STUDY OF THE INTERACTIONS EXISTING BETWEEN ORGANIC MOLECULES AND INORGANIC PARTICLES USED IN FORMULATING CERAMIC GLAZES

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ABSTRACT

A ceramic glaze, both in the form of a suspension and as agglomerates, is made up of inorganic particles (frits, raw materials, etc.) and organic molecules (bonding agents, binders, etc.), which interact with each other to provide the required rheological characteristics, manageability, pressability, etc.

Since the organic molecule-inorganic particle interactions take place at the particle surface, the present study has focussed on achieving a greater understanding of the chemical character of this surface and its affinity for organic molecules. For this, a study has been carried out by inverse chromatography at infinite dilution, in which the Surface Energy of the different glaze components (organic and inorganic) has been determined, evaluating its specific and non-specific component. Other aspects, such as the influence of temperature or milling medium on the Surface Energy of the materials have also been studied in this work.

Subsequently, to determine the specific surface interaction between two concrete components, the solid-liquid adsorption isotherms were established and analysed in aqueous medium.

These studies enable obtaining information, for example, on the affinity between different glaze components or on the minimum quantity of an organic compound required to form a single layer on particles of a certain frit or raw material.

1. INTRODUCTION

The aesthetic finish and technical properties of ceramic floor and wall tiles have evolved in a spectacular way in the last few decades. Today one can acquire tiles that are hardly distinguishable from natural stones, with highly elaborate designs and profiles, high abrasion resistance, etc., which have required numerous applications to produce. This has entailed a parallel evolution in the composition and appearance of ceramic glazes. Research has been done on new frit formulations, the number and nature of the raw materials used have increased, new additives are used, a great variety of glazes have been developed for dry applications (spray dried, micronised or flakes), etc.

On the other hand, independently of its use or appearance, a ceramic glaze mainly consists of particles of frits and raw materials, and organic additives. The interactions between the inorganic particles and the organic additives basically provide the required rheological characteristics, manageability, pressability, etc. These interactions take place at the particle surface and they depend fundamentally on their chemical character. In the specific case of frits, there is a wide variety of chemical compositions, in which each atom's contributing effect on final behaviour is different. Moreover, by their own glassy nature, frits have a disordered chemical structure, while at the same time, a layer a few Angstroms thick is generated with an amorphous structure at their surface by bond break-up in the milling process. All this, together with other aspects such as the great variety of raw materials used, the presence of water in larger or smaller proportions, or the different nature of the organic additives used, provides some idea of the complexity of the interactions that can take place in a ceramic glaze.

Most of the studies found in the literature on this issue have been mainly directed toward measuring a series of characteristics (rheological parameters, granule strength, etc.), which contribute information in an indirect way on the arising phenomena. However, numerous questions remain to which an appropriate answer has yet to be given.

It was therefore considered convenient to conduct a study that directly addressed the interaction arising between organic additives dispersed in liquid medium and the particle surface of inorganic materials. For this, several procedures are available, although the most widely used method consists of determining the solid-liquid adsorption isotherms, which in turn depend on the physico-chemical characteristics of the surfaces that come into contact with each other. Beforehand it is convenient to establish the characteristics of these surfaces, determining their acid-base character and Surface Energy by means of inverse chromatography at infinite dilution, a method of proven validity for a multitude of materials, from paper pulp to pure metals, glasses, etc. Other methods, such as surface chemical analysis by X-ray photoelectron spectroscopy, infrared spectroscopy or reflection raman, provide an idea of the existing chemical composition at the surface, but not of their surface energy. Equally, measurement of the solid-liquid contact angle, the most common method for determining surface energy, cannot be used in this case since it is not valid for powdered materials.

2. THEORETICAL FUNDAMENTALS

Before proceeding to set out the objectives of the work, the experimental procedure used and the results obtained, it is useful to briefly review the theoretical fundamentals of the technique known as Inverse Gas Chromatography at Infinite Dilution[1].

As the very name indicates, Gas Chromatography is involved in which the chromatographic column is filled with the problem solid, injecting probe molecules into a carrier gas and measuring their retention time. Retention time, t_R, carrier gas flow, F_O, and sample weight, W, then enable calculating the retention volume, V_R, from the following equation:

$$V_R = t_R \, . \, F_O \, / \, W \qquad [1]$$

The non specific or dispersive component of the surface energy of a solid can be found using n-alkanes as probe vapours, while the specific component is determined using vapours with acid-base properties. Figure 1 presents two elution peaks corresponding to a neutral vapour and another with acid-base characteristics.

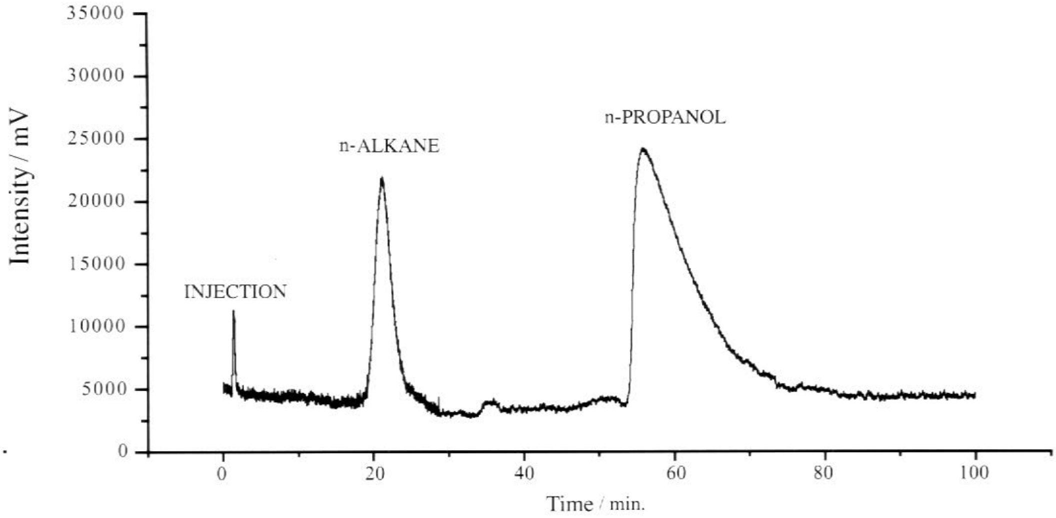

Figure 1. Elution peaks in a chromatography column.

According to Fowkes[2], the work of adhesion W_A between a liquid and a solid is the summation of two factors, the work done by non specific or dispersive interactions and the work done by specific interactions. Fowkes demonstrated that work of adhesion is the product of solid and liquid surface tensions , g_S and γ_L, respectively, i.e.:

$$W_A = 2(\gamma_S{}^d \, . \, \gamma_L{}^d)^{1/2} + 2(\gamma_S{}^{sp} \, . \, \gamma_L{}^{sp})^{1/2} \qquad [2]$$

where the superscripts d and sp respectively indicate dispersive and specific. This equation [2] is equally valid for gas or vapour adsorption onto a solid, as occurs in Inverse Gas Chromatography, simply substituting g_L by g_G.

When n-alkanes are used, the specific component, $\gamma_G{}^{sp}$, is zero since they are nonpolar, so that the previous equation becomes:

$$W_A = 2(\gamma_S{}^d \, . \, \gamma_G{}^d)^{1/2} \qquad [3]$$

On the other hand, when using vapours, the work of adhesion is really the change in adsorption free energy when these vapours are adsorbed onto the surface of the solid, which is found from:

$$\Delta G_A = -RTLn(V_R) + C \qquad [4]$$

Multiplying expression [3] by the Avogadro number (N_A) and by the area of the probe molecule (a_L) expressed in m^2.molecule, and setting this equal with expression [4], finally gives equation [5].

$$- RTLn(V_R) + C = 2\ N_A \cdot a_{L.} (\gamma_S^{\ d})^{1/2}. (\gamma_G^{\ d})^{1/2} + C \qquad [5]$$

In accordance with this equation, plotting - RTLn(V_R) versus $a_L(\gamma_G^{\ d})^{1/2}$, i.e., retention volume of different n-alkanes as a function of the surface tension of each one of these, a straight line is found, whose slope enables calculating the dispersive component of the free energy of the analysed solid surface ($\gamma_S^{\ d}$).

With regard to the specific component of solid surface free energy, this is determined by adsorption of a vapour with acid-base properties on this surface.

The equation that governs this interaction is found from equations [2] and [4], in which the following holds:

$$- RTLn(V_R) + C = (2(\gamma_S^{\ d} \cdot \gamma_G^{\ d})^{1/2} + 2(\gamma_S^{\ sp} \cdot \gamma_G^{\ sp})^{1/2})\ N_A \cdot a_L + C \qquad [6]$$

The specific interactions can be of the Brönsted acid-base, Lewis acid-base, hydrogen bond, interaction with p electrons, dipole-dipole, induced dipole-dipole type, etc. It is generally considered that all these specific interactions can be included in the ones defined by the Lewis acid-base concept, so that they are generally called Lewis interactions.

The acid or basic characteristics of any molecule are defined by their acceptor (AN) or donor numbers (DN) of electrons. Table 1 sets out these values for different molecules, as well as their acid-base character[3].

Now it is necessary to keep in mind that the acid-base probe molecules also interact in a non specific way with the surface of the solid, so that it is necessary to eliminate this last contribution of the acid-base itself, to find only the specific interaction. For this, the retention volume is determined of the different specific probe molecules and n-alkanes, plotting -RTLn(V_R) as a function of a certain property of the probe molecule (vapour pressure of the corresponding liquid, boiling temperature, vaporisation enthalpy, polarizability, topographical number, etc.) as Figure 2 shows. The specific interaction is considered to be the difference that exists between the interaction of each specific molecule with regard to the line that the n-alkanes follow, since these only interact in a non-specific way.

MOLECULE	Symbol	DN	AN	CHARACTER
n-pentane	C5	0	0	Neutral
n-hexane	C6	0	0	Neutral
n-heptane	C7	0	0	Neutral
n-octane	C8	0	0	Neutral
1,2 Dichloroethane	DCE	0	16.7	Acid
Carbon tetrachloride	TCC	0	8.6	Acid
Chloroform	CL	0	23.1	Acid
Benzene	BZ	0.1	8.0	Acid
Acetone	AC	17.0	12.5	Amphoteric
Ethyl acetate	AE	17.1	9.3	Amphoteric
Diethyl ether	DE	19.2	3.9	Alkaline
Tetrahydrofuran	THF	20.0	8.0	Alkaline

Table 1: Acid-base characteristics of the various probe molecules.

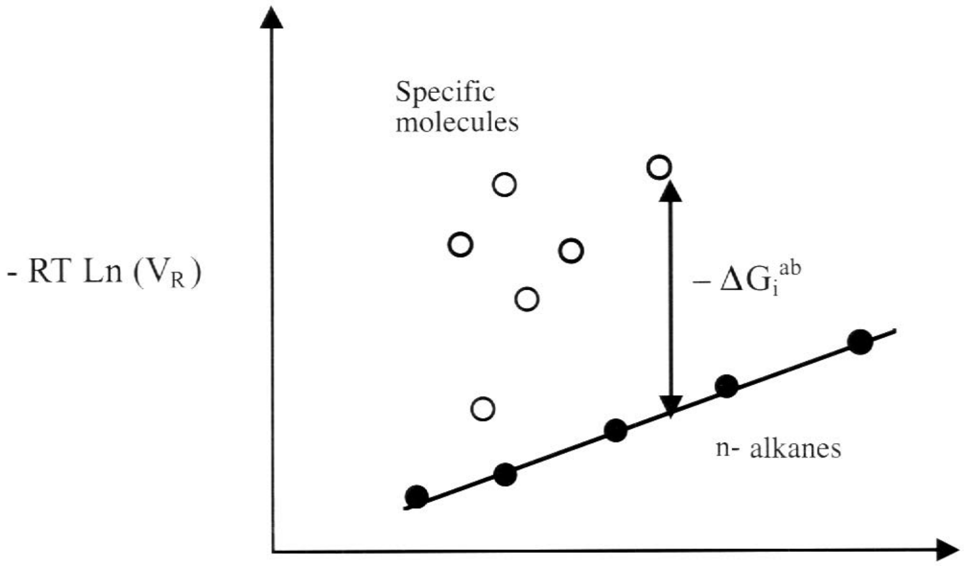

Figure 2. Determination of the specific interaction of a probe molecule (the superscript sp, indicating specific, has been replaced by ab, indicating Lewis acid-base).

After finding $-\Delta G_{Ai}^{ab}$ for each probe molecule at different temperatures, enthalpy ΔH_{Ai}^{ab} is calculated from the equation:

$$-\Delta G_{Ai}^{ab} = \Delta H_{Ai}^{ab} - T\Delta S_{Ai}^{ab} \qquad [7]$$

This enthalpy is related to the specific component of the solid surface, defined by constants k_a and k_b which express the acidity and basicity of the solid surface:

$$\Delta H_{Ai}^{ab} = k_a \, . \, DN + k_b \, . \, AN \qquad [8]$$

Dividing both parts of the equality by AN yields a straight line of slope k_a and ordinate at the origin k_b, i.e., the acid and basic constants of the solid surface.

3. OBJECTIVES

Keeping in mind the above, the present work sought to further the knowledge of the interaction that takes place between the surface of the frit and raw materials particles, and organic additives used in formulating ceramic glazes, for which the following studies were undertaken:

- Determination of the Surface Energy of the components of a glaze, differentiating the non specific or dispersive component from the acid-base or specific one.
- Determination of the solid-liquid adsorption isotherms corresponding to the molecules of organic additives dissolved in water with frit and raw materials particles.

4. EXPERIMENTAL

4.1. MATERIALS

To conduct the present work three frits of different chemical composition were used, involving kaolin, zirconium silicate and two binders, all being widely used materials in the ceramic industry. Table 2 details the chemical analyses of the frits. To be noted is the presence of B_2O_3 in frit F2 compared to F1 and the high network modifier element content in frit F3. To carry out the Inverse Chromatography tests, frit F2 and F3 were milled in water (F2H and F3H), while frit F1 was dry milled (F1S) as well as in water (F1H), to enable evaluating the effect of the milling medium on the studied parameters. A carboxymethylcellulose of low molecular weight (A1) was chosen as a binder, together with an acrylic binder (A2).

	F1	F2	F3
SiO_2	56	53	49
B_2O_3	---	6	3
Al_2O_3	5	5	17
CaO	9	10	1
Na_2O	--	--	15
K_2O	5	5	2
ZrO_2	9	8	12
MgO	3	2	1
ZnO	12	11	--

Table 2: Average chemical composition of the frits used.

4.2. EXPERIMENTAL PROCEDURE

4.2.1.- Gas Chromatography at Infinite Dilution

The chromatographic column consisted of a Teflon tube with a 3 mm diameter, approximately 100 cm long. This column was filled with particles of controlled size of the material to be analysed in each case (frit, kaolin, etc.), compacting these as best as possible to reduce dead or non-retained volume, V_{NR}, between the particles to a maximum. The probe molecules were injected with a Hamilton 1 μl syringe, using Helium as carrier gas at a flow rate of 20 ml.min-1. Retention volume was found from equation [1], after performing at least five measurements under the same conditions. To calculate dead volume, V_{NR}, methane was injected, which is not retained at the test temperatures used. Corrected retention volume, V_N, is thus:

$$V_N = (V_R - V_{NR}) \qquad [9]$$

The analysis temperatures were 40, 50 and 60 °C for the frits and binders, and 120, 130 and 140 °C for the kaolin and zirconium silicate. All the samples analysed were previously heated at a higher temperature than that of the evaporation temperature of the organic compound used as a probe.

4.2.2. Solid-liquid adsorption isotherms

The solid-liquid adsorption isotherms were found by dispersing 2 grams of the solid involved (frit, kaolin or zirconium silicate) in 20 ml of deionised water in which a certain percentage (between 0.5 and 20%) of binder A1 or A2 had been previously dissolved according to each case. The dispersion was stirred for 24 hours at test temperature (25, 35 and 45 °C). The dispersion was then centrifuged, separating the solid from the liquid. The solid was dried in an oven at 50°C for 24 h and the existing carbon content was analysed with a LECO CS-200 analyser. Solid carbon content was related to the quantity of adsorbed organic compound by means of a reference straight line established previously.

In all the cases, final dispersion pH was measured; minimal variation with the concentration of either of the added binders was observed, so that the results can be considered independent of pH.

5. RESULTS AND DISCUSSION

5.1. GAS INVERSE CHROMATOGRAPHY AT INFINITE DILUTION

5.1.1. Non-specific interactions (dispersive)

The non specific interactions were found from the retention volume of the n-alkanes. As an example, Figure 3 plots the results obtained with frit F2H at the different test temperatures. Similar graphs were found with the other analysed materials. In Figure 4 the plots obtained with the frits and the binders at 60°C, and with the kaolin and zirconium silicate at 120 °C, are compared. The slope of all these straight lines and equation [5] were used to calculate the dispersive component of the surface free energy. These values are detailed in Table 3.

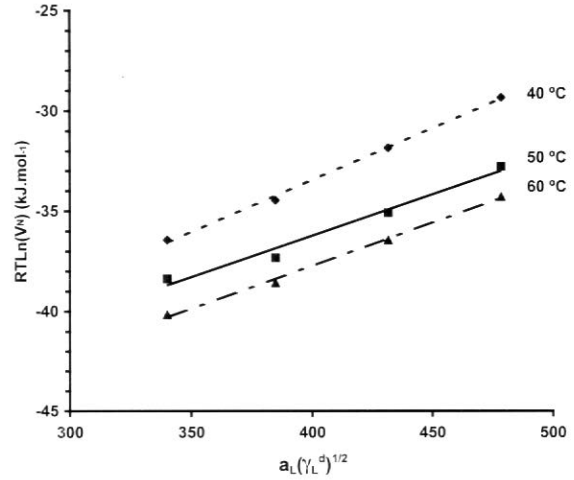

Figure 3. Variation of n-alkane retention volume with F2H at different temperatures.

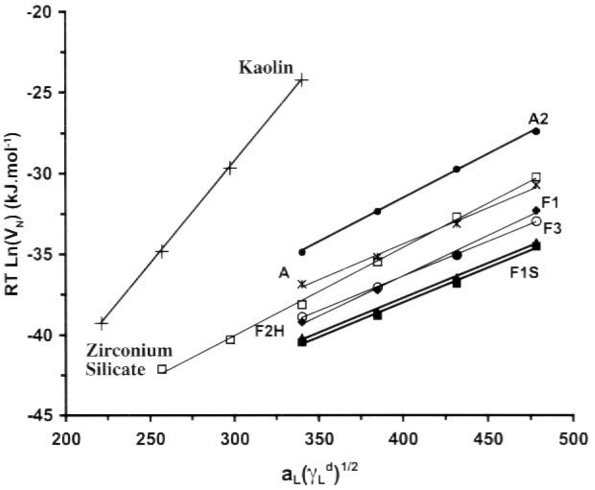

Figure 4. Variation of n-alkane retention volume with the different studied materials.

T (°C)	F1H	F1S	F2H	F3H	Kaolin	Zirconium silicate	A1	A2
40	36.0	35.9	26.2	24.2	274 *	129 *	27.8	39.7
50	32.7	34.0	23.2	22.4	254 *	121 *	24.2	36.4
60	28.2	28.5	19.4	18.6	245 *	113 *	23.6	34.1
120					167.6	50.4		
130					159.0	40.9		
140					148.2	34.6		

Table 3: Dispersive component γ_S^d of surface energy (mJ.m^{-2}).
(Values extrapolated from the results found between 120 and 140 °C).*

Based on the data listed in Table 3, a series of remarks can be made on the surface energy of the studied samples.

In the first place, if only the inorganic materials are considered, strong dependence of the surface energy dispersive component is observed to exist with the crystallinity of the material in question. Thus the frits, which are glassy, exhibit the lowest values for this parameter, while the kaolin and zirconium silicate, which are crystalline materials, present the highest values. This fact is in agreement with the values reported by other researcher for similar materials. Indeed, Saint-Flour and Papirer[5] obtained a value of 34.7 mJ.m^{-2} for rock wool glass fibres and Baptist et al.[6] 39.3 mJ.m^{-2} for silica glass-alumina fibres. In the case of kaolin, similar values have been reported for other types of clays, such as bentonite, sepiolite or pyrophyllite[7]. Similarly, Papirer[8] and Rubio[9] obtained values of 138.0 and 120.4 mJ.m^{-2} respectively at 100 and 120 °C for zirconia. In the case of the binders A1 and A2 similar values were also found to those of other organic compounds such as PVC (38.8 mJ.m^{-2}), polyethylene (35 mJ.m^{-2}), nylon (29 mJ.m^{-2}) and cellulose (37 mJ.m^{-2})[10]. All these data show the validity of the method for assessing the dispersive component of the surface energy of the studied ceramic materials.

If we focus on the frits, an important variation of the parameter studied with frit composition is observed. Thus, the incorporation of boron causes the surface energy dispersive component to decrease, a drop that is even more pronounced in frit F3, which contains a larger quantity of network modifiers, which produce break-up of the glassy network. The use of water as a milling medium is also observed not to modify frit F1 γ_S^d.

Finally, in all the cases dispersive energy decreases with temperature, as is fitting for a thermodynamic magnitude that describes surface energy. This variation can be defined from the equation:

$$\gamma_S^d = h_S^d - T\, s_S^d \qquad [10]$$

where h_S^d is dispersive enthalpy and s_S^d dispersive entropy of solid surface energy.

The plot of γ_S^d/T vs. $1/T$ yields a straight line of slope h_S^d. The data are given in Table 4.

	F1H	F1S	F2H	F3H	Kaolin	Zirconium silicate	A1	A2
h_S^d	158.4	151.2	131.9	77.8	549.8	361.2	95.1	126.4
s_S^d	-0.39	-0.36	-0.34	-0.17	-0.97	-0.79	-0.22	-0.28

Table 4: Dispersive enthalpy h_S^d (mJ.m^{-2}) and entropy s_S^d (mJ.m^{-2}.K^{-1}).

The kaolin and zirconium silicate present a great variation of dispersive energy with temperature, which indicates that small changes of temperature will have an important influence on the interaction between the materials and the n-alkane molecules. For the rest of the studied materials the g_S^d variation with temperature is much smaller, albeit still quite significant. It is to be noted that frit F3H presents the least tendency to vary its behaviour with temperature, while milling in water does not seem to affect the frit F1 surface.

5.1.2. Specific interactions (acid-base)

The Lewis acid-base surface energy components of the studied solids were determined based on the retention volume of the specific vapours detailed in Table 1.

Again, by way of example, Figures 5 and 6 show the variation of adsorption free energy versus the polarizability of the probe molecule for frit F1H and binder A1 at 40°C. The distance between the straight line of the n-alkanes and each specific molecule corresponds to the specific interaction I^{SP} $(-\Delta G_{Ai}^{ab}$ indicated in the equation [7].

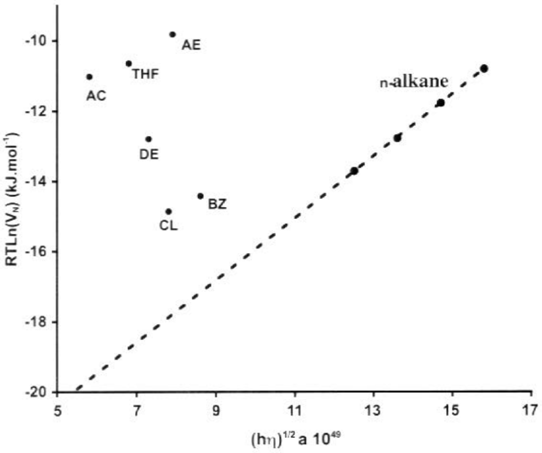

Figure 5. Variation of n-alkane retention volume with frit F1H.

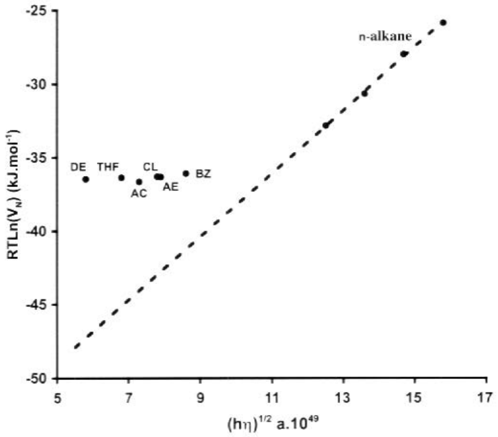

Figure 6. Variation of n-alkane retention volume with binder A1.

Table 5 details the values of I^{SP} at 60°C for the frits and binders, and at 140 °C for the kaolin and zirconium silicate. Using these values obtained at different temperatures and equations [7] and [8] enables calculating the acid and basic constant of the surface of each studied material. These data are given in Table 6.

Molec.	F1H	F1S	F2H	F3H	Kaolin	Zirconium silicate	A1	A2
BZ	5.6	2.6	1.4	4.8	10.2	8.8	2.5	2.0
CL	7.3	4.4	2.5	5.9	7.8	6.2	5.1	3.8
DCM	8.0	3.3	1.6	--	--	--	--	--
AC	6.8	15.8	12.5	18.2	39.7	33.0	9.9	20.1
AE	10.9	11.6	6.6	23.5	31.9	33.6	5.6	20.1
DE	7.7	10.6	5.6	10.6	30.2	24.2	6.1	15.2
THF	8.2	11.5	9.4	15.9	36.7	31.1	7.9	15.6
T (°C)	60	60	60	60	140	140	60	60

Table 5: I^{SP} values for the different molecules and starting materials.

	F1H	F1S	F2H	F3H	Kaolin	Zirconium silicate	A1	A2
$k_A \cdot 10^2$	49	30	32	45	150	114	45	74
$k_B \cdot 10^2$	32	41	32	68	95	93	5	36
k_A / k_B	1.53	0.73	1.00	0.66	1.57	1.22	9.00	2.05

Table 6: Acid and basic constants of the studied materials.

With regard to the absolute value of the acidity and basicity constants, Table 6 shows that kaolin and zirconium silicate present the highest values for both constants, indicating their greater tendency to react with other materials. Binder A2 and frit F3H present an intermediate behaviour, while the rest of the frits and the binder A1 are the least reactive.

It can also be observed that dry milling of frit F1 lowers its acidity and raises its basicity constant.

Based on the quotient kA / kB some remarks can be made relating to the predominantly acid or basic character of the studied materials. In general, except for the frit that contains boron (F2) and the one that bears a high number of network modifiers (F3), the other materials are acids. To be noted is the cellulosic binder, due to the great number of hydroxyl groups that it possesses. Dry milling of frit F1 affects both its acidity and basicity, causing its character to change, going from acid to basic.

5.1.3. Overall interaction

In a ceramic glaze, the frit and raw materials particles enter into contact with the molecules of additives, water, etc. The overall interaction that arises in this system can be considered the summation of the partial interactions that take place between the organic and inorganic compounds. Given the mainly polar character of the materials used, the dispersive component is negligible compared to the acid-base interactions, so that only the latter are taken into account. It is usual in classical thermodynamics to consider the total interaction to be the summation of the products of the partial interactions. Thus in inorganic-organic binary systems, the following expression can be written:

$$IG = k_{A1}\, k_{B2} + k_{A2}\, k_{B1} \qquad [11]$$

where subscript 1 corresponds to the inorganic materials (frit, kaolin or zirconium silicate depending on each case) and subscript 2 to the binders (A1 or A2).

Figure 7 shows the results to be expected based on the data in Tables 3 and 6, using equation [11].

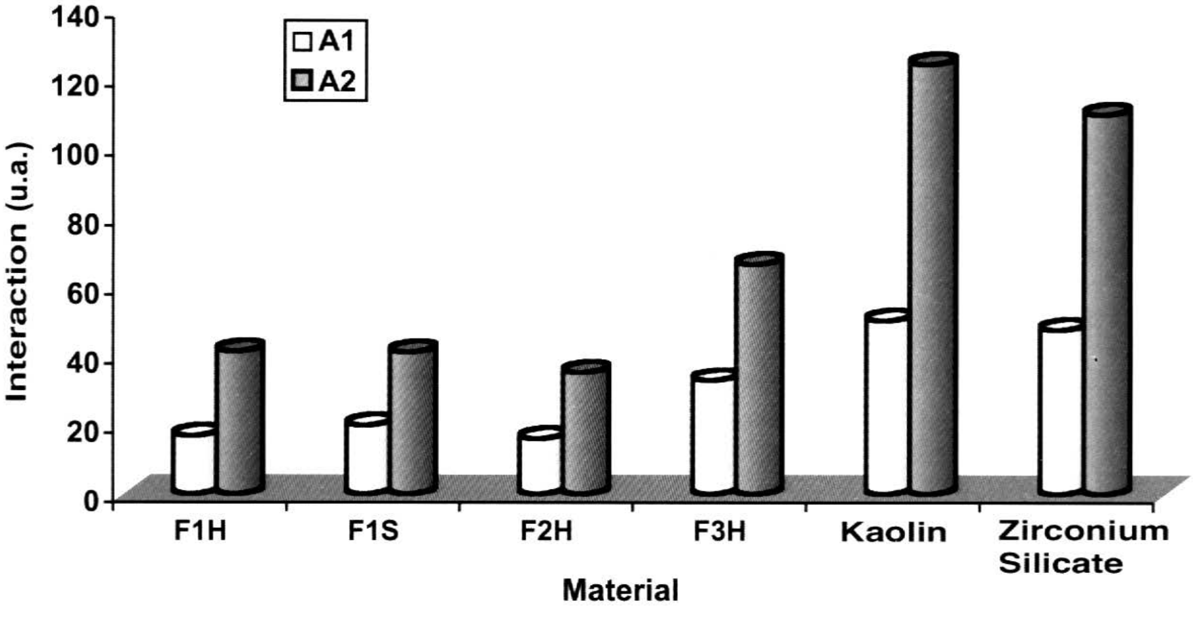

Figure 7. Overall interaction in binary systems.

As can be observed, the crystalline materials present much higher interaction values than the frits. In the frits, frit F3 interacts with the binders to a greater extent than the other two studied frits, mainly due to its high basicity constant, while frit F2 does so least. On the other hand, wet milling slightly reduces frit F1 interaction with binder A1, which remains unaltered when binder A2 is used.

Figure 8 plots the overall interaction of binder A2 versus that of A1. All the points fit a straight line of slope 2.4 and ordinate at the origin close to zero, which indicates that the acrylic binder interacts with a little over twice the energy of the carboxymethylcellulose with all the studied materials.

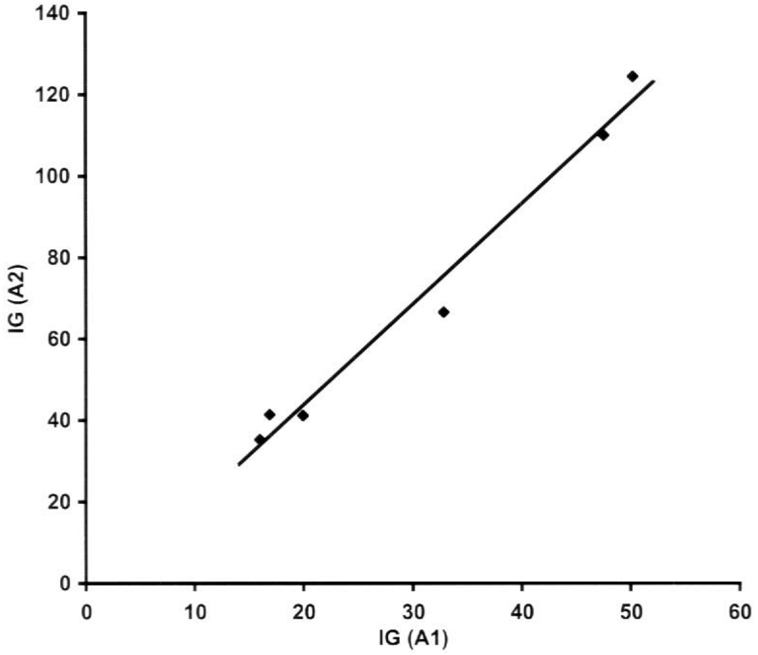

Figure 8. Overall interaction of binder A2 versus that of A1.

Thus, a change in the quantity of one of the materials making up the ceramic glaze will alter the required binder quantity, a change that will not just depend on the modified quantity, but also on the greater or lesser interaction of the component involved, making it convenient to know the magnitude of this interaction, a priori. Equally, depending on the acid or basic character of the frits and raw materials, the most appropriate binder can be selected or specific binders can be chosen for each component.

5.2. SOLID-LIQUID ADSORPTION ISOTHERM

Figure 9 shows the adsorption isotherms of the cellulosic binder (A1) in frit F1 at three temperatures, in which rapid binder adsorption is observed at very small equilibrium concentrations, adsorption then continuing in a practically linear way. The adsorbed quantity decreases with temperature, the same behaviour being observed with all the materials used in the study.

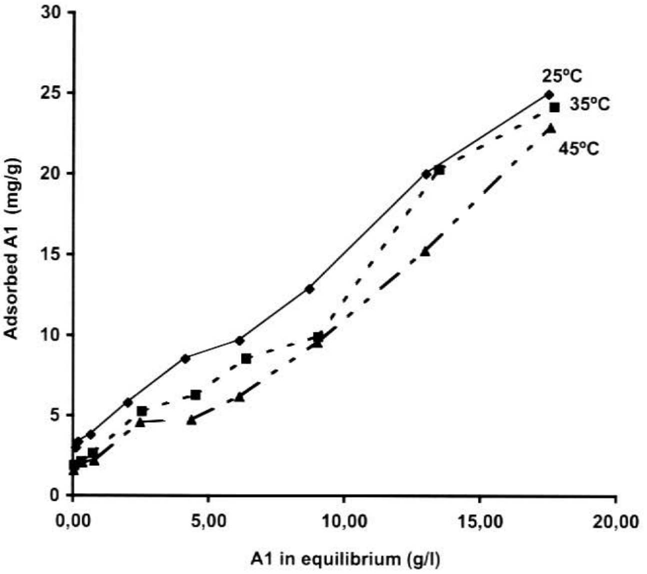

Figure 9. Adsorption isotherm of binder A1 on frit F1.

Figures 10 and 11 show the isotherms corresponding to the two organic compounds with all the solids studied at 25°C. In every cases there is rapid adsorption at very small equilibrium concentrations, indicating a great affinity of these organic compounds to frit, kaolin and zirconium silicate surfaces. At low equilibrium concentrations the biggest adsorption takes place for kaolin, independently of the organic compound used, although binder A2 is observed to produce greater differences between the solids, and in every case greater adsorption than binder A1. This last fact agrees with the greater overall interaction mentioned previously (Figures 7 and 8). In contrast, at high equilibrium concentrations the adsorption of a certain material with a different binder tends to equal out, due to the formation of multiple layers on the particles.

An interesting parameter to be determined when formulating ceramic glazes is the minimum quantity of organic compound molecules needed to form a single layer (V_M) on the surface of the inorganic compounds, which can be calculated from different theoretical equations such those proposed by Freundlich, Langmuir, Brunauer-Emmet-Teller (BET)[11], etc. In view of the shape of the experimental isotherms shown in Figures 9 to 11, it was decided to use the BET equation, of the form:

$$\frac{(C_E/C_O)}{(1-C_E/C_O)V_A}=\frac{1}{V_M K}+\frac{K-1}{V_M K}(C_E/C_O) \qquad [12]$$

C_E and C_O are quantities of organic compound in equilibrium and saturation, V_A and V_M are the quantities of adsorbed organic compound needed to form a single layer and K is a constant. As C_E and V_A are known, since they are the values used in elaborating Figures 9 to 11, while C_O has been determined in water for binders A1 and A2, equation [12] can be considered an ordinate straight line at the origin $1/V_M K$ and slope $K-1/V_M K$. With these two data, V_M can be calculated, whose values for the different studied solids and binders are detailed in Table 7.

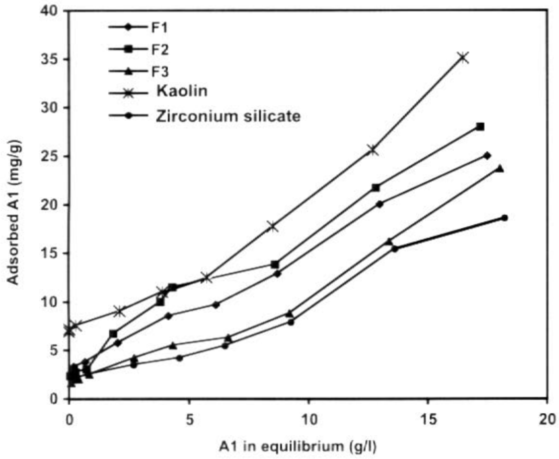

Figure 10. Adsorption isotherms of binder A1 at 25 °C.

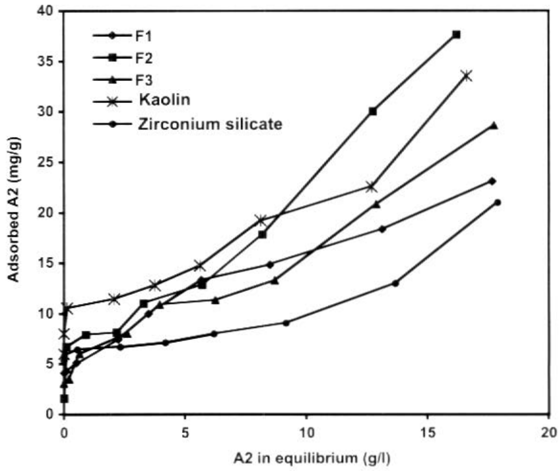

Figure 11. Adsorption isotherms of binder A2 at 25 °C.

Material	Se (m^2/g)	A1		A2	
		V_M (mg/g)	V_M (mg/m^2)	V_M (mg/g)	V_M (mg/m^2)
F1	1.12	6.0	5.4	9.0	8.0
F2	1.06	9.6	9.1	11.0	10.4
F3	1.10	4.5	4.1	11.0	10.0
Kaolin	14.00	11.0	0.8	13.0	0.9
Zirconium silicate	6.20	4.2	0.7	7.0	1.1

Table 7: Quantity of binder required to form a single layer (VM) and specific surface of the various studied solids.

These results show that a few grams of organic compound are required per gram of inorganic compound to complete a single layer, which is due to the large size of these organic molecules. In all the cases, binder A2 presented the largest values of V_M, indicating that for certain work conditions, a larger quantity of binder A2 is needed than of A1 to cover all the solid particles.

As regards the inorganic materials, kaolin needs the largest quantity of organic compound to be covered, due to its larger specific surface area, as shown in Table 7. Nevertheless, the whole kaolin surface may not be accessible to the binder molecules, owing to its laminar structure and the distance between sheets. Zirconium silicate is the material that adsorbs the smallest quantity to form a single layer, while in the frits the binder A1 is more selective than A2, since it presents a larger variation of V_M depending on the frit used.

As the binder molecules have a certain size and during adsorption onto the inorganic materials they gradually cover these surfaces, the adsorbed quantity will be a function of the specific surface exposed by each material, so that is convenient to express V_M as a function of specific surface to eliminate its influence (Table 7). Moreover, V_M will thus be expressed in the same way as interaction energy, i.e., per square meter adsorbing solid. These results show that the frits need a larger quantity of binder to cover 1 m^2, indicating that the organic molecules probably adsorb perpendicularly to the frit surface, while in the case of kaolin or zirconium silicate they do so in a parallel form.

Indeed, the different orientations that the organic molecules can adopt on adsorbing onto the surface of the inorganic particles depend on the existing interactions. Thus, if the interaction is very strong, the organic molecule will tend to orient itself parallel to the surface, whereas if the interaction is weak, the organic molecule will orient itself perpendicularly to the surface, only interacting by the most active centres. These types of interactions are those that probably occur in the systems studied in this work. In fact, plotting the overall interaction (IG), depicted in Figure 7, versus the values of V_M expressed as a function of the specific surface area given in Table 7, yields Figure 12, in which it can be observed that as the overall interaction increases, the binder quantity needed to cover the particle surface decreases.

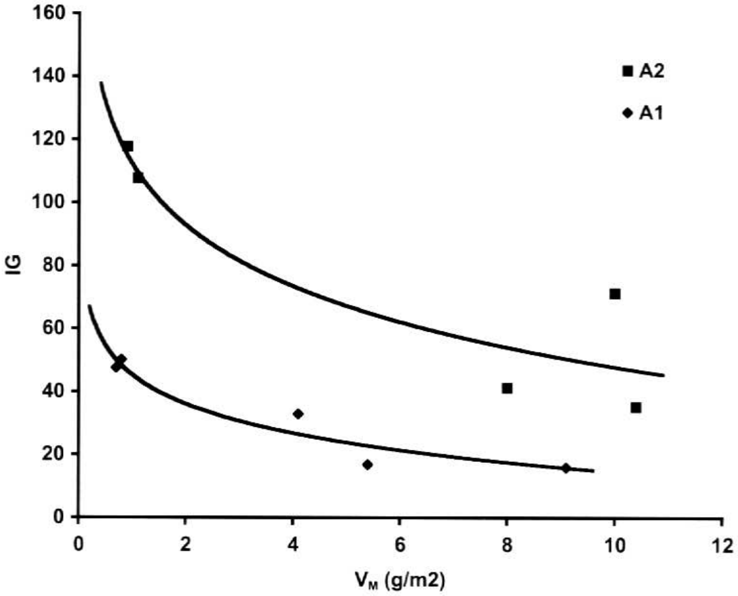

Fig. 12: Relation between Overall Interaction and quantity required to form a single layer for the two binders.

Another way of approaching the issue of different adsorbed molecule orientations is in terms of the size of these molecules, which can be calculated from the following expression:

$$\sigma = M / V_M.N_A \qquad [13]$$

where σ is the area of the molecule, M its molecular weight and N_A the Avogadro number. For a single molecule the quotient M / N_A is constant, so that σ is inversely proportional to V_M. According to the data in Table 7, V_M changes for each studied material, so that σ will also have to change. As it can be assumed that there will be no great variation in molecule size on being adsorbed onto one material or another, the variation of σ must be due to the different orientation that the molecules adopt on the particle surface.

6. CONCLUSIONS

The results of the study enable drawing the following conclusions:

1. - The surface of different frits has been characterised for the first time from a physico-chemical point of view, establishing the specific and non-specific components of

the energy of these surfaces. At the same time, these components were also established for other materials typically used in ceramic glaze formulation , such as kaolin, zirconium silicate, a cellulosic binder and an acrylic binder.

2. – Both the specific component, characterised by the acidity and basicity constants, and the dispersive component of Surface Energy, vary as a function of the crystallinity of the studied material. Crystalline compounds such as kaolin or zirconium silicate present much higher values for these parameters than glassy materials like frits.

3. - Both components also vary with frit composition. Thus, the incorporation of boron or modifying elements that distort the glassy network lower the dispersive part, while at the same time increasing the basic character of the frits.

4. - The overall interaction has been calculated which exists between the inorganic compounds (frits, kaolin and zirconium silicate) and the organic binders, always finding a larger interaction with the acrylic than with the cellulosic binder, due to the higher value in the acidity and basicity constants exhibited by the former. It was also observed that, independently of the binder used, kaolin and zirconium silicate were the solids that presented the greatest interaction, followed by the frit with network modifiers, while frits F1 and F2 interacted least.

5. - The solid-liquid adsorption isotherms were established of the organic binders on the particles of inorganic materials, always finding a typical multilayer formation behaviour.

6. – It was shown that typical ceramic process variables, such as type of milling or temperature, affect frit and raw materials particle surface characteristics as well as the quantity of binder adsorbed on these surfaces.

7. - The quantity of organic binder needed to form a single layer on the surface of the different studied inorganic materials was calculated. It was found that when this parameter was expressed per unit surface area of the solid involved the frits exhibited the highest values. However, if it was expressed by unit weight of the solid, it was the kaolin that required a larger quantity, due to its high specific surface. Moreover, it was found that for the frits, the cellulosic binder was more selective than the acrylic binder, presenting a larger variation of V_M as a function of the frit used.

8. - It was observed that as the overall interaction increased between a given inorganic material and an organic binder, the quantity required to form a single layer decreased, indicating the different orientations that binder molecules adopt with adsorption. Thus, when adsorption takes place on low energy surfaces (frit) the preferential orientation is perpendicular to the surface, while if a high energy surface is involved (kaolin or zirconium silicate), the orientation is parallel.

REFERENCES

[1] J. CONDER, J.H. PURNELL. "Gas chromatography at finite concentrations". Trans. Far. Soc. 65, 839-848 (1969).

[2] F. M. FOWKES. "Calculations of work of adhesion by pair potential summation". J. Colloid Interface Sci. 28 (3/4), 493-505 (1968).

[3] V. GUTMAN. The donor – acceptor approach to molecular interactions. Ed. Plenum Press. N.Y. 1978.

[4] J. RUBIO, F. RUBIO, J.L. OTEO. "Energía y heterogeneidad energética de la superficie del vidrio". Bol. Soc. Esp. Ceram. Vidrio. 36 (5) 485-495 (1997).

[5] C. SAINT FLOUR, E. PAPIRER. "Gas-solid chromatography. A method of measuring surface free energy charactaristics of short glass fibres"" Ind. Eng. Chem. Prod. Res. Dev. 221, 337-341 (1982).

[6] M.C. BAUTISTA, J. RUBIO, J.L. OTEO. "Surface thermodynamics analysis of cleared silicoaluminate glass fibres". J. Mater. Sci. 30, 1595-1600 (1995).

[7] T. J. BANDOSZ, K. PUTYERA, J. JAGIELLO, J.A. SCHWARTZ. "Application of inverse gas chromatography to the study of the surface properties of modified layered minerals". Microporous Mat- 1, 73-79 (1993).

[8] E. BRENDLÉ, E. PAPIRER. "A New Topological Index for Molecular Probes used in Inverse Gas Chromatography for the Surfce Nanorugosity Evaluation"J. Colloid Interface Sci. 194, 207-216 (1997).

[9] F. RUBIO. "Estudio químico-físico de la preparación por el método sol-gel de materiales del sistema SiO_2-ZrO_2". Tesis Doc. U. Complutense. Madrid 1994.

[10] G. M. DORIS, D. G. GRAY. "Adsorption of n-alkanes at zero surface coverage on cellulose paper and wood fibres". J. Collid Interface Sci. 77 (2), 353-362 (1980).

[11] S. BRUNAUER, P.H. EMMETT, E. TELLER. "The adsorption of gases in multimolecular layers". J. A. Chem. Soc. 60, 309-319 (1938).