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Overhauser-driven dynamic nuclear polarization for petroleum systems: literature survey and comparing with experiments

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Abstract. Overhauser dynamic nuclear polarization (ODNP) in solutions of various paramagnetic complexes has been studied for 60 years, but only in recent years has found applications of broad interest to biophysical and biomedical sciences, for the investigation of soft materials and biomolecules. Relatively few applications are focused on the ODNP in petroleum dispersed systems (PDS) like oils, bitumen, their fractions and solutions. This work presents a short review of the ODNP studies of PDS with aim to introduce the basic concepts and key values for the effective petroleum ODNP in low and high magnetic fields. Experimental results obtained in our Laboratory by using home-made spectrometer are included. The study can be used for designing ODNP spectrometers, proton precession magnetometers for geological and geophysical exploration, investigation of supramolecular organisation of PDS and their components.

1. Introduction

Nuclear magnetic resonance (NMR) is a powerful method for the routine analysis and detailed studies of diverse hydrocarbon systems (petroleum dispersed systems, PDS). For decades, NMR logging tools have been developed that allow in situ determination of a number of petrophysical parameters such as porosity, permeability, water content, gas, and oil saturation, oil viscosity etc. Analyses of the NMR relaxation times are used for the *in situ* and non-invasive investigations, to measure fluid properties in porous, oil containing media [1], [2]. Electron paramagnetic resonance (EPR) is also known since 1950s as a convenient tool for PDS detection and investigation due to the existence in PDS various paramagnetic centers [3], [4]. Application of modern pulsed and high-frequency EPR techniques last decade broaden significantly the EPR abilities for PDS analysis [5]-[7].

However, despite this body of literature, there is a surprisingly small amount of publications reporting on the use of double resonance techniques like dynamic nuclear polarization (DNP) in which both EPR (microwave, MW) and NMR (radiofrequency, RF) electromagnetic waves are applied to crude oils and their fractions [1], [8]-[15] and references therein. Possible reasons for this are, apart from the complexity of the natural samples, the lack of available instrumental tools and limited models available for interpreting data of double resonance experiments. Obviously, investigations of the coupling between the electronic spin reservoir S and the nuclear spin reservoir I in PDS and their components can provide insight into the structure and dynamics of these complex materials, but at the same time, the coupling itself can be used to enhance the NMR signal by spin polarization transfer from S to I by means of DNP techniques, thus increasing sensitivity by one or two orders of magnitude [10], [11]. Indeed, as



it was firstly shown by Poindexter [12], 15 fold NMR enhancement could be achieved in the low-viscous oil in the magnetic field of $B_0 = 1.55$ mT while potentially up to 45 in solutions of asphalt in chlorobenzene at $B_0 = 7.4$ mT [15].

Since crude oil is conventionally considered as a viscous liquid, the Overhauser type mechanism (ODNP) for the hyperpolarization is supposed to be the most effective because relatively high mobility of oil molecules and compounds including paramagnetic radicals implies a sufficiently strong modulation of electron-nuclear interaction leading to effective polarization transfer between electrons and nuclei in oil [12], [16]. The key property of ODNP is the fact that the maximal effect of electron polarization transfer on the nuclear system occurs when the frequency of the microwave pumping is exactly in resonance with the EPR transition, i.e. $\nu_{MW} = \nu_S$. This work is a short review of the classical liquid state DNP papers [17]-[24] as applied to PDS [8], [9], [12]-[15] with aim to introduce the basic concepts and key values of ODNP between “free” radicals and protons in PDS. The presented results can be used for designing ODNP spectrometers, proton precession magnetometers for geological and geophysical exploration, investigation of supramolecular organisation of PDS and their components.

2. Basic concepts of ODNP in PDS, simple semi-classical approach, and comparing with experiments

In the high permanent homogenous external magnetic field B (along which we choose z - axis of the laboratory coordinate system) the spins precess around z with the Zeeman (Larmor) angular frequency

$$\omega_S = -\gamma_S B, \quad \omega_I = \gamma_I B, \quad (1)$$

where γ_S and γ_I are the gyromagnetic ratios of electron and nuclear spins (γ_S is negative) which result in $\nu_S = 280$ MHz for the unpaired electron and $\nu_I = 425$ kHz for protons in the magnetic field $B = 10$ mT ($\omega = 2\pi\nu$). If the mean distance, r , between S and I is sufficiently large ($r \geq d \approx 10$ Å, where $d \approx 10$ Å is a typical distance of the closest approach for the asphaltenes solutions, [15]) to assume that dipole-dipole interaction dominates over scalar.

The majority of paramagnetic centers in PDS are concentrated in asphaltenes. They frequently exist in the form of stable carbonaceous “free” radicals (FR) – unpaired electrons delocalized over many conjugated or aromatic chemical bonds [3]. However, the exact nature and structure of the intrinsic paramagnetic centres in PDS remains unclear due to the complexity of the investigated material and the different forms of aggregation of its larger constituents. Usually in PDS, FR is detected by conventional X-band ($\nu_{MW} \approx 9.5$ GHz) EPR as a single line ($S = 1/2$) with the peak-to-peak linewidth of $\Delta H_{pp} = 0.4$ - 0.8 mT and a g -factor between 2.0008 and 2.0081 (the typical range of 2.0027-2.0036 – see Figure 1, [3], [9]). It is shown that in low magnetic fields of 1.44-10 mT the values of g -factor and ΔH_{pp} are roughly the same [25]-[27].

To flip nuclear spin I , the energy of its interaction with the environment should be time-dependent, i.e. fluctuating local magnetic field, B_{local} , should exist Fourier component of which with ω_I would cause nuclear spin reorientation. One of the sources of such “modulation” field is an electron spin S generating on the nuclei B_{local} . In liquids these fluctuations could be caused by the further reasons:

- rotational motion of the paramagnetic molecule (characterized by the rotational correlation time τ_{rot});
- exchange (Heisenberg) interaction between the electron spins or between the molecules with $\tau_{ex} = \tau_H = 1/\omega_{ex}$;
- translational motion (diffusion) of the molecules in the solvent with τ_{tr} .

Then the „integrated“ correlation time of the z -component of the electron spin, S_z , is (assuming that the values are independent and are not correlated)

$$1/\tau = 1/\tau_{tr} + 1/\tau_{rot} + 1/\tau_{ex}, \quad (2)$$

i.e. the correlation time is mainly defined by the shortest term(s). Concentration of FR in asphaltenes of heavy oils and bitumen is in the range of 10^{16} - 10^{20} spins/g or 1 FR on 10-10000 asphaltenes molecules

[3], [9] and, therefore, exchange interaction (that can be operative at high concentration of paramagnetic centres), can be excluded from further consideration.

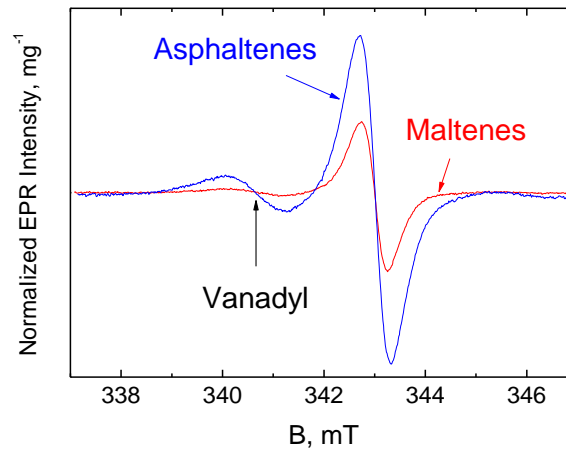


Figure 1. EPR spectra of FR ($g = 2.0030$, $\Delta H_{pp} = 0.54$ mT (15 MHz)) in asphaltenes ($C = 9(1) \cdot 10^{18}$ spin/g) and maltenes ($C = 4.0(5) \cdot 10^{18}$ spin/g) fractions of the oxidized bitumen at $T = 300$ K in X-band normalized to the sample masses. Additional line in the low-field part of the asphaltenes spectrum belongs to the paramagnetic vanadyl complexes [27].

The probability of nuclear flipping caused by the relaxation of $S = \frac{1}{2}$ (per time unit) located at the distance r drops with r and magnetic field strength as [21]

$$\frac{3}{10} \frac{(g\beta)^2}{\tau B^2} \frac{1}{2r^6}. \quad (3)$$

It follows that high nuclear polarization via electron spin is achievable only in the case of sufficiently rapid relative motion of S and I in low magnetic fields. Conventionally, the condition for ODNP observation can be written as [18]

$$\omega_S \tau < 1. \quad (4)$$

Therefore, ODNP is most effective in (low-viscous) liquids, metals and semi-conductors [16]-[23]. From Eq. (4) for $B = 10$ mT ($\nu_S = 280$ MHz, $\omega_S = 1.76 \cdot 10^9$ rad/s), $\tau < 560$ ps.

The most of the ODNP results in liquids, including those for PDS, were explained by using translational motions models only in which (for the isotropic diffusion)

$$\tau \approx \tau_{tr} \approx d^2/D_{\text{solvent}}, \quad (5)$$

where D_{solvent} is the diffusion (self-diffusion) coefficient of diamagnetic particles of solvent molecules. Large sizes and high-molecular mass of asphaltenes (250-1500 a.m. u. [3], [25]), their propensity to self-aggregation lead to the fact that the radical diffusion is too slow to be accounted. Therefore, τ_{tr} is mainly defined by the movement of the solvent molecules rather than radical-containing structures.

Poindexter [15] in 1972 reported extensive DNP studies of asphalts and asphaltenes in various solvents at near room temperature in a magnetic field of 7.4 mT (the proton NMR frequency is 320 kHz and the EPR of 210 MHz). He found that the best ODNP enhancement could be observed in chlorobenzene and toluene and estimated τ_{tr} as varying from 36 ps for toluene to 700 ps in *n*-dodecylbenzene. The shortest time of 36 ps implies that perceptible ODNP effect can be potentially observed in PDS solvents in the magnetic fields up to 150 mT ($\nu_S = 4.3$ GHz, $\nu_I = 6.5$ MHz). It means

that one can rarely expect ODNP detection in the conventional for EPR X-band range ($\nu_s = 9$ GHz, $B_0 = 320$ mT) even for the diluted solutions.

Figure 2 demonstrates the ODNP effect in toluene solvent of the oxidized bitumen in home-made DNP equipment operating in pulsed mode at $B_0 = 10$ mT. The technical description of NMR/DNP spectrometer is given in ref. [8]. The ODNP effect reveals as a disappearing of NMR signal with the EPR pumping as a sign of the prevailed dipole-dipolar electron-nuclear coupling [18], [24] and due to the solvation of stable asphaltenes-resins aggregates [3] while no ODNP effect is observed for the initial bitumen. It gives a potential opportunity to follow the processes of asphaltenes disaggregation by magnetic resonance techniques [15].

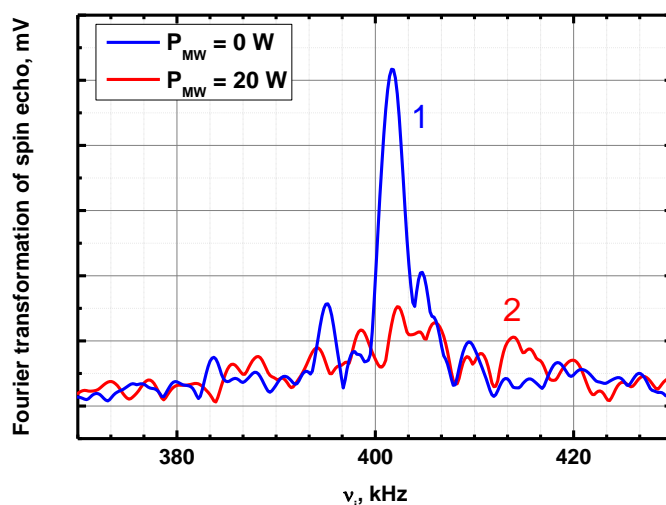


Figure 2. Change of the Fourier-transformed NMR spectrum (1) from the oxidized bitumen dissolved in toluene (1:10, v:v) in a magnetic field of 10 mT and $\nu_l = 420$ kHz with EPR pumping at $\nu_s = 280$ MHz (2).

Translational correlation time is a function of microspic parameters such as temperature and viscosity. For a spherical molecule of radius R in a pure solvent, one can write the dependence of the diffusion coefficient (Stokes-Einstein-Smoluchowski equation) on temperature and viscosity (η) as

$$D = k_B T / 6\pi\eta R, \quad (6)$$

where k_B is a Boltzmann constant. Then from the Eq. (5) it follows that

$$\tau_{tr} \propto \eta(T)/T. \quad (7)$$

Because viscosity is also a function of temperature and generally decreases sharply with T [27], ODNP effect should be more pronounced at higher temperatures and, as it was already mentioned, for the low viscous systems. It gives a potential opportunity to monitor thermal and catalytic PDS changes in the well-boring operations by applying DNP techniques. For the investigated bitumen the viscosity of the initial sample was measured to be 44 Pa·s at $T = 313$ K. Therefore, any ODNP effect could be hardly expected for the undiluted species.

3. Conclusion

Although NMR has been extensively used to characterize petroleum feedstocks, products, and catalysts while ODNP in low and high magnetic fields has found broad applications in biophysical, biomedical, surface characterization sciences, for the investigation of soft materials and biomolecules last decades, there is surprisingly small amount of PDS related ODNP research and utilization. We believe that PDS

DNP has a great potential to provide valuable information on supramolecular properties of PDS such as asphaltene aggregation and can be used to effectively enhance NMR signals for various PDS NMR employment.

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