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A STUDY ON THE ADHESION OF ANCHORING GROUPS TO PIGMENT SURFACES

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Abstract A method is described for the comparison of the adhesion of anchoring groups to pigment or filler surfaces, using simple model compounds. Energies of adsorption and the amount of anchoring groups per gram of pigment can be estimated.

1. INTRODUCTION

The development of dispersants for pigments and fillers in paints, or solid matrices like plastics or rubber, requires knowledge about anchoring groups, i.e. groups having a strong affinity to the pigment surface and thus connecting the dispersant molecule to the pigment or filler particles.

Anchoring groups are usually selected by trial and error. Dispersants bearing different groups are prepared and tested in the selected systems. This is a cumbersome and time-consuming procedure. Moreover, if a dispersant fails in a given system, it is not always clear why it fails: insufficient anchoring, insufficient stabilization or some other

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cause. Therefore, a more effective method for selection of anchoring groups would allow a more focused development of pigment dispersants.

In this paper we describe a method which allows an easy comparison of pigment/anchoring-group combinations without the preparation and testing of pigment dispersants. We measured the adsorption of model compounds from an aqueous solution[*] onto a pigment surface. These model compounds consisted of an anchoring group X and an ethyl tail. So propionic acid, ethane sulfonic acid, ethyl amine, etc. were used to test the anchoring properties of the carboxylic-acid group, the sulfonic-acid group and the amino group, respectively. It was assumed that the small ethyl tail has only a minor effect on adsorption. Moreover, as the ethyl group is kept constant throughout the investigation, a direct comparison of anchoring groups is always possible, even though the absolute results may be slightly incorrect due to the effect of the ethyl rest.

The method has been described before (Ref. 1) for transparent iron oxide, but has been extended here to other pigments.

2. ANCHORING

2.1 Theory of adsorption

If a solution of a model compound M in a solvent S is brought into contact with a surface, e.g. a pigment surface P, both solvent and model compound will adsorb onto this surface. After some time an equilibrium (with equilibrium constant K_{ads}) will develop between the adsorbed and the free model compound:

$$M + PS \rightleftharpoons PM + S \qquad (1)$$

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[*] Although we used water as a "solvent" in this investigation, there is probably no reason not to do similar measurements with solutions in organic solvents.

$$K_{ads} = \frac{[PM]*[S]}{[PS]*[M]} \tag{2}$$

where PS and PM are molecules of the solvent S and the model compound M, respectively, adsorbed on the pigment surface P. It is assumed that the whole pigment surface is covered either with solvent or with model compound, so that

$$[PM] + [PS] = [P_{sat}] \tag{3}$$

The value of K_{ads} will of course depend on the nature of both the anchoring group, the solvent and the pigment surface. Eliminating [PS] in **(2)** by means of **(3)** and rearranging the result gives the equation for the well known Langmuir isotherm:

$$\frac{[PM]}{[P_{sat}]} = \Theta = \frac{K_{ads}[M]}{K_{ads}[M] + [S]} \tag{4}$$

or

$$[M] = [S] * \frac{\Theta}{(1 - \Theta)} * \frac{1}{K_{ads}} \tag{5}$$

where

[PM] = actual concentration of the model compound at the pigment surface

$[P_{sat}]$ = maximum concentration of the model compound at the pigment surface, i.e. the concentration at full monolayer adsorption. [PM] and $[P_{sat}]$ may be expressed either in mol/gram, mol/m^2, or as a mol fraction. As they always appear as a quotient, their dimensions may be chosen, as long they are the same.

Θ = coverage of the pigment surface, i.e. the fraction of the available anchor sites occupied by the model compound ($0 \leq \Theta \leq 1$)

K_{ads} = equilibrium constant of adsorption for equilibrium **(1)**

[M] = mol fraction of the model compound in the solution

[S] = mol fraction of the solvent

2.2 Real vs. apparent adsorption

In principle K_{ads} and $[P_{sat}]$ can be determined by preparing a series of model-compound solutions of known initial mol fractions $[M_0]$, adding a known amount of the pigment and measuring the mol fraction of model compound again after the equilibrium has been settled. [PM] is then calculated from the decrease in mol fraction $[M_0] - [M]$ and the amount of pigment. The series of [PM]- and [M]-values thus obtained are fitted to the Langmuir equation **(4)**, resulting into $[P_{sat}]$ and K_{ads}.

This method has been used in our lab for several pigment/anchoring-group combinations, using the Langmuir equation or a more sophisticated one (Ref. 2). In several cases this method is too simple, however, and does not account for a number of other effects which have been found. We could improve our results considerably by accounting for the fact that when a molecule of the model compound is adsorbed, a number of solvating solvent molecules will be adsorbed as well. As a result, both model compound and solvent molecules are withdrawn from the liquid phase, and the concentration of the model compound changes in a much more complicated way than described above. It is even possible, that when much more solvent than model compound is adsorbed, the mol fraction of the model compound increases and a negative apparent adsorption is found.

The solvation of the adsorbed molecules can be accounted for by assuming that a molecule of the model compound M is coadsorbed together with n molecules of solvent S, resulting in a "molecule" PMS_n.

$$PM + n\,S \rightleftharpoons PMS_n \tag{6}$$

$$K_{solv} = \frac{[PMS_n]}{[PM]*[S]^n} \tag{7}$$

In that case the mol fraction of the adsorbed model compound [PM] in **(2)** must be replaced by the sum of adsorbed model compound [PM] and solvated adsorbed model compound $[PMS_n]$. Equations **(2)** and **(3)** then change into:

$$K_{ads} = \frac{([PM] + [PMS_n]) * [S]}{[PS] * [M]} \quad (8)$$

and $$[P_{sat}] = [PS] + [PM] + [PMS_n] \quad (9)$$

Of course this does not mean that each adsorbed molecule of the model compound forms a well defined complex with n molecules of the solvent. The model is only used to account for the fact that, apart from the model compound, a considerable amount of solvent is adsorbed as well. Similar models, using e.g. a Freundlich-type function for the coadsorption of solvent, have been used by other authors (Refs. 3, 4, 5).

From **(7)**, **(8)** and **(9)** expressions can be derived for the decrease of the mol fraction of the model compound on addition of pigment, and for [PM], [PMS$_n$], [S] and [M] as a function of K_{ads}, K_{solv}, n and the adsorption capacity A. The latter is defined as the maximum number of mols that can be adsorbed by 1 gram of pigment. Fitting of a series of values of initial concentrations [M$_0$], concentrations after adsorption [M] and the amount of pigment P to these equations allows calculation of K_{ads}, K_{solv}, n and A.

3. EXPERIMENTAL

In a typical experiment about 10 aqueous solutions of a model compound were prepared, with known concentrations in the range between 0 and 20 mmol/l. Constant amounts of these solutions were injected in an HPLC apparatus in order to prepare a calibration curve. A very good linear correlation ($R^2 > 0.99$) between the concentration and the areas under the detector curves was found in all cases.

40 grams of these standard solutions were stirred overnight with 10 grams of pigment and the pigment was removed by centrifugation. An overview of the pigments used is given in table 1. No pH adjustment was carried out, unless otherwise stated. The concentration of the model compound in the liquid phase was measured again by means of HPLC using the calibration line prepared as described above. The data were fitted to the model described above.

Table 1 Overview of the pigments used in this study

type	name	supplier
transparant iron oxide	Sicotrans Red L2816	BASF
phthalocyanine	Heliogen Blue L7101 F	BASF
carbon black	Farbruß 200	Degussa
aluminum oxide	-	Acros

4. INFORMATION FROM THE ADSORPTION MEASUREMENTS

In this chapter we work out the adsorption of the carboxylic-acid group and the amide group (i.e. the model compounds propionic acid and propionamide, respectively) to the transparent iron oxide pigment Sicotrans Red L 2816, to demonstrate which information can be obtained from the parameters K_{ads}, K_{solv}, n and A and how it can be used. In the next chapter we will give an overview of the results of all pigment-anchoring group combinations we tested.

In figure 1 the measured and the calculated **apparent** adsorption (both expressed as $\Delta[M]$) as a function of the mol fraction [M] of the model compound in the liquid phase are shown for propionic acid and propionamide, respectively. A good to fair correlation (R^2 = 0.997 and 0.888) between measured and calculated values was found.

The figure clearly shows the effect of the coadsorption of water: a Langmuir isotherm alone (or a Freundlich isotherm) could never account for the concave curve, as was found for propionic acid, or the apparently negative adsorption for propionamide. The coadsorption of water causes a dip in the apparent adsorption of propionic acid and even causes a negative apparent adsorption for propionamide.

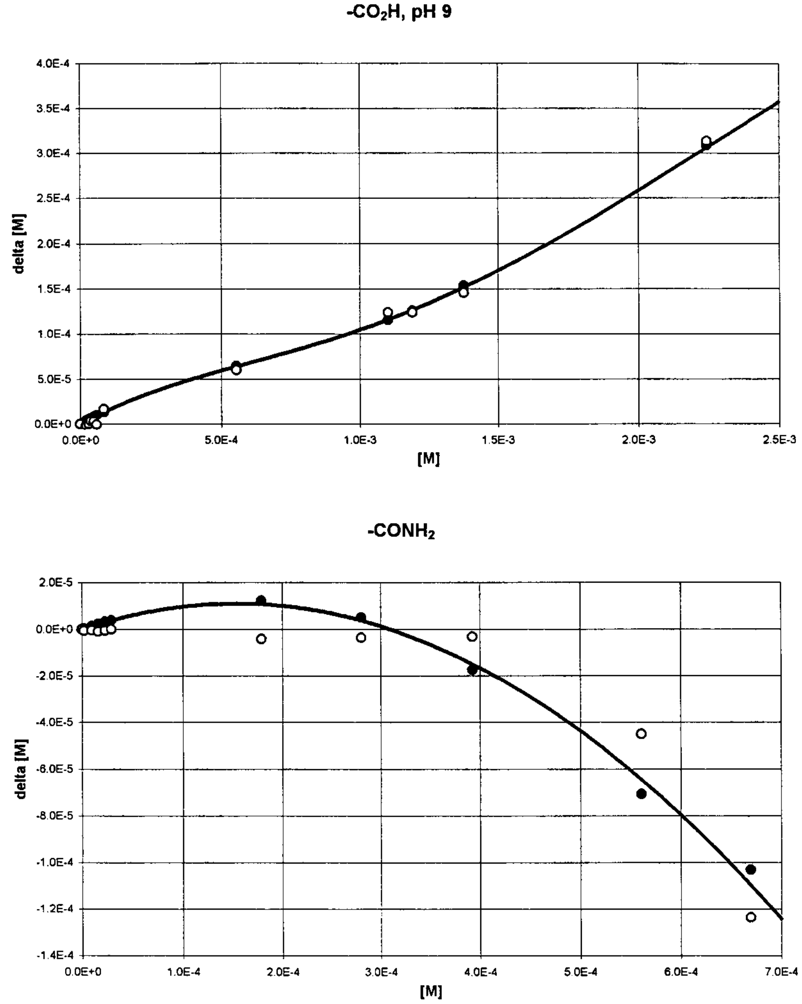

Figure 1 The measured (o) and the calculated (●) apparent adsorption of propionic acid (above) and propionamide (below) on iron oxide as a function of their mol fractions in the liquid phase, using the adsorption parameters as given in table 2

4.1 The adsorption capacity A

An adsorption capacity A of 3.56 mmol/gram was found for the combination propionic acid/iron oxide. For propionamide 1.78 mmol/gram was found. This corresponds to 0.07 and 0.14 nm^2 per molecule or an average distance of 2.8 and 4 Å between neighboring molecules. These distances are in fair agreement with the size of anchoring groups as estimated from bond lengths. The difference between propionic acid and propionamide might be caused by different degrees of solvation of the model compounds.

The adsorption capacity may be used to estimate how much of a dispersant can be used to fully cover a given amount of pigment. However, the results must be interpreted with some care. The estimation of the maximum adsorption capacity is based on an enormous extrapolation, as for both anchoring groups mentioned here at the highest measured concentration a coverage of only 2 % was attained. For other model compounds coverages as high as 80 % have been measured, which of course results in a much more reliable measurement of A.

4.2 The strength of adsorption

The equilibrium constant K_{ads} gives an impression of the strength of the adsorption of an anchoring group to a pigment surface. A higher value of K_{ads} means that the anchoring group has a higher tendency to adhere to the pigment surface. From K_{ads} the free energy of adsorption ΔG_{ads} can be calculated with formula **(10)**:

$$\Delta G_{ads} = -RT\ln K_{ads} \qquad \textbf{(10)}$$

with

R = gas constant, 8.314 $J.K^{-1}.mol^{-1}$

T = absolute temperature, 295 K in our experiments

ΔG_{ads} values of -6.1 and -7.2 KJ/mol were found for propionic acid and propionamide, respectively. A more negative ΔG_{ads} indicates a stronger interaction between the pigment and the anchoring group.

Once K_{ads} is known, **(4)** can be used to plot a Langmuir isotherm (the **real** adsorbed amount or the degree of coverage θ as a function of the mol fraction in the liquid phase, see figure 2).

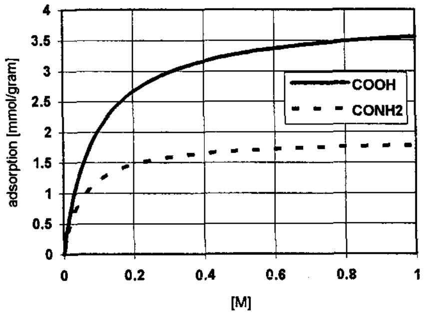

Figure 2 Real adsorption of propionic acid and propionamide on iron oxide, as calculated from the data in table 2

The free energy of adsorption ΔG_{ads} may also be used to select adhesion-promoting functional groups for coatings.

4.3 Coadsorption of solvent

The parameters K_{solv} and n account for the coadsorption of the solvent, water in our study. They can be used to calculate the total amount of adsorbed water as a function of the mol fraction of the model compound, just by summing [PS] and n*[PMS$_n$].

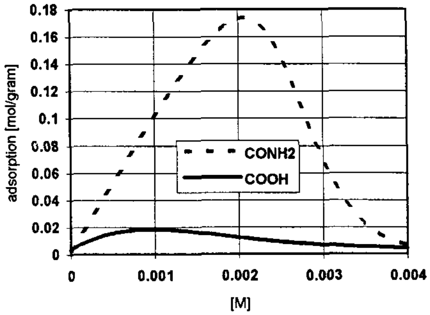

Figure 3 Coadsorption of water on iron oxide as a function of the mol fraction of model compound in the liquid phase

Figure 3 gives the result for the carboxylic-acid group and the amide group. The amount of coadsorbed water first increases with the amount of adsorbed model compound, but at a given concentration of model compound in the water phase it decreases again, as water is required for solvation of the free model compound.

Of course the coadsorption of solvent by adsorbed model compounds is of much less interest for the understanding of the behavior of dispersants than the adsorption of anchoring groups. In real pigment dispersants the solvation of the anchoring groups is probably unimportant in comparison to the solvation of the soluble tails, as these are specially designed to be freely soluble in the paint system. We are currently investigating a similar method as described here to measure the degree of solvation of soluble tails and so to estimate their effectiveness.

5. DISCUSSION

In table 2 an overview of the results for several pigment/anchoring group combinations is given. A good correlation between predicted and measured adsorption was found in most cases. The poor correlation for the adsorption of the amino and diethylamino group on iron oxide is probably caused by the low affinity and the resulting small change in concentration during the measurement of the adsorption. The data for the aromatic amines 2-ethylpyridine and 2-ethylpyrazine suggest a stronger interaction with this pigment. Due to the poor correlation, these data should be interpreted with care, however. A strong interaction is found for the pyridyl group and carbon black and the organic pigment phthalocyanine. The amino group is a well known anchoring group for carbon black (Ref. 6).

In spite of the poor correlation, the glycol ethers (model compounds ethyl glycol and ethyl diglycol) show a surprising consistency: a very strong adsorption (high K_{ads}) of a very low amount of model compound (low A). Due to the very low level of the adsorption the concentration measurements become less reliable, with a bad correlation as a result and the results should be interpreted with care. The low adsorption capacity of these groups makes them useless as anchoring groups in waterborne systems.

Table 2. Adsorption parameters for model compounds C_2H_5-X to pigments or fillers

Pigment or filler	Anchoring group X	R^2	A (mmol/ gram)	area (nm^2/ molecule)	K_{ads}	ΔG_{ads} (KJ/mol)	K_{solv}	n (mol)
transparant iron oxide	carboxylic acid, pH 3	0.9166	0.25	0.66	1164	-17.3	2.8	2.55E4
	carboxylic acid, pH 9	0.9973	3.6	0.047	11.8	-6.1	1.4	1400
	sulfonic acid, pH 2	0.9340	1.5	0.11	64.4	-10.2	4.3	2.1E4
	sulfonic acid, pH 7	0.9979	1.2	0.14	6.8	-4.7	0.97	2.5E4
	sulfonic acid, pH 9	0.9923	1.2	0.14	3.15	-2.8	1.7	4.8E3
	4-phenylol	0.9972	0.1	1.66	148	-12.2	3.1	1.08E4
	amino acid, pH 7	0.9754	1.5	0.11	48.9	-9.5	2.1	1800
	amino acid, pH 9	0.9856	0.24	0.69	158	-12.4	9.9	162
	amino	0.3694	0.36	0.46	18.1	-7.1	11.6	1960
	diethylamino	0.6032	4.8	0.035	1.13	-0.3	6.8E3	3730
	2-pyridyl	0.5070	0.12	1.35	63.3	-10.2	3.0	8300
	2-pyrazinyl	0.0667	0.016	10.4	224	-13.3	1010	5400
	amide	0.8876	1.8	0.093	18.7	-7.2	3.1E3	3070
	acetyl, pH 7	0.9842	0.079	2.1	857	-16.7	1.7	888
	acetyl, pH 9	0.9901	0.18	0.93	248	-13.5	1.2	663
	methyl ester	0.9513	0.76	0.22	163	-12.5	1.2E3	1400
	$-OC_2H_4OC_2H_4OH$	0.1299	0.0010	166	1E4	-22.6	1E4	4E4
	$-OC_2H_4OH$, pH 7	0.5971	0.0013	121	1.1E4	-22.8	1E3	980
	$-OC_2H_4OH$, pH 9	0.2679	3.9E-5	4.3E3	5.4E3	-21.1	2E7	4.1E4
carbon black	4-phenylol	0.9752	0.519	0.32	8.04E4	-27.7	-	-
	2-pyridyl	0.9797	0.245	0.68	4.1E4	-26.0	-	-
	4-pyridyl	0.9327	0.276	0.60	5.15E4	-26.6	-	-
phthalo-cyanine	2-pyridyl	1.000	0.126	1.32	7.51E3	-21.9	1.05	1.3E4
	4-pyridyl	1.000	0.26	0.63	4.15E3	-20.4	1.64	7.7E3
aluminum oxide	4-phenylol	0.2360	0.506	0.32	62.4	-10.7	6.16	5.8E3

Much better results are obtained for iron oxide with the carboxylic-acid group, which is of course a well known anchoring group in many dispersants, and with the (weakly) acidic phenylol group. The effectiveness decreases however, at high pH values. The anchoring properties of the amino-acid group (model compound 2-amino butyric acid) persist, even at high pH values. Surprisingly the sulfonic-acid group, which is known to be a very strong solubilizing group, is a very poor anchoring group, unless it is used at low pH values.

Both the acetyl group and the ester group seem to be effective anchoring groups in water. This may be due to their low solubility in water. Measurements in solvents other than water might show a very different adsorption pattern.

6. CONCLUSION

A method has been presented which allows measurement of the free energy of adsorption of anchoring groups to a pigment or filler surface. This method may be used to select anchoring groups for a given pigment and thus allows a more focused development of pigment dispersants. More generally, the method may also be used to select functional groups which improve adhesion to a given surface.

The same method also yields information of the amount of solvent which is coadsorbed on adsorption of a model compound. When used for polymers, this method can allow comparison of the effectiveness of stabilizing groups in pigment dispersants.

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