THE USE OF DYNAMIC NUCLEAR POLARIZATION IN COAL RESEARCH

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1. Introduction

In a variety of articles it has been shown that the presence of unpaired electrons in coal makes it possible to enhance the ^{1}H and ^{13}C NMR signals of this material by irradiating at or near the electron Larmor frequency: the Dynamic Nuclear Polarization (DNP) effect (ref. (1)-(5) + references cited therein). It is found that in favourable cases the nuclear polarization can be enhanced by one to three orders of magnitude, which can e.g., be used as a fast method to characterize coal via ^{13}C NMR. In this paper the DNP enhancement will be investigated as a function of coal rank, and the observed behavior will be explained. Furthermore, special DNP experiments will be given which provide information about the carbon percentage detected via ^{1}H-^{13}C cross-polarization (CP).

2. Experimental

For an extensive treatment of the experimental set-up we refer to the references (1) and (3). The external field strength was 1.4 T, corresponding to a proton Larmor frequency of 60 MHz, a ^{13}C Larmor frequency of 15 MHz and an electron Larmor frequency of 40 GHz. The microwave power was provided by a 10 W Klystron, in our set-up resulting in an amplitude B_1 of the microwave field of about .05 mT. All experiments shown in this paper except for the ^{13}C (DNP)-CPMAS experiments were performed on coal samples which were dried and degassed and have been put into pyrex tubes. (We found that both drying and degassing caused an increase in both the ^{1}H and ^{13}C Zeeman relaxation times as well as in the respective DNP enhancements). All measurements have been performed at room temperature.

3. The DNP enhancement as a function of coal rank.

In a solid several types of DNP effects can occur, depending on the nature and time-dependence of the spin-spin interaction term H_{en} between the electrons and the solids[3],[5]: (i) an Overhauser effect is observed when H_{en} is time-dependent on a scale comparable to the inverse electron Larmor frequency ω_e^{-1}; (ii) a solid state effect occurs when H_{en} is (partially) time-independent; (iii) a thermal mixing effect can be found when H_{en} is time-independent and when the electron concentration is so large that the broadening of the ESR line becomes homogeneous in character. In the latter case the polarization corresponding to this broadening can be enhanced via microwave irradiation, and this enhanced polarization is transferred towards the nuclear Zeeman system either via electron-nucleus relaxation interactions (the direct thermal mixing effect) or via so-called forbidden transitions (the indirect thermal mixing effect).

The ^{1}H and ^{13}C DNP enhancement in coal has been investigated extensively in the ref. (3) to (5). It has been found that, though all DNP mechanisms are present in the coal, the ^{1}H polarization enhancement becomes a maximum when the microwave frequency $\omega = \omega_e - \omega_H = \omega_e - 60$ MHz and that for this value of ω the enhancement is mainly due to a combinaton of the solid state effect and the indirect thermal mixing effect. The ^{13}C polarization becomes maximal when $\omega \simeq \omega_e - \omega_{\frac{1}{2}}$, $\omega_{\frac{1}{2}}$ being the ESR linewidth (half width at half height) and is mainly caused by the direct thermal mixing effect. These results appeared to be the same for all coals we have investigated, with the exception of a meta-anthracite, where the Overhauser effect dominated.

We investigated the maximum ^1H and ^{13}C enhancements, $(P_H)_{max}$ and $(P_C)_{max}$, respectively, of more than sixty coal samples of different rank and origin, with a volatile matter percentage % VM varying from 6.8 to 91% (dmmf) and a carbon content %C varying from 96% to 66% (dmmf). The meta-anthracite has been omitted. We found that for a microwave amplitude B_1 of ca 0.05 mT $(P_C)_{max}$ was about 8 times larger than $(P_H)_{max}$, independent of the coal rank, so that we can confine ourselves by showing the proton results.

Figure 1 shows $(P_H)_{max}$ as a function of %C, from which we observe that $(P_H)_{max}$ becomes maximal when %C > 92% and that for %C < 75% no enhancement is found. In order to explain this we use an approximate equation for $(P_H)_{max}$ [3]-[5]:

$$(P_H)_{max} \quad 1 + c\, N_e (W_z^H)^{-1} (\Delta B_{\frac{1}{2}})^{-1} \qquad 1)$$

N_e is the number of organic radicals, W_z^H is the proton Zeeman relaxation rate, $\Delta B_{\frac{1}{2}} = 2\gamma_e \omega_{\frac{1}{2}}$ is the ESR linewidth and c is a constant, among others proportional to B_1^2. For $B_1 = 0.05$ mT c is given by $c = 2.4\ 10^{-24}$, if N_e is expressed in m^{-3} (dmmf), W_z^H in sec^{-1} and $\Delta B_{\frac{1}{2}}$ in mT. As $\Delta B_{\frac{1}{2}}$ varies only between 0.8 and 1.3 mT for all the coal samples, the change in $(P_H)_{max}$ as a function of coal rank is mainly due to variations in N_e and W_z^H. Figure 2 shows N_e as a function of % VM, from which we observe that N_e is decreasing for decreasing coal rank. In fact two dependencies are observed, curve 1 and curve 2, and it was found that the coals with the large N_e value (curve 2) almost all originated from the southern hemisphere. Moreover, it was found that for these coals only a part contributed to the DNP enhancement, so that presumably not all the radicals in these coals are present in the organic part of the coal. Figure 3 shows W_z^H as a function of the oxygen content. We observe that W_z^H increases with increasing %O, which probably means that a part of the oxygen is present as paramagnetic oxygen, because it is well-known that even a small percentage of paramagnetic oxygen causes a strong increase in the Zeeman relaxation rate. The increase in W_z^H for small oxygen percentages is caused by an increased number of organic radicals.

By inserting the observed values of $\Delta B_{\frac{1}{2}}$, N_e (except for the coals of the southern hemisphere, where only a part of Ne is causing the DNP effect, see above) and W_z^H into Equation 1) it was found that this equation predicts the observed proton enhancement very satisfactorily. We like to emphasize that, as the constant c in Equation 1) is proportional to B_1^2, both $(P_H)_{max}$ and the region of coals for which a DNP enhancement is observed, will increase if more microwave power were available (this does not hold for the ^{13}C enhancement, as for the used B_1 value $(P_C)_{max}$ is already close to the largest possible value).

4. How much carbon do we observe in coal?

A long standing problem is the percentage of carbons observed via the ^1H-^{13}C cross-polarization technique, because it is possible that a substantial fraction of especially the aromatic carbons may be too remote from the protons to be measured via this method. In the literature this problem has been approached via a variety of different experiments [6]-[9], and the found percentage differed between 50 and 100% so that the problem is still unresolved. The best way to determine this percentage is to compare the ^{13}C CP spectrum with the ^{13}C FID spectrum, where the ^{13}C signal is obtained after a 90° pulse applied at the ^{13}C Larmor frequency, but this is almost impossible to do because of the many scans needed and the long recycle delay between the scans. Therefore, we used an alternative approach and compared the ^{13}C CP spectra with ^{13}C FID spectra, obtained by enhancing the ^{13}C polarization via DNP. In figure 4, ^{13}C spectra are given of a medium volatile bituminous coal (31% VM, 87.4% C, 5.2% H, 5.3% O, all dmmf) obtained via CP, DNP-CP (here the ^1H signal was enhanced with a factor 16 via DNP before the CP experiment) and DNP-FID (here the ^{13}C signal was enhanced with a factor 130 before the 90° pulse), both with and without

Magic-Angle Spinning (MAS). We observe that within the signal-to-noise ratio the ^{13}C CP(MAS) and DNP-CP (MAS) spectra are the same, indicating that the proton polarization is enhanced uniformly. However, in the ^{13}C DNP-FID (MAS) spectra the aliphatic carbons are suppressed. Two explanations are possible: (i) in the DNP-FID experiment we are indeed observing more aromatic carbons than in the (DNP)-CP experiments; (ii) in the DNP-FID experiment, the DNP enhancement of the aliphatic carbons is less than that of the aromatic carbons, which is possible if the radicals are located mainly in the aromatic part of the coal. In order to investigate this we performed the following experiments:

a. $T_{1\rho}^{C}$ experiments. It is known that the electron Zeeman relaxation time T_{1e} in coal is of the order of μsec, which means that this provides an efficient way of relaxing the ^{13}C nuclei in the rotating frame[4] as T_{1e} is of the same order of magnitude as the inverse lock field. As the ^{13}C-^{13}C spin diffusion is very slow, the relaxation of the ^{13}C magnetization M_C in the rotating frame is given by[5],[10].

$$M_c(t) = M_c(0)\exp\left\{ -(t/T_{1\rho}^{C})^{\frac{1}{2}} \right\} \qquad 2)$$

Equation 2) holds provided that all the carbon nuclei are observed. If a percentage s of the carbons close to the electrons are not observed, Equation 2) is valid only for larger values of t, whereas for short values of t $M_c(t)$ is almost independent of t and given by 1-s.

Figure 5 shows the rotating frame relaxation of the aromatic carbons of the medium volatile bituminous coal, measured via the DNP-FID and DNP-CP experiment. It follows that in the first case we measure about 90% of the carbons, probably because carbons very close to the electrons are shifted out of the ^{13}C DNP-FID spectrum. In the DNP-CP experiment only 65% of the aromatic carbons are observed, which means that another 25% of the carbons are too remote from the protons to be observed via ^{1}H-^{13}C cross-polarization.

b. The back-match experiment. The contact times T_{CH} between the carbons and protons, which determine the increase of the carbon polarization during a ^{1}H-^{13}C CP experiment, depend on the strengths of the C-H interactions, and therefore on the carbon-proton distances.[11] The values of T_{CH} can be determined by varying the matching time t_M during which the cross-polarization takes place. Figure 6a shows the result of such an experiment for the aromatic carbons in the medium volatile bituminous coal. We see that for about 35% of the carbons T_{CH} = 30 μsec (direct C-H bonds) whereas for the remaining 65% T_{CH} = 350 μsec (C-C-H bonds). Figure 6b shows a similar experiment, but now for a $^{13}C \rightarrow {}^{1}H$ cross-polarization experiment (the 'back-match' experiment), after enhancing the ^{13}C polarization directly via DNP. We observe a much slower decay than in Figure 6a, because for about 40% of the aromatic carbons T_{CH} = 1600 μsec, which is not observed via the usual $^{1}H \rightarrow {}^{13}C$ CP experiment. Hence in the latter experiment about 40% of the aromatic carbons are not observed, a percentage which is comparable to the one obtained via the $T_{1\rho}^{C}$ experiments. Similar results were obtained for a high volatile bituminous coal and an anthracite.

However, if we correct the aromatic part of the ^{13}C (DNP)-CP(MAS) spectra for the percentage of carbons not observed, still the percentage of aliphatic carbons in these spectra is larger than that obtained via the DNP-FID method. This means that indeed in the latter experiment the aliphatic carbons are enhanced less than the aromatic ones. Therefore, we conclude that both types of experiments are necessary to obtain the true percentages of the aliphatic and aromatic carbon atoms, and that the ^{13}C aromaticity in coal is larger than the apparent aromaticity following from the ^{13}C CP spectra.

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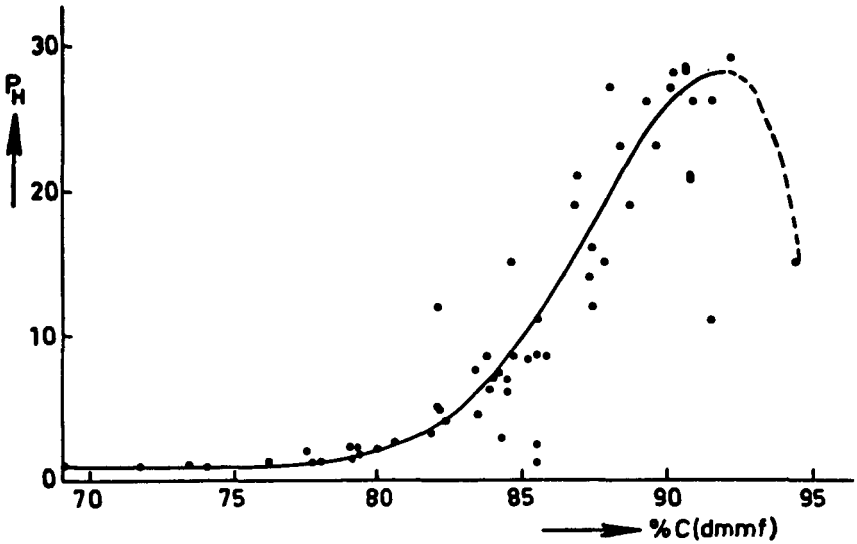

Figure 1. The maximum proton enhancement as a function of the carbon content.

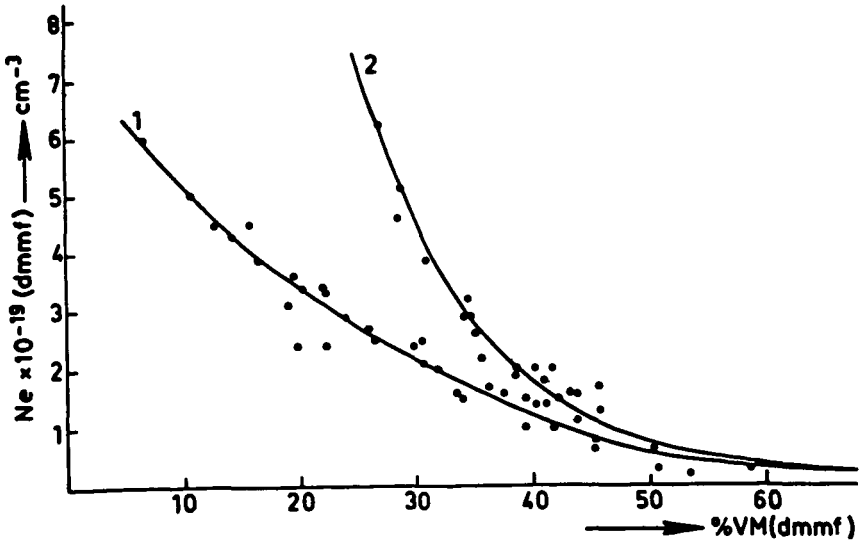

Figure 2. The number of unpaired electrons as a function of the percentage volatile matter.

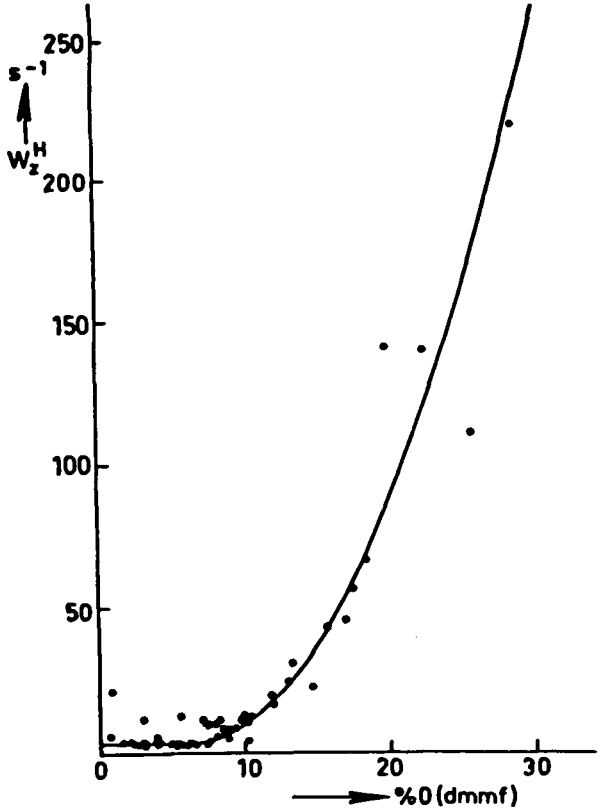

Figure 3. The proton Zeeman relaxation rate as a function of the oxygen content.

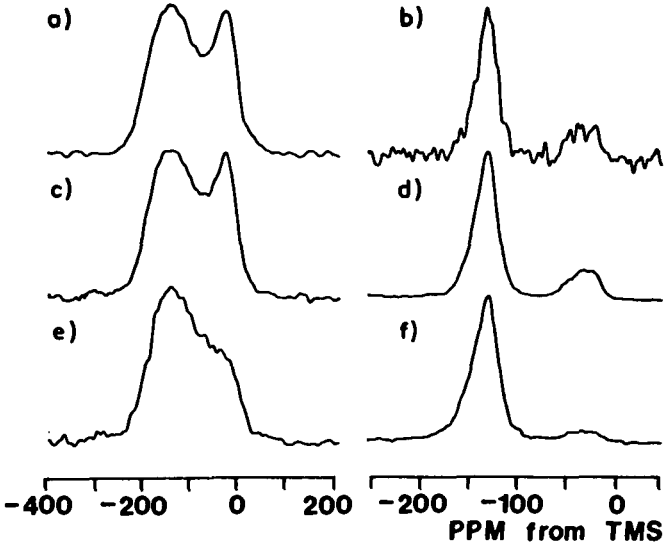

Figure 4. ^{13}C spectra of a medium volatile bituminous coal measured via different techniques. a) CP. Match time - 0.9 msec; acquisition time = 5 msec; match field - proton decoupling field = 50KHz; number of scans = 20,000; recycle delay = 0.6 sec. A Lorentzian broadening of 200 Hz is applied. b) CPMAS. Spinning frequency = 3.5 KHz; acquisition time = 15 msec; number of scans = 10,000; no broadening is used. Other parameters as in a). c) DNP-CP. Number of scans = 400. Other parameters as in a). d) DNP-CPMAS. Number of scans = 10,000. Other parameters as in b). e) DNP-FID. Duration $\pi/2$ pulse = 6 μsec; acquisition time = 5 msec; proton decoupling field = 50 KHz; number of scans = 8; recycle delay = 60 sec; Lorentzian broadening = 200 Hz. f) DNP-FIDMAS. Spinning frequency = 3.4 KHz; acquisition time = 15 msec; number of scans = 70; no broadening. Other parameters as in e).

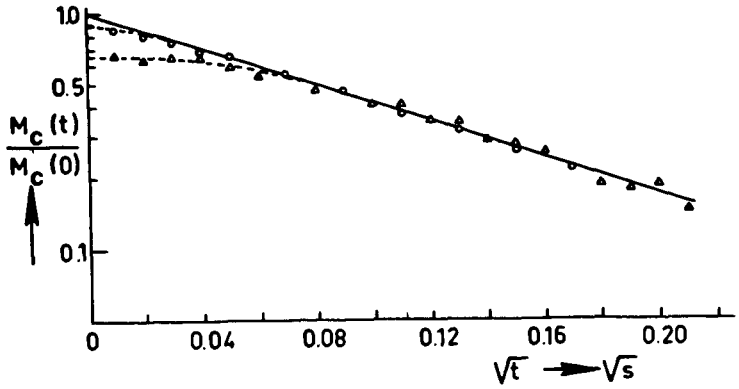

Figure 5. The rotating frame relaxation of the aromatic carbons of a medium volatile bituminous coal. The amplitude of the lock field = 40 KHz. circles : measured via DNP-FID; triangles: measured via DNP-CP.

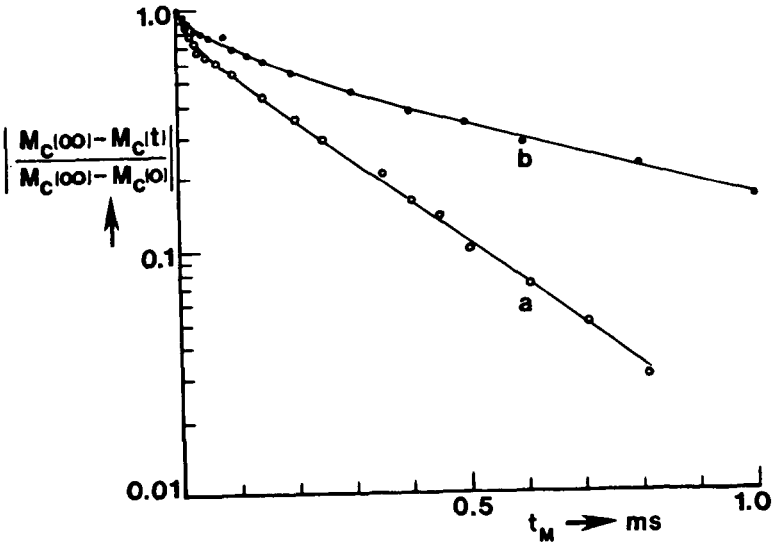

Figure 6. The magnitude of the aromatic ^{13}C signal as a function of the matching time. a: After ^{1}H DNP and $^{1}H \rightarrow {}^{13}C$ CP; b: After ^{13}C DNP and $^{13}C \rightarrow {}^{1}H$ CP.