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CORRELATION OF MECHANICAL PROPERTIES OF CLAY FILLED POLYAMIDE MOULDINGS WITH CHROMATOGRAPHICALLY MEASURED SURFACE ENERGIES

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ABSTRACT

Inverse gas chromatography, IGC, has been used to investigate the surface properties of calcined kaolins and the effect of the mechanical properties of a Nylon-6 composite containing the clay. Modification of the kaolin with an aminosilane coupling agent lowered its surface energy so that it was comparable with that of the polymer matrix and changed the surface from being acidic to being predominantly basic. The surface of the nylon was also found to be basic but susceptible to hydrogen bonding. Incorporation of the kaolin into nylon changed the mechanical properties, raised the modulus and toughness of the materials. Better results were achieved for the coated kaolin than the uncoated material and this correlated with the surface energy measurements.

Keywords: Inverse Gas Chromatography; Kaolinite, Calcined kaolin; surface energy; surface modification, nylon-6.

INTRODUCTION

Reinforced polyamides (PA's) have been in use since the 1950s. While glass fibre reinforcement [1] has been used to increase toughness, abrasion resistance, tensile strength and modulus, the current trend is to use mineral fillers such as calcined clays [2]. These reinforced thermoplastics find many applications, a major use being in the automotive industry. The use of kaolins, natural aluminosilicates, as fillers in thermoplastics is an area of current interest since they offer a range of properties not given by other fillers. Among systems that have been studied are polyethylene [3], polystyrene [4], silicones [5], polypropylene [6] and polyimides [7] as well as polyamides [8] [9] [10] [11].

To ensure good mechanical properties, calcined kaolins are often treated with silane coupling agents to increase compatibility through hydrogen bonding and acid-base interactions [12], [13]. While there have been a number of studies of compatibility in such systems, a complete understanding of the factors influencing the mechanical properties in these systems is yet to be achieved. Characterisation of the surface chemistries of both the calcined kaolins and PA are essential in predicting end performance.

A number of methods are available for investigating the surfaces of polymers and fillers but Inverse Gas Chromatography, IGC, has been shown to be useful for this type of work [14] [15] [16]. Small amounts of "probe" solvents are injected into a flow of carrier gas over the material under investigation and the retention time depends on the interactions between the probe and the surface. By using probes with a range of properties, the nature of the surface can be defined with good accuracy. The technique has been applied to the measurement of a number of physicochemical properties of a range of polymers [16] [17]. More recently IGC has been used to characterise a varied range of solid surfaces. IGC studies of a number of different clay minerals have also been reported including pillared smectites, [18] [19] montmorillonite and bentonite [20]. The surface properties of illites and kaolinite clays from various origins were measured by IGC and the use of branched alkane probes

allowed characterisation of the surface morphology [21]. In addition to this work on kaolins, IGC has been used at high temperature to investigate the interactions of small molecules with nylons [22]. The surface properties of related polymers such as Kevlar [23] and polyamides [24] have been determined by IGC.

In this paper, we report IGC measurements of the surface properties of two calcined kaolins that were coated with an aminosilane as an adhesion and dispersion aid. The properties were compared with the uncoated kaolin and with those of a nylon-6 polyamide. The kaolins were compounded in the nylon and the mechanical properties of the composites measured to determine the effect of the coating.

EXPERIMENTAL

Materials: Two commercial grades of calcined kaolins, PoleStar 200R and PoleStar 400, were obtained from Imerys Minerals Ltd. The calcined kaolins, coded here as CC1 and CC2 were from different feed sources with CC2 having approx. double the surface area and a significantly smaller particle size than CC1. The calcined kaolins were coated with γ -aminopropyl triethoxysilane, $\text{NH}_2-(\text{CH}_2)_3-\text{Si}-(\text{O}-\text{C}_2\text{H}_5)_3$, by mixing in a Steele and Cowlshaw high-speed mixer for fifteen minutes. The modified kaolins were conditioned in an air circulating oven for three days at 60 °C to remove residual ethanol and water before measurements were made. The characteristics of the calcined kaolins are shown in Table 1.

The polyamide used was Durethan 30S Nylon 6 from Bayer. It had a density of 1140 kg m^{-3} , softening temperature and melting point of 200 and 222 °C respectively. PA-kaolin composites containing 30 wt.% filler were prepared with an APV2030 twin screw extruder with a screw speed of 250 rpm and torque maintained at 40 to 45 %. An un-coated version of CC1 (Un-CC1) and the unfilled polymer were also included as comparisons. After drying in

a desiccant drier for 8 hours at 80 °C, the materials were dried for two hours in a vacuum oven before moulding. Using this procedure, no degradation of the polymer has been observed.

Mechanical testing: Plaques for mechanical testing were injection moulded on an Arburg 320M using a mould temperature profile of 200 - 260 °C, with an injection speed of 100 cm³ s⁻¹ and an injection pressure to 1250 bar. Mechanical properties of the materials were measured after conditioning for a minimum of 14 days at 23 °C, 50 % relative humidity. The notched and un-notched Izod strength of the bars was measured with a Ceast pendulum tester (ISO 180-1982), the results reported being the mean of ten measurements. The flexural modulus was measured with a Monsanto T10 tensometer by the three-point bend technique (BS 2782: Part 3: Method 335A). The tensile strength was also measured with a Monsanto T10 tensometer according to BS2782: Part 3: Method 320B. Here five measurements were made of each property. The deviations in the results were within that specified in the test methods.

Chromatography: The GC mineral fractions were prepared by compacting the kaolins, grinding and sieving to a particle size 425 – 850 µm particle size. The polymer stationary phases were prepared by milling in liquid nitrogen to give the same range of particle sizes. Stainless steel columns ¼ in o.d. of length 0.90 – 1.0 m were packed with 10-15 g of packing and conditioned under a flow of carrier gas at 250 °C for 24 hours, before further conditioning for twelve hours at the required experiment temperature.

A Perkin-Elmer Autosystem XL gas chromatograph employing FID detection was used. The column temperature was measured to ± 0.2 °C on a calibrated RDT thermometer and the carrier flow rate measured to ± 0.3 cm³ min⁻¹ with a FP-407 (Chrompack) solid state calibrated dual flow and pressure meter. Oxygen-free nitrogen, passed through a Perkin-Elmer three-stage drying and purification system, was used as the carrier gas. Barometric pressure was measured at the beginning and end of each run using a BDH precision aneroid

barometer. The instrument was located in a temperature-controlled laboratory, maintained at $23\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$.

After conditioning, a series of $\sim 0.1\text{ }\mu\text{L}$ aliquots of the vapour of the probes used were injected by Hamilton syringe over a range of temperatures. All probes were chromatographic grade (BDH). Retention times were recorded and processed by the PE-Nelson Turbochrom data management software. Methane was used as a non-interacting marker to determine the void volume of the column. Each value reported is the result of at least three elutions agreeing to within experimental uncertainty. The usual checks were carried out to ensure that results were recorded at infinite dilution.

RESULTS AND DISCUSSION

Inverse Gas Chromatography and measurement of Surface Energies

The primary measurement in IGC is the net retention volume, V_n , given [25] by

$$V_n = J f (t_r - t_0) \quad (1)$$

where t_r is the retention time taken for the probe and t_0 that for the non-interacting marker and f is the carrier gas flow rate corrected to S.T.P. J is the correction factor for the pressure drop across the column and carrier gas compressibility. For solid minerals and polymers below their glass transition, absorption into the bulk is negligible and retention therefore solely due to adsorption onto the solid surface. Under these conditions, it is readily shown that the retention volume is related to the Gibbs free energy of adsorption, ΔG_a° by [25]

$$\Delta G_a^{\circ} = - RT \ln (V_n) + k \quad (2)$$

where k is a constant depending on the standard states chosen for the free energy. The approach of de Boer [25] is commonly adopted and hence, ΔG_a° can be calculated over a series of temperatures from measurement of V_n allowing the calculation of the enthalpy of adsorption.

$$\Delta G_a^\circ = \Delta H_a^\circ - T\Delta S_a^\circ \quad (3)$$

Thus, if ΔG_a° is plotted *versus* T, ΔH_a° can be calculated from the intercept and ΔS_a° from the slope, with the assumption that both parameters do not depend on temperature over the range investigated.

The plots of ΔG_a° versus temperature for a series of alkane probes on the materials are exemplified for the coated and uncoated CC1 calcined clays in Figures 1 and 2. Those for the other clay and for the Nylon were similar in appearance. The enthalpies of adsorption for the probes were determined and are given in Table 2.

The enthalpies of adsorption on each of the silane-coated kaolins were similar to each other with CC2 being $\sim 2 \text{ kJ mol}^{-1}$ lower although this difference is within the experimental uncertainty of the measurements. The values are also close to those for the polymer. Balard et al. evaluated the degree of surface modification of silicas by IGC [26] and found a strong correlation between the degree of coating and adsorption enthalpy. Since CC1 and CC2 gave similar results, it can be assumed that each clay is covered to approximately the same degree; from the coating conditions used, the surface should be completely covered. The comparable adsorption enthalpies for PA and the surface-modified minerals indicated that the interactions between the two materials would also be similar.

The ΔH_a° values for alkane probes on the uncoated calcined kaolin were significantly higher. Previous work [27] showed that they were in turn lower than those for the hydrous kaolins from which CC1 and CC2 were derived. After calcination, the kaolin retained some surface polarity, presumably from strongly bound hydroxyl and oxide groups. The silane coating would have reacted with these groups, leading to the reduction of ΔH_a° .

It is common in this type of work to follow the approach of Fowkes [28] whereby the surface energy of the solid, γ_s can be considered as consisting of two components, one due to

van der Waals or dispersion forces, γ_s^d , and one due to other specific interactions such as polar, acid-base etc., γ_s^{sp}

$$\gamma_s = \gamma_s^d + \gamma_s^{sp} \quad (4)$$

The non-specific or dispersive component of the substrate surface energy, γ_s^d , can be calculated from the elution data for saturated hydrocarbon vapours, which are assumed to interact only with dispersion intermolecular forces. The free energy change for the adsorption of a single methylene group, $\Delta G_a^{\circ, CH_2}$, is found from the difference in free energies of adsorption for succeeding alkanes in an homologous series

$$\Delta G_a^{\circ, CH_2} = -RT \ln \left(\frac{V_n^{\circ}(n+1)}{V_n^{\circ}(n)} \right) \quad (5)$$

where n is the number of carbons in the linear alkane. γ_s^d can then be calculated from [29], [28]

$$\gamma_s^d = \frac{1(-\Delta G_a^{\circ, CH_2})^2}{\gamma_{CH_2}(2N \cdot a_{CH_2})} \quad (6)$$

where N is Avogadro's number; γ_{CH_2} is the surface tension of a hypothetical surface containing only methylene groups and a_{CH_2} is the cross-sectional area of a methylene group ($\approx 0.06 \text{ nm}^2$). Thus at constant temperature, for a series of alkane probes, a plot $RT \ln(V_n)$ versus the number of carbon atoms should give a straight line from which $\Delta G_a^{\circ, CH_2}$ can be found. It is clear that this will not give an exact value of γ_s^d under all circumstances since, for example, a_{CH_2} will be somewhat temperature dependent. However, comparison of relative results across a series of systems should allow reasonable conclusions as to the surface behaviour to be made. The value of γ_s^d represents the interaction of the surface with an alkane and hence is a measure of how easily the surface can polarise the probe. At infinite dilution therefore, the probes will interact most strongly with the high surface energy sites so, for a

heterogeneous surface, the γ_s^d results will predominantly reflect these, rather than being an average across the whole surface.

The plots for the systems studied here are exemplified by Figure 3; again the plots for all the systems were similar in appearance. Data for the elution of decane, undecane and dodecane were not collected for the kaolins due to the excessive retention times at the temperatures of study. Similarly, those for pentane and hexane on PA were not used, as they were too short to be sufficiently accurate for reliable calculations. All showed the expected linear relationships and the values of γ_s^d calculated are given in Table 3.

The surfaces of native clays such as kaolin are strongly acidic, related to layer defects and hydroxyl and oxygen atoms in the aluminium structures and silicate layers [30]. Strong Lewis acidic sites are formed by cations of interlayer materials. On calcination, these sites are altered as the interlayered structure collapses and a proportion of the highest energy surface sites are removed. However, there is still some hydroxyl functionality present so that a relatively high energy surface remains.

A considerable reduction of γ_s^d occurs on treatment with the aminosilane which will react with these remaining hydroxyl groups. The reduction in γ_s^d clearly bears this out. The γ_s^d results for PA showed little variation with temperature and are in good agreement with a literature value for nylon of 46 mJ m^{-2} [31]. Those for the coated kaolins were higher than PA but there were statistically significant differences between the two materials, particularly as the temperature increased. Tsutsumi and Ohsuga [32] evaluated the effect of silane coupling agents on glass fibres and observed a reduction of 20 – 50 % on the dispersive component of surface energy with surface modification. Osmont and Schreiber [33] also reported the effect of treating glass fibres with silanes and showed that, by varying the silane used, a range of acidic or basic character could be imparted to the surface. Significantly for the current work, treatment with aminopropylsilane was found to make the surface basic.

Interactions at the surfaces of the kaolins involved in our work were further characterised by using non-alkane probes to estimate γ_s^{sp} , due to non-dispersion interactions. Saint-Flour and Papirer [34] suggested that a plot of ΔG_a° as a function of the probe saturated vapour pressure should give a straight line which could act as a standard. The results for the alkane probes are again used to determine a reference line. Given the nature of the alkanes, p° is a reflection of the strength of dispersion forces. Deviations from the line will be due to specific interaction energies and the degree of difference allows estimation of the interaction energies. While there are difficulties in assigning exact quantitative significance to the values obtained, useful comparative information can be obtained. In particular, use of probes with acidic (acceptor), basic (donor) and amphoteric properties allows conclusions to be drawn on the nature of the solid.

A number of workers have used this approach and demonstrated its usefulness and equivalence to more thermodynamically rigorous treatments. A range of polar probes were injected at 100 °C, typical plots being shown in Figures 4 and 5. Specific interaction energies were calculated and are summarised in Table 4. While it was not possible to use the same probes on all of the materials studied, the limited selection of results obtained allows some preliminary conclusions to be drawn on the nature of the surfaces and the effect of coating.

The strongly acidic alcohols gave large specific interactions with the PA surface, although the retention times were too small to measure on the clays indicating the different nature of the surfaces. Results for carbon tetrachloride, a weaker acid, showed only minimal interactions with PA. The amphoteric probes interacted weakly, as did THF, a strongly basic probe. The result for the predominantly basic diethyl ether was negative compared with the non-polar alkanes. These all indicate that the surface of the polyamides is predominantly basic. In addition, it can undergo hydrogen bonding via the carbonyl functionality with hydroxyl groups resulting in the large specific interaction energies for the alcohol probes.

On silane treatment the specific interactions on the filler change from being acidic, electron acceptor-type for Un-CC1 to those of mainly weakly basic, electron donor-type. Thus specific interaction results for the acids, carbon tetrachloride and chloroform were negative for Un-CC1 and positive for CC1 and CC2. Results for the alkenes showed the opposite effect, with a reduction in specific interaction energy on surface modification. These data are consistent with the presence of the amine functional group at the mineral surface. It is also known that some siloxane functionality is introduced due to hydrolysis of the triethoxysilane. In other work[27] we have shown that surface modification with long chain alkyl carboxylic acids effectively produces an alkane-like layer at the surface with γ_s^d values in the region of 30 mJ m^{-2} .

Results for the two coated kaolins were similar, with no strong interactions observed. While the results are within experimental uncertainty, the interactions for CC1 were marginally stronger. A marginally higher specific interaction was, however, seen for cyclohexane on CC2 compared with CC1, possibly indicating a somewhat higher surface accessibility to a bulky probe for the former.

Mechanical Properties of Composites

To assess the effect of surface modification on the polymer-mineral interactions, some physical properties of the composites were measured, the results being shown in Table 5. The notched Izod results for all the systems were similar. This is unsurprising, as the method is relatively insensitive to small variations. However, the un-notched data revealed significant differences between the four systems. The addition of a calcined kaolin reduced the strength of the composite compared with the unfilled polymer. This phenomenon is well documented [35], [36] as is due to filler particles acting as stress concentrators. The relevance of coating becomes clear when comparing the filled polymers. The impact strength for the composite

with non-coated kaolin was less than half that for the systems containing the coated kaolins. In the coated system the interphase region formed between the kaolin and the polymer has some ductility and permits distribution of the impact energy over a larger area. The effect is more profound with a larger number of smaller particles (as observed with CC2).

The flexural modulus and yield strength were increased with calcined kaolin addition. In this case, the poor bonding of Un-CC1 to the polymer increased the matrix modulus as the polymer may orient around the particles during deformation and the polymer will work harden. This behaviour has been previously reported in these materials [11] [9]. Flexural modulus is known to be influenced by particle shape and surface area (volume fraction), with the higher surface area calcined kaolin (CC2) giving a slightly higher modulus.

Tensile properties are affected by filler packing fraction and interfacial characteristics. Addition of a fine, calcined kaolin increased the tensile breaking strain compared with the unfilled polymer. However the peak and breaking stresses were only increased significantly with CC1 and CC2. Under tensile load, movement of the polymer matrix may be restricted by the immobile particles, resulting in greater tensile strength. As the test specimen is placed under tensile load the particles adhering to the matrix undergo uniform displacement, resulting in a greater reinforcing effect than with the uncoated calcined kaolin.

Further discussion

Good dispersion of a mineral in a molten polymer requires the polymer to wet the mineral surface but also needs to have the particles well separated and stabilised to prevent agglomeration. This requires the surface energies of the components to be carefully matched. The uncoated kaolin had a relatively high surface energy. Addition of aminosilane reduced this and made it comparable to that of the polyamide. This assists in the wetting of the filler by the matrix. Silane treatment also modifies the interphase region of the composite. The

mechanical strengths of the composites containing CC1 and CC2 were greater than that based on Un-CC1 reflecting the more closely matched surface energies. While there are relatively small differences between the two coated kaolins with CC2 having the slightly higher dispersive components, this also correlates with the somewhat higher modulus, yield strength and Izod strength. However, it is important that the interaction between polymer and filler is not too strong since it will prevent energy dissipation during flexing or cracking.

A number of workers have commented on the importance of acid-base interactions in determining the interfacial properties and hence promoting filler compatibility [37] and also in polymer-polymer blend [14] systems. However, other workers have suggested that these interactions should not be considered to be of primary importance in the interfacial region [38]. The results reported here support the suggestion that the predominant factor to promote good mechanical properties in PA-clay is the match between the surface energies so that efficient wetting and dispersion of the filler takes place.

The mechanism of silane interactions with inorganic substrates has been characterised by FTIR [39], Raman spectroscopy [40] and XPS [41]. Two regions are formed on a reactive substrate comprising chemisorbed and physisorbed layers with a composition gradient believed to exist at the interface. Physically adsorbed silanes also exist on the substrate surface. This layer comprises predominantly small oligomeric siloxanes. These act as lubricating agents in a polymer melt and also inhibit any preferred interactions between the functional groups at the surface and specific sites on the polymer chain. Thus, the interface will not consist simply of an interaction region between the filler and the matrix.

The use of polar probes allowed some characterisation of the acid-base behaviour of the modified surface and the polymer. The calcined kaolin surface was found to change from a predominantly acidic one to one that was predominantly basic, supporting the evidence for the presence of exposed amine groups. This permitted the formation of strong interactions

with the carbonyl groups of the polyamide, resulting in a stronger composite than one containing unmodified calcined kaolin.

CONCLUSIONS

Inverse Gas Chromatography has been used to characterise the surfaces of a nylon-6 polyamide, a calcined kaolin and kaolins that were coated with an aminosilane coupling agent. The enthalpies of adsorption for alkane probes on all the materials were similar. However, the dispersive component of the surface free energy for the uncoated kaolins was much higher than the polyamide. Treatment with the silane reduced the value so that it was comparable with the polymer. The use of a small selection of probes which display specific interactions suggests that the PA has a predominantly basic surface although the capacity for hydrogen bonding was also strong. Silane treatment modified the behaviour of the acidic calcined kaolin, also resulting in a mainly basic surface.

Measurements of the mechanical properties of PA composites containing the kaolins showed that incorporation of the kaolins raised the flexural modulus and also increased their strength. However, the properties were better when the silane coated kaolins were used. The results further illustrate the potential of IGC to characterise composite materials in order to optimise their performance.

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Table 1: Physical properties of calcined clays.

		CC1	CC2
ISO Brightness		88.8	91.2
ECC Yellowness		4.9	3.5
BET Surface area (m⁻² g)		7.0	16.0
Particle size (wt.%)	> 10 μm	5	1
	> 5 μm	15	5
	< 2 μm	49	90
	< 1 μm	12	80
	< 0.5 μm	< 5	40
	< 0.25 μm	< 5	6
Composition (wt.%)	SiO ₂	55.8	52.8
	Al ₂ O ₃	41.0	44.2
	Fe ₂ O ₃	0.59	1.0
	TiO ₂	0.06	1.49
	CaO	0.01	0.08
	MgO	0.19	0.01
	K ₂ O	2.21	0.07
	Na ₂ O	0.01	0.01
	Loss on ignition	0.30	0.40

Table 2: Enthalpy of adsorption data for PA, calcined kaolins and silane treated kaolin.

Probe	Enthalpy of Adsorption / kJ mol⁻¹			
	PA	Un-CC1	CC1	CC2
Pentane		35 \pm 2	44 \pm 1	43 \pm 1
Hexane		46 \pm 4	47 \pm 1	45 \pm 1
Heptane	53 \pm 2	58 \pm 3	52 \pm 1	50 \pm 1
Octane	57 \pm 1	73 \pm 4	59 \pm 1	57 \pm 1
Nonane	68 \pm 1	87 \pm 4	66 \pm 1	64 \pm 1
Decane	88 \pm 1			
Undecane	105 \pm 2			
Dodecane	112 \pm 2			

Table 3: Dispersive component of surface free energy data for PA and kaolins.

	Dispersive component of surface free energy (mJ m⁻²)			
Temperature (°C)	PA	Un-CC1	CC1	CC2
60	41 ± 3			
70	40 ± 3			
80	42 ± 2	139 ± 4	58 ± 2	64 ± 5
90	42 ± 3	137 ± 3	58 ± 2	65 ± 2
100	45 ± 3	132 ± 3	63 ± 3	65 ± 4
110			65 ± 3	66 ± 4
120		130 ± 2	58 ± 2	70 ± 2
130			56 ± 2	67 ± 3
140		130 ± 3	56 ± 3	69 ± 2

Table 4: Specific interaction energies for polar probes for PA and kaolins.

	Specific interaction – $\Delta G_{\text{specific}}$ (kJ mol⁻¹)			
Probe	PA	CC1	CC2	Un-CC1
Methanol	12.4			
Ethanol	10.9			
Butanol	12.0			
Carbon tetrachloride	1.5	2.2	2.0	-2.7
Chloroform		4.1	4.0	-1.8
Cyclohexane		-1.0	-2.5	-4.3
Acetone	4.0			NPD
Ethyl acetate	4.4			NPD
Diethyl ether	-2.4			NPD
Pentene		2.2	1.8	4.9
Hexene		1.8	1.8	4.0
Octene		1.8	1.4	3.8
THF	3.1			

NPD – no peak detectable

Table 5: Physical properties of injection mouldings.

		PA + Un-CC1	PA + CC1	PA + CC2	PA
Izod strength	Notched (kJ m⁻²)	6.9 (1.5)	6.4 (0.4)	5.8 (1)	6.8 (0.3)
	Un-notched (kJ m⁻²)	80 (2)	181 (16)	208 (18)	340 (8)
Flexural properties	Modulus (MPa)	2760 (70)	2305 (103)	2440 (83)	1525 (46)
	Yield strength (MPa)	87 (2)	83 (1)	86 (1)	67 (1)
Tensile properties	Peak stress (MPa)	68 (1)	74 (1)	75 (1)	66 (1)
	Break stress (MPa)	66 (1)	73 (1)	73 (1)	47 (10)

Standard deviations given in parenthesis.

CAPTIONS FOR FIGURES

- Figure 1:** Plot of ΔG_a° versus temperature for alkane probes on calcined kaolinite CC1 coated with aminosilane.
- Figure 2:** Plot of ΔG_a° versus temperature for alkane probes on uncoated calcined kaolinite Un-CC1
- Figure 3:** Plot of $RT \ln V_n$ versus number of alkane carbon atoms for calcined clay CC1 coated with aminosilane.
- Figure 4:** Plot of ΔG_a° versus $\log P_o$ for PA polymer to determine specific interaction energies
- Figure 5:** Plot of ΔG_a° versus $\log P_o$ for coated calcined clay CC1 to determine specific interaction energies

Figure 1: Plot of ΔG_a° versus temperature for alkane probes on calcined kaolinite CC1 coated with aminosilane.

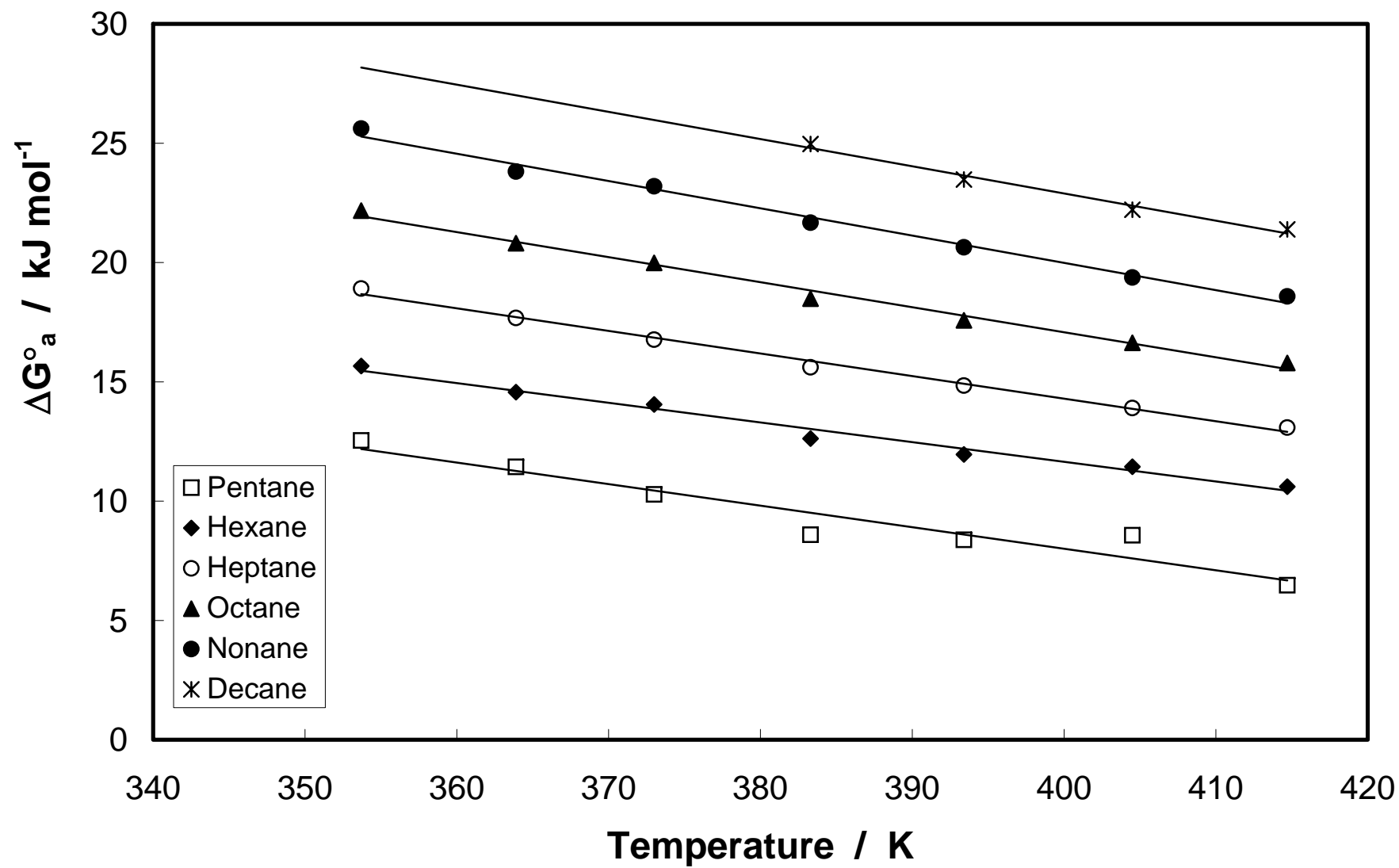


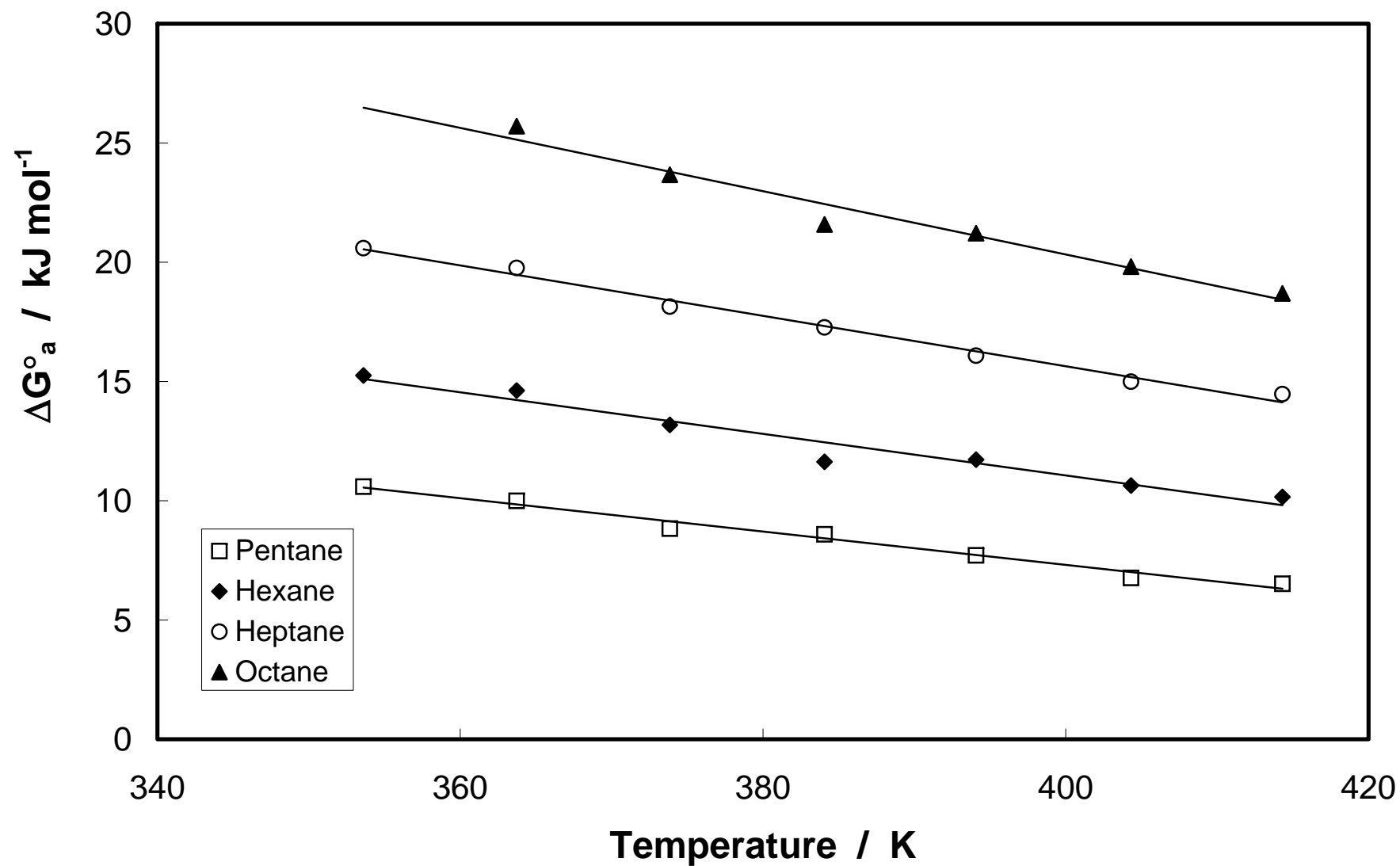
Figure 2: Plot of ΔG_a° versus temperature for alkane probes on uncoated calcined kaolinite Un-CC1

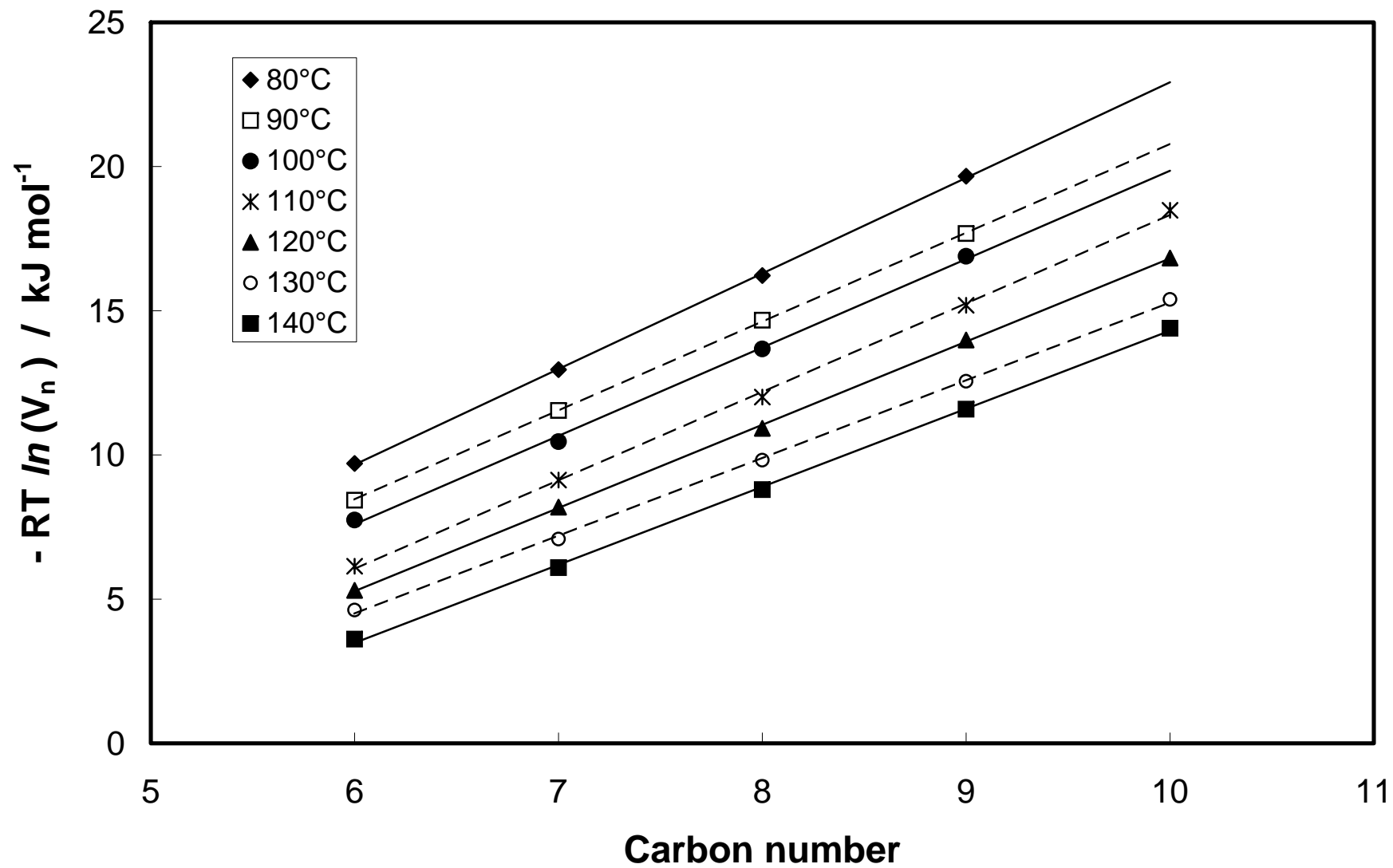
Figure 3: Plot of $RT \ln V_n$ versus number of alkane carbon atoms for calcined clay CC1 coated with aminosilane.

Figure 4: Plot of ΔG_a° versus $\log P_o$ for PA polymer to determine specific interaction energies

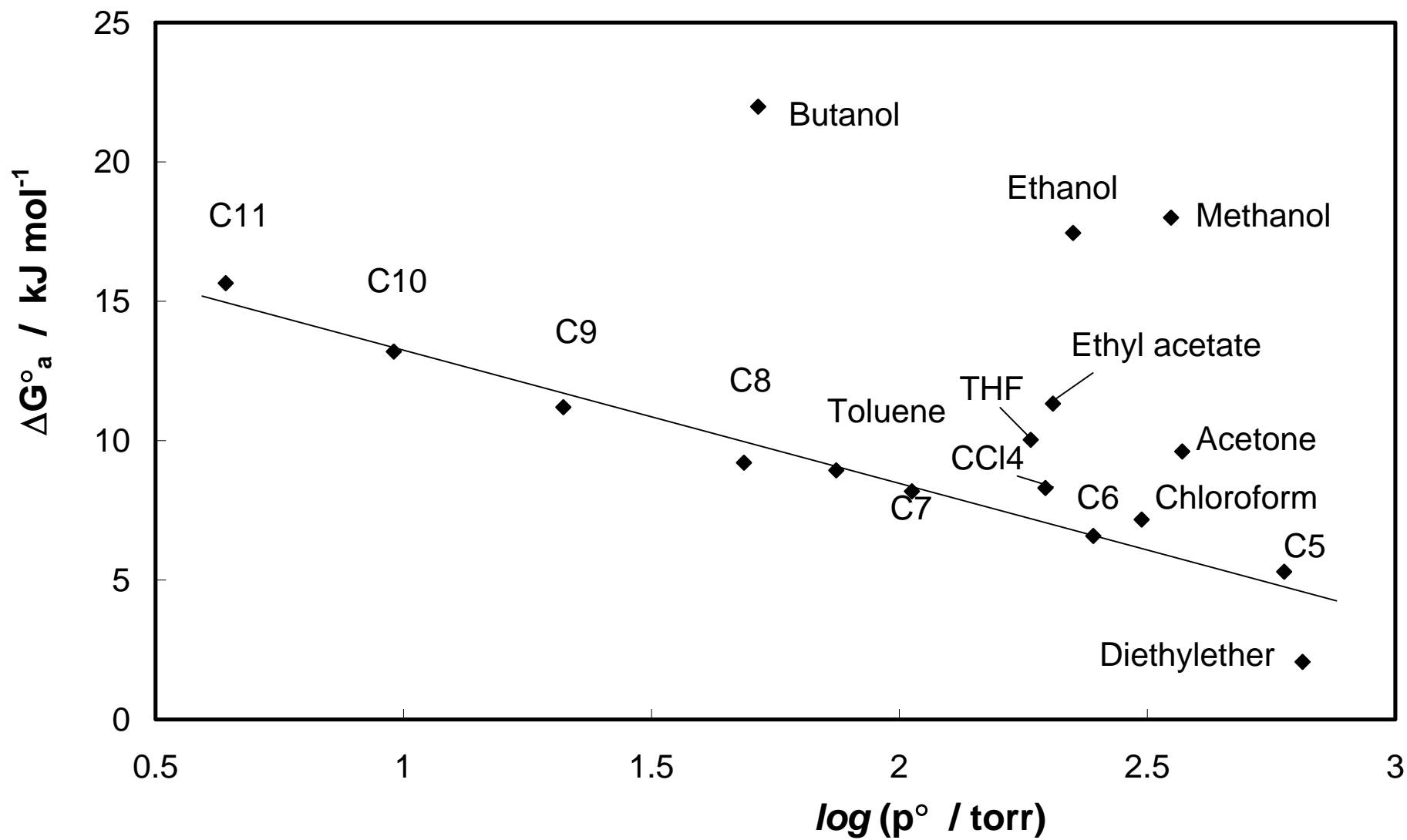


Figure 5: Plot of ΔG_a° versus $\log P_0$ for coated calcined clay CC1 to determine specific interaction energies