



Determination of Acid-base Component of the Surface Energy by Inverse Gas Chromatography

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This paper describes the application of the IGC SEA technique to determine the Acid-Base component of the surface energy of solid samples. The acid-base surface energy of a solid can be determined using two mono-polar probes of known γ_l^- and γ_l^+ based on the van Oss-Chaudhury and Good approach. The applied mono-polar probes have different strengths so the calculated γ_s^{ab} can vary. Also the γ_l^- and γ_l^+ can vary as a function of the model chosen (either Della Volpe or vOCG). This represents the limitation of current theories.

Introduction

The data analysis software of the SEA gives an option to determine the acid-base (short range forces) component of the surface energy of solid materials (γ_s^{ab}). This is sometimes also termed the specific surface energy. In inverse gas chromatography, two mono-polar probes are injected to determine this parameter. In this study the effects of mono-polar probe selection were investigated as well as the model used in data analysis.

According to Fowkes, the total surface energy (γ_s) can be divided into two parts; a dispersive (long range forces), γ_s^d , and an acid-base component (short range forces), γ_s^{ab} :

$$\gamma_s = \gamma_s^d + \gamma_s^{ab}$$

Van Oss, Chaudhury and Good extended this method to allow the determination of the acid and base components of the surface energy in 1988 [5,6]. Based on this approach, the specific surface energy of a solid (or a liquid) can be also

divided into two parts, the acid component (γ_s^+) and the base component (γ_s^-). The specific surface energy γ_s^{ab} can thus be calculated by the following equation:

$$\gamma_s^{ab} = 2\sqrt{\gamma_s^- \gamma_s^+}$$

And the terms γ_s^- and γ_s^+ can be calculated from two mono-polar probes with the following equation:

$$\Delta G^{sp} = Na2(\sqrt{\gamma_l^- \gamma_s^+} + \sqrt{\gamma_l^+ \gamma_s^-})$$

Where the ΔG^{sp} is the specific free energy of the polar probe in [J/mol], the N is the Avogadro's number ($N=6.022 \times 10^{23} \text{ mol}^{-1}$) and the a is the cross sectional area of the polar probe in [m^2]. Commonly used mono-polar solvents are ethyl-acetate and the dichloromethane, but chloroform and toluene can be used as well.

In case of the Contact Angle (CA) measurements the polar solvent used can be also different including diiodomethane, formamide, ethylene-glycol. But the reported specific surface energy



components of the solvents can also vary. The disadvantage of CA approach is well known [4] and this is one of the critical points in both methods. In this study diverse mono-polar probes will be used to calculate the specific surface energy of solids and the effect of probe selection will be illustrated.

However, there is another critical point in the CA measurement. It is the assumption that the acid-base surface tension for water is neutral ($\gamma_l^- = \gamma_l^+ = 25.5 \text{ mJ/m}^2$ - vOCG Scale) whereas it is known to be a stronger Lewis acid than a Lewis base – Della Volpe Scale [3,4]. Both scales can be applicable using the inverse gas chromatographic technique, and the Cirrus Plus Software of the iGC-SEA system which allows the user the opportunity to choose the scale used.

The surface tension components of the mono-polar solvents are listed in the Table 1. In this study the effect of the applied scale will be also demonstrated.

Table 1.: Surface Tension Components of Liquid probes [mJ/m^2]

	Della Volpe		vOCG	
	γ_l^+	γ_l^-	γ_l^+	γ_l^-
Water	65.0	10.0	25.5	25.5
Ethyl-acetate	0	475.67	0	19.2
Dichloromethane	124.58	0	5.2	0
Chloroform	1.27	0	3.8	0
Toluene	0	16.23	0	2.3

Method

In the case of the IGC SEA experiments a powder sample was packed in a column with 30 cm length and a 3 mm ID. All IGC analyses were carried out

using iGC Surface Energy Analyzer (SMS, Alpertown, UK) and the data were analysed using both standard and advanced SEA Cirrus Plus Analysis Software. Samples were run at a series of surface coverages with alkanes and mono-polar probe molecules to determine the dispersive surface energy distribution as well as the acid-base surface energy distribution. For the analysis, the Dorris and Gray method was employed for the dispersive component [1]. The acid-base contribution was determined by first measuring the free energy of desorption based on the polarisation approach [2]. The specific surface energies were determined based on the van Oss methodology using both the Della Volpe scale and vOCG scale [3]. Each column was pre-conditioned for 2 hours at 30°C and 0% RH with helium carrier gas to remove any physisorbed water. All experiments were carried out at 30°C with 10sccm total flow rate of helium, using methane for dead volume corrections.

Results

Surface Energy Profiles

Three different solid samples (a polymer based fabric, lactose monohydrate and an $\alpha\text{-Al}_2\text{O}_3$ – CRM-170) were used during the investigation of the specific surface energy.

Acid-base surface energy (γ_s^{ab}) values were determined using different mono-polar probe pairs by Della-Volpe Scale, as shown in Figures 1-3. Despite the fact that similar or nearly the same γ_s^{ab} values were expected, significant variations are observed, depending on the solvent pairs used. And using the Della-Volpe scale the dispersive surface energy (γ_s^d) contributes the major part of the total surface energy (Figure 4) except for the Toluene-Chloroform pair (Figure 5).

Similar conclusions was made in case of each of these 3 samples, so the results show systematic variation in the calculation.

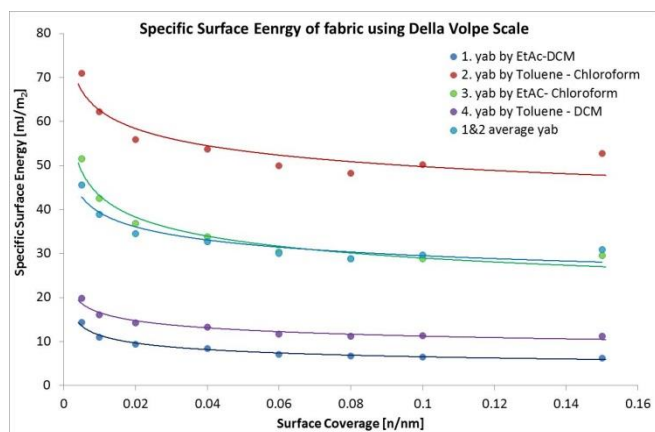


Figure 1. Calculated acid-base surface energies of fabric using diverse monopolar pairs and the Della Volpe Scale.

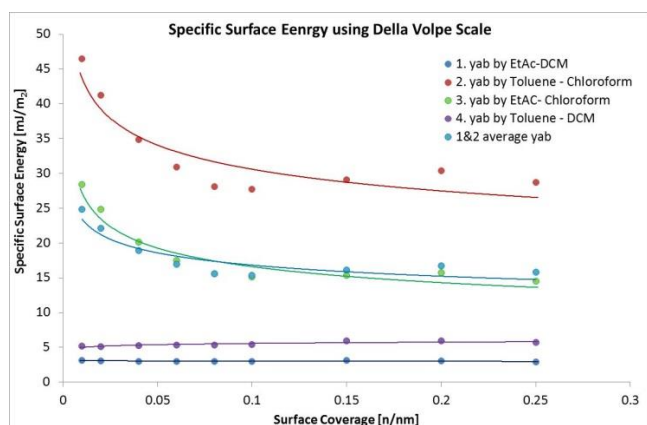


Figure 2. Calculated acid-base surface energies of lactose monohydrate using diverse monopolar pairs and the Della Volpe Scale.

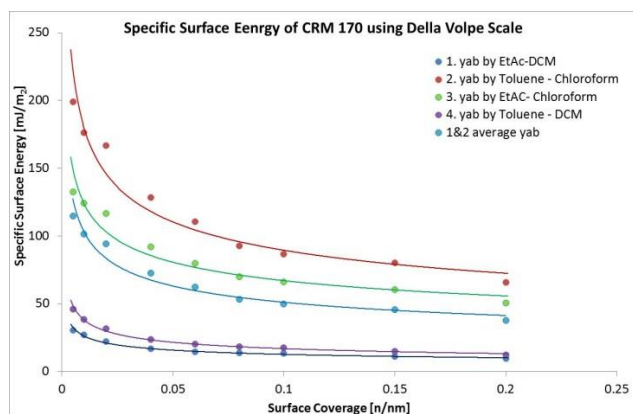


Figure 3. Calculated specific surface energies of alpha-alumina (CRM-170) using diverse monopolar pairs and the Della Volpe Scale.

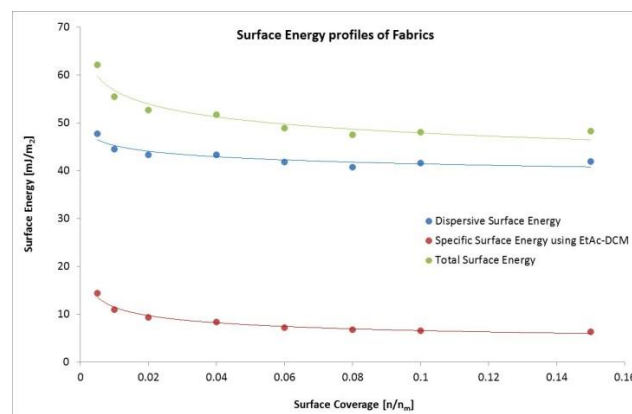


Figure 4. Surface energy components of fabric using ethyl-acetate and dichloromethane to determine the acid-base component by Della Volpe approach.

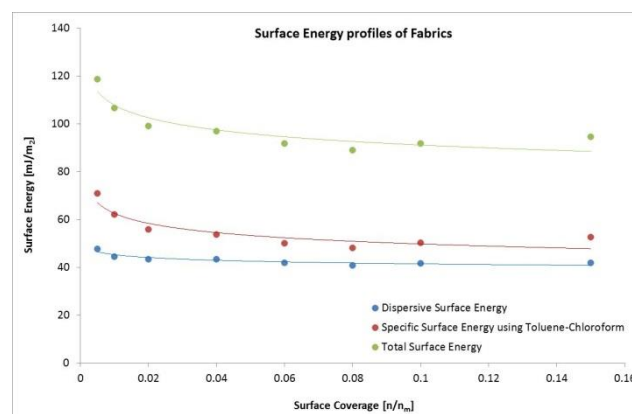


Figure 5. Surface energy components of fabric using Toulene and Chloroform to determine the acid-base component by the Della Volpe approach.

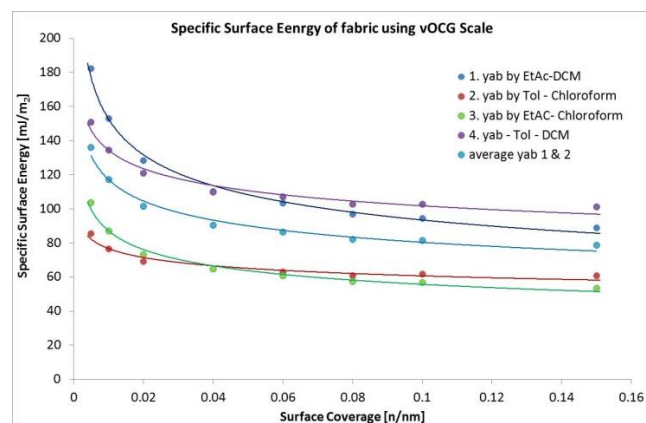


Figure 6. The calculated acid-base surface energies of fabric using diverse mono-polar pairs applying the vOCG Scale.

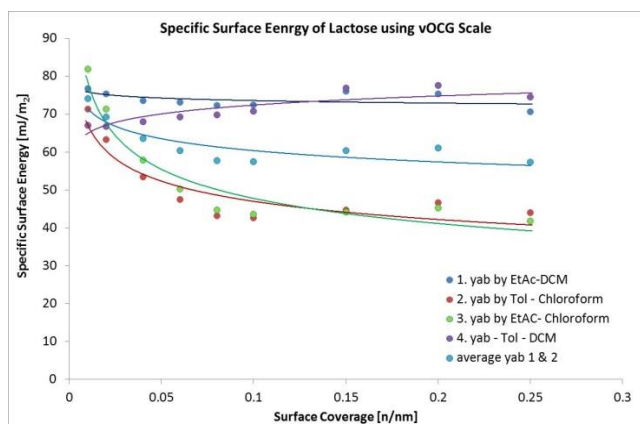


Figure 7. Calculated acid-base surface energies of lactose monohydrate using diverse mono-polar pairs applying the vOCG Scale.

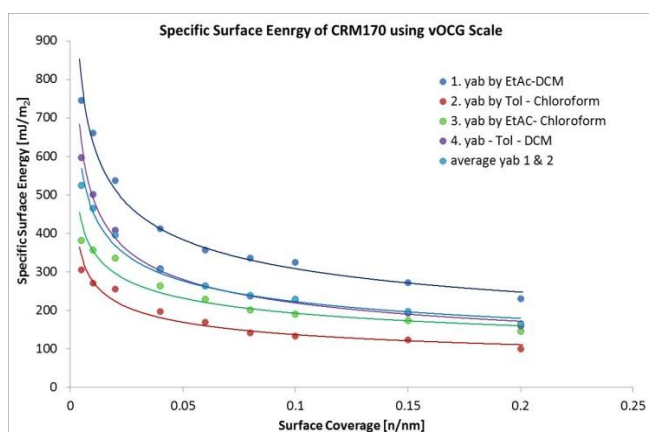


Figure 8. Calculated acid-base surface energies of alpha – alumina (CRM 170) using diverse mono-polar pairs applying the vOCG scale.

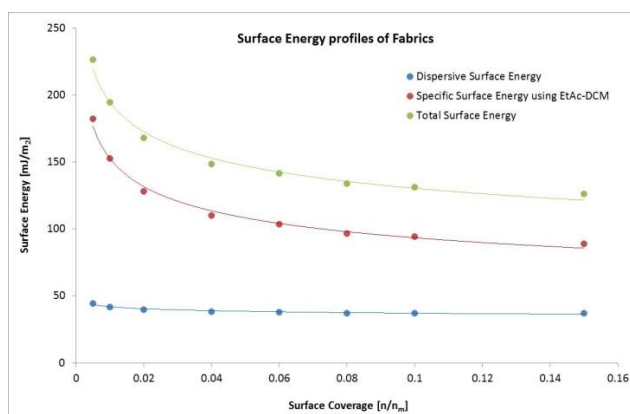


Figure 9. Surface energy components of fabric using ethyl-acetate and dichloromethane pair to determine the acid-base component by vOCG approach.

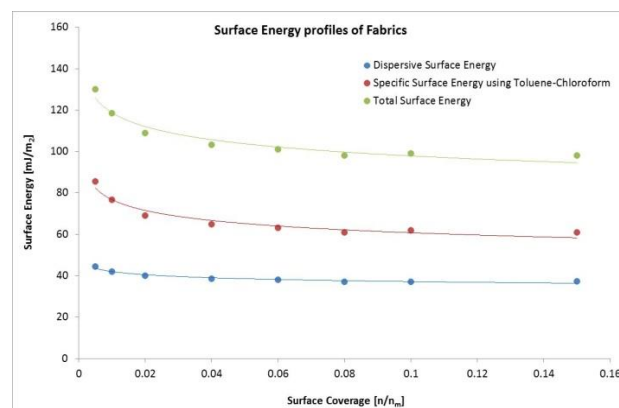


Figure 10. Surface energy components of fabric using toluene and chloroform pair to determine the specific part by vOCG approach.

Variable specific surface energy values can also be determined using different mono-polar pairs by vOCG Scale. Nevertheless, significantly higher specific surface energy values are observed using the vOCG Scale (Figure 6-8), thus contributing the major part of the total surface energy (Figure 9-10) in case of each mono-polar pairs. All sample surfaces are strongly polar based on these results, which are questionable.



Conclusion

Both IGC and contact angle methods have serious limitations in determining acid-base surface energy values which can affect the absolute results obtained. These limitations can be diminished in IGC when the Della Volpe Scale is used and the energetic heterogeneity is considered. Using different models of the surface tension components, caution must be exercised as some sets of γ_i^- , γ_i^+ values used may result in unrealistically high specific surface energies for solids. This caution has been defined earlier for contact angle measurements, and now it also can be stated for the inverse gas chromatography.

The uncertainty in both γ_i^- and γ_i^+ values for monopolar solvents, as well as a lack of validation of the models, means that the obtained estimates for γ_s^{ab} depends heavily on the solvent pairs chosen for data analysis. Although caution must be used in selecting the mono-polar probes and model for absolute acid-base surface energy values, trends between samples are still valid and internally resistant when all measurements use the same probe pairs and model. Therefore, determining relative differences between samples and measurement conditions can be done using any probe/scale combination. The SMS Team is working to develop the specific surface energy calculation and to improve the accuracy of these methods.

References

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