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**NMR responsive paramagnetic [M-EDTA] (M = Fe³⁺, Mn²⁺, Cu²⁺) complexes
to differentiate T₂-distribution signals of crude oil and brine**

Shahid Ali ^{a,*}, Safyan A. Khan ^{a,*}, Syed R. Hussaini ^b, Zain H. Yamani ^a, Julian Eastoe ^c

^a Center of Research Excellence in Nanotechnology, King Fahd University of Petroleum and
Minerals, Dhahran 31261, Saudi Arabia

^b Center for Integrative Petroleum Research, College of Petroleum Engineering & Geosciences,
King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

^c School of Chemistry, University of Bristol, Cantock's Close, BS8 1TS, Bristol, UK

(*) Corresponding authors at: Center of Research Excellence in Nanotechnology, King Fahd
University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia.

E-mail addresses: shali@kfupm.edu.sa (S. Ali), safyan@kfupm.edu.sa (S.A. Khan).

Abstract

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

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

1. Introduction

Fluid characterization and analysis of oil reservoirs are the most challenging areas of research for oil exploration industries¹. The oil industries frequently faced with the difficulty and uncertainty in the quantitative estimation of various fluids (brine, light, and heavy crude oil) confined in the reservoir rocks. This information will help the mapping of oil-bearing formations and predict the physiochemical properties of oil reservoirs. Since the early 1990s, the phenomenon of nuclear

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

The estimation of crude oil is one of the unique outputs that NMR well logging tools can potentially provide by the interpretation of T_2 -relaxation signals and their T_2 -distributions. However, it is challenging to apply conventional NMR T_2 -distribution measurements to quantify the actual fractions of crude oil and brine due to their spectral overlap. It is because the crude oil is a mixture of several components called SARA fractions (Saturates, Aromatics, Resin, and Asphaltenes) ⁶, so it usually has a broad relaxation signal and diffusivity distribution, thus overlaps with the T_2 -signal of brine. Therefore, several models based on various pulse sequences have been adopted to resolve the NMR T_2 -distribution signals coming from brine and crude oil. It is reported that NMR response from crude oil can be distinguished from brine and the viscosity of crude oil can be estimated by **constituent viscosity model** ⁷. Late in 2004, Freedman et al. ⁸ introduced a magnetic resonance fluid (**MRF**) characterization method to reveal the discrimination of crude oil and water signals which help to determine the flushed-zone saturation and oil viscosities. This NMR-based diffusion method is useful for developing 2D maps of relaxation times and molecular diffusion rates to investigate various fluids in complex environments. Moreover, the log-inject-log method also utilized to differentiate between the two logs which is preferably helpful for water-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 ⁹. 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 T₂-values.

9 The presence of **paramagnetic minerals** such as Fe³⁺ and Cu²⁺ ions have a significant influence
10 on the NMR relaxation time of liquids ^{10,11}. 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)₃], iron(III) 2-ethyl hexanoate, and iron(II) naphthenate to
18 separate the proton relaxation phenomenon in crude oil sample ¹². 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 (**H₄EDTA**) is a commercially available and
23 remarkable chelating agent. Its conjugate base (EDTA⁴⁻) has the capability to chelate with metal

cations to form stable and soluble [M-EDTA] complexes¹³. As such DTA is an electron donor hexadentate ligand which allows multiple bindings in its coordination complex. However, the choice of metal ion is very important to develop paramagnetic characteristics in the complexes. [M-EDTA] complexes have been extensively utilized for various applications such as analytical titrations¹⁴, biological catalysts¹⁵, waste treatments^{16,17}, chelation therapy¹⁸ and additives in the food industry¹⁹. However, these complexes, particularly paramagnetic, have not been investigated yet for the possible detection of crude oil in the reservoirs using logging-while-drilling (LWD) NMR probes developed by various oil exploration companies (Saudi Aramco, Schlumberger, and Halliburton)²⁰⁻²².

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

2. Experimental

2.1. Chemicals

All the chemicals were purchased from various commercial sources as follows: ethylene diamine tetraacetic acid disodium salt dihydrate ($\text{EDTA-Na}_2 \cdot 2\text{H}_2\text{O}$, 99%, Sigma-Aldrich), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$, Sigma-Aldrich), manganese(II) sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $>99\%$, Fluka), and copper(II) chloride (CuCl_2 , 99.9%, Aldrich) were utilized for preparation of [M-EDTA] complexes.

2.2. Preparation of [M-EDTA] complexes

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 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 CuCl_2 (0.1 M) stock solutions were prepared by dissolving 2.703, 1.690, and 1.345 g of salts in 100 mL of DI water, respectively. Finally, each [M-EDTA] ($\text{M} = \text{Fe}^{3+}$, Mn^{2+} , Cu^{2+}) complex having conc. 0.05 M was prepared by mixing an equal volume of the EDTA and respective metal ion solutions. The synthesized complexes were named as follows: $[\text{Fe-EDTA}]^-$, $[\text{Mn-EDTA}]^{2-}$, and $[\text{Cu-EDTA}]^{2-}$.

2.3. Stability test of [M-EDTA] complexes

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

2.4. Characterization techniques

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

2.5. Preparation of carbonate and sand packs

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

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

2.6. NMR T_2 -distribution measurements

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

3. Results and discussion

3.1. Chemistry of paramagnetic complexes

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

unpaired electrons in their valence shells exhibiting magnetic moments $5.92 \mu_B$, $5.92 \mu_B$, and $1.73 \mu_B$, respectively. When disodium salt of EDTA is dissolved in deionized water, it behaves like an amino acid with double zwitterions. The ligand $[\text{H}_2\text{-EDTA}]^{2-}$ chelates with metal cations (Fe^{3+} , Mn^{2+} , and Cu^{2+}) in 1:1 molar ratio forming stable complexes; $[\text{Fe-EDTA}]^-$, $[\text{Mn-EDTA}]^{2-}$, and $[\text{Cu-EDTA}]^{2-}$, as shown in the balanced chemical equations (1-3). The reason behind the extraordinary stability of these complexes is the multiple binding sites available within the ligand. These sites oriented to generates a cage-like structure where the metal cation is effectively trapped in EDTA and isolated from solvent molecules²⁵. Fig. 1 displays the proposed three-dimensional (3D) ball and stick model representing the binding motif in M-EDTA complexes. The central metal cation is coordinated with two amino and four carboxyl groups forming a stable and soluble [M-EDTA] complex making a cage-like structure.

3.2. Formation of paramagnetic complexes

Metal-EDTA complexes have been extensively explored using various techniques such as cyclic voltammetry²⁶, X-ray crystallography²⁷, mass spectrometry²⁸, electron paramagnetic resonance (EPR)²⁹, nuclear magnetic resonance (NMR)³⁰, X-ray photoelectron (XPS)³¹, and Fourier transform infrared (FTIR) spectroscopy³². However, we have applied UV-visible spectroscopy to characterize these [M-EDTA] complexes³³. Fig. 2(a) depicts UV-visible reference spectra of (i) DI water, (ii) brine, and (iii) EDTA-brine. The brine and EDTA-brine solutions exhibit the absorption maxima (λ_{max}) at 215 and 218 nm, respectively. Fig. 2(b-d) represents UV-visible spectra of various paramagnetic (b) Fe^{3+} , (c) Mn^{2+} , and (d) Cu^{2+} ions in the presence of DI water,

brine, and EDTA-brine solutions. It was observed that Fe^{3+} ions in DI water display characteristic absorption maxima at 291 nm (Fig. 2b)³⁴. However, the observed spectrum gets broaden and absorption intensity increased by almost three times for the same concentration of Fe^{3+} ions by the addition of EDTA solution, which indicates their chemical interactions and formation of stable $[\text{Fe-EDTA}]^-$ complexes. Similar behavior and interactions were observed for Mn^{2+} and Cu^{2+} ions in EDTA solution signifying the formation of $[\text{Mn-EDTA}]^{2-}$ and $[\text{Cu-EDTA}]^{2-}$ complexes (Fig. 2c,d). Moreover, it was observed that Fe^{3+} and Cu^{2+} ions are unstable in the brine solution and show broad absorption spectra suggesting the possible formation of their insoluble hydroxides³⁵.

3.3. Stability of paramagnetic complexes

The chemical stability of paramagnetic ions (Fe^{3+} , Mn^{2+} , Cu^{2+}) in DI water and brine solution was compared with the stability of $[\text{M-EDTA}]$ complexes in the brine solution. Fig. 3 exhibits the (a-c) percent transmittance and (d-f) backscattering intensities of various solutions (Fe^{3+} , Mn^{2+} , Cu^{2+}) recorded via a Turbiscan optical analyzer after 24 h of mixing. It was observed that the Fe^{3+} (Fig. 2d) and Cu^{2+} (Fig. 2f) ions are completely unstable in the brine solution, as confirmed from the increase in backscattering intensity at the bottom of vial due to sedimentation phenomenon. However, their corresponding complexes, i.e., $[\text{Fe-EDTA}]^-$ and $[\text{Cu-EDTA}]^{2-}$ were found stable in the brine solution. Interestingly, Mn^{2+} ions remained stable in brine solution up to 24 h (Fig. 2e). It is well-known that the uncapped ions are unstable and may adsorb on rock surfaces and/or react with various salts of brine. Therefore, capping of these metal cations has significant worth for their ultimate use in the oil reservoir. It was also observed that the synthesized complexes have chemical stability in the brine solution for a couple of months. Moreover, the precipitation and sedimentation behavior of these Fe^{3+} and Cu^{2+} ions in the presence of brine solution was also examined up to 240 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_2 -distributions for oil/water signal separation**

6 NMR T_2 -relaxation curves were attained for various sample packs and the signals transformed into
7 T_2 -distributions via Laplace inversion technique using GIT system software coupled with the
8 spectrometer. The standard brine solution (36.03 g L⁻¹) and ALCO (API ~35) were utilized as
9 water and oil phases, respectively, to mimic the reservoir conditions. NMR T_2 -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_2 -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_2 -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_2 -distributions of carbonate and sand packs saturated with brine and ALCO
17 mixture in a porous medium. The observed T_2 -distribution for carbonate pack (CP) is partially
18 overlapped (T_2 ~296 ms, ~1730 ms), while the signal for sand pack (SP) is completely overlapped
19 (T_2 ~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_2 -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.

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

4. Conclusions

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

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