Surface Measurement Systems
World Leader in Sorption Science

iGC SEA Application Note 211

An Investigation of Minerals used in Asphalt by Inverse Gas Chromatography at Infinte Dilution

Surface Measurement Systems Ltd.

The affinity of minerals to bitumen is highly important for the quality of the asphalt composition. In order to predict this affinity a detailed knowledge of the physico-chemical properties of the mineral surface is required. Inverse Gas Chromatography (IGC SEA) is a fast and sensitive method for the characterisation of solid powders. In the current study dispersive as well as acid-base properties have been investigated for different minerals.

Introduction

Asphalt is a building material consisting of minerals and bitumen. The latter acts as the binder. Bitumen is produced from heavy fractions during crude oil refining and contains linear and cyclic alkanes, olefines and aromatic compounds. The quality of the asphalt depends strongly on the interaction between the minerals and the binder. Despite its importance a reliable parameter for the description of such interactions has yet not been identified.

In practice it is often observed that similar minerals give different affinities with the same bitumen. As demonstrated in the following example surface energy experiments can be a good measure for this affinity. Moreover, specific interactions with polar probe molecules can provide interesting information about the acid-base chemistry of the surface.

Theory

Generally IGC SEA elution experiments can be configurated in two ways: as a discontinuous pulse or a continuous frontal experiment. In a pulse measurement an injection of a known vapour probe molecule (adsorbate) is done. This pulse is transported by the carrier gas, which is helium for the SMS-*iGC* SEA, through the GC to the column. The amount adsorbed by the solid sample in the column is eluted by the carrier gas. The retention time of the probe molecule is detected by the flame ionisation detector (FID). The retention time can be converted into the net retention volume VR0 by Equation 1:

$$V_R^0 = j / m \cdot F \cdot (t_R - t_0) \cdot \frac{T}{273.15} \qquad (1),$$

where T is the column temperature, m the sample mass, F the exit flow rate at 1 atm and 273.15K; t_R is the retention time for the adsorbing probe and t0 is the mobile phase hold-up time (dead-time). j is the James-Martin correction, which corrects the retention time for the pressure drop in the column bed [1].

To measure the dispersive surface energy (γ_S^D) of solid materials by IGC SEA, a series of alkanes with different carbon chain lengths is injected at a constant column temperature. The logarithm of the net retention volume of each probe molecule is plotted versus a property of the probe molecules. Usually this is the product of cross sectional area a and square root of the liquid tension γ_L^D. The alkanes form a straight line in this plot and the dispersive contribution of the

surface energy can be calculated from the slope according to Equation 2.

$$RT \ln V_R^0 = 2N_A \left(\gamma_S^D\right)^{1/2} a \left(\gamma_L^D\right)^{1/2} + const. \qquad (2).$$

N is the Avogadro constant and R the gas constant [2]. These measurements are carried out at infinite dilution where only a very few probe molecules are available for the interaction with the surface. For this reason only the higher energy sites on the surface are covered which provides the highest sensitivity of the measured parameters.

If polar probe molecules are injected in addition then specific interactions can be measured. The experimental points for the polar probe molecules are located beyond the alkane straight line in the surface energy plot. The distance between each point and the straight line represents the specific contribution of the interaction, which is expressed as the free energy, ΔG. A detailed description of these calculations can be found elsewhere [3].

Free energies can be converted into acid-base parameters if acid-base concepts are applied. One of the most commonly used approaches is the theory of van Oss et al [4,5].

$$\Delta G = N_A * a * 2 * ((\gamma_L^+ * \gamma_S^-)^{1/2} + (\gamma_L^- * \gamma_S^+)^{1/2}) \qquad (3)$$

In this equation γ_S^+ and γ_S^- are the electron acceptor and donor parameters of the surface and γ_L^+ and γ_L^- are the electron acceptor and donor parameters of the probe molecule. If experiments are carried out with monopolar probe molecules γ_S^- and γ_S^+ can be obtained by measuring the free energy of just one acidic and one basic probe molecule.

After the γ_S^+ and γ_S^- values have been calculated the specific contribution of the surface energy can simply be obtained by the geometrical mean [**Error! Bookmark not defined.**] of the acid-base parameters (Equation 4).

$$\gamma_S^{AB} = 2 \cdot \sqrt{\gamma_S^+ \cdot \gamma_S^-} \qquad (4)$$

Method

Four different minerals were investigated: pure mineral quartz with a poor affinity to bitumen, quartz sand (good affinity), calcite sand (good affinity) and potassium feldspar (medium affinity).

Various columns (2 mm ID, 300 mm long) were packed. All sorption experiments were carried out on an SMS-*iGC* 2000. Measurements were done with several probe molecules, all HPLC grade, supplied by Aldrich. Before measurement, samples were pre-treated for 2 h at 423 K to remove physisorbed water and impurities adsorbed on the surface. After pre-treatment, pulse injections were carried out with a 0.25 ml gas loop at 323K and an injection concentration of 0.03 p/po. The carrier gas (Helium) flow rate was 10 ml/min. Measurements were analysed using the SMS *iGC* Analysis Software v1.12.

Results

Table 1 summarises the results for minerals investigated in this study.

Table 1. Surface and free energy results for minerals used in this study.

	Quartz, pure	Quartz-sand	Calcite-sand	Pot.-Feldspar
γS^D [mJ/m^2]	31.84	73.99	78.85	31.16
ΔG (DCM)	-	9.19	11.78	6.31
ΔG (Ethyl acetate) [kJ/Mol]	7.41	16.56	11.87	5.56
ΔG (1-Butanol) [kJ/Mol]	-	14.42	17.87	13.76
ΔG (Toluene) [kJ/Mol]	3.56	2.70	3.32	1.92
ΔG (Acetone) [kJ/Mol]	5.56	-	10.98	-
Affinity to bitumen	bad	good	very good	intermediate

The results for the dispersive contribution of the surface energy are shown in Figure 1.

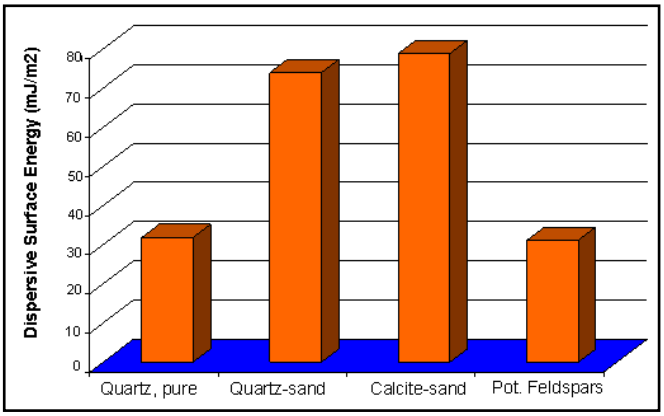

Figure 1. Dispersive surface energies of different minerals measured by a series of alkane injections between heptane and decane.

The two samples with the best affinity, calcite and quartz-sand show a significantly higher surface energy than the other two samples. This suggests that the dispersive surface energy is a good indicator for the affinity and that the affinity is related to the adhesion between mineral and bitumen.

Polar probes were also studied for potassium feldspar, calcite and quartz sand. Figure 2 shows the results for dichloromethane, ethyl acetate, 1-butanol and toluene.

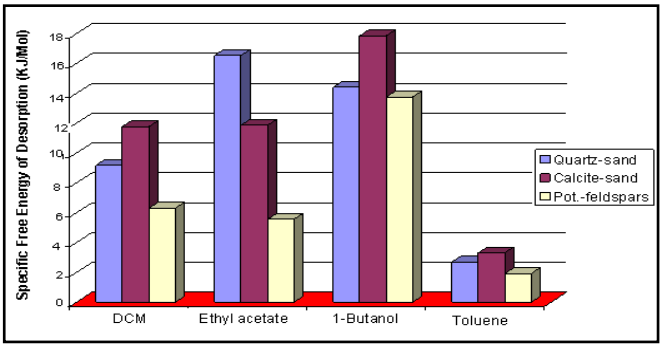

Figure 2. Free energies of desorption for different minerals. Measurements were carried out with dichloromethane, ethyl acetate, 1-butanol and toluene (left to right).

All minerals show their hydrophilic character by a strong interaction with ethyl acetate and butanol. Butanol gives a significantly stronger interaction with calcite and feldspar demonstrating the basic character of these minerals since butanol is a Lewis-acid. Quartz shows its slightly acid character by giving the strongest interaction with the Lewis-base ethyl acetate.

As mentioned above free energies can be converted into acid-base numbers by using the van Oss concept. Ethyl acetate and dichloromethane are used as base and acid respectively. The γ_S^+ and γ_S^- value as as well as the acid-base and total surface energy, obtained from the free energy values are listed in Table 2.

Table 2. Surface energies and acid-base numbers for minerals used in this study.

	Quartz-sand	Calcite-sand	Pot.-Feldspars
γ_S^D [mJ/m^2]	73.99	78.85	31.16
γ_S^{AB} [mJ/m^2]	259.74	238.64	59.88
γ_S^T [mJ/m^2]	333.73	317.49	91.04
γ_S^+ [mJ/m^2]	90.42	46.45	10.19
γ_S^- [mJ/m^2]	186.53	306.49	87.94

For calcite and feldspar the γ_S^+ and γ_S^- show the same trend as expected from the consideration of the free energy values, reflecting the basic character of the surface. For quartz the van Oss numbers show a more amphoteric behaviour but dominating basic properties. This opposes the expected dominance of acid groups. One possible reason is that these calculations are only based on two mono-polar probe molecules. Although results should be independent of the probe molecule in theory, it often appears in practise that they depend on the choice of vapour probe. More reliable results could be obtained by using several bipolar probe molecules. Such a calculation would be less dependent on the nature of the probe molecule.

The numbers for van Oss and acid-base contributions seem to be unusually high compared to typical results of wettability experiments. This could be due to the different concentration regime. Wettability experiments are carried out with a drop of liquid saturating all energy sites while IGC SEA measurements at infinite dilution reflect only the interaction with the highest energy sites. Interaction with the latter therefore involve higher energies. Another explanation could be that the concept of van Oss is inappropriate due to its various oversimplifications.

Conclusion

Dispersive, acid-base and total surface energies as well as van Oss acid and base numbers have been determined on different minerals by IGC SEA. IGC SEA was shown to be a fast and accurate method for the characterisation of mineral surfaces in terms of their dispersive and acid-base properties. The results can also be used to predict affinities to bituminous components.

Acknowledgement:

Surface Measurement Systems acknowledge the contributions of Frank Thielmann, Duncan Pearse towards this application note.

And also to 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]Condor, J. and Young, C., Physicochemical Measurement by Gas Chromatography, John Wiley and Sons, Chichester, 1979
[2]Mukhopadhyay, P. and Schreiber, H., Colloid and Surfaces A 100 (1995), 47.
[3]Thielmann, F., SMS Application Note 221, (2005).
[4Goss, K., J. Coll. Interf. Sci. 190 (1997), 241.
[5]van Oss, C, Good, R. and Chaudhury, M., Langmuir 4 (1988), 884.

Head Office:
Surface Measurement Systems, Ltd
5 Wharfside, Rosemont Road
London HA0 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