

# Methodological approach for the estimation of the experimental surfactant:clay ratio in the production of large-scale organo-mineral complexes

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## INTRODUCTION

Organoclays are used in the production of nanomaterials in electronic devices, pharmaceutical and cosmetic industry, textile processes, energy, agricultural field, etc. Their relevance is motivated because of its capability to undergo tailor-surface modification by introducing organic functional moieties. Montmorillonite has been extensively the most widely used clay mineral due to its high surface area, high cation exchange capacity and expansive properties. The hydrophilic surface of this mineral can be fully or partially changed to hydrophobic by adsorption of cationic surfactants, usually of the quaternary alkylammonium cation type (QACs). On an industrial scale, it is necessary to use in its production a methodology that allows to establish a priori the surfactant:clay mineral ratios to be used to obtain the expected surfactant loading, in the sorption processes used. This work shows a methodology based on the Scatchard-Langmuir equation.

## MATERIALS AND METHODS

The QACs selected were octadecyltrimethylammonium (ODTMA), didodecyldimethylammonium (DDAB), dodecyldimethylammonium (DAB), hexadecyltrimethylammonium chloride (HDTMA) and benzalkonium chloride (BK). A sodium bentonite provided by Clariant Iberica, with a CEC of 0.8 mmol/g, was used. Sorption isotherms of the surfactants on the clay were carried out in triplicate by mixing 15 mL of solutions of each one (0-10 mM) prepared in distilled water with 24 mg of clay. After shaking for 24 h at 20 °C, the suspensions were centrifuged at 12000 g for 10 min, the pellets were dry-frozen and the analyte content determined by elemental analysis of C and N by using a LECO CHNS micro analyser (model TRUSPEC). Modeling of the sorption isotherm was performed by using the Langmuir-Scatchard equation:

$$\frac{L_0 - L}{L} = \frac{R_0 * K}{1 + K * L}$$

where  $L_0$  and  $L$  denote the molar concentration of total and free surfactant, respectively,  $R_0$  is the molar concentration of sorption sites and  $K$  is the binding coefficient.

## RESULTS AND DISCUSSION

The fit to the experimental data using the Langmuir-Scatchard equation was very good, with  $R^2$  values ranging between 0.85 and 0.98 (Fig. 1). This theoretical model estimates that there is homogeneity in the adsorption sites and formation of a monolayer resulting in their saturation. This requires an estimation of  $R_0$  which is obtained experimentally through the value reached in the adsorption plateau. Once this data is fixed, the value of  $K$  can be easily calculated. With both parameters, the theoretical value can be predicted for other surfactant:clay ratios of those previously used, depending on the loading to be obtained (Table 1). This is crucial to determine in reaction tanks the amount and feasibility of production of organo-mineral complexes.

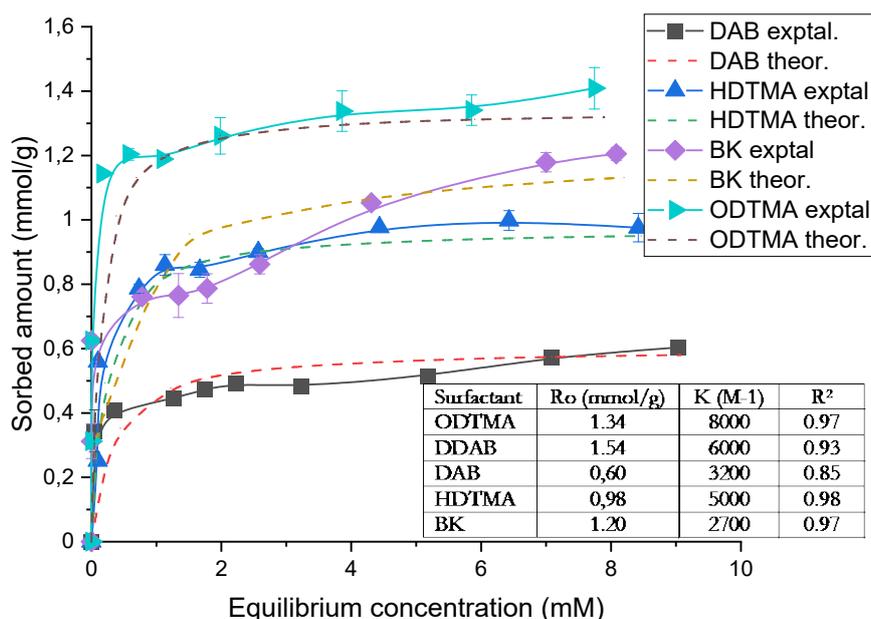


Fig. 1. Sorption isotherms of QACs on bentonite and their modeling. Fitting data included.

The fit of the experimental data to the model does not guarantee that the assumptions of the model are being fulfilled. The adsorption of surfactants above the cation exchange capacity is associated with a state in which after adsorption of molecules by electrostatic interactions with the negatively charged sites of the clay, additional molecules are adsorbed by hydrophobic interactions on pre-adsorbed surfactant molecules. Both processes are each described by a different binding coefficient:  $K_1$  describes the electrostatic reactions while  $K_2$  describes the hydrophobic interactions. Such binding coefficients were determined for HDTMA ( $K_1=2000 \text{ M}^{-1}$ ;  $K_2=50 \text{ M}^{-1}$ ) and ODTMA ( $K_1=8000 \text{ M}^{-1}$ ;  $K_2=200 \text{ M}^{-1}$ ) (Mishael et al., 2002). In addition, adsorption resulted in different loadings on the clay depending on whether the surfactant was adsorbed as a monomer or micelles.

Surfactant	Clay conc. (g/L)	Surf. conc. (g/L)	Theor loading (mmol/g)	Exptal loading (mmol/g)
DAB	36	4.4	0.37	0.38
DDAB	10	4.0	1.20	1.42
HDTMA	15	14	0.81	0.93
ODTMA	5	1.5	0.73	0.77
BK	10	4.5	1.03	1.19

Table 1. Experimental and predicted loading of surfactants on bentonite by using different ratios to those used in the determination of the fitting parameters.

## CONCLUSIONS

A methodological approach was established for obtaining clay-surfactant complexes at the expected loading, even though the procedure is a mathematical artifact since the model assumptions are not actually given. Spectroscopic evidence should be obtained to determine the mechanistic operating.

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## REFERENCES

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