Using a Mageleka *M*agno*M*eter XRS™ *R*elaxo*M*eter to Determine the Hansen Solubility Parameters for a Carbon Black

Introduction

Carbon blacks are used extensively in industrial applications. Major uses are in the production of tires and formulation of paints and inks but they are also used extensively as a conductive additive in Li-ion batteries to improve the fast-charging ability of anodes. Indeed, improvements in energy and power densities, charge and discharge times, cost, lifetime and safety are all critical to the success of next generation batteries.

Another use is in the development of engine oil. Harmful debris generated during operation of an engine includes, among other materials, soot particles that can thicken the oil, cause wear, and plug oil filters. Engine oil additives are critical as they disperse the debris by helping to reduce the formation of deposits on metal surfaces and inhibit soot agglomeration via stable micelle formation. Carbon black is used as a surrogate for soot for the development and testing of suspensing and dispersing agents (i.e., additives) because of the technical difficulty in obtaining sufficient soot.

The particle morphology and surface properties of a carbon black directly affects its performance behavior, so accurate and repeatable evaluation of those characteristics is important. The surface chemical properties of carbon blacks are equally important and they can vary considerably because they are determined, to a large extent, by the presence of functional groups such as oxygen, nitrogen, and sulphur that arise because of possible different sources of the raw feed material and/or processing (such as the thermal dehydrogenation of hydrocarbons). Further, the ability to predict the most appropriate liquid(s) to use for wetting/dispersing a given carbon black is of considerable interest to the formulator.

In any application, including those involving carbon blacks, accurate, quantitative, and reliable characterisation and analysis methods are needed – right through from checking incoming raw materials to developing new formulations and quality control within high volume manufacturing. However, in addition to being opaque, many real-world suspensions of carbon blacks can also be pasty/thick and/or viscous, so analysis of them by traditional particle characterization instrumentation is difficult, if not impossible.

The use of NMR relaxation time overcomes these difficulties and provides a versatile means of interrogating virtually any solid-liquid or liquid-liquid dispersion, including carbon blacks. The relaxation time can be measured directly using an NMR spectrometer, such as the Mageleka *M*agno*M*eter XRS *R*elaxo*M*eter. The NMR relaxation time is a fundamental *intrinsic* property of solids and liquids and it

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is sensitive to both the extent of wetted surface in a suspension as well as the chemical nature of a particle surface and so measurements will reflect the contribution of both features.

NMR relaxation is quantifiable and fast, without the need for dilution or other sample preparation and so offers practical advantages as a technique to directly characterize, and quantitatively discriminate, the interaction of solvents with carbon blacks (see Mageleka Application Note 16). Moreover, the *M*agno*M*eter *R*elaxo*M*eter is a small benchtop device that is easy to employ, requires limited input data and provides rapid measurements. The instrument can work with any industrially relevant solids concentration and with virtually any liquid. Due to its easy-to-use software, it also has the benefit that it can be operated by a non-NMR specialist. The *R*elaxo*M*eter can be used at every stage of manufacture – from quality control (QC) of incoming materials through formulation R&D and process monitoring to quality assurance (QA) of final commercial products (see the series of Mageleka Technical Notes at www.mageleka.com) – to help improve efficiency and to reduce costs.

This Application Note describes the theory behind using NMR relaxation time measurements to determine the Hansen Solubility Parameters (HSP) for carbon blacks. The key phenomenon underpinning dispersibility is how a liquid wets a particle surface. Wetting depends crucially on the morphology and chemical nature of the material but is related to the *strength* of solvent-surface interaction.

The relative NMR relaxation rates of different solvents in contact with solid surfaces are indicative of a relative interaction strength (or affinity) between the specific solvent and the chosen solid surface. Liquids exhibiting strong interactions with a particle surface have a faster NMR relaxation rate than liquids with weak interactions. Since strong interactions indicate a high affinity of solvent with the surface, the single solvent, or solvent mixture, that exhibits the highest enhancement in relaxation rate would be the most suitable fluid to use for the initial wetting/dispersion process.

The HSP for a material can be calculated using NMR relaxation time data. Once known, solvent blends – *even mixtures of individually poor solvents* – having volume average HSP values similar to that for the powder surface will be most effective in wetting the material and producing high quality dispersions. Further, the HSP can be used to probe and discriminate the surface chemical nature of materials. Understanding this allows a formulator to more efficiently and better optimize the preparation of a suspension.

Here, we present data demonstrating the procedure in practice using a commercially-available carbon black. Measurements were made directly on the homogenized non-aqueous suspensions using a Mageleka *R*elaxo*M*eter.

Using NMR relaxation data to derive the HSP for a carbon black

Hansen suggested that particle-solvent interactions can be characterized by splitting the total cohesion energy (E) of a liquid into three separate energies: dispersion energy (D), polar-dipolar energy (P), and hydrogen bonding energy (H). These HSP can be used to select the most appropriate solvents for wetting and dispersing particulate powder materials.

NMR solvent relaxation measurements are sensitive to the same intermolecular forces (and dynamics) between solvent and materials that affect HSP. Hence, a logical step is to combine quantitative relaxation data (relaxation number values) from

the *R*elaxo*M*eter with computational analysis using commercially available HSPiP software to determine accurate and precise HSP values for the carbon black material used in this study.

Note: The relaxation number, R_{no}, is defined as:

$$R_{no} = [R_{suspension}/R_{solvent}] - 1$$

Where, $R = 1/T$ and T is the relaxation time (ms).

R_{no} is, thus, a useful dimensionless parameter in which the effect of the solvent, which could include dispersants, additives, etc., is normalized out. This allows us to rank the strength of solvent-surface interaction, as shown in Table 1.

The HSP approach requires the user to input solvent quality information into the calculation of the HSP. A solvent with known energy characteristics is characterized as either a "good" solvent or a "poor" solvent, depending on its ability to interact with a surface. Solvents can be rank ordered as "good/poor" (i.e., strong/weak interaction) based on visual observations or, using a more quantitative technique, analytical centrifugation (AC). The AC method is time-consuming and requires dilute suspensions to avoid hindered settling.

In contrast, determination of R_{no} is straightforward and fast, and it provides a direct measurement of "solvency". Utilizing R_{no} values provides a reliable, quantitative means to categorize solvents as good or poor. The *R*elaxo*M*eter provides R_{no} values as a default output when analyzing any suspension.

The procedure for ranking the strength of solvent-surface interaction is iterative, as follows:

1. Order the R_{no} values from smallest to largest for the range of solvents used.
2. Assign the three highest R_{no} values a score of 1 (for strong affinity), with the rest being scored 0 (for weak affinity).
3. Use the HSPiP software to construct an initial Hansen sphere for the boundary between the strong and weak affinity solvents.
4. Sequentially expand the number of solvents scored as a "1" until it is no longer possible to fit a spherical boundary between the strong and weak affinity solvents.
5. The center of this "best-fit sphere" is the effective HSP for the surface under investigation. The HSP locations of the final solvents with a score of "1" define the maximum value for the radius of the Hansen sphere.

In essence, this solvent relaxation-based protocol is used to (i) accelarate the whole process of HSP determination and (ii) to provide a well-defined evaluation procedure for the reliable ranking of good and poor solvents for dispersing the particles.

For a specific material, although the choice of solvents is somewhat arbitrary, the solvents must encompass a range of behavior characteristics from highly polar to highly non-polar. Hansen recommends that a minimum of twelve probe solvents be used in order to ensure maximum interrogation of a material and, hence, the most precise construction of the 3-D sphere. In this study we used 17 solvents.

Analysis Results

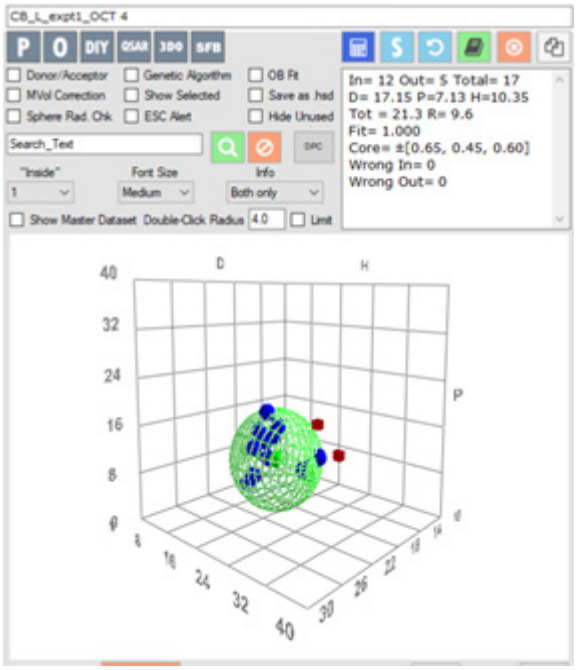
In this study, a commercial carbon black, CABOT Mogul L, was used. Suspension and solvent quality information are summarized in Table 1.

Table 1. Solvent quality ratings for CABOT Mogul L.

Solvent	Relaxation Data					
	Suspension		Solvent		Relaxation Number, R_{no}	Ranking
	T_2 (ms)	R_2 (x10^4)	T_2 (ms)	R_2 (x10^4)		
NMP	523	19.2	1894	5.28	2.62	2
Acetone	1335	7.49	3216	3.11	1.41	4
MEK	1182	8.46	2420	4.13	1.05	5
Cyclohexanone	785	12.74	1542	6.49	0.96	6
Xylene	1089	9.18	2060	4.85	0.89	=7
Ethanol	904	11.06	1707	5.86	0.89	=7
IPA	776	12.89	1134	8.82	0.46	9
Butanol	677	14.77	960	10.42	0.42	11
Hexane	1536	6.51	2044	4.89	0.33	13
Dodecane	812	12.32	974	10.27	0.20	14
Trichloroethylene	1089	9.18	1557	6.42	0.43	10
DMF	220	45.45	1078	9.28	3.90	1 (best)
n-Pentane	2144	4.66	2227	4.49	0.04	16 (worst)
Ethylene Glycol	310	32.26	369	27.10	0.19	15
Monoethanol-amine	210	47.62	288	34.72	0.37	11
DMSO	1162	8.61	2026	4.94	0.74	8
1,4 Dioxane	895	11.17	2239	4.47	1.50	3

The best affinity was shown by NMP and the least by n-pentane, followed by dodecane.

Here, the cut-off value for R_{no} was arbitrarily set as 0.40 (i.e., smaller values implying too weak solvent-particle interaction). Thus, for the creation of the Hansen sphere using the HSPiP software, the solvents n-pentane, hexane, dodecane, monoethanolamine, and ethylene glycol were assigned a score = 0 and the rest a score = 1. The result is shown in Figure 1.



No.	Solvent	δD	δP	δH	Score	RED	MVol	CAS	SMILES
521	n-Methyl-2-Pyrrolidone (N...	18	12.3	7.2	1	0.564	96.6	872-50-4	CN1C(CC...
1271	1,4-Dioxane (High P)	17.1	6.8	7.8	1	0.234	85.7	123-91-1	C1COCCO1
7	Acetone	15.5	10.4	7	1	0.500	73.8	67-64-1	CC(C)=O
481	Methyl Ethyl Ketone (Mek)	16	9	5.1	1	0.540	90.2	78-93-3	CC(CC)=O
183	Cyclohexanone	17.8	8.4	5.1	1	0.511	104.2	108-94-1	O=C1CCC...
697	p-Xylene	17.8	1	3.1	1	0.981	121.1	106-42-3	CC1=CC=...
325	Ethanol	15.8	8.8	19.4	1	0.997	58.6	64-17-5	CCO
303	Dimethyl Sulfoxide (Dmso)	18.4	16.4	10.2	1	0.912	71.3	67-68-5	O=S(C)C
570	2-Propanol	15.8	6.1	16.4	1	0.723	76.9	67-63-0	OC(C)C
649	Trichloroethylene	18	3.1	5.3	1	0.691	90.1	79-01-6	[H]/C(Cl)=...
92	1-Butanol	16	5.7	15.8	1	0.666	92	71-36-3	CCCCO
326	Ethanolamine	17	15.5	21	0	1.364	60.3	141-43-5	OCCN
417	Hexane	14.9	0	0	0	1.342	131.4	110-54-3	CCCCCC
316	Dodecane	16	0	0	0	1.288	228.6	112-40-3	CCCCCC...
368	Ethylene Glycol	17	11	26	0	1.658	55.9	107-21-1	OCCO
297	Dimethyl Formamide (Dmf)	17.4	13.7	11.3	1	0.617*	77.4	68-12-2	[H]C(N(C)...
550	Pentane	14.5	0	0	0	1.370	116	109-66-0	CCCCC

Figure 1. Hansen Sphere for the carbon black CABOT Mogul L and solvent scores (good=1; poor=0).

Using the iterative procedure above, the average HSP values for CABOT Mogul L are:

$$\delta D = 17.15,\ \delta P = 7.13,\ \delta H = 10.35$$

These HSP values lie within the wide range of literature values (Table 2) found for available diverse commercial carbon blacks.

Table 2. Range of HSP values found for commercial carbon blacks.

	δD	δP	δH
Carbon Low	16.5	9.1	6.8
Carbon High	20.4	10.9	13.0

The HSP values from NMR relaxation are similar to those found using analytical centrifugation (AC) for a sample of the carbon black Printex L, obtained from EVONIK (δD= 17.2, δP= 8.5, δH=11.6). However, determination by NMR relaxation is considerably simpler and faster than AC. The production of relaxation number values using the *R*elaxo*M*eter takes one or two minutes in comparison to total analysis times for AC, which can take up to an hour.

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Characterizing the surface quality of the carbon black so that it is a known quantity is important since it allows a formulator a better choice of dispersants in a solvent of choice. Dodecane is often used as a "model" solvent for carbon black studies. The HSP values for dodecane are δD=16.00, δP=0, δH=0, and so it would not be a good wetting solvent for the carbon black used in this study (CABOT Mogul L). This conclusion is also apparent from the relaxation number for dodecane/Mogul L which was found to be one of the lowest (0.2) amongst the 17 solvents tested in this study. Importantly, based on the hypothesis that "like dissolves like", solvent blends – *even mixtures of individually poor solvents* – having volume average HSP values similar to that for a carbon black will be effective. This provides the formulator with greater flexibility to improve any carbon black dispersion.

As mentioned, the HSP of carbon blacks are sensitive to manufacturing variables such as the feed stock used and so, potentially, can be used as a quality control parameter of the surface quality of a carbon black. It is also possible to track the surface quality of a source of any carbon black by cross-referencing its relaxation number, obtained in just a few selected solvents, without carrying out a complete HSP analysis, which also makes the process less time-consuming.

Determination of the HSP of an engine oil would allow the most suitable solvent to be selected for experimental evaluation of suspending and dispersing aids. It may very well be that dodecane, for example, is an appropriate liquid for such studies, since the goal may not be to completely wet the carbon black but to provide a realistic fluid substitute that mimicks the wetting behavior of an engine oil. However, until representative oils are evaluated, this remains unknown. The HSP of an oil (including diesel) may be obtained by assessing its miscibility with a range of good and poor solvents with known HSP values. Solvent relaxation NMR may be used to quickly determine the interaction of the candidate oil with solvents. Then, as described above, the relaxation number R_{no} can be rank ordered and inputted into the HSPiP software to compute the HSP of the oil.

Although the data here were obtained on a specific carbon black (CABOT Mogul L), the HSP methodology and analysis employed using the *R*elaxo*M*eter can be applied to any applications involving non-aqueous dispersions of carbon blacks of any type/grade, such as those used as a conductive additive in Li-ion batteries.

For more information, to send samples, to arrange a demonstration of the MagnoMeter at your facility, or to talk to one of Mageleka's technical applications specialists, please email roger@mageleka.com

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