



Khan, S. A., Ali, S., Yamani, Z. H., Hussaini, S. R., Eastoe, J., Khan, A. M., & Sarfraz, S. (2019). NMR-Responsive Paramagnetic [M-EDTA] (M = Fe<sup>3+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>) Complexes to Differentiate T<sub>2</sub>-Distribution Signals of Crude Oil and Brine. *Energy and Fuels*, 33, 12278-12285. [12]. <https://doi.org/10.1021/acs.energyfuels.9b02984>

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1 **NMR responsive paramagnetic [M-EDTA] (M = Fe<sup>3+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>) complexes**  
2 **to differentiate T<sub>2</sub>-distribution signals of crude oil and brine**

3

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15

16

1 **Abstract**

2 Nuclear magnetic resonance (NMR) well logging tools are being commercially utilized for the  
3 characterization of various fluids confined within reservoir rocks. Conventional NMR  $T_2$ -  
4 distribution measurements are unable to quantify the actual fractions of crude oil and brine  
5 simultaneously present in the reservoir rocks. Herein, we reported NMR responsive paramagnetic  
6 [M-EDTA] ( $M = Fe^{3+}, Mn^{2+}, Cu^{2+}$ ) complexes having the capability to differentiate NMR  $T_2$ -  
7 distribution signals coming from crude oil and brine by accelerating the water ( $^1H$ ) relaxation. The  
8 formation of these [Fe-EDTA] $^-$ , [Mn-EDTA] $^{2-}$  and [Cu-EDTA] $^{2-}$  complexes was explored by UV-  
9 visible spectroscopy, and their chemical stability in brine solution was monitored by measuring  
10 the change in percent transmittance and backscattering intensities with time. Spin-spin ( $T_2$ )  
11 relaxation signals and  $T_2$ -distribution spectra of various carbonate and sand packs were recorded.  
12 The separation of NMR  $T_2$ -distribution signals was achieved using the optimized concentration of  
13 synthesized paramagnetic complexes. The separation of NMR  $T_2$ -distribution signals with  
14 optimum concentration of complexes and their long-term chemical stability in brine solution  
15 suggest them to be commercially reliable contrast agents for the characterization of various rock  
16 fluids confined in the oil reservoirs.

17 **Key Words:** Paramagnetic complexes;  $T_2$ -distributions; NMR logging; Reservoir monitoring.

18 **1. Introduction**

19 Fluid characterization and analysis of oil reservoirs are the most challenging areas of research for  
20 oil exploration industries <sup>1</sup>. The oil industries frequently faced with the difficulty and uncertainty  
21 in the quantitative estimation of various fluids (brine, light, and heavy crude oil) confined in the  
22 reservoir rocks. This information will help the mapping of oil-bearing formations and predict the  
23 physiochemical properties of oil reservoirs. Since the early 1990s, the phenomenon of nuclear

1 magnetic resonance (**NMR**) spectroscopy has been applied commercially to the oil well logging <sup>2</sup>.  
2 NMR spectra provide the real-time analysis of bottom-hole fluid fractions confined within porous  
3 media of reservoir rocks. The low field NMR well logging tool (~2 MHz) is evidently compatible  
4 with the down-hole reservoir environment <sup>3</sup>. The technology is dedicated to measuring the <sup>1</sup>H  
5 relaxation times, both longitudinal ( $T_1$ ) as well as transverse ( $T_2$ ), and occasionally diffusivity <sup>4</sup>.  
6 The resolved NMR spectra can help to estimate a wide variety of petrophysical reservoir properties  
7 such as porosity, permeability, wettability, and viscosity of crude oil <sup>3,5</sup>.

8 The estimation of crude oil is one of the unique outputs that NMR well logging tools can  
9 potentially provide by the interpretation of  $T_2$ -relaxation signals and their  $T_2$ -distributions.  
10 However, it is challenging to apply conventional NMR  $T_2$ -distribution measurements to quantify  
11 the actual fractions of crude oil and brine due to their spectral overlap. It is because the crude oil  
12 is a mixture of several components called SARA fractions (Saturates, Aromatics, Resin, and  
13 Asphaltenes) <sup>6</sup>, so it usually has a broad relaxation signal and diffusivity distribution, thus overlaps  
14 with the  $T_2$ -signal of brine. Therefore, several models based on various pulse sequences have been  
15 adopted to resolve the NMR  $T_2$ -distribution signals coming from brine and crude oil. It is reported  
16 that NMR response from crude oil can be distinguished from brine and the viscosity of crude oil  
17 can be estimated by **constituent viscosity model** <sup>7</sup>. Late in 2004, Freedman et al. <sup>8</sup> introduced a  
18 magnetic resonance fluid (**MRF**) characterization method to reveal the discrimination of crude oil  
19 and water signals which help to determine the flushed-zone saturation and oil viscosities. This  
20 NMR-based diffusion method is useful for developing 2D maps of relaxation times and molecular  
21 diffusion rates to investigate various fluids in complex environments. Moreover, the log-inject-log  
22 method also utilized to differentiate between the two logs which is preferably helpful for water-  
23 based mud (WBM). It is known that the mobility of various components within the crude oil phase

1 is significantly lower than the mobility of water. Therefore, there is another possibility to resolve  
2 the NMR signal overlapping arising from crude oil and water by diffusion experiments using a  
3 combined pulsed field gradient spin echo (**PFGSE**) – Carr-Purcell-Meiboom-Gill (CPMG)  
4 sequence <sup>9</sup>. However, NMR studies based on diffusion experiments have several disadvantages  
5 such as: (i) the diffusion technique interrupts the earth magnetic field, (ii) cannot be easily  
6 performed for bore-hole experiments, (iii) it is a time-consuming technique, and (iv) requires  
7 expensive equipment. Moreover, only diffusion experiments could not differentiate the crude oil  
8 and water signals in the real environment until they have different T<sub>2</sub>-values.

9 The presence of **paramagnetic minerals** such as Fe<sup>3+</sup> and Cu<sup>2+</sup> ions have a significant influence  
10 on the NMR relaxation time of liquids <sup>10,11</sup>. During reservoir logging, this effect can be utilized to  
11 reduce the relaxation time of brine and remove its spectral overlap with crude oil. However, the  
12 uncapped metal ions are unstable and may get adsorb on the rock surface and/or react with various  
13 salts present in the brine solution and precipitate. Therefore, NMR signals cannot provide reliable  
14 qualitative and quantitative information of the fluids confined in the porous rocks. Recently,  
15 **organic complexes** have also been utilized as oil-soluble contrast agents to differentiate the NMR  
16 relaxation signals of crude oil. Zhang et al. proposed various iron-based complexes such as  
17 iron(III) acetylacetonate [Fe(acac)<sub>3</sub>], iron(III) 2-ethyl hexanoate, and iron(II) naphthenate to  
18 separate the proton relaxation phenomenon in crude oil sample <sup>12</sup>. However, these commercially  
19 available complexes are organic in nature and cannot easily be removed from the crude oil with  
20 an applied external magnetic field. Therefore, it is desirable to find alternatives to oil-soluble  
21 contrast agents that are compatible with water-based mud (WBM).

22 It is well-known that ethylene diamine tetraacetic acid (**H<sub>4</sub>EDTA**) is a commercially available and  
23 remarkable chelating agent. Its conjugate base (EDTA<sup>4-</sup>) has the capability to chelate with metal

1 cations to form stable and soluble [M-EDTA] complexes <sup>13</sup>. As such DTA is an electron donor  
2 hexadentate ligand which allows multiple bindings in its coordination complex. However, the  
3 choice of metal ion is very important to develop paramagnetic characteristics in the complexes.  
4 [M-EDTA] complexes have been extensively utilized for various applications such as analytical  
5 titrations <sup>14</sup>, biological catalysts <sup>15</sup>, waste treatments <sup>16,17</sup>, chelation therapy <sup>18</sup> and additives in the  
6 food industry <sup>19</sup>. However, these complexes, particularly paramagnetic, have not been investigated  
7 yet for the possible detection of crude oil in the reservoirs using logging-while-drilling (LWD)  
8 NMR probes developed by various oil exploration companies (Saudi Aramco, Schlumberger, and  
9 Halliburton) <sup>20-22</sup>.

10 Herein, we have developed NMR responsive paramagnetic [M-EDTA] (M = Fe<sup>3+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>)  
11 complexes and determined their chemical stability in harsh saline water. The research was carried  
12 out at the lab scale to explore the response of crude oil and brine present in various sample packs.  
13 The work signifies a novel application of well-known [M-EDTA] complexes by overcoming the  
14 spectral overlap coming from crude oil and water, which is the real issue of implementing the  
15 NMR-based well logging tools to acquire reliable qualitative and quantitative information of  
16 various fluids confined in the reservoir rocks.

## 17 **2. Experimental**

### 18 **2.1. Chemicals**

19 All the chemicals were purchased from various commercial sources as follows: ethylene diamine  
20 tetraacetic acid disodium salt dihydrate (EDTA-Na<sub>2</sub>.2H<sub>2</sub>O, 99%, Sigma-Aldrich), iron(III)  
21 chloride hexahydrate (FeCl<sub>3</sub>.6H<sub>2</sub>O, ≥99%, Sigma-Aldrich), manganese(II) sulfate monohydrate  
22 (MnSO<sub>4</sub>.H<sub>2</sub>O, >99%, Fluka), and copper(II) chloride (CuCl<sub>2</sub>, 99.9%, Aldrich) were utilized for  
23 preparation of [M-EDTA] complexes.

## 1    **2.2.    Preparation of [M-EDTA] complexes**

2    EDTA- $\text{Na}_2 \cdot 2\text{H}_2\text{O}$  (0.1 M) stock solution was prepared by dissolving 3.722 g of salt in 100 mL of  
3    deionized (DI) water. Similarly,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.1 M),  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (0.1 M), and  $\text{CuCl}_2$  (0.1 M)  
4    stock solutions were prepared by dissolving 2.703, 1.690, and 1.345 g of salts in 100 mL of DI  
5    water, respectively. Finally, each [M-EDTA] ( $\text{M} = \text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ) complex having conc. 0.05  
6    M was prepared by mixing an equal volume of the EDTA and respective metal ion solutions. The  
7    synthesized complexes were named as follows:  $[\text{Fe-EDTA}]^-$ ,  $[\text{Mn-EDTA}]^{2-}$ , and  $[\text{Cu-EDTA}]^{2-}$ .

## 8    **2.3.    Stability test of [M-EDTA] complexes**

9    The chemical stability of transition metal ions ( $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ) in DI water and brine solutions  
10    was examined and compared with the stability of [M-EDTA] complexes in a brine solution. For  
11    this purpose, various  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Cu}^{2+}$  ionic solutions having overall conc. 0.01 M were  
12    prepared in DI water and brine. Similarly, [M-EDTA] complexes having conc. 0.01 M were also  
13    prepared by diluting the complexes with brine solution. The standard brine (ASTM D1141)  
14    solution having salinity  $\sim 36.03 \text{ g L}^{-1}$  was utilized as described in our recently published work <sup>23,24</sup>.

## 15    **2.4.    Characterization techniques**

16    UV-visible spectra of various NMR responsive paramagnetic complexes were recorded using UV-  
17    visible spectrometer (USB-2000, Ocean Optics, USA). The long-time stability of complexes in  
18    brine solution were examined by measuring the percent transmittance and backscattering  
19    intensities via Turbiscan LAB optical analyzer (Formulation, USA).

## 20    **2.5.    Preparation of carbonate and sand packs**

21    Various carbonate and sand sample packs were prepared to mimic the actual oil reservoir  
22    conditions. For each sample pack, standardized calcium carbonate gravels or sand were mounted  
23    in a glass bottle (30 mL). For standardization of sand, the fine sand was passed through the mesh-

1 45 (354 microns) followed by the mesh-80 (177 microns). It means that 90 % or more of the sand  
2 passed through a 45-mesh and retained by an 80-mesh sieve. The particles size of the collected  
3 sand was in the range of -45 / +80 mesh. The standard brine (ASTM D1141) solution having  
4 salinity  $\sim 36.03 \text{ g L}^{-1}$  and Arabian light crude oil (ALCO) having API gravity 35 were utilized as a  
5 continuous phase. The desired amount  $\sim 10 \text{ mL}$  of fluid (brine and oil) was filled in the sample  
6 packs having final diameter  $\sim 2.83 \text{ cm}$ , length  $\sim 4.77 \text{ cm}$ , and volume  $\sim 30.0 \text{ cm}^3$ . The sample packs  
7 were placed in a dedicated NMR sample holder for measurements.

## 8 **2.6. NMR $T_2$ -distribution measurements**

9 NMR  $T_2$ -relaxation experiments were performed using a dedicated rock core analyzer (GeoSpec2,  
10 Oxford Instruments, UK). The NMR spectrometer has the capability to scan the rock cores having  
11 maximum dimensions of 2" x 5". The built-in Q-Sense signal enhancement technology permits the  
12 detection of extremely small pores ( $\sim 1 \text{ nm}$ ). The spectrometer is coupled with Green Imaging  
13 Technologies (GIT) Systems software which allows the fast, reliable, and non-destructive  
14 acquisition of standard NMR experiments for reservoir applications. The experiments were  
15 performed at fixed-field strength with a resonating frequency of 2.2 MHz at ambient temperature  
16 and pressure. The standard Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence was executed  
17 while keeping the tau ( $\tau$ ) value constant (0.053 ms) between the initial  $90^\circ$  and  $180^\circ$  pulses. The  
18 signal to noise ratio (SNR) for each experiment was kept at 150 after 16 scans. Each experiment  
19 was conducted three times to check the reproducibility of NMR  $T_2$ -distribution measurements.

## 20 **3. Results and discussion**

### 21 **3.1. Chemistry of paramagnetic complexes**

22 It is well-known that the paramagnetic ions have unpaired electron/s in their outermost valence  
23 shells. The selected transition metal cations, i.e.,  $\text{Fe}^{3+}$  ( $5e^-$ ),  $\text{Mn}^{2+}$  ( $5e^-$ ), and  $\text{Cu}^{2+}$  ( $1e^-$ ) have



1 unpaired electrons in their valence shells exhibiting magnetic moments  $5.92 \mu_B$ ,  $5.92 \mu_B$ , and  $1.73$   
 2  $\mu_B$ , respectively. When disodium salt of EDTA is dissolved in deionized water, it behaves like an  
 3 amino acid with double zwitterions. The ligand  $[\text{H}_2\text{-EDTA}]^{2-}$  chelates with metal cations ( $\text{Fe}^{3+}$ ,  
 4  $\text{Mn}^{2+}$ , and  $\text{Cu}^{2+}$ ) in 1:1 molar ratio forming stable complexes;  $[\text{Fe-EDTA}]^-$ ,  $[\text{Mn-EDTA}]^{2-}$ , and  
 5  $[\text{Cu-EDTA}]^{2-}$ , as shown in the balanced chemical equations (1-3). The reason behind the  
 6 extraordinary stability of these complexes is the multiple binding sites available within the ligand.  
 7 These sites oriented to generates a cage-like structure where the metal cation is effectively trapped  
 8 in EDTA and isolated from solvent molecules <sup>25</sup>. Fig. 1 displays the proposed three-dimensional  
 9 (3D) ball and stick model representing the binding motif in M-EDTA complexes. The central metal  
 10 cation is coordinated with two amino and four carboxyl groups forming a stable and soluble [M-  
 11 EDTA] complex making a cage-like structure.



### 13 3.2. Formation of paramagnetic complexes

14 Metal-EDTA complexes have been extensively explored using various techniques such as cyclic  
 15 voltammetry <sup>26</sup>, X-ray crystallography <sup>27</sup>, mass spectrometry <sup>28</sup>, electron paramagnetic resonance  
 16 (EPR) <sup>29</sup>, nuclear magnetic resonance (NMR) <sup>30</sup>, X-ray photoelectron (XPS) <sup>31</sup>, and Fourier  
 17 transform infrared (FTIR) spectroscopy <sup>32</sup>. However, we have applied UV-visible spectroscopy to  
 18 characterize these [M-EDTA] complexes <sup>33</sup>. Fig. 2(a) depicts UV-visible reference spectra of (i)  
 19 DI water, (ii) brine, and (iii) EDTA-brine. The brine and EDTA-brine solutions exhibit the  
 20 absorption maxima ( $\lambda_{\text{max}}$ ) at 215 and 218 nm, respectively. Fig. 2(b-d) represents UV-visible  
 21 spectra of various paramagnetic (b)  $\text{Fe}^{3+}$ , (c)  $\text{Mn}^{2+}$ , and (d)  $\text{Cu}^{2+}$  ions in the presence of DI water,

1 brine, and EDTA-brine solutions. It was observed that  $\text{Fe}^{3+}$  ions in DI water display characteristic  
2 absorption maxima at 291 nm (Fig. 2b) <sup>34</sup>. However, the observed spectrum gets broaden and  
3 absorption intensity increased by almost three times for the same concentration of  $\text{Fe}^{3+}$  ions by the  
4 addition of EDTA solution, which indicates their chemical interactions and formation of stable  
5  $[\text{Fe-EDTA}]^-$  complexes. Similar behavior and interactions were observed for  $\text{Mn}^{2+}$  and  $\text{Cu}^{2+}$  ions  
6 in EDTA solution signifying the formation of  $[\text{Mn-EDTA}]^{2-}$  and  $[\text{Cu-EDTA}]^{2-}$  complexes (Fig.  
7 2c,d). Moreover, it was observed that  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions are unstable in the brine solution and  
8 show broad absorption spectra suggesting the possible formation of their insoluble hydroxides <sup>35</sup>.

### 9 **3.3. Stability of paramagnetic complexes**

10 The chemical stability of paramagnetic ions ( $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ) in DI water and brine solution was  
11 compared with the stability of  $[\text{M-EDTA}]$  complexes in the brine solution. Fig. 3 exhibits the (a-  
12 c) percent transmittance and (d-f) backscattering intensities of various solutions ( $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ )  
13 recorded via a Turbiscan optical analyzer after 24 h of mixing. It was observed that the  $\text{Fe}^{3+}$  (Fig.  
14 2d) and  $\text{Cu}^{2+}$  (Fig. 2f) ions are completely unstable in the brine solution, as confirmed from the  
15 increase in backscattering intensity at the bottom of vial due to sedimentation phenomenon.  
16 However, their corresponding complexes, i.e.,  $[\text{Fe-EDTA}]^-$  and  $[\text{Cu-EDTA}]^{2-}$  were found stable in  
17 the brine solution. Interestingly,  $\text{Mn}^{2+}$  ions remained stable in brine solution up to 24 h (Fig. 2e).  
18 It is well-known that the uncapped ions are unstable and may adsorb on rock surfaces and/or react  
19 with various salts of brine. Therefore, capping of these metal cations has significant worth for their  
20 ultimate use in the oil reservoir. It was also observed that the synthesized complexes have chemical  
21 stability in the brine solution for a couple of months. Moreover, the precipitation and sedimentation  
22 behavior of these  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions in the presence of brine solution was also examined up to 240  
23 min (Fig. 4). The precipitation of Fe and Cu was observed up to 60 and 20 minutes, respectively,

1 followed by sedimentation. The transmittance intensity was decreased during the precipitation,  
2 while it gradually increased from the top of bottle during sedimentation (Fig. 4a,c). Moreover, the  
3 backscattering intensity was gradually increased from the bottom of specimen due to the  
4 sedimentation of particles (Fig. 4b,d).

### 5 **3.4. NMR T<sub>2</sub>-distributions for oil/water signal separation**

6 NMR T<sub>2</sub>-relaxation curves were attained for various sample packs and the signals transformed into  
7 T<sub>2</sub>-distributions via Laplace inversion technique using GIT system software coupled with the  
8 spectrometer. The standard brine solution (36.03 g L<sup>-1</sup>) and ALCO (API ~35) were utilized as  
9 water and oil phases, respectively, to mimic the reservoir conditions. NMR T<sub>2</sub>-distribution  
10 measurements are presented before and after the addition of [M-EDTA] complexes in the brine  
11 solution which clearly show the enhancement of water relaxation. Fig. 5(a) shows T<sub>2</sub>-distributions  
12 of three sample packs in the continuous phase, i.e., brine, ALCO, brine-ALCO (1:1) mixture. The  
13 sample packs exhibited 100 % porosity as the measurements were performed in continuous phases.  
14 The observed T<sub>2</sub>-times for brine and ALCO are 2488 and 335 ms, respectively. Moreover, the  
15 brine-oil mixture did not show any signal overlapping due to their different relaxation times. Fig.  
16 5(b) represents the T<sub>2</sub>-distributions of carbonate and sand packs saturated with brine and ALCO  
17 mixture in a porous medium. The observed T<sub>2</sub>-distribution for carbonate pack (CP) is partially  
18 overlapped (T<sub>2</sub> ~296 ms, ~1730 ms), while the signal for sand pack (SP) is completely overlapped  
19 (T<sub>2</sub> ~142 ms). CP and SP exhibited the porosity value around ~35 and ~30 %, respectively. The  
20 SP exhibited less porosity than CP due to the homogenous and smaller size of sand particles,  
21 explaining why the T<sub>2</sub>-relaxation curve for SP slightly shifted downward.

22 NMR responsive paramagnetic complexes were prepared in a brine solution to shift the brine  
23 signal downward. Case-1 presents various CPs saturated with brine and oil in the porous medium.

1 Fig. 5(c) shows  $T_2$ -distributions of four CPs, i.e., blank (black line),  $\text{Fe}[\text{EDTA}]^-$  (red line),  
2  $\text{Mn}[\text{EDTA}]^{2-}$  (blue line), and  $\text{Cu}[\text{EDTA}]^{2-}$  (green line) saturated with crude oil and brine. By the  
3 addition of paramagnetic  $[\text{M-EDTA}]$  complexes, the notable enhancement in  $T_2$ -relaxation was  
4 observed and  $\text{Mn}[\text{EDTA}]^{2-}$  (0.01 M) complex solution completely resolved the brine ( $T_2 \sim 14$  ms)  
5 and oil ( $T_2 \sim 312$  ms) signals as demonstrated in Fig. 5c. Similarly, Case-2 exhibits various SPs  
6 saturated with brine and oil in the porous medium. Fig. 5(d) exhibits four SPs, i.e., blank (black  
7 line),  $\text{Fe}[\text{EDTA}]^-$  (red line),  $\text{Mn}[\text{EDTA}]^{2-}$  (blue line), and  $\text{Cu}[\text{EDTA}]^{2-}$  (green line) saturated with  
8 brine and oil mixture. The significant enhancement in  $T_2$ -relaxation was observed by the addition  
9 of complexes and  $\text{Mn}[\text{EDTA}]^{2-}$  (0.01 M) solution completely resolved  $T_2$ -signal into its  
10 components, i.e., brine ( $T_2 \sim 13$  ms) and oil ( $T_2 \sim 248$  ms). Therefore, NMR responsive  
11 paramagnetic complexes have the capability to resolve the  $T_2$ -spectral overlap of brine and oil  
12 phases confined in reservoir rocks.

#### 13 **4. Conclusions**

14 We have successfully engaged the paramagnetic metal cations with EDTA ligand to develop  $[\text{M-}$   
15  $\text{EDTA}]$  complexes. The synthesized complexes have chemical stability in the brine solution for a  
16 couple of months. The innovative aspect of this research work, which leads to our research  
17 motivation, is the utilization of these NMR responsive paramagnetic complexes to differentiate  $T_2$ -  
18 distribution signals coming from crude oil and brine. We successfully discriminated the NMR  
19 response of crude oil and brine in porous media by enhancing the  $T_2$ -relaxation of brine using  
20 stabled paramagnetic complexes. This will help to extract the qualitative and quantitative  
21 information from NMR spectra, which cannot resolved by other NMR-based diffusion methods  
22 published in the literature [Ref]. The obtained information will also help to predict the  
23 physiochemical properties and mapping of oil-bearing formations.

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2 JCIS, Volume 484, 15 December 2016, Pages 125–134

3

4 <http://dx.doi.org/10.1016/j.jcis.2016.08.082>

5

6

7

## 8 **Acknowledgment**

9 The authors would like to acknowledge the financial support received from "Center of Research  
10 Excellence in Nanotechnology (CENT) at King Fahd University of Petroleum and Minerals  
11 (KFUPM) in the Kingdom of Saudi Arabia".

12

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