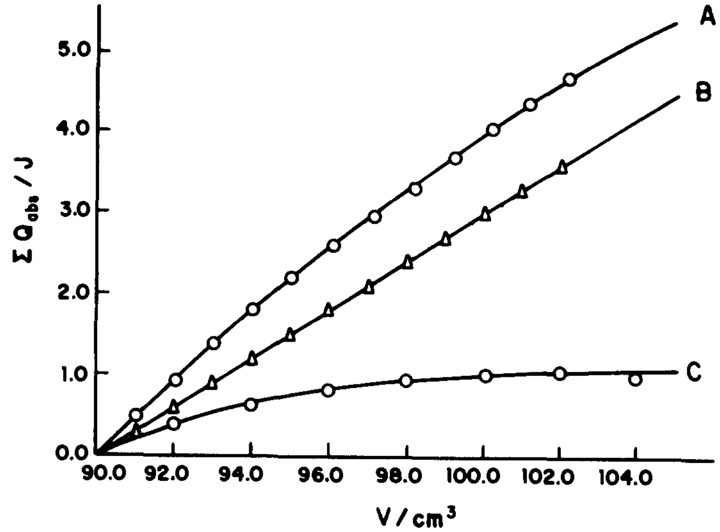

Fig. 1. Calorimetric titration of 0.2027 g of ≡Sil–ac suspended in 90.0 cm$^3$ of ethanol with ZnCl$_2$ (4.90 × 10$^{-3}$ mol dm$^{-3}$) at 298.15 K: A, thermal effect of surface-cation interaction ($Q_1$); B, thermal effect of cation dilution ($Q_2$); C, net thermal effect of adsorption ($Q$).

The exothermic values for free energies for all reactions indicate a favourable system. The variation in ethalpies for nickel and mercury in ethanol are highly exothermic, − 137.70 ± 1.38 and − 102.20 ± 1.02 kJ mol$^{-1}$, respectively, and contrast with the only endothermic value in this solvent, found for zinc, of 52.64 ± 0.53 kJ mol$^{-1}$, which

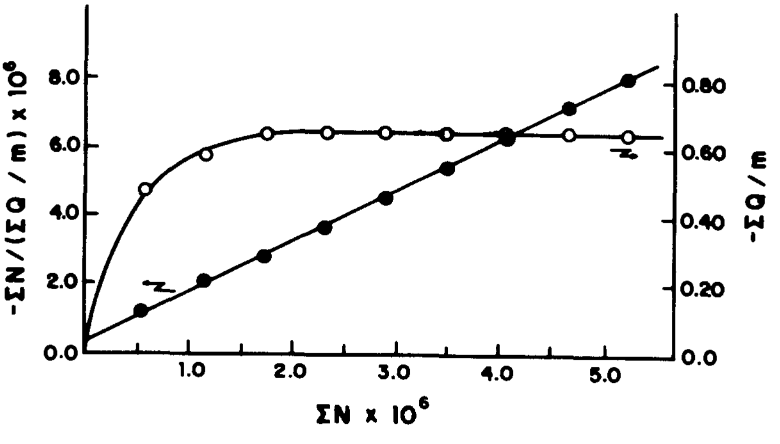

Fig. 2. Isotherm obtained through calorimetric titration of ≡Sil–ac suspended in acetone with CuCl$_2$ (4.25 × 10$^{-3}$ mol dm$^{-3}$) at 298.15 K and the respective linearization of the isotherm.

Table 2
Thermodynamic data for cation/$\equiv$Sil–ac interactions at 298.15 K

| $MCl_2$ | Solvent | $Qm$/J $g^{-1}$ | $n \times 10^4$/mol $g^{-1}$ | $\Delta H$/kJ $mol^{-1}$ | ln $Ke$ | $-\Delta G$/kJ $mol^{-1}$ | $-\Delta S$/J$k^{-1}$ $mol^{-1}$ |
|---|---|---|---|---|---|---|---|
| Co | Ethanol | −9.17 | 1.89 | −48.52 ± 0.49 | 9.40 | 23.29 | +85 |
|  | Acetone | +20.40 | 4.88 | +41.80 ± 0.42 | 9.31 | 23.08 | −218 |
| Ni | Ethanol | −16.67 | 1.21 | −137.70 ± 1.38 | 8.70 | 21.55 | +390 |
| Cu | Ethanol | −0.67 | 2.12 | −3.16 ± 0.03 | 15.70 | 38.89 | −120 |
|  | Acetone | −58.55 | 6.27 | −93.38 ± 0.94 | 13.09 | 32.43 | +205 |
| Zn | Ethanol | +8.47 | 1.61 | +52.64 ± 0.53 | 11.18 | 27.70 | −270 |
|  | Acetone | +0.75 | 3.15 | +2.38 ± 0.02 | 11.63 | 28.82 | −105 |
| Cd | Ethanol | −10.04 | 2.39 | −42.00 ± 0.42 | 11.51 | 28.52 | +45 |
| Hg | Ethanol | −38.02 | 3.72 | −102.20 ± 1.02 | 11.60 | 28.74 | +247 |

is also endothermic in acetone, 2.38 ± 0.02 kJ mol$^{-1}$. The enthalpic value for copper in acetone is $-93.38 \pm 0.94$ kJ mol$^{-1}$, while zinc and cobalt, 41.80 ± 0.42 kJ mol$^{-1}$ presented endothermic values. This tendency of copper in displaying the largest exothermic values in acetone is observed in other systems [27]. In this case, the enthalpy is nearly twice the value found for an immobilized bidentate diamine [15]. In many circumstances the release of the solvent during the complexation is considered to be an important feature that gives some explanation about the entropic contribution [18, 19, 26]. In fact, it is thought that the complexation causes a disturbance due to desolvation, and consequently an enhancement in entropy is expected. An increase in entropy is clearly observed for cobalt and zinc in acetone at 218 and 105 J K$^{-1}$ mol$^{-1}$, respectively. Copper and zinc in ethanol presented favourable entropic values at 120 and 270 J K$^{-1}$ mol$^{-1}$, respectively. In conclusion, the immobilized acetylacetone/silica system gives a series of thermodynamic results which clearly illustrate the great ability of the bidentate oxygen ligand in coordinating cations from non-aqueous solvents.

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