Indian Journal of Chemical Technology
Vol. 29, March 2022, pp. 195-200

Effect of sample age of fluorocarbons on MC800 asphaltene on dynamic nuclear polarization parameters

Hüseyin & Ovalioglu*
Bursa Uludag University, Facult of Arts and Sciences, Physics Department, 16059, Bursa, Turkey
E-mail: ovali@uludag.edu.tr

Received 23 January 2022; accepted 22 February 2022

Nuclear Magnetic Resonance and Overhauser effect type dynamic nuclear polarization (DNP) experiments were performed to study suspensions of asphaltene in the fluorocarbons at a low magnetic field of 1.53 mT at room temperature. Asphaltene was extracted from MC800 liquid asphalt, which was Heavy Iran origin. Each sample of the solvent medium was produced at three different concentrations of asphaltene. These samples were kept for a period of seven years until DNP parameters were discovered through new DNP tests. The influence of sample age on parameters of DNP was studied and then the findings were analyzed. It was found that the ρ nuclear-electron coupling parameter was smaller. In low magnetic fields the nuclear-electron coupling parameter. ρvaries from +0.5 (pure dipolar) to -1.0 (pure scalar), and new ρ obtained values are between these limits. New ρ values in our study are positive and this shows that the dipolar part of intermolecular spin-spin interactions is dominant.

Keywords: Asphaltene, Dynamic nuclear polarization, Fluorobenzene, Overhauser effect

Crude oils are sophisticated liquids that have a broad range variety of viscosities, at this point, "heavy oils" are typically considered to have a viscosity over 100 mPa’s[1]. Conventionally, the components of SARA (saturated, aromatic, resin, and asphalt) are differentiated in these materials utilizing a well-defined separation method. Asphaltenes (identified as the n-alkane insoluble, toluene soluble fraction) and resins are accepted to be the main reasons for having average molecular weight high viscosity characteristics for oils[2-10]. In addition, crude oils have paramagnetic characteristics[5,6, 11,12]. In resins and asphalts, many paramagnetic centers are favourably clustered which often occur in the shape of consistent carbonaceous FR (Free Radicals), unpaired electrons dislocated over several conjugated or aromatic chemical bonds.

The heaviest and most viscous element in crude oil is Asphaltene. Additionally, it is the most polar element, soluble in aromatic solvents like toluene and xylene, but in typical aliphatic hydrocarbons like as n-heptane and n-hexane, it is insoluble[13-15]. Asphaltene only precipitates under unstable conditions. Different parameters, such as the pressure, temperature and properties of crude oil mixes, impact its stability[16,17].

Asphaltenes, which apart of petroleum, are considered to be polar species, have greater aromatic complexes, and consist of heteroatoms (e.g. O, S, and N), alkyl chains, and certain metals[18]. Asphaltenes have unpaired electrons, which are observed in crude petroleum by using the ESR (Electron Spin Resonance) experiments[11].

DNP (Dynamic Nuclear Polarization) uses liquid state interactivities between nucleus and unpaired electron spins to produce enhanced Nuclear Polarization (NP) after the saturation of ESR radical transitions. The maximum DNP enhancement rate of the NMR signal is calculated by the electron-to-nuclear gyro magnetic ratio, $\gamma e/\gamma n$. For ^{19}Fs pin, this ratio is 700.

It becomes apparent that studies of the coupling between I, nuclear spin reservoir, and S, electronic spin reservoir, may put forward insight into the dynamics and structure of these sophisticated materials. However, while the coupling itself can also utilize DNP techniques to increase the NMR signal via spin polarization starting from S to I. Therefore, sensitivity increases by[3] or[4] orders of magnitude[19]. For hyperpolarization, the ODNP (Overhauser Type Mechanism) should be the most effective, as crude oil is handled as a viscous liquid in the past[20]. Since the comparably high mobility, including radicals, of oil molecules, requires an appropriate regulation of electron-nuclear interactivity, this condition leads to an efficient propagation of polarization between nuclei and electrons in oil. The main aspect of ODNP is that when the microwave pumping frequency is in precisely the same resonance as the EPR transition, namely, f MW= fe, the entire influence on the nuclear system is acquired via electro-polarization conversion. In fact, Poindexter [21,22] recorded Overhauser form of DNP at B_0= 18 G of the external magnetic field on protons of "medium" or "light" crude oil that have a viscosity of 25-40 mPa·s as early as the 1950s.

The nuclear spins in this sample have been the ^{19}F spins, which represent the center of the solvent medium in the ^{19}F center, while electron spins have been the unbound electrons exit on the asphalt micelles. Unpaired electrons have been dislocated to the unfilled carbon bonds of asphaltene particles' compact aromatic structure[23]. We revealed a dipolar interactivity between the solvent fluorine atoms and unpaired colloidal asphaltene electrons through the DNP process. In a low magnetic field, electron spin saturation, as well as DNP improvements, were achieved, and also DNP parameters have been determined.

This study aimed to investigate the DNP parameters of fluorocarbons solvents in MC800 asphaltene free radical against time at room temperature at 1.53 mT low magnetic field.

Experimental Section

The spectrometer used in this study is a continuous wave weak field dual resonance NMR spectrometer. Additional material is available in the literature on the DNP principle and implementations for liquid samples[24-27]. DNP experiments were performed at 1.53mT with 61.2kHz resonance frequency for the^{19} Nuclei and the electrons 45.5MHz resonance frequency. Asphaltene was taken from MC800 fluid asphalt. This asphalt was obtained from the Turkish Petroleum Refineries Corporation in Kırıkkale province of Turkey. Three distinct asphalt ratios were taken to prepare the suspensions. The solvent was bought from the US, Aldrich Chemical Co.

The main properties of selected solvents in Figure 1 used as a solvent in this study are given in Table I.

Degasification of the samples was carried out with the Leybold-Heraeus vacuum system and the lowest pressure value seen in our studies was recorded as $1\cdot10^{-5}$ Pa. As seen in Fig. 2, the samples were sealed and degassed in Pyrex tubes.

Results and Discussion

EPR spectra

To test DNP parameters in the magnetic field, it is important to obtain a free radical EPR spectrum. ESR

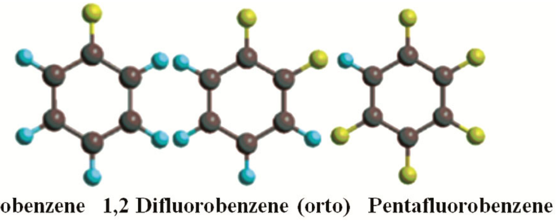

Fig. 1 — Structure of fluorobenzene, 1,2 Difluorobenzene (orto), and Pentafluorobenzene molecules (green color “flourine”; blue color “hydrogen” and grey color “carbon”).

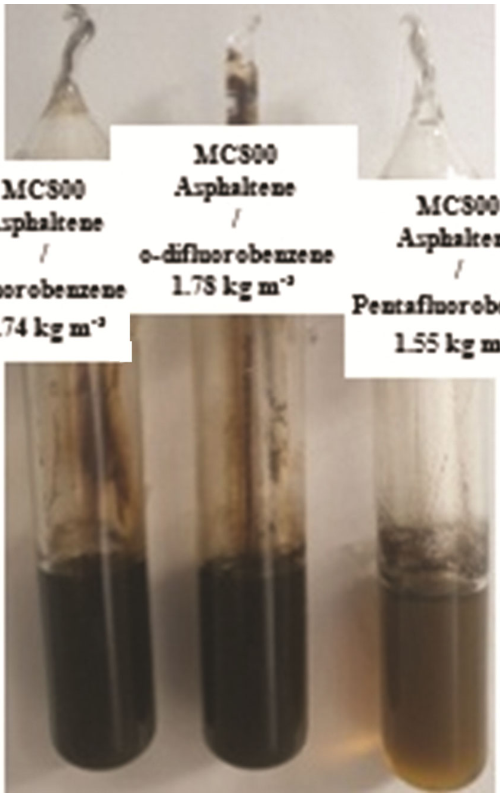

Fig. 2 — The sample in Pyrex tubes were sealed and degassed.

Table 1 — Basic constants and NMR sensitivity of the selected solvents.

Solvent	Molecular weight(g mol^{-1})	Melting point (°C)	Boiling point (°C)	Density (g cm^{-3})	Viscosity (cP)	Dipole moment (D)	NMR Sensitivity (x10^{22} spin/cm^3)
Fluorobenzene (C_6H_5F)	96,10	-42	85	1,024	0,545	1,68	0,64
o-Difluorobenzene($C_6H_4F_2$)	114,09	-34	92	1,158	0,548	2,40	1,22
Pentafluorobenzene (C_6HF_5)	168,06	-48	85	1,514	-	1,59	2,71

spectrum should not be affected by the solvents[28]. Figure 3 shows the EPR spectrum of this work and the EPR spectrum obtained by[24]. As shown in Figure 3, the spectrum obtained for asphaltene/fluorobenzene at a concentration of 3.00 kg/m^3 is best fit to measured values by a Gaussian, and obtained fit can be given by the following equation:

$$y = A \cdot e^{\left[-\frac{1}{2}\frac{(x-x_c)^2}{\sigma^2}\right]} \qquad \ldots(1)$$

The spectrum was presented as single Gaussian, created by the overlay of many Lorentzians. Additionally, the measured values of these concentrations are fit with Gaussian functions given by the following equations:

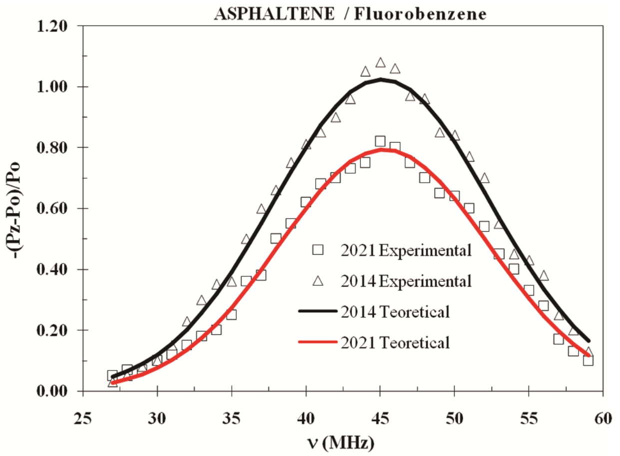

Fig. 3 — EPR spectrum of this work (□) and the EPR spectrum obtained by Kirimli (2014)(Δ)[24].

$$-\frac{(P_z-P_0)}{P_0} = 0.793\exp\left[-\frac{(\nu_s-45.25)^2}{99.00}\right] \qquad \ldots(2)$$

DNP Parameters

The NMR enhancement factor is calculated as follows[29]

$$A = -\frac{(P_z-P_0)}{P_0} = \rho \cdot f \cdot s\left|\frac{\gamma_s}{\gamma_I}\right| \qquad \ldots(3)$$

Where P_z and P_0 are the NMR signal amplitudes with and without ESR saturation power. On the other side, γ_s and γ_I symbolize electronic and nuclear gyromagnetic ratios, f is the nuclear relaxation leakage factor, s is the saturation factor equivalent to 1 for the whole EPR saturation, and lastly, is the nuclear-electron coupling parameter that is a measurement of the nuclear-electron interaction. All of the saturation measurements have been saturated at 45.5 MHz.

The variation of $\left[\frac{(P_z-P_0)}{P_0}\right]^{-1}$ versus V_{eff}^{-2} for asphaltenefluorobenzene derivatives sample is seen at 3 distinct concentrations in Fig. 4. For the maximum attainable EPR power, A^{-1} and A_{end}^{-1} are equal. The reciprocal enhancement factor is extrapolated for the infinite ESR power if the saturation condition is met. At complete EPR saturation A_∞ is the enhancement factor and it is calculated as follows:

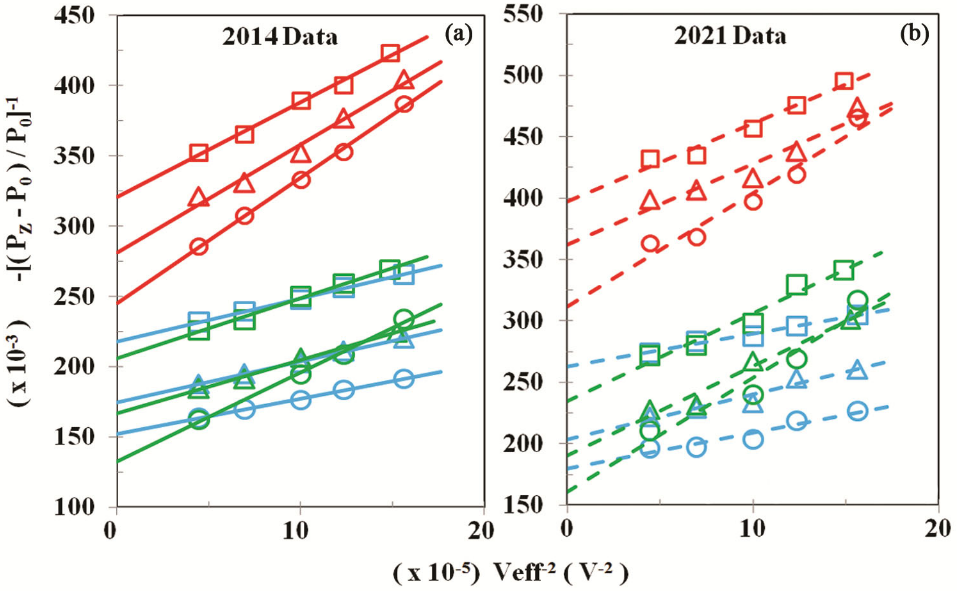

Fig. 4 — Variation of $\left[\frac{(P_z-P_0)}{P_0}\right]^{-1}$ versus V_{eff}^{-2} for asphaltene/ fluorobenzene derivatives sample at 3 distinct concentrations. Here, A_∞^{-1} values equivalent to the intersection points of the extrapolated best-fit and the $V_{eff}^{-2} = 0$ lines. (The red lines represent Pentafluorobenzene, the blue lines represent 1,2-difluorobenzene, and the green lines represent fluorobenzene.) (a)[24] data and (b) 2021 data.

$$A_\infty = -\rho \cdot f \left|\frac{\gamma_S}{\gamma_I}\right| \qquad \ldots (4)$$

U_∞, the ultimate enhancement factor, can easily be determined, as A_∞^{-1} values are well proportioned to the reciprocal concentration of the sample c^{-1} as depicted in Figure 5. Here the ρ values can be calculated after determining U_∞.

$$\rho = -\frac{U_\infty}{700} \qquad \ldots (5)$$

In the formula, for each concentration f value was figured by using the A_∞/U_∞ ratio and the s value was computed by using the A_{end} to A_∞ ratio. A_∞, U_∞, f, and s parameters which are parameters of the dynamic nuclear polarization are provided in Table 2.

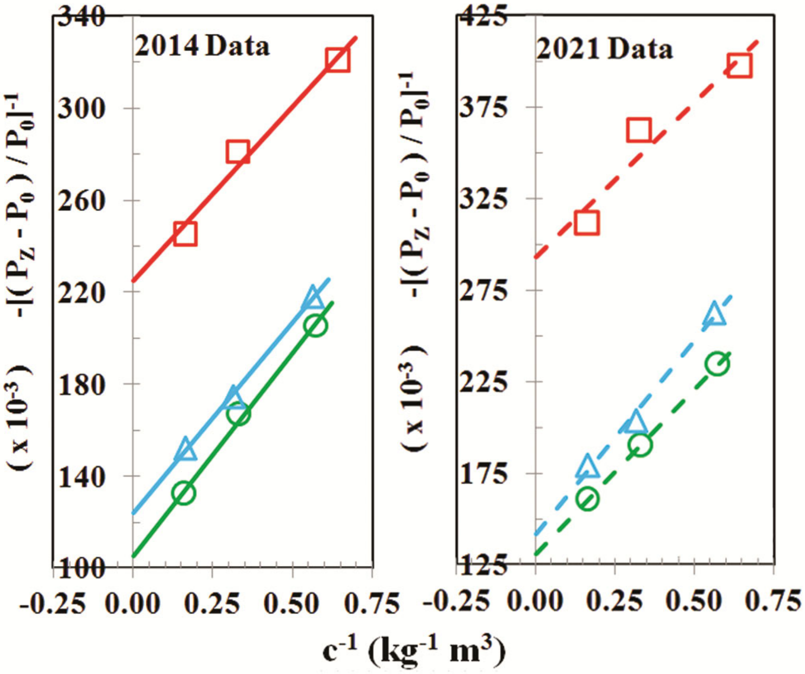

Fig. 5 — Examples of ultimate enhancement factor evaluations measured at room temperature. Here, the U_∞^{-1} values are equivalent to the intersection points of extrapolated best-fit lines and the c^{-1} = 0 line[24]2014& 2021 data).

Table 2 — DNP parameter values for the suspensions of fluorobenzene derivatives with MC800 asphaltene. (a) 2021 data and (b) 2014 data [24].

(a)

Solvent medium	C (kg m^{-3})	A_∞	U_∞	ρ	f	s	K
Fluorobenzene C_6H_5F	1,7	-4,3	-7,6	0,011	0,559	0,863	0,968
	3,00	-5,3			0,689	0,835	
	6,20	-6,2			0,816	0,763	
1,2 Difluorobenzene$C_6H_4F_2$	1,8	-3,8	-7,1	0,010	0,539	0,959	0,970
	3,2	-4,9			0,696	0,917	
	6,1	-5,6			0,790	0,914	
PentafluorobenzeneC_6HF_5	1,6	-2,5	-3,4	0,005	0,738	0,919	0,985
	3,1	-2,8			0,809	0,907	
	6,1	-3,2			0,941	0,857	

(b)

SolventMedium	C (kg m^{-3})	A_∞*	U_∞*	ρ*	f*	s*	K*
Fluorobenzene C_6H_5F	1,7	-4,9	-9,5	0,014	0,513	0,911	0,843
	3,00	-6,0			0,632	0,906	
	6,20	-7,5			0,797	0,818	
1,2 Difluorobenzene$C_6H_4F_2$	1,8	-4,6	-8,1	0,012	0,568	0,940	0,947
	3,2	-5,7			0,710	0,929	
	6,1	-6,6			0,814	0,931	
PentafluorobenzeneC_6HF_5	1,6	-2,8	-4,6	0,007	0,679	0,910	0,983
	3,1	-3,1			0,774	0,876	
	6,1	-3,5			0,888	0,858	

Experimental saturations range from 76% to 96%. The value of A_∞ varies between -2.5 and -6.2. The value of U_∞ varies between -3.4 and -7.6.The value of ρ varies between 0.005 and 0.011.For all samples, it shows an increase with the rise in the concentration of the sample. All A_∞ and U_∞ parameters have negative values since P_z and P_0 NMR signals are opposite to each other. This condition also leads ρ, nuclear coupling parameter, to have a positive value for solvent medium. Therefore, the dipole-dipole interaction, which is proportional to $1/r^3$, reciprocal cube of the distance between proton and electron spins, is predominant for the intermolecular spin-spin interaction.

The smallest absolute U_∞(so, ρ)value has been obtained for the pentafluorobenzene solvent medium. This indicates that fluorobenzene and 1,2-difluorobenzene disperse and suspend the asphaltene more effectively. Having the lowest electrical dipole moment is the pentafluorobenzene.

Conclusion

The Overhauser effect type dynamic nuclear polarization are used to study some colloidal suspensions with fluorobenzene, 1,2difluorobenzene, and pentafluorobenzene solvent media of MC800 asphaltene in a weak magnetic field of 1.53 mT at room temperature. For each sample solvent medium, the samples are prepared in three different asphaltene concentrations. The total sample number is nine. The spectrum of MC800 asphaltene in the fluorobenzene solvent medium was observed to be a single Gaussian which was peaked around 45.5 MHz in the EPR spectra of the asphaltenes. The form of EPR spectrum is in good agreement with Kirimli's work (2014)[(Ref.24)].

After the samples, which have formed colloidal suspensions with fluorobenzene, 1,2 difluorobenzene, and pentafluorobenzene solvent media of MC800 asphaltene are held seven years, it is found that the ρ nuclear-electron coupling parameter is smaller. In low magnetic fields the nuclear-electron coupling parameter. ρ varies from +0.5 (pure dipolar) to -1.0 (pure scalar), and new ρ obtained values are between these limits. New ρ values in our study are positive and this shows that the dipolar part of intermolecular spin-spin interactions is dominant.

K, for the importance of depend scalar coupling parameter in nearly all of the samples. This means that the scalar part of intermolecular spin –spin interactions increases in the waited samples i.e., dipolar part of interactions decrease.

In biological samples, the detailed information of chemical environment could be obtained with aromatic fluorinated solvents and free radicals which are inclined to the scalar interaction in EPR oximetry supported by the Overhauser effect[30,31].

This work contribute to study of the asphaltene surface and support these studies with dynamic nuclear polarization results. In addition, dynamic nuclear polarization studies are useful applications for empirical characterization of asphaltene solutions.

References

1 Briggs P J, Baron P R, Fulleylove R J & Wright M S, *J Petrol Technol*, 40 (1988) 206.

2 Gizatullin B, Gafurov M, Rodionov A, Mamin G, Mattea C, Stapf S &Orlinskii S, *Energy Fuels*, 32 (2018) 11261.

3 Shukla A K, *Analytical Characterization Methods for Crude Oil and Related Products*. JohnWiley & Sons Ltd: Hoboken, New Jersey (2018) 13.

4 Martyanov O N, Larichev Y V, Morozov E V, Trukhan S N & Kazarian S G, *Russ Chem Rev*, 86 (2017)999.

5 Yen T & Chilingarian G, *Asphaltenes and asphalts,* Elsevier, New York, 40A (1994) 7.

6 Yen T & Chilingarian G, *Asphaltenes and asphalts,* 2 edn Elsevier, New York, 40B (2000) 1.

7 Chilingarian G V & Yen T F, Bitumens, *Asphalts and Tar Sands*. Elsevier, New York, 7 (1978) 155.

8 Evdokimov I N, *Petrol SciTechnol*, 28 (2010) 756.

9 Ilyin S O & Strelets L A, *Energy Fuels*, 32 (2018) 268.

10 Chen J J, Hȕrlimann M, Paulsen J, Freed D, Mandal S & Song Y Q, *Oils Chem Phys Chem*, 15 (2014) 2676.

11 Gutowsky H S, Roger Ray B, Rutledge R L & Unterberger R R, *J Chem Phys*, 28 (1958)744.

12 O'Reilly D E, *J Chem Phys*, 29 (1958) 1188.

13 Mahmood M S A & Al-L Hamad A, *J Petrol SciEng*, 201 (2021) 1.

14 Alrashidi H, Afra S & Nasr-El-Din H A, *J Petrol SciEng*, 172 (2019) 724.

15 Campen S, Moorhouse S J & Wong J S, *J Petrol SciEng*, 184 (2020)106502.

16 Junior L C R, Ferreira M S & da Silva Ramos A C, *J Petrol Sci Eng*, 51 (2006) 26.

17 Vargas F M, Creek J L & Chapman W G, *Energy Fuels*, 24 (2010) 2294.

18 Evdokimov I N, Eliseev N Y & Akhmetov B R, *Fuel*, 85 (2006) 1465.

19 Sapunov V, Denisov A, Saveliev D, Soloviev A, Khomutov S, Borodin P, Narkhov E, Sergeev A & Shirokov A, *MagnReson Solids*, 18 (2016) 16209.

20 Pradhan A, Ovalles C & Moir M, Characterization of Heavy Petroleum Fractions by NMR Techniques. In The Boduszynski Continuum: Contributions to the Understanding of the Molecular Composition of Petroleum. Ovalles, C., Moir, M., Eds. ACS Symposium Series; OUP: Washington, DC (2018) 73.

21 Poindexter E, *Nature,* 182 (1958) 1087.

22 Poindexter E H & Torrey H C, *Overhauser effect well logging. U.S. Patent*, US 3096476A (1963).

23 Griesinger C, Bennati M, Vieth H M, Luchinat C, Parigi G, Hofer P, Engelke F, Glaser S J, Denysenkov V & Prisner T F, *Magn Reson Spectrosc*, 64 (2012) 4.

24 Kirimli H E &Ovalioglu H, *Asp J Dispers Sci Technol*, 35 (2014) 255.

25 Hausser K H & Stehlik D, *Adv Magn Opt Reson*, 3 (1968) 79.

26 Potenza J, *Adv Mol Relax Process*, 4 (1972) 229.

27 Müller-Warmuth W & Meise-Gresch K, *Adv Magn Opt Reson*, 11 (1983) 1.

28 Yalciner A, *Commun Facul Sci Univ Ankara*, 27 (1978) 1.

29 Kramer K D & Müller-Warmuth W, *Z Naturforsch C*, 19a (1964) 375.

30 Guiberteau T & Grucker D, *J Magn Reson*, 124 (1997) 263.

31 Murugesan R, English S, Reijnders K, Yamada K, Cook J A, Mitchell J B, Subramanian S & Krishna M C, *Magn Res Med*, 48 (2002) 523.