Surface Measurement Systems
World Leader in Sorption Science

DVS Application Note 43

Determination of Surface Energetics of Mineral Aggregates by Dynamic Vapour Sorption

Frank Thielmann, Majid Naderi and Dan Burnett, Surface Measurement Systems Ltd.

The quality of asphalt depends strongly on the affinity of the mineral aggregates to the bitumen binder. This affinity is directly related to the surface energetics of the individual components. Dynamic gravimetric vapour sorption is an accurate and reliable method for the characterisation of solid powders. In the current study dispersive and specific (acid-base) contributions to the surface energy have been measured for six different mineral aggregates.

Introduction

Asphalt is a building material consisting of mineral aggregates and bitumen. The latter acts as the binder. Bitumen is produced from heavy fractions during crude oil refining and contains linear and cyclic alkanes, olefins and aromatic compounds. The quality of the asphalt depends strongly on the interaction between the mineral aggregates and the binder. Such interaction can be quantified by the work of adhesion [1]. The work of adhesion is calculated from the surface energies of the individual bitumen and aggregate components. While bitumen surface energies are usually obtained by wettability measurements such experiments are difficult to perform on the aggregates due to the particular nature of these materials.

Vapour sorption measurements are an accurate and reliable alternative for the determination of aggregate surface energies [1, 2]. This application note describes how to obtain surface energies of various different mineral aggregates by dynamic gravimetric vapour sorption experiments (DVS).

Theory

The surface energy, γ is directly related to the work of adhesion, W_{adh} by Equation 1. From a practical point of view the work of adhesion can be seen as a measure for the strength of interaction between a component 1 and 2.

$$W_{adh} = 2(\gamma_1 * \gamma_2)^{1/2} \quad (1)$$

This means that the work of (component) adhesion in an asphalt sample can be directly calculated from an individual surface energy measurement of the aggregate and the binder. The surface energy can be split into a dispersive contribution, γ^d describing Lifshitz-van der Waals interactions and a specific component, γ^{sp} reflecting Lewis acid-base (electron acceptor/donor) interactions [3]. In older literature the term “polar” is often used instead of “specific”. However, the former is misleading since it is easily confused with the polar contribution of the Keesom or Debye forces to the Lifshitz-van der Waals interactions while specific interaction are based on Lewis acid-base forces. Good and van Oss suggested to replace the general expression for the specific contribution with an acid and base

parameter, γ^+ and γ^- [4]. The specific surface energy is the geometric mean of the acid and base number (Equation 2).

$$\gamma^{SP}=2\sqrt{\gamma^+\cdot\gamma^-} \quad (2)$$

The solid-solid work of adhesion W^{ss}_{total} (between aggregate and binder) can then be calculated according to Equation 3.

$$W^{ss}_{total} = 2(\gamma_1^d * \gamma_2^d)^{1/2} + 2((\gamma_1^+ * \gamma_2^-)^{1/2} + (\gamma_1^- * \gamma_2^+)^{1/2}) \quad (3)$$

For the determination of the different contributions of the surface energy, DVS adsorption isotherms of a non-polar probe as well as of an acidic and basic vapour need to be measured. From the isotherms a spreading pressure is calculated that is directly related to the surface energy. The calculation is described in reference [5] in more detail.

Method

DVS is a well-established method for the determination of vapour sorption isotherms. The DVS Advantage instrument used for these studies measures the uptake and loss of vapour gravimetrically using a highly sensitive recording ultra-balance with a mass resolution of ±0.1 µg. The high mass resolution and excellent baseline stability allow the instrument to measure the adsorption and desorption of very small amounts of probe molecule. The vapour partial pressure around the sample is controlled by mixing saturated and dry carrier gas streams using electronic mass flow controllers. The temperature is maintained constant ±0.1 °C, by enclosing the entire system in a temperature-controlled incubator.

Aggregate samples were provided by DLR Hanover, Germany and were collected in different geological regions of Germany. Between 30 and 65 mg of the aggregate samples were placed into a DVS-Advantage instrument and preconditioned in a 100-sccm stream of dry air (< 0.1% relative humidity) for several hours. Octane was used as a non-polar probe while ethyl acetate and chloroform were selected as basic and acidic vapour, respectively. The sample was exposed to the following vapour partial pressure profile: 0.01, 0.02, 0.03, ... , 0.10, 0.20, .., 0.90, and 0.95 p/po. For the selected samples the partial pressure was then decreased in an identical manner back down to 0.00 p/po to check for irreversible adsorption. The sorption isotherms were calculated from the equilibrium mass values at each partial pressure.

Results

Figure 1 shows the sorption isotherms of octane, ethyl acetate and chloroform on the Augite sample.

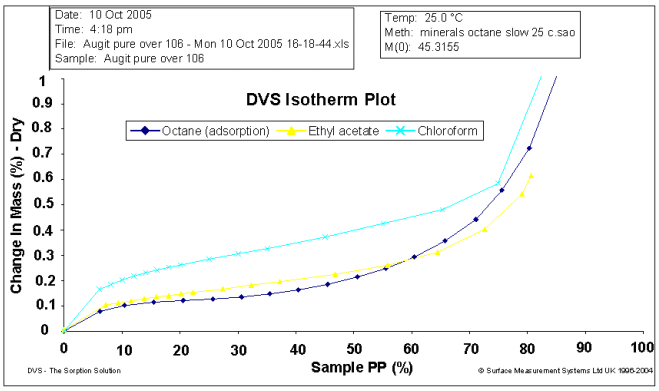

Figure 1. Adsorption isotherms for octane, ethyl acetate and chloroform on the Augite sample at 25 °C. The isotherm is only shown up to 85% p/po to visualise the differences at lower partial pressures.

No irreversible adsorption has been observed in this or any other experiment where a complete adsorption/ desorption cycle has been recorded. For this reason only the adsorption branch was analysed. To obtain the surface energy for the different aggregates the spreading pressures and vapour-solid work of adhesion values were calculated from the adsorption isotherms using the DVS Advanced Analysis suite v4.3. Table 1 summarises the results for the samples investigated in this study. The surface area is also given as it is required for the calculation. It has been simultaneously determined from the octane adsorption isotherms as described in reference [6].

Table 1. Surface and free energy results for aggregates investigated in this study.

	Vapour	π_e [mJ/m²]	W^{sv}_{adh} [mJ/m²]	S_{BET} [m²/g]
Augite	Octane	70.9	113.2	3.19
	Chloroform	92.6	145.9	x
	Ethyl acetate	73.5	120.3	x
Basalt	Octane	101.9	144.2	2.09
	Chloroform	100.5	153.8	x
	Ethyl acetate	104.6	151.3	x
Calcite	Octane	43.5	85.8	1.03
	Chloroform	64.7	118.1	x
	Ethyl acetate	104.8	151.6	x
Feldspars	Octane	30.4	72.6	0.79
	Chloroform	27.4	80.8	x
	Ethyl acetate	32.5	79.2	x
Granite	Octane	28.4	70.7	0.20
	Chloroform	27.7	81.1	x
	Ethyl acetate	53.0	99.8	x
Quartz	Octane	46.8	89.1	2.25
	Chloroform	51.2	104.5	x
	Ethyl acetate	66.2	113.0	x

The dispersive contribution of the surface energy can be directly obtained from the octane data. The acid and base contribution to the surface energy is calculated from the work of adhesion and spreading pressure obtained for the acid and base probe vapour [4, 7, 8]. It should be emphasised that the work of adhesion, W^{sv}_{adh} reported in Table 1 represents the interaction between the solid surface and the vapour. This is different and should not be confused with the work of adhesion W^{ss}_{total} between aggregate and binder in Equation 3.

The acid and base numbers can now be either calculated based on the original scale from van Oss [4] or the modified scale of Della Volpe et al. [8]. The former has the disadvantage that the acid and base parameter, γ^+ and γ^- are not directly comparable due to inaccurate starting parameters. It also leads to an overestimation of the basic contribution and the absolute values for the specific surface energy. To solve these problems Della Volpe et al. optimized the values for probe liquids in wettability experiments. This scale was later extended by Thielmann and Burnett for vapour phase probes [9].

Finally, the total surface energy may be obtained from the sum of the specific surface energy (Equation 2) and the dispersive contribution. The results are shown in Table 2a (van Oss scale) and b (Della Volpe scale).

Table 2a. Surface energies and acid-base numbers for aggregates (van Oss).

Sample	γ_S^D [mJ/m²]	γ_S^+ [mJ/m²]	γ_S^- [mJ/m²]	γ_S^{total} [mJ/m²]
Augite	151.40	1.67	34.49	166.59
Basalt	245.90	2.05	0.58	248.08
Calcite	87.10	61.89	40.18	186.83
Feldspars	62.40	1.13	0.20	63.35
Granite	59.20	13.05	1.11	66.80
Quartz	93.90	9.62	3.84	106.05

Table 2b. Surface energies and acid-base numbers for aggregates (Della Volpe).

Sample	γ_s^D [mJ/m²]	γ_s^+ [mJ/m²]	γ_s^- [mJ/m²]	γ_s^{total} [mJ/m²]
Augite	151.40	0.05	111.09	156.40
Basalt	245.90	0.06	0.88	246.35
Calcite	87.10	2.44	128.73	122.52
Feldspars	62.40	0.04	1.34	62.86
Granite	59.20	0.51	4.84	62.34
Quartz	93.90	0.36	14.22	98.44

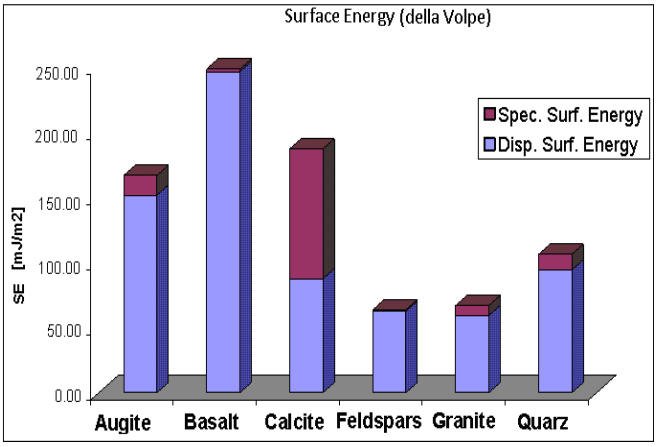

Figure 2b. Dispersive and specific surface energies of the different aggregate samples. Specific surface energies have been obtained using the Della Volpe scale.

For all samples the total surface energy is dominated by the dispersive contribution with the exception of calcite where a significant specific surface energy is observed on both scales. The dispersive, specific and total surface energies are illustrated in Figures 2a and b.

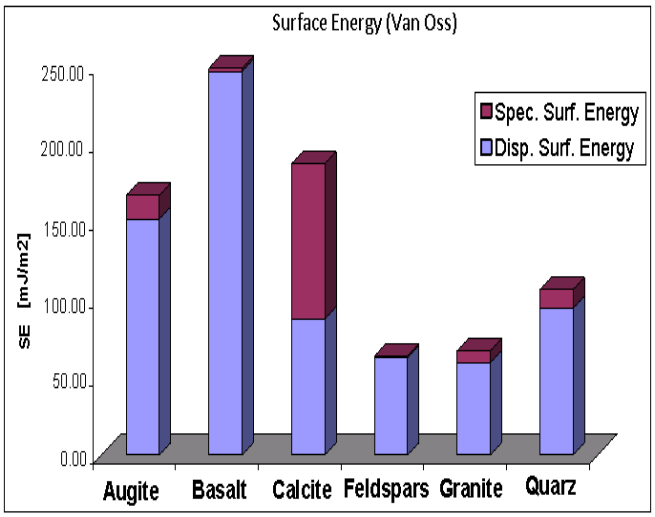

Figure 2a. Dispersive and specific surface energies of the different aggregate samples. Specific surface energies have been obtained using the van Oss scale.

The Della Volpe scale gives more realistic specific surface energies although it doesn't solve the problem of an overestimation of the basic contribution to the specific surface energy as described in the previous discussion of acid-base scales.

If the samples are ranked by their total surface energy the following sequence is obtained (on the Della Volpe scale): Basalt >Augite> Calcite > Quartz >Feldspars~Granite.

The results obtained on the van Oss scale show a similar trend with the exception that Calcite and Augite change positions. However, the latter is most likely an artefact due to the overestimation of the specific contribution to the surface energy.

The sequence found in this study agrees in general with the empirical observation that these aggregates show a similar order of affinity to the most common asphalt binders. The only unexpected observation is the position of Quartz in this sequence as it is known to have generally a very poor affinity. However, one has to keep in mind that only one sample of each aggregate type has been investigated and that different sources (different geological regions) could have a strong impact on purity level and morphology, all factors that can affect the surface energy significantly.

Conclusion

Dispersive, specific and total surface energies as well as acid and base numbers have been determined for different mineral aggregate samples by DVS. The results for the acid and base numbers and therefore for the specific surface energies depend on the scale used for the calculation. It was found that the Della Volpe scale produces more realistic specific surface energies although the overall impact on the trend in total surface energy was smaller than expected. DVS was shown to be a reliable and accurate method to determine dispersive and acid-base properties of particulate materials. If surface tensions of binders are known the affinity between aggregates and binders could be quantified by calculating the work of adhesion from the surface energies of the aggregates obtained in this study.

Acknowledgement:

The authors would like to greatfully acknowledge Dr. Dieter Schreier from DRL in Hannover, Germany for supplying the mineral samples used in this study and for collaborating with our staff to share his expertise in this area.

References

[1]Cheng, D.X. et al, Proc. TRB 2003 Annual Meeting, Washington, (2003).
[2]Thielmann, F. and Pearse, D., SMS Application Note 211, (2005).
[3]Mukhopadhyay, P. and Schreiber, H., Colloid and Surfaces A 100 (1995), 47.
[4]van Oss, C, Good, R. and Chaudhury, M., Langmuir 4 (1988), 884.
[5]Levoguer, C. and Williams, D., SMS Application Note 17, (2002)
[6]Levoguer, C. and Williams, D., SMS Application Note 18, (2003).
[7]Thielmann, F. et al., SMS Application Note 221, (2005).
[8]Della Volpe, C. and Siboni, S., J. Adh. Sci. Techn. 14 (2000), 235.
[9]Thielmann, F. And Burnett, D., paper submitted to Intern J. Pharm.

Head Office:
Surface Measurement Systems, Ltd
5 Wharfside, Rosemont Road
LondonHA0 4PE, UK
Tel: +44 (0)20 8795 9400
Fax: +44 (0)20 8795 9401
Email: science@surfacemeasurementsystems.com

United States Office:
Surface Measurement Systems, Ltd, NA
2125 28th Street SW, Suite I
Allentown PA, 18103, USA
Tel: +1 610 798 8299
Fax: +1 610 798 0334