



HAL
open science

Calorimetric screening of co-operative effects in adsorption of Co(II) on γ -alumina surface in the presence of Co-complexing anions in aqueous solution

Mouhamad Ali Ahmad, Benedicte Prelot, Jerzy Zajac

► To cite this version:

Mouhamad Ali Ahmad, Benedicte Prelot, Jerzy Zajac. Calorimetric screening of co-operative effects in adsorption of Co(II) on γ -alumina surface in the presence of Co-complexing anions in aqueous solution. *Thermochimica Acta*, 2020, 694, pp.178800. 10.1016/j.tca.2020.178800 . hal-03025070

HAL Id: hal-03025070

<https://hal.science/hal-03025070>

Submitted on 26 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

**Calorimetric screening of co-operative effects in
adsorption of Co(II) on γ -alumina surface in the presence
of Co-complexing anions in aqueous solution**

Mouhamad Ali Ahmad, Benedicte Prelot, Jerzy Zajac*

*Institut Charles Gerhardt, UMR-5253 CNRS-UM-ENSCM,
Université de Montpellier, Place E. Bataillon, F-34095 Montpellier cedex 5, France*

*Corresponding author:

J. Zajac, e-mail: jerzy.zajac@umontpellier.fr, ORCID: 0000-0002-9529-4624

ABSTRACT

The understanding of the mechanism of co-operative adsorption of Co(II) cations and acetate or citrate anions onto γ -Al₂O₃ from aqueous solutions has been refined on the basis of comparison between the enthalpies of displacement measured in single-solute and bi-solute systems by means of isothermal titration calorimetry. The data processing procedures were adapted to take into account the occurrence of a cobalt-ligand complex in the bulk solution. Considering the bridging role of the adsorbed cobalt cations as a starting point to reproduce the enthalpy of displacement in the cobalt-acetate system, each ligand unit was suggested to bind preferentially to more than one adsorbed metal species and to interact additionally with some electrically neutral binding sites on the oxide surface. In the case of cobalt-citrate couple, the formation of a 1:1 stoichiometry solid-ligand-metal complex and simultaneous adsorption of cobalt cations as bidentate inner-sphere complexes reproduced best the experimental data.

Keywords:

γ -alumina, cobalt adsorption, organic ligands, isothermal titration calorimetry, co-operative effects

1. Introduction

Alumina-supported cobalt catalysts, such as Co(II)/ γ -Al₂O₃, offer promising perspectives for mitigation of nitrogen oxides, oxidation of volatile organic compounds, hydrodesulfurization reactions, or Fischer-Tropsch production of clean fuels while reducing energy inputs and CO₂ emissions [1-7]. It is commonly admitted that the catalytic activity chiefly depends on metal-support interactions as a function of such factors as the concentration and dispersion of cobalt species, surface chemistry of the support, and the type of functionalization method or thermal treatment applied. One notable example is the impregnation of alumina with small amounts of Co(II) nitrate solution, followed by a thermal treatment in air and subsequent reduction in hydrogen. The addition of oxygenated organic additives is probably the most effective way to control and modulate the deposition of the cobalt species, thereby enhancing the catalytic performance of Co(II)/ γ -Al₂O₃ catalysts [8-12].

In order to consider the potential impact that Co-complexing additives may have on the metal binding to the catalytic support, it is necessary to study the retention of cobalt under the conditions similar to those used during the supported catalyst preparation. In the previous paper [12], Co(II) retention on γ -Al₂O₃ in the presence of acetate, citrate, tricarballoylate, and nitrilotriacetate anions was quantified through measurements of the isotherms of individual adsorption of the components in bi-solute systems under the unadjusted pH condition. To mimic the usual preparation procedures, cobalt and additive species were adsorbed simultaneously from equimolar aqueous solutions (N-ligand-Co systems) or the adsorption of cobalt from a single-component solution was preceded by pre-loading γ -alumina with an aqueous solution containing only the additive (S-ligand-Co systems); sample drying was also carried out as an intermediate step (D-ligand-Co systems). In all cases, both the co-operative and competitive adsorption of the ligand and cobalt were evidenced on the basis of a comparison among the experimental adsorption isotherms, in accordance with the observed small changes in the pH of

the equilibrium solid-liquid suspension and the results of potentiometric titrations. In accordance with published literature on the subject [13, 14], the formation of ternary surface complexes of type A (i.e., solid-metal-ligand) or type B (i.e., solid-ligand-metal) was considered to describe the co-operative adsorption at least in a qualitative manner.

The objective of the present study was to employ the isothermal titration calorimetry (ITC) to quantify the enthalpy effects accompanying the co-operative adsorption from aqueous solutions containing equimolar quantities of Co(II) cations and acetate or citrate anions. The resulting calorimetry data were intended to be used as a basis for shedding more light on the nature of interactions involved in the formation of surface complexes. In order to attain this objective, the calorimetry operating procedures were adjusted accordingly to reproduce, at best, the experimental conditions under which the previous adsorption study was made [12]. Among others, it was necessary to develop a new data processing procedure allowing the formation of a cobalt-ligand complex in the bulk solution to be taken into account. The analysis of the calorimetric data was based on the adsorption isotherms measured previously for the N-ligand-Co systems. The research strategy applied here relied on a comparison between the cumulative enthalpy of displacement accompanying adsorption from aqueous solutions of cobalt cations and acetate or citrate anions and the analogous quantities obtained when each solute was retained on the solid surface from a single-solute solution.

Interpreting the heat quantities measured upon adsorption from ionic solutions at an electrified solid-liquid interface is never an easy task since the total thermal effect is composed of several hardly separable contributions which may be exothermic or endothermic, often depending on the nature of the adsorbate-adsorbent couple, surface coverage ratio, or pH of the solid suspension [15-18]. This usually includes the heat effects related to: (i) adsorption of solute molecules or ions, as well as co-adsorption of counter-ions, (ii) desorption of solvent molecules, other molecules or ions pre-adsorbed at the solid-liquid interface, (iii) changes in

the structure of the vicinal water (e.g., surface dewetting), (iv) changes in the hydration layers of the adsorbing and desorbing species, (v) changes in the electrical charge and potential of the solid surface. It is possible to conclude correctly on the affinity between a given solute and the solid surface if the related contribution is dominant over the others or/and the other contributions are constant over the adsorption range studied. This is argued to be true for the systems studied here and used as a key prerequisite for further analysis of the experimental enthalpy of displacement.

2. Materials and Methods

2.1. Materials

Gamma-alumina ($\gamma\text{-Al}_2\text{O}_3$) was prepared by calcination, in air at 500 °C for 4 h, of Pural SB3 boehmite supplied by Sasol Germany Ltd. The powdered sample had a BET specific surface area of $212 \pm 11 \text{ m}^2 \text{ g}^{-1}$ [12]. Cobalt(II) nitrate hexahydrate (purity $\geq 98\%$), ammonium acetate (purity $\geq 98\%$), and ammonium citrate tribasic (purity $\geq 97\%$) were purchased from Sigma-Aldrich. All chemicals were used without further purification. MilliQ water (18.2 M Ω cm) was used to prepare aqueous solutions.

2.2. Calorimetric measurements of the enthalpy of displacement

The individual adsorption isotherms for cobalt and additive species from single-solute and bi-solute aqueous solutions at 298 K were determined previously under the unadjusted pH condition [12]. In the present paper, the corresponding enthalpy changes were monitored by means of a TAM III multi-channel calorimetric device described elsewhere [19].

Prior to each adsorption run, a single-solute (cobalt or anionic ligand) or bi-solute (cobalt with a given anionic ligand) stock solution was placed in the micro-syringe. This stock solution was prepared by dissolving appropriate salts in ultrapure water. Stock solutions corresponding

to the following concentrations were used in adequate calorimetry runs: 30 mmol L⁻¹ for cobalt, 80 mmol L⁻¹ for acetate, and 50 mmol L⁻¹ for citrate salts. In the case of bi-solute solutions, cobalt and anionic ligand were mixed together in equimolar proportions. The concentrations of the two solutes in the bi-solute stock solutions were as follows: 50 mmol L⁻¹ for cobalt-citrate system and 30 mmol L⁻¹ for the other. All these concentrations were adjusted accordingly in order to cover the range of low and moderate adsorption quantities where the individual adsorption isotherms represented monotonously increasing functions of the concentration (i.e., the competitive effects did not manifest themselves on the adsorption isotherms).

In a typical adsorption experiment, about 800 μ L of deionized water and 10 mg of γ -Al₂O₃ were poured into a 1 ml glass ampoule serving as a calorimetric cell. After the attainment of the thermal equilibrium inside the calorimetric device at 298 K, successive injections of the 10- μ L aliquots of a given stock solution during 10 sec were performed, thus resulting in the heat flows recorded with an equilibration time of 45 min between 2 injections. The data processing procedures resulting in plots of the *cumulative enthalpy of displacement*, $\Delta_{dpl}H_{cum}$, as a function of the total amount adsorbed in single-solute and bi-solute systems are detailed in Supplementary material (see sections S1 and S2).

Generally, special attention should be paid when determining the heat contribution due to the dilution phenomenon. In the present case of alumina-cobalt or alumina-ligand systems, the adsorption of metal or ligands ions was accompanied by the transfer of potential-determining H₃O⁺ and OH⁻ ions between the solid-liquid interface and the supernatant solution, thereby causing progressive changes in the solution pH. Nevertheless, the observed pH changes were rather small in the adsorption range covered by the calorimetry experiments. In consequence, the thermal effects recorded upon dilution of cobalt or ligand solution in ultrapure water may be thus considered as a good estimate of the enthalpy of dilution.

The same isothermal titration calorimeter by TAM Instruments was used to determine the equilibrium dissociation constants for Co-ligand aqueous complexes. For this purpose, a $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ stock solution was placed in the syringe and about 800 μL of an aqueous $\text{NH}_4\text{CH}_3\text{CO}_2$ or $\text{HOC}(\text{CO}_2\text{NH}_4)(\text{CH}_2\text{CO}_2\text{NH}_4)_2$ solution were introduced into the calorimetric cell. Successive injections of the 10- μL aliquots of the Co-containing stock solution resulted in the absorbed or released heat recorded in the form of peaks. These thermal peaks were further integrated to obtain the corresponding values of heat of injection.

Given the complexity of the data processing procedures applied in the present study, the measurement uncertainty was not determined on the basis of error propagation law. Instead, the uncertainty in measured adsorption and enthalpy quantities was assessed directly by duplicating the adsorption and calorimetry experiments [12, 19]. The repeatability-reproducibility was found to be within:

- 5%, for the measurement of the amount adsorbed,
- 7%, for the determination of the dissociation constants,
- 10%, for the determination of the enthalpy of displacement.

3. Results and Discussion

The detailed analysis of the calorimetric results obtained with the aid of an Isothermal Titration Calorimetry (ITC) device will be separated in two subsections devoted, respectively, to single-solute and bi-solute systems. The principal motivation behind this separation is the difference in the data processing procedures applied in each case.

3.1. Enthalpy effects of displacement in single-solute systems

In principle, the calorimetry measurements do not involve too much difficulty and the cumulative enthalpy curves may be quite easily obtained based on the routine processing

procedures detailed in Supplementary material (see section S1). The enthalpy change accompanying the adsorption from single-solute aqueous solution represents the displacement effect according to the competitive character of the phenomenon. In consequence, such a displacement may be exothermic or endothermic and the results of ITC measurements usually differ greatly from the isosteric heats of adsorption which are calculated from the temperature dependency of the individual adsorption isotherms [20-22]. A recent study of fluoride adsorption onto mesoporous hierarchical alumina microspheres provides new experimental arguments for the direct determination of the heat of adsorption by ITC against the van't Hoff procedure [18].

Figure 1 shows the plots of the cumulative enthalpy of displacement, $\Delta_{dpl}H_{cum}$, as a function of the relative solute adsorption onto γ -alumina from single-solute solutions. Note that the relative solute adsorption was calculated by dividing the adequate amount adsorbed by its maximum value measured in the concentration range studied, according to the data reported in the previous article [12]. The relative adsorption scale has been chosen to draw all enthalpy curves on one graph with the same x-axis for comparison. Otherwise, the absolute adsorption ranges are quite different for various systems, namely up to: 0.092 mmol g⁻¹, cobalt; 0.017 mmol g⁻¹, acetates; 0.14 mmol g⁻¹, citrates. Moreover, the differential enthalpy values indicated in Fig.1 have been inferred from the plots of $\Delta_{dpl}H_{cum}$ against the absolute quantity of adsorption (expressed in mmol g⁻¹).

In the case of cobalt cations and citrate anions, the displacement phenomenon appears exothermic (i.e., negative $\Delta_{dpl}H_{cum}$ values) in the whole adsorption range. Even though the enthalpy of displacement cannot be practically decomposed into individual enthalpy terms, the most plausible explanation here is that the strong solute-surface interaction is dominant over all other contributions. Furthermore, the enthalpy curves take the form of straight lines and a change in the slope is observed for higher adsorption values, particularly visible for citrates.

The linearity of $\Delta_{dpl}H_{cum}$ vs. adsorption plots gives a strong indication that the partial mechanisms provide rather constant contributions to the total enthalpy. Each slope value is related to the differential molar enthalpy of displacement, thus giving an idea about the intensity of solute-surface interactions [23]. The method of least squares for fitting straight lines to experimental data has been employed and the resulting differential enthalpy values are as follows (together with the maximum measurement uncertainty): $-1.5 \pm 0.2 \text{ kJ mol}^{-1}$ and $-12.4 \pm 1.9 \text{ kJ mol}^{-1}$ for Co(II); $-12.5 \pm 1.9 \text{ kJ mol}^{-1}$ and $-25.4 \pm 3.8 \text{ kJ mol}^{-1}$ for citrates.

The exothermic character of the competitive adsorption of cobalt or citrate species is consistent with the hypothesis of the formation of inner-sphere complexes induced by strong specific interactions between $\text{Co}(\text{H}_2\text{O})_6^{2+}$ or $\text{C}_6\text{H}_5\text{O}_7^{3-}$ ions and the surface of $\gamma\text{-Al}_2\text{O}_3$ [12]. It is worth noting that the cumulative enthalpy of displacement is much more negative for citrate anions than that of cobalt cations. Since the pH conditions are not far from the point of zero charge of the solid sample, the sign and the density of the surface charge may vary according to the charge regulation mechanism. In consequence, the retention of both cations and anions on the surface is possible. Besides the difference in affinity for solid surface between the two types of ions, the proton release to the equilibrium aqueous phase accompanying the retention of cobalt cations or the proton uptake paralleling the adsorption of citrate anions obviously contribute, in an opposite manner, to the overall enthalpy effect. Indeed, for mineral oxides, the formation of negative surface charge by desorption of protons from surface hydroxyl groups is endothermic, whereas the surface protonation is exothermic [24]. Furthermore, partial dehydration of a cobalt cation upon adsorption is certainly more endothermic than that of a citrate anion, firstly, due to the presence of a hydrophobic moiety in the latter and, secondly, because cations are generally characterized by much higher enthalpies of hydration compared to anions [25].

The change in the slope of the linear plot of $\Delta_{dpl}H_{cum}$ against the relative solute adsorption occurs at a relative value of 0.48 (i.e., 0.086 mmol g⁻¹) for Co(II) and 0.54 (i.e., 0.093 mmol g⁻¹) for citrates. Beyond these limit values, the intensity of the exothermic character of the competitive adsorption greatly increases for both types of species. This may suggest the formation of multi-dentate surface complexes within the ionic double layer. According to the literature of the subject [26], divalent cobalt cations are capable of forming mono- and bidentate inner-sphere complexes with negatively charged surface hydroxyl groups, whereas trivalent citrate anions may be attached to the alumina surface by means of one or two carboxyl groups and a hydroxyl one.

The precise mode of ion binding to the surface has a very important impact on the eventual formation of ternary surface complexes in bi-solute systems. In view of further discussion, it should be mentioned here that the existence of bidentate cobalt and tridentate citrate complexes on the solid surface would diminish the bridging capacity of the adsorbate species and thus greatly reduce the occurrence of ternary surface complexes.

The case of monovalent acetate anion, C₂H₃O₂⁻, appears somewhat more complicated to rationalize. Firstly, the displacement phenomenon is endothermic in a relative adsorption range up to 0.31 (i.e., 0.013 mmol g⁻¹). Here, the differential molar enthalpy of displacement is +8.7 ± 1.3 kJ mol⁻¹. The observed endothermic character of the overall displacement phenomenon points out rather weak acetate binding to the surface γ -Al₂O₃, which is in line with the formation of outer-sphere surface complexes, as has been envisaged previously [12]. It seems likely that the exothermic effect of hydrogen bonding of acetate anions at a greater distance of approach to the alumina surface is over-compensated by some endothermic phenomena, which also result in an increase in the entropy of the system. These endothermic phenomena may be related to: (i) the displacement of some other anionic species (e.g., hydroxide anions) from the interface so as to maintain the electroneutrality of the ionic double

layer and (ii) the displacement of vicinal water necessary for the formation of a cavity to make space for an oncoming acetate anion. Additionally, each acetate moiety in outer-sphere complexes may potentially induce an endothermic deprotonation of a surface hydroxyl, since it has been proven to be capable of capturing a proton from the surface group to form an acid molecule [27].

Then, the slope of the linear plot surprisingly changes from positive to negative with the concomitant change in the differential molar enthalpy of displacement from $+8.7 \pm 1.3$ to -23.8 ± 3.6 kJ mol⁻¹. The hypothesis of adsorption via inner-sphere complexation becomes plausible here, especially in the light of the conclusions drawn from density functional theory calculation of surface complexation of acetate on aluminosilicate surfaces: in addition to the covalent bonding of one carboxylate oxygen to a surface aluminium atom, the other oxygen atom may either form another covalent bond with the same Al atom or interact via hydrogen-bonding with a surface OH group attached to this surface atom [27].

3.2. Enthalpy effects of displacement in bi-solute systems

In the case of adsorption from bi-solute solution onto γ -alumina, the data processing becomes more difficult on account of the occurrence of Co-ligand complexes already in the aqueous phase before it enters into contact with the solid surface. Therefore, the enthalpy effects of dilution for any aqueous solution containing equimolar quantities of Co(II) and ligand species may also include a contribution coming from the dilution of these complexes. The adequate Co-ligand speciation diagrams simulated with a Medusa modelling software (e.g., see Supplementary Material section in the previous article [12]) have revealed the presence of the following predominant species in the pH range applied for each Co-ligand pair: $\text{Co}(\text{H}_2\text{O})_6^{2+}$ but also $\text{Co}(\text{CH}_3\text{COO})^+$ to a much smaller extent (up to 30%) for the cobalt-acetate systems, $\text{Co}(\text{C}_6\text{H}_5\text{O}_7)^-$ for the cobalt-citrate systems. As a consequence of this complexation in the bi-

solute systems, the stock solution placed in the micro-syringe, the solution collected in the calorimetric cell after each injection during the dilution experiment, or the supernatant solution remaining in equilibrium with the currently adsorbed species onto solid particles during the adsorption experiment may contain some quantity of Co-ligand complex in addition to free cobalt or ligand species.

The knowledge of dissociation constants (K_d) in the systems studied is thus necessary to extract the concentration of free and complex species from the overall concentrations of cobalt and ligand in various solutions. Figure 2 presents the results of additional ITC experiments carried out to determine the heat of successive injections of a Co-containing stock solution into a ligand-containing aqueous solution placed in the calorimetric cell. Here the so-obtained heats of injection are plotted as a function of the Co-to-ligand molar ratio. The experimental heat values were fitted to the independent site binding model by using NanoAnalyze™ Software offered by TA Instruments, thus leading to the determination of the equilibrium dissociation constants for both types of Co-ligand complex. The best fitting curves are shown in Fig. 2 together with the resulting dissociation constants: $K_d = 4.2(\pm 0.3) \times 10^{-2}$ mol L⁻¹ for the Co-acetate system; $K_d = 2.7(\pm 0.2) \times 10^{-5}$ mol L⁻¹ for the Co-citrate system.

On the basis of the partial concentrations of free and complex species, it was possible to determine the corresponding dilution effects contributing to the total enthalpy change recorded in each displacement experiment with the use of a bi-solute solution (see section S2 in Supplementary material). The cumulative enthalpies of displacement corrected for dilution effects have been collected in Fig. 3. They are plotted on the relative adsorption scale constructed by dividing the sum of the quantities of cobalt and ligand adsorption by its maximum value obtained in the concentration range studied [12]. Since cobalt is a common component of the two bi-solute systems, the variations of $\Delta_{dpl}H_{cum}$ recorded upon its adsorption from single-solute solution have been added to Fig. 3 for comparison purposes.

In order to rationalise these experimental results on more theoretical grounds, two alternative hypotheses are compared here: (1) *independent adsorption* of both components on the solid surface and (2) *co-operative adsorption* of the two components. To a first approximation, the assumption of the additivity of enthalpy contributions given individually by each solute component to the total displacement effect has been taken as a starting point for comparison. In consequence, the theoretical enthalpy of displacement in a bi-solute system may be calculated from the following expression:

$$\Delta_{dpl}H_{cum}^{12} = \Delta_a n_{Co}^{12} \cdot \Delta_{dpl}h_{Co}^{12} + \Delta_a n_L^{12} \cdot \Delta_{dpl}h_L^{12} \quad (1)$$

where $\Delta_a n_{Co}^{12}$ and $\Delta_a n_L^{12}$ correspond to the quantities of individual adsorption for cobalt and ligand, respectively, onto γ -alumina in the bi-solute system (taken from the appropriate experimental curves), $\Delta_{dpl}h_{Co}^{12}$ and $\Delta_{dpl}h_L^{12}$ denote the molar enthalpies of displacement accompanying the adsorption of each solute from bi-solute solutions. The latter may be approximated by the molar enthalpies of displacement measured in single-solute systems (i.e., the slopes of the various linear segments in Fig.1) or they may be calculated from the comparison between the experimental enthalpy values and those obtained by imposing a particular mode of ligand and metal attachment to the surface of γ -alumina.

In the two bi-solute systems, the displacement is clearly an exothermic process in line with the exothermic effects accompanying the attachment of cobalt and citrate species from single solute solutions and contrary to the endothermic effects when acetates alone form outer-sphere complexes on the oxide surface. Within the framework of the *hypothesis of independent adsorption*, the enthalpy contribution due to the ligand, $\Delta_{dpl}h_L^{12}$, should be thus negative for Eq. 1 to reproduce correctly the negative values of $\Delta_{dpl}H_{cum}$. Nevertheless, further data analysis has revealed that none of the combinations based on the slopes of the linear segments in Fig.1 can reproduce well the experimental results in the whole adsorption range. Figure 4 illustrates the lack of concordance between $\Delta_{dpl}H_{cum}^{12}$ and $\Delta_{dpl}H_{cum}$ for the cobalt-citrate

system in which the metal and ligand ions seem to adsorb in an independent manner only in the very beginning (at the most, the two first points on the enthalpy curve). The theoretical enthalpy values become far too negative for further points, (i.e., the exothermic character of the phenomenon is greatly overestimated).

The enthalpy modelling on the basis of the *hypothesis of the co-operative adsorption* has been more successful, as illustrated in Fig. 4. Indeed, the differences between the two types of enthalpy values are within experimental error for most experimental points. Here the theoretical enthalpy of displacement is obtained by imposing firstly a particular mode of attachment to the surface of γ -alumina via the metal (or ligand) and calculating its contribution to the experimental enthalpy of displacement as $\Delta_a n_{Co}^{12} \cdot \Delta_{dpl} h_{Co}^1$ (or $\Delta_a n_L^{12} \cdot \Delta_{dpl} h_L^2$), where $\Delta_{dpl} h_{Co}^1$ (or $\Delta_{dpl} h_L^2$) is taken as corresponding to the first or the second linear segment of the enthalpy curve in Fig. 1. The procedure applied to determine the quantities of adsorption $\Delta_a n_{Co}^{12}$ and $\Delta_a n_L^{12}$ from the individual adsorption isotherms in the bi-solute systems is detailed in Supplementary material (see section S2). Then an estimation of the molar enthalpy contribution for the other solute, i.e., $\Delta_{dpl} h_L^{12}$ or $\Delta_{dpl} h_{Co}^{12}$, is deduced directly from Eq.1 developed for $\Delta_{dpl} H_{cum}$ determined experimentally. For example, when considering the direct metal attachment to the oxide surface as the starting hypothesis, one can obtain for the ligand enthalpy contribution in the bi-solute system:

$$\Delta_{dpl} h_L^{12} = \frac{\Delta_{dpl} H_{cum} - \Delta_a n_{Co}^{12} \cdot \Delta_{dpl} h_{Co}^1}{\Delta_a n_L^{12}} \quad (2)$$

Nevertheless, the question arises as to whether these simplified models can explain the observed behaviour of each metal-ligand couple in an adequate way.

The case of cobalt-acetate couple is considered first. The best fitting model was related to the *hypothesis of co-operative adsorption* and it took into account the bridging role of the cobalt species directly attached to the solid surface. The theoretical metal contribution to the

total enthalpy of displacement recorded in the cobalt-acetate system was fixed at a value equal to the differential enthalpy corresponding to the first linear segment of the enthalpy curve in Fig. 1, i.e., $\Delta_{dpl}h_{Co}^{12} = -1.5 \text{ kJ mol}^{-1}$. The fitting of Eq. 1 to the $\Delta_{dpl}H_{cum}$ data resulted in a theoretical ligand contribution, $\Delta_{dpl}h_L^{12}$, being equal to about $-7.5 \pm 1.2 \text{ kJ mol}^{-1}$ over the whole $\Delta_a n_L^{12}$ interval. Figure 4 shows that there is quite good concordance between the experimental $\Delta_{dpl}H_{cum}$ and theoretical $\Delta_{dpl}H_{cum}^{12}$ values.

It is worth noting that the stock solution used in the present calorimetry experiments has allowed the following maximum amounts adsorbed to be obtained: 0.086 mmol g⁻¹ for Co (i.e., the end of the first linear segment of the enthalpy curve in Fig. 1) and 0.071 mmol g⁻¹ for acetates. Within these adsorption ranges, the individual adsorption of the metal does not show much change compared to the single-solute system (see the inset graph in Fig. 3). Furthermore, the pH of the solid suspension is practically the same as that observed when only cobalt is present in the aqueous phase. Hence there should not be much difference in the cobalt interaction with the surface of γ -alumina between the two types of system and it is realistic to postulate the mono-dentate scheme of the metal attachment to the surface. On the other side, the individual adsorption of acetate anions is greatly enhanced compared to the single solute system. The ratio between the amounts in moles of cobalt and the ligand adsorbed on the oxide surface is on average close to 1.3 and it hardly changes over the adsorption range studied. All of this suggests that one ligand unit is bound preferentially to more than one adsorbed cobalt cations. Nevertheless, the negative value of $\Delta_{dpl}h_L^{12}$ is not fully consistent with the previously established image of a ternary surface complex of type A having a stoichiometry of 1:1 in which the ligand does not interact directly with the solid surface. The comparison with the two characteristic enthalpy values reported in Fig. 1 for acetate species alone in the aqueous phase gives an indication that acetate units interact additionally with some neighbouring surface sites. Such an interaction should not be of electrostatic type and thus imply changes in the pH of the

suspension. Already considered in the previous section, hydrogen bonding between acetate units and surface OH groups may be advanced in order to account for this effect.

The case of cobalt-citrate couple is different. First of all, the maximum quantities of adsorption attained in this system are equal to 0.333 and 0.235 mmol g⁻¹ for cobalt and citrates, respectively. These adsorption ranges extend far beyond the maximum adsorption values recorded in the corresponding single-solute systems and thus the individual adsorption of both the metal and the ligand is greatly enhanced in the bi-solute system (e.g., see the adsorption curve for cobalt in the inset of Fig. 3). The best fitting models predict the direct attachment to the γ -Al₂O₃ surface for all citrate anions and, at least, 30% of the cobalt cations. The two solutes should thus interact independently with the appropriate surface sites in accordance with the local electric charge of the γ -alumina surface and this explains why the pH of the solid suspension lies somewhere between the values observed when only cobalt or citrate species are present in the aqueous phase [12].

Up to the second point on the enthalpy curve ($\Delta_a n_{Co}^{12} = 0.99$ mmol g⁻¹ and $\Delta_a n_L^{12} = 0.077$ mmol g⁻¹), the metal and ligand ions are regarded as being adsorbed fully independently, with the differential molar enthalpies of displacement corresponding to the first linear segments in Fig. 1. Then, the best fitting model based on the hypothesis of cooperative adsorption foresees the formation of a ternary complex having a stoichiometry of 1:1 (i.e., one cobalt cation for each citrate anion). To construct this model, the theoretical molar enthalpy contribution due to citrate has been taken as being equal to -12.5 kJ mol⁻¹ (i.e., the first linear segment in Fig. 1). When applying Eq. 1, the individual enthalpy contribution ascribed to cobalt involved in these complexes is about $+10.5 \pm 1.6$ kJ mol⁻¹. In line with the endothermic displacement effects observed in this work for the formation of outer-sphere complexes in the single-solute systems, this molar enthalpy value at least suggests that the corresponding cobalt species are retained at a farer distance from the solid surface. Such particular modes of cobalt and ligand adsorption

onto γ -alumina may be interpreted to be consistent with the formation of a ternary complex of type B in which citrate anions form the bidentate inner-sphere complexes, thereby providing negative sites for binding cobalt cations [12]. Given the stoichiometry of such a ternary complex, its formation represents an exothermic process with a total enthalpy balance of about -2 kJ mol^{-1} . Additional cobalt species (almost 0.1 mmol g^{-1} at the end of the adsorption range studied here) appear to bind to the surface by forming bidentate inner-sphere complexes. It is important to note that the enthalpy value imposed for this attachment (i.e., $\Delta_{dpl}h_{Co}^{12} = -12.4 \text{ kJ mol}^{-1}$) is of the same order of magnitude as that of citrate anion alone and much more negative than that of the ternary complex. For this reason, it is understandable that some cobalt cations continue to adsorb on adequate binding sites even in the presence of citrate species. Note that the formation of the bidentate inner-sphere complexes prevents the construction of solid-metal-ligand structures on the γ -alumina surface.

4. Conclusion

By applying the isothermal titration calorimetry (ITC) for a determination of the cumulative enthalpy of displacement, $\Delta_{dpl}H_{cum}$, as a function of the quantity of adsorption of cobalt cations and acetate or citrate anions onto γ -alumina from single-solute and equimolar bi-solute solutions in water, a net progress in the description of the co-operative adsorption effects could be achieved. In the case of single-solute systems, the apparent linearity of the enthalpy plots in two successive intervals was firstly interpreted as an indication of the formation of inner-sphere (exothermic) and outer-sphere (endothermic) surface complexes. Based on the resulting differential enthalpy values, a simple modelling was proposed to rationalise the experimental results in the two bi-solute systems where the displacement appeared to be an exothermic process in the whole adsorption range studied. The mono-dentate scheme of the metal attachment to the surface in the cobalt-acetate system was considered to be hardly

perturbed in comparison with that observed when the metal was retained from the single-solute solution. This provided the positively charged binding sites for the ligand units which additionally interacted with some electrically neutral binding sites on the γ -alumina surface. In the case of cobalt-citrate system, the metal and the ligand units were postulated to adsorb independently in the range of low adsorption values. Then the two solutes likely formed the ternary surface complexes having a stoichiometry of 1:1, with only the ligand units being attached directly to the oxide surface. Other cobalt cations were envisaged to form bidentate inner-sphere complexes.

The picture above constitutes a much more detailed description of the phenomenon in the range of low and moderate quantities of adsorption compared to that gained previously from the data analysis, relying mostly on the adsorption isotherms, pH changes, and potentiometric titration curves.

CRedit Author Statement

Mouhamad Ali Ahmad: investigation, data curation. **Benedicte Prelot:** conceptualization, project administration, methodology, supervision. **Jerzy Zajac:** methodology, visualization, writing-reviewing, editing.

Acknowledgment

The authors greatly acknowledge the financial support of this work by the ANR SLIMCAT project ‘Solid-Liquid Interface at Molecular-scale for Catalysis’ (ANR-14-CE08-0019).

Supplementary Material: The online version of this article contains supplementary data, which are available to authorized users.

Captions to Figures

Fig. 1 Variations of the cumulative enthalpy of displacement accompanying the individual adsorption of cobalt (circles) and anionic ligands onto γ -alumina from single-solute aqueous solutions at 298 K under the unadjusted pH condition: acetates (stars) and citrates (triangles). The numbers represent the differential molar enthalpy of displacement (in kJ mol^{-1}) corresponding to each of the two linear parts (dashed lines) of the enthalpy curve; the non-zero values of y-intercepts are given in brackets. The inset shows the related individual adsorption isotherms published previously [12]; the dashed horizontal lines mark the upper limits of the adsorption range covered here by the enthalpy data for each system.

Fig. 2 ITC heat data corresponding to successive injections of a Co-containing stock solution into a ligand-containing aqueous solution placed in the calorimetric cell at 298 K; the solute concentrations, respectively, in the syringe and in the cell are as follows: 2 mol L^{-1} Co and 300 mmol L^{-1} acetate solutions (upper panel), 60 mmol L^{-1} Co and 5 mmol L^{-1} citrate solutions (lower panel). The two dissociation constants, K_d , obtained by fitting the heat experimental values (filled circles) to the independent site binding model (solid lines) are indicated.

Fig. 3 Variations of the cumulative enthalpy of displacement accompanying the solute adsorption onto γ -alumina from single-solute and bi-solute aqueous solutions at 298 K under the unadjusted pH condition: cobalt alone (circles), cobalt-acetate (stars), and cobalt-citrate (triangles). The inset shows the individual isotherms of cobalt adsorption from single solute (circles) and bi-solute (stars and triangles) solutions [12]; the dashed horizontal lines mark the upper limits of the metal adsorption range covered here by the enthalpy data for each system.

Fig. 4 Comparison between the experimental enthalpy values, $\Delta_{dpl}H_{cum}$, measured for cobalt-acetate (stars) or cobalt-citrate (triangles) systems and the theoretical ones, $\Delta_{dpl}H_{cum}^{12}$, corresponding to the best results of enthalpy modelling on the basis of Eq. 1: *independent adsorption model* (circles connected by dash-dot lines drawn to guide the eye), *co-operative adsorption model* (circles connected by dash lines drawn to guide the eye). The uncertainty in the enthalpy measurement is represented by error bars. The enthalpy values shown inside the panel indicate the differential molar enthalpy of displacement (in kJ mol^{-1}) for ligand or cobalt imposed or estimated in the numerical calculations.

References

- [1] T. Maunula, J. Ahola, H. Hamada, Reaction mechanism and kinetics of NO_x reduction by propene on CoO_x/alumina catalysts in lean conditions, *Applied Catalysis B: Environmental*, 26 (2000) 173-192. [https://doi.org/10.1016/S0926-3373\(00\)00118-1](https://doi.org/10.1016/S0926-3373(00)00118-1)
- [2] M.-f. Luo, X.-x. Yuan, X.-m. Zheng, Catalyst characterization and activity of Ag–Mn, Ag–Co and Ag–Ce composite oxides for oxidation of volatile organic compounds, *Applied Catalysis A: General*, 175 (1998) 121-129. [https://doi.org/10.1016/S0926-860X\(98\)00210-5](https://doi.org/10.1016/S0926-860X(98)00210-5)
- [3] H. Topsøe, B.S. Clausen, N.-Y. Topsøe, P. Zeuthen, Progress in the Design of Hydrotreating Catalysts Based on Fundamental Molecular Insight, in: D.L. Trimm, S. Akashah, M. Absi-Halabi, A. Bishara (Eds.) *Studies in Surface Science and Catalysis*, vol., Elsevier, 1989, pp. 77-102. [https://doi.org/10.1016/S0167-2991\(08\)61061-7](https://doi.org/10.1016/S0167-2991(08)61061-7)
- [4] R. Bechara, D. Balloy, D. Vanhove, Catalytic properties of Co/Al₂O₃ system for hydrocarbon synthesis, *Applied Catalysis A: General*, 207 (2001) 343-353. [http://doi.org/10.1016/S0926-860X\(00\)00672-4](http://doi.org/10.1016/S0926-860X(00)00672-4)
- [5] M.E. Dry, Practical and theoretical aspects of the catalytic Fischer-Tropsch process, *Applied Catalysis A: General*, 138 (1996) 319-344. [http://doi.org/10.1016/0926-860X\(95\)00306-1](http://doi.org/10.1016/0926-860X(95)00306-1)
- [6] A.A. Adesina, Hydrocarbon synthesis via Fischer-Tropsch reaction: travails and triumphs, *Applied Catalysis A: General*, 138 (1996) 345-367. [http://doi.org/10.1016/0926-860X\(95\)00307-X](http://doi.org/10.1016/0926-860X(95)00307-X)
- [7] J. Hu, F. Yu, Y. Lu, Application of Fischer–Tropsch Synthesis in Biomass to Liquid Conversion, *Catalysts*, 2 (2012) 303-326. <https://doi.org/10.3390/catal2020303>
- [8] A. Jean-Marie, A. Griboval-Constant, A.Y. Khodakov, F. Diehl, Influence of sub-stoichiometric sorbitol addition modes on the structure and catalytic performance of alumina-supported cobalt Fischer–Tropsch catalysts, *Catalysis Today*, 171 (2011) 180-185. <http://doi.org/10.1016/j.cattod.2011.04.002>
- [9] J.S. Girardon, E. Quinet, A. Griboval-Constant, P.A. Chernavskii, L. Gengembre, A.Y. Khodakov, Cobalt dispersion, reducibility, and surface sites in promoted silica-supported Fischer–Tropsch catalysts, *Journal of Catalysis*, 248 (2007) 143-157. <http://doi.org/10.1016/j.jcat.2007.03.002>
- [10] J.-F. Boily, J.B. Fein, Experimental study of cadmium-citrate co-adsorption onto α -Al₂O₃, *Geochimica et Cosmochimica Acta*, 60 (1996) 2929-2938. [http://doi.org/10.1016/0016-7037\(96\)00131-7](http://doi.org/10.1016/0016-7037(96)00131-7)
- [11] J.A. Davis, Complexation of trace metals by adsorbed natural organic matter, *Geochimica et Cosmochimica Acta*, 48 (1984) 679-691. [http://doi.org/10.1016/0016-7037\(84\)90095-4](http://doi.org/10.1016/0016-7037(84)90095-4)
- [12] M. Ali Ahmad, J. Zajac, B. Prelot, The effect of chelating anions on the retention of Co(II) by γ -alumina from aqueous solutions under the unadjusted pH condition of supported catalyst preparation, *Journal of Colloid and Interface Science*, 535 (2019) 182-194. <https://doi.org/10.1016/j.jcis.2018.09.091>
- [13] P.W. Schindler, Co-adsorption of metal ions and organic ligands; formation of ternary surface complexes, in: J. M. F. Hochella, A. F. White (Ed.) *Mineral-water interface geochemistry*, *Reviews in Mineralogy and Geochemistry*, vol. 23, Mineralogical Society of America, Washington, DC, 1990, pp. 281-307.
- [14] J.B. Fein, The effects of ternary surface complexes on the adsorption of metal cations and organic acids on mineral surfaces, in: R. Hellmann, S. A. Wood (Ed.) *Water-Rock Interactions, Ore Deposits, and Environmental Geochemistry - A Tribute to David A. Crerar*, vol. Special Publication No.7, The Geochemical Society, St. Louis, Missouri, USA, 2002, pp. 365-378.
- [15] B. Prelot, S. Lantenois, M.-C. Charbonnel, F. Marchandeu, J.M. Douillard, J. Zajac, What are the main contributions to the total enthalpy of displacement accompanying the adsorption

- of some multivalent metals at the silica–electrolyte interface?, *Journal of Colloid and Interface Science*, 396 (2013) 205-209. <https://doi.org/10.1016/j.jcis.2012.12.049>
- [16] B. Prelot, S. Lantenois, C. Chorro, M.-C. Charbonnel, J. Zajac, J.M. Douillard, Effect of nanoscale pore space confinement on cadmium adsorption from aqueous solution onto ordered mesoporous silica: a combined adsorption and flow calorimetry study, *The Journal of Physical Chemistry C*, 115 (2011) 19686-19695. <http://doi.org/10.1021/jp2015885>
- [17] B. Prelot, M. Araïssi, P. Gras, F. Marchandea, J. Zajac, Contribution of calorimetry to the understanding of competitive adsorption of calcium, strontium, barium, and cadmium onto 4A type zeolite from two-metal aqueous solutions, *Thermochimica Acta*, 664 (2018) 39-47. <https://doi.org/10.1016/j.tca.2018.04.006>
- [18] S.G. Lanas, M. Valiente, E. Aneggi, A. Trovarelli, M. Tolazzi, A. Melchior, Efficient fluoride adsorption by mesoporous hierarchical alumina microspheres, *RSC Advances*, 6 (2016) 42288-42296. <http://dx.doi.org/10.1039/C5RA27371D>
- [19] B. Prelot, I. Ayed, F. Marchandea, J. Zajac, On the real performance of cation exchange resins in wastewater treatment under conditions of cation competition: the case of heavy metal pollution, *Environmental Science and Pollution Research*, 21 (2014) 9334-9343. <http://doi.org/10.1007/s11356-014-2862-3>
- [20] S. Builes, S.I. Sandler, R. Xiong, Isosteric Heats of Gas and Liquid Adsorption, *Langmuir*, 29 (2013) 10416-10422. <http://doi.org/10.1021/la401035p>
- [21] I. Anastopoulos, G.Z. Kyzas, Are the thermodynamic parameters correctly estimated in liquid-phase adsorption phenomena?, *Journal of Molecular Liquids*, 218 (2016) 174-185. <http://doi.org/10.1016/j.molliq.2016.02.059>
- [22] U. Zafar, M.A. Bhatti, A. Akram, Kinetics and Thermodynamics Studies of Cobalt (II) Adsorption onto Alumina, 2018, 19 (2018) 11. <http://doi.org/10.21743/pjaec/2018.06.05>
- [23] C.J. Penn, J.M. Gonzalez, I. Chagas, Investigation of Atrazine Sorption to Biochar With Titration Calorimetry and Flow-Through Analysis: Implications for Design of Pollution-Control Structures, *Frontiers in Chemistry*, 6 (2018). 10.3389/fchem.2018.00307
- [24] W.H. Casey, Enthalpy Changes for Brønsted Acid-Base Reactions on Silica, *Journal of Colloid and Interface Science*, 163 (1994) 407-419. <https://doi.org/10.1006/jcis.1994.1120>
- [25] Y. Marcus, A simple empirical model describing the thermodynamics of hydration of ions of widely varying charges, sizes, and shapes, *Biophys. Chem.*, 51 (1994) 111-127. [http://doi.org/10.1016/0301-4622\(94\)00051-4](http://doi.org/10.1016/0301-4622(94)00051-4)
- [26] K. Bourikas, C. Kordulis, J. Vakros, A. Lycourghiotis, Adsorption of cobalt species on the interface, which is developed between aqueous solution and metal oxides used for the preparation of supported catalysts: a critical review, *Advances in Colloid and Interface Science*, 110 (2004) 97-120. <https://doi.org/10.1016/j.cis.2004.04.001>
- [27] X. Liu, X. Lu, R. Wang, H. Zhou, S. Xu, Surface complexes of acetate on edge surfaces of 2:1 type phyllosilicate: Insights from density functional theory calculation, *Geochimica et Cosmochimica Acta*, 72 (2008) 5896-5907. <https://doi.org/10.1016/j.gca.2008.09.026>