

Addendum

Addendum: Taylor, S.E., et al. Metal Ion Interactions with Crude Oil Components: Specificity of Ca^{2+} Binding to Naphthenic Acid at an Oil/Water Interface. *Colloids Interfaces* 2018, 2, 40.

Spencer E. Taylor ^{1,*} , Hiu Tung Chu ² and Ugochukwu I. Isiocha ³

¹ Centre for Petroleum and Surface Chemistry, Department of Chemistry, University of Surrey, Guildford, Surrey GU2 7XH, UK

² TÜV Rheinland, 10-16 Pun Shan Street, Tsuen Wan, N.T., Hong Kong; christy.chu@tuv.com

³ Department of Chemistry, University of Surrey, Guildford, Surrey GU2 7XH, UK; ui00015@surrey.ac.uk

* Correspondence: s.taylor@surrey.ac.uk; Tel.: +44-1483-681999

Received: 25 October 2018; Accepted: 2 November 2018; Published: 6 November 2018



In the article recently published in *Colloids and Interfaces* [1], it was erroneously stated that a hydrated form of calcium chloride, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, was the source of Ca^{2+} ions used to compare with other alkali and alkaline earth ions on the interfacial behavior the metal ions at aqueous/*n*-heptane interfaces containing commercial naphthenic acid exhibit. We have since determined that the real source of Ca^{2+} ions was in fact anhydrous CaCl_2 (supplied by Fisher Scientific Ltd., Lot 1496876), which was inadvertently prescribed by the main author. As a consequence, the authors wish to make the readers aware that the interpretations given are not necessarily correct in the original account [1].

In particular, the use of anhydrous CaCl_2 causes an increase in pH of the aqueous solutions. In the original paper, an average pH value of the chloride salt solutions of ~6 was reported. This was true for all the salts used, but did not include solutions derived using anhydrous CaCl_2 . It is correct, however, for the hydrated salt $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

On the other hand, as shown in Figure 1, the pH of aqueous solutions derived from anhydrous CaCl_2 increases steadily throughout the concentration range covered in reference [1], that is, 0.01–1 mol/L. As far as we have been able to ascertain, however, there is little quantitative information relating to the solution properties of anhydrous CaCl_2 in the literature, except for indications of its alkaline character given in manufacturers' specification sheets (e.g., Sigma–Aldrich state “<1% free alkali as $\text{Ca}(\text{OH})_2$ ” for an equivalent product [2]). This characteristic is most likely a consequence of CaCl_2 being obtained commercially as a byproduct of the Solvay process for sodium carbonate manufacture. The purer hydrated forms obtained by crystallization are devoid of such impurities.

The significance of the pH change accompanying the increase in Ca^{2+} concentration is shown in Figure 2, in which the minimum interfacial tension (from Figure 7a in reference [1]) is seen to decrease linearly with the OH^- concentration (determined from the pH, i.e., $[\text{OH}^-] = 10^{-(14 - \text{pH})}$), indicating that OH^- , and not Ca^{2+} ions are responsible for the observed interfacial tension behavior.

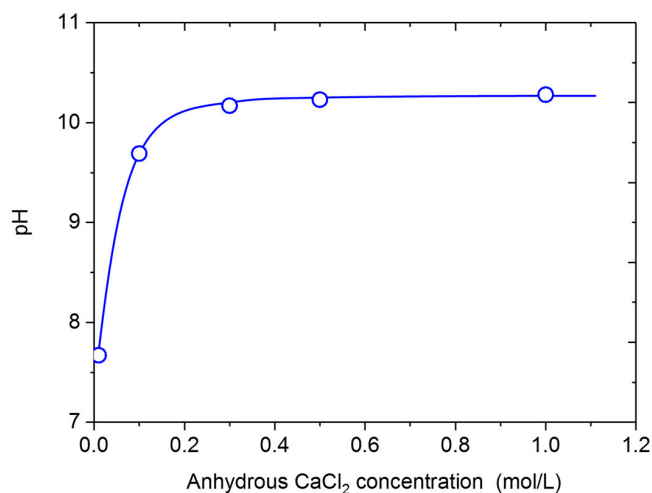


Figure 1. Effect of anhydrous CaCl₂ concentration on solution pH.

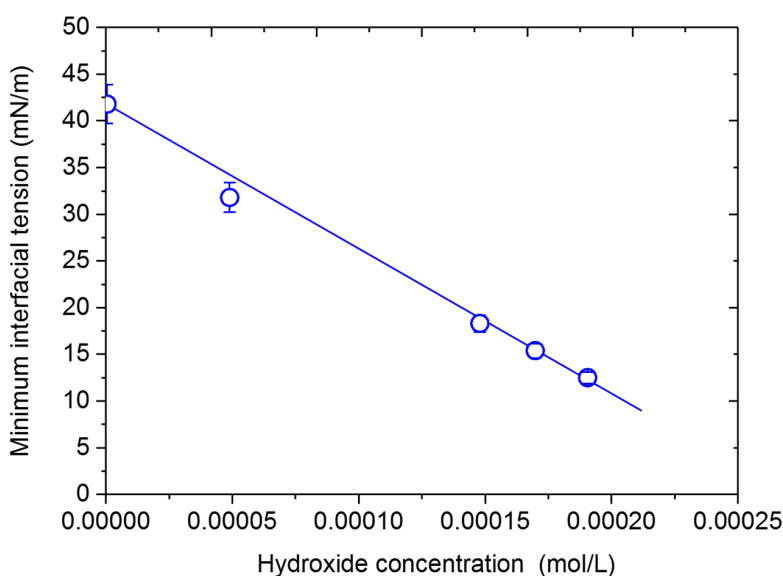


Figure 2. Relationship between the minimum interfacial tension and hydroxide ion concentration.

Notwithstanding the inaccurate reporting of the type of CaCl₂ used in the original paper [1], the interfacial tension data were correctly and precisely determined and we believe will make a useful contribution to the literature. However, we appreciate that we can no longer claim that the interpretation and data-fitting regarding the role of Ca²⁺ ions that we presented are unequivocally correct. The original authors would therefore like to apologize for any inconvenience and confusion caused by this disclosure.

References

1. Taylor, S.E.; Chu, H.T. Metal Ion Interactions with Crude Oil Components: Specificity of Ca²⁺ Binding to Naphthenic Acid at an Oil/Water Interface. *Colloids Interfaces* **2018**, *2*, 40. [CrossRef]
2. Available online: http://www.merckmillipore.com/GB/en/product/Calcium-chloride,MDA_CHEM-102083?bd=1#anchor_Specifications (accessed on 17 October 2018).

