Brazilian Journal
of Chemical
Engineering

ISSN 0104-6632
Printed in Brazil
www.abeq.org.br/bjche

Vol. 30, No. 01, pp. 55 - 62, January - March, 2013

SPECIFIC ION EFFECTS ON THE INTERFACIAL TENSION OF WATER/HYDROCARBON SYSTEMS

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(Submitted: June 13, 2012 ; Accepted: June 27, 2012)

Abstract - Specific ion effects – also known as Hofmeister effects – are ubiquitous in several areas of chemistry, chemical engineering and biology. The interfacial tension corresponds to the energy per unit of area at the interface. Thus, the presence of different salts in different concentrations changes the interfacial tension of a system containing an aqueous phase. This effect can be explained based on the concentration profile of different ions in the vicinity of the interface. In order to study this effect we measured the surface tension of aqueous electrolyte solutions and the interfacial tension of various systems containing hydrocarbons and different aqueous electrolyte solutions as a function of the ionic strength of the aqueous phase. We classify the tested ions for their ability to alter the interfacial tension of each system. These data provide valuable information that can be related to the stability of the corresponding emulsions, since the ions with higher capability of increasing the interfacial tension tend to be more effective in destabilizing the corresponding emulsion.

Keywords: Surface tension; Interfacial tension; Ion specificity; Hofmeister; Tensiometer.

INTRODUCTION

Colloids are present in several industrial processes. Colloid science concerns systems in which one or more of the components have at least one dimension between 1 nm and 1 μm (Shaw, 1975). Colloidal systems in which both phases – dispersed phase and dispersion medium – are in the liquid state are called emulsions.

Colloids present high A/V (interfacial area/ volume) ratios. Because of this, surface properties such as surface tension and interfacial tension are extremely important for the characterization and study of these systems.

The interfacial tension corresponds to the Gibbs free energy per unit of area at the interface between the phases, or the force per unit of length acting at the interface (Adamson and Gast, 1997). This information about the interfacial energy can be used to predict the interaction between the drops (or particles) of an emulsion.

Since van't Hoff's experimental measurements of osmotic pressure more than 120 years ago, electrolyte solutions have fascinated physicists, chemists, and biologists alike. At about the same time, Hofmeister and colleagues reported in a series of articles, interesting results about the influence of different ions on the solubility of proteins (Kunz *et al*., 2004). The authors found that different species of ions affect differently the stability of aqueous solutions of a globular protein – lysozyme – found in chicken eggs. They classified the ions studied as to their

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This article is an extended version of a work presented at CBTermo-2011 - VI Brazilian Congress of Applied Thermodynamics 2011, Salvador, Bahia, Brasil.

ability to coagulate the referred protein. This classification was called by them the lyotropic series, later becoming known as the Hofmeister series.

Heydweiller (1910) measured the surface tensions of various electrolyte solutions and observed that they were higher than the surface tension of pure water. While the dependence on the type of cation was weak, a strong variation of the excess surface tension was found with the type of anion. The sequence was the reverse of the famous Hofmeister series. An explanation for this behavior was provided by Wagner (1924) and Onsager and Samaras (1934) (WOS), who argued that, when ions approach the dielectric air/water interface, they sense their image charge and are repelled from it. This produces a depletion zone which, with the help of thermodynamics, can be related to the excess surface tension (Levin *et al*., 2009).

However, the theory developed by WOS was unable to account for the Hofmeister series and showed strong deviations from the experimental measurements above 100 mM concentrations, indicating that not all ions were repelled by the interface as they proposed.

According to the classical theory, for the air/electrolyte interface, more polarizable ions tend to adsorb more at the interface. This is in alignment with the Gibbs adsorption isotherm:

$$\Gamma_i = -\frac{1}{k_B T}\left(\frac{\partial \gamma}{\partial \ln c_i}\right), \tag{1}$$

where k_B is the Boltzmann constant, T is the temperature of the system, c_i is the concentration of ion i within the fluid phase where it is dissolved (number of ions per unit volume), and Γ_i is the excess of ion i at the interface, that is, the number of ions in excess at the surface per unit area.

The Gibbs isotherm shows that, if the surface (or interfacial) tension increases with increasing ion concentration (positive derivative in Eq. (1)), then Γ_i is negative, i.e., there is a depletion of concentration of that component in the vicinity of the surface, exactly as predicted by WOS theory presented above. This is the general behavior of most ions. On the other hand, if the increasing concentration of component i results in a decrease of the interfacial tension (negative derivative), there is an accumulation of that component near the interface ($\Gamma_i > 0$). This is what happens with detergents.

Several years passed before the Hofmeister effects were again studied systematically. These studies showed that Hofmeister effects are ubiquitous in chemistry, biochemistry, biology and chemical engineering. Some examples are: protein solutions (Boström *et al*., 2011); air-water interfaces (Matubayasi, 1999a, 1999b; Henry and Craig, 2010); micellization and emulsion stability (Ivanov *et al*., 2011); and hydrophobic and hydrophilic colloidal particles (López-León *et al*., 2008).

In particular, these effects have been well studied for air/water interfaces, but not for the hydrocarbon/water interface. In this paper we focus on the measurement of the interfacial tension of these systems and show that the trends are not the same as for air/water systems.

For air/water systems, according to Henry and Craig (2010), the stability (coalescence) of air bubbles depends on the partitioning of ions within the surface. Levin *et al*. (2009) presented a quite convincing theory that better explains the influence of different salts on the air/water surface tension. Although using an adjustable parameter – the hydration radius of sodium – the theory of Levin *et al*. was able to reasonably predict the effect of sodium salts on the surface tension of water.

The authors confirm a trend that had already been observed in several previous works: larger ions, such as chloride and iodide, for example, tend to accumulate at the interface due to their large polarizability and low hydration. In addition, the authors take into account the cavity potential, i.e., the energy associated with the disturbance caused by the presence of the ion in the structure of the solvent.

Santos and Levine (2012) applied the same theory to the water-oil interface indicating that iodide and perchlorate ions adsorb to the surface while kosmotropic anions and potassium and sodium cations are repelled from the interface. They once again call attention to the cavitational hydrophobic energy.

Nenningsland *et al*. (2010) measured the interfacial tension of water/fractions of crude oil systems using a ring tensiometer. They studied the influence of pH and reported ion specific effects on the surface pressure of the system. Wojciechowski *et al*. (2011) studied Hofmeister effects on zeta potential measurements of toluene/water systems stabilized with cetyltrimethylammonium bromide (CTAB). Despite the large experimental errors presented they conclude that there is low ion-specificity in that system. In fact, this was expected because the interface was already saturated with surfactant molecules. Ivanov *et al*. (2011) suggest that the factor controlling Hofmeister effects is the counterion specific adsorption energy.

Boström *et al*. (2011) pointed out that a complete model would include the finite ion size, ion-size dependent dispersion forces acting between ions and surfaces and between ions, the surface dehydration of certain ions, and ion-ion correlations.

The data obtained in the present paper will be used in the future in conjunction with a complete theory that accounts for van der Waals interactions, ion hydration and ion size. The validation of the model to be proposed in this future work will be done by comparison with the experimental results obtained here.

METHODOLOGY

In order to measure the surface and interfacial tensions we used a pendant drop tensiometer OCA 15E by Dataphysics. In this equipment, for measuring the interfacial tension between two phases, a liquid is placed inside a glass cell and another liquid in a syringe. The syringe is pressed, forming a droplet on the tip of the needle, immersed in the liquid inside the cell. The droplet size is controlled automatically by a computer, with a precision of tenths of a microliter. A high-resolution camera captures the image of the drop. According to the size and shape of the drop, the software calculates the interfacial tension between the phases. It uses axisymmetric drop shape analysis (ADSA). All the measurements were made in static conditions. The details about the ADSA method will be omitted here and are described by del Río and Neumann (1997). Briefly, it uses the Young-Laplace equation:

$$\Delta P = \gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right), \qquad (2)$$

where ΔP is the difference between the pressure inside the droplet and the external pressure, γ is the interfacial tension, and R_1 and R_2 are the characteristic radii of the droplet. To calculate ΔP one needs to know the pressure inside the drop, which is obtained from its shape and size. The more spherical the drop, the greater the pressure difference. In addition, the software performs a force balance in which the surface tension acts in the opposite direction to the weight force and keeps the droplet attached to the needle tip. Figure 1 shows an image captured by the tensiometer for the system water/ cyclohexane. The measured value of the interfacial tension in this case was 50.20 mN / m, in agreement with the value reported in the database of the equipment.

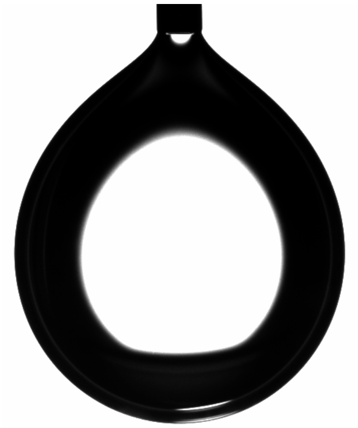

Figure 1: Image captured by the OCA 15E tensiometer for measuring the interfacial tension of the water-cyclohexane system. A needle with an outer diameter of 0.714 mm was used.

Two very important parameters input to the software are the outer diameter of the needle used and the density of the liquids. From the outer diameter, by counting pixels, the software calculates the volume of the drop. And from this volume and the density of both liquids (fluids), it is possible to calculate the weight of the pendant drop and the thrust force that acts on it. When the less dense liquid is placed into the syringe (e.g. a drop of cyclohexane in water), a needle with a hook shape is required, because the drop is upside down (see Figure 2).

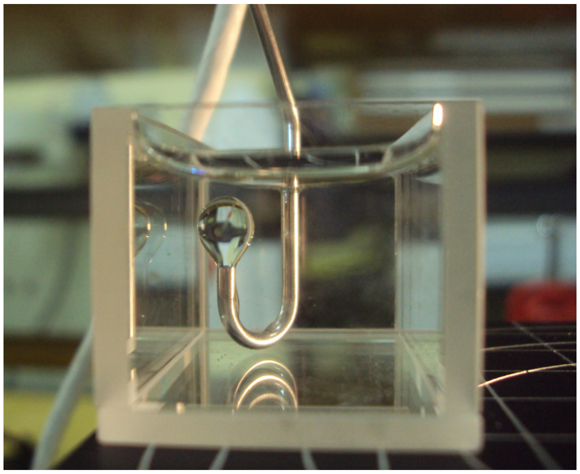

Figure 2: Inverted drop image used to measure the water-oil interfacial tension. The water was placed into the glass cell and the oil in the syringe, requiring a needle with a hook shape, given the lower density of the oil.

Materials

In the experiments described in the following section, deionized Milli-Q water and freshly distilled water were used. Both gave the same results for surface tension and were considered equivalent for the measurements pursued here. The outer diameter of the needle was measured with a digital micrometer. The following salts were used: KCl, supplied by Merck, and NaCl, NaI, $NaNO_3$, $CuSO_4$, Na_2SO_4, KI, K_2SO_4, $MgSO_4$, NaAc, $Ca(Ac)_2$, $CaCl_2$ and $CuCl_2$, all P.A. salts provided by Vetec. In addition, the following solvents were used: cyclohexane P.A., by Vetec, and n-heptane 99% pure provided by Tedya.

Methods

The solutions were prepared using an analytical balance and 50mL volumetric flasks. After preparation, the solutions as well as the organic solvent to be used were placed into a thermostatic bath at 20 °C for at least 30 min.

Before starting the measurements for each solution, at least 3 measurements of the interfacial tension with pure water at 20 °C were carried out. The average value of these preliminary measurements was compared with the value reported in the data bank of the software in order to infer whether there was any contamination. Once it was ensured that the measured value for water was in agreement with the expected value, the measurements with the prepared solutions were carried out. This first step is essential since any residual contamination in the glassware or in the reagents used may go to the interface and drastically change the interfacial tension.

Temperature control during the measurements was performed by coupling the tensiometer to a Huber thermostatic bath. The density data of the solutions required as an input by the software were obtained from the fitting expressions of Laliberté (2007) and Laliberté (2009). These data are close enough to the experimental results reported in the references cited therein. The data for pure solvents were taken from the software database.

For measuring the interfacial tension between hydrocarbons and aqueous solutions, the syringe was filled with the solution and immersed into a glass cell containing the hydrocarbon. Several batches of at least 7 measurements were carried out. The whole batch was discarded in case of the slightest sign of impurity. When impurities were detected the measurements with pure water were repeated in order to ensure its removal. The first drop measurements were always discarded and we started measuring the interfacial tension only after liquid-liquid solubility saturation had been achieved.

The influence of the electrolyte on the interfacial tension was then obtained as follows:

$$\Delta\gamma = \gamma_{\text{sol.-hidrocarbon}} - \gamma_{\text{water-hidrocarbon}}, \tag{3}$$

where $\gamma_{\text{sol.-hydrocarbon}}$ is the interfacial tension between the solution and the hydrocarbon, and $\gamma_{\text{water-hydrocarbon}}$ is the interfacial tension between pure water and the hydrocarbon. This difference ($\Delta\gamma$) is known as the excess interfacial tension. The error bars included in all figures presented in this paper refer to the propagation of errors implicit in both measurements. We consider that the standard variance of $\Delta\gamma$ is the sum of the standard variances of $\gamma_{\text{sol.-hydrocarbon}}$ and $\gamma_{\text{water-hydrocarbon}}$, resulting in the following equation for the standard deviation of $\Delta\gamma$:

$$\sigma(\Delta\gamma) = \sqrt{\sigma^2(\gamma_{\text{sol-hidrocarbon}}) + \sigma^2(\gamma_{\text{water-hidrocarbon}})}\ . \tag{4}$$

Note that by using Eq. (4) we are neglecting the covariance of these measurements.

RESULTS AND DISCUSSION

The first experiments were performed with systems involving the air/electrolyte interface in order to compare the results of excess surface tension obtained with those reported in the literature. For these results, the electrolyte solution was placed into the syringe, without the use of the glass cell. For some salts, we tested the results obtained by placing the electrolyte into the cell and air in the syringe, obtaining the same results.

Only a few points were collected because the objective here was only to compare the results with those from the literature. This validation of the experimental procedure is important because the interfacial tension measurements are very sensitive to the presence of any impurity in the system, including (and specially) detergents. This aspect demands special care in the washing procedure.

Figure 3 shows the excess surface tension ($\Delta\gamma$) measured for NaCl, KCl, NaI and KI as a function of the ionic strength of the electrolyte. As expected, all salts presented a positive excess surface tension. The results obtained are in agreement with those presented by Matubayasi *et al.* (1999a; 1999b) for NaCl and KCl and with those presented by Aveyard and Saleem (1976). These results also follow the same trend reported by Pegram and Record (2007) and references therein. As one can see, the results for all these 1:1 electrolytes are about the same for excess surface tension.

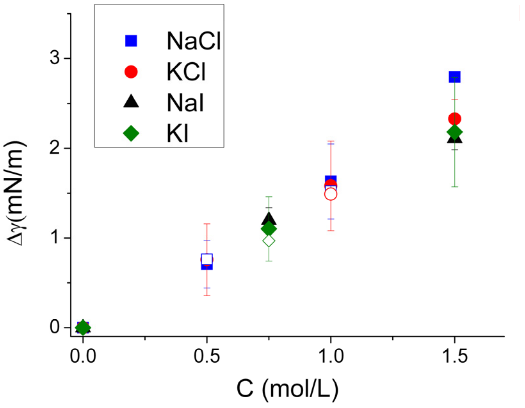

Figure 3: Excess surface tension (Δγ) as a function of salt concentration for two electrolytes: NaCl (blue squares), open symbols from Matubayasi *et al.* (1999a); KCl (red circles), open symbols from Matubayasi *et al.* (1999b); NaI (black triangles); and KI (green diamonds), open symbols from Aveyard and Saleem (1976).

Measurements for systems containing hydrocarbons and electrolyte solutions were carried out. The first hydrocarbon tested was cyclohexane. Its interfacial tension against pure water is 50.2±0.3 mN/m, in accordance with the databank provided by Dataphysics. For n-heptane, it was 50.7±0.2 mN/m, 0.5 mN/m below the value provided by the Dataphysics databank. Figure 4 presents some results obtained for cyclohexane interacting with different sulfate salt solutions: $CuSO_4$, $MgSO_4$, Na_2SO_4.

According to Figure 4, the Hofmeister series obtained is $CuSO_4$ > $MgSO_4$ > Na_2SO_4. Hence $CuSO_4$ is the most effective salt in increasing the interfacial tension of water/cyclohexane systems. Since the anion is the same for the three salts we have a cation effect. In this case, Cu^{2+} – the larger ion – is responsible for the higher interfacial tension. This means that the most polarizable cation is more repelled by the surface than the other cations studied. Hence we have an effect which is different from that of Figure 3, meaning that there is no simple explanation for the sequence obtained. A more complete explanation for the whole picture requires an adequate model to reproduce the results obtained here, because many effects are present competing with each other. As suggested by Levin *et al.* (2009), the explanation may require a model that accounts for ionic polarizability, ionic hydration and cavity potentials.

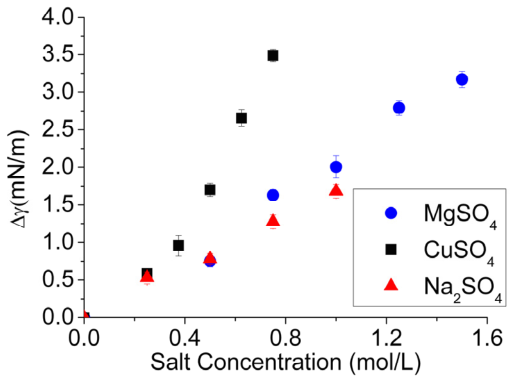

Figure 4: Excess interfacial tension (Δγ) for cyclohexane interacting with 3 electrolyte solutions: $CuSO_4$ (squares), $MgSO_4$ (circles), Na_2SO_4 (triangles) as a function of salt concentration.

In Figure 5 we present a similar study for n-heptane interacting with three different salt solutions: $CuSO_4$, K_2SO_4 and Na_2SO_4. Comparing Figure 5 to Figure 4 we can see that the difference between the results for $CuSO_4$ and Na_2SO_4 is larger for cyclohexane than for n-heptane. Moving from cyclohexane to n-heptane, $CuSO_4$ (a 2:2 electrolyte) is less effective in raising the interfacial tension, while the opposite occurs for the other (1:2) salts. Hence, the conformation of the hydrocarbon plays an important role in this phenomenon. Nevertheless we also note that the trend is the same as for Figure 4: the larger the ion the higher the interfacial tension.

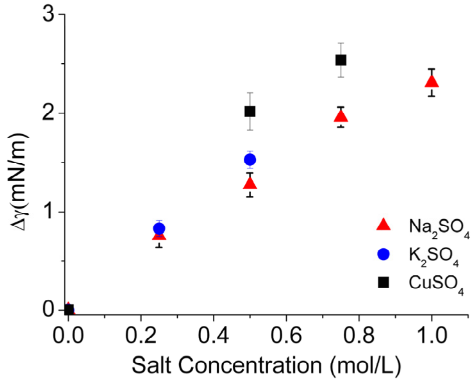

Figure 5: Excess interfacial tension (Δγ) for n-heptane interacting with 3 electrolytes: $CuSO_4$ (squares), K_2SO_4 (circles), Na_2SO_4 (triangles) as a function of salt concentration.

The reason for the behavior presented in Figures 4 and 5 is still under discussion. As mentioned before, a definitive explanation could come from a complete model accounting for all the different contributions.

In order to study the anion effect, Figure 6 presents the excess interfacial tension for n-heptane interacting with different sodium salts. The sequence obtained at intermediate concentrations is: Na_2SO_4 > NaCl ~ $NaNO_3$ > NaI > NaAc.

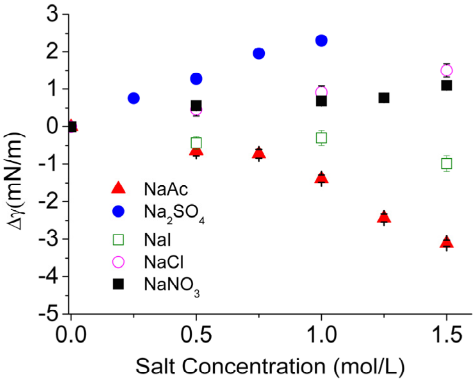

Figure 6: Excess interfacial tension (Δγ) for n-heptane interacting with 5 sodium electrolytes: NaAc (triangles), Na_2SO_4 (circles), NaCl (open circles) $NaNO_3$ (squares), and NaI (open squares), as a function of salt concentration.

Sodium acetate (NaAc) decreased the interfacial tension of water, presenting negative values of Δγ in the entire concentration range. This was expected because the acetate ion is a kind of surfactant. On the other hand, Na_2SO_4 was the most effective salt in increasing the interfacial tension. This occurs especially because sulfate is a divalent and large anion. NaCl and $NaNO_3$ presented a very similar behavior.

The most interesting behavior in Figure 6 was revealed by NaI, which acts as a surfactant, decreasing the interfacial tension of the water-heptane system. Despite being less effective than acetate ion in decreasing the interfacial tension, the results suggest that iodide is attracted to the surface in this system. This is a clear competition between at least two dominating effects that corroborates the need for a complex model to describe the system.

Based on this result we decided to compare the interfacial tension curves for NaI with those for KI, as presented in Figure 7. These results confirm the negative effect of iodide (1:1) salts in aqueous solution on the interfacial tension with n-heptane, for the two cations studied. The results for KI solutions against n-heptane are similar to those reported by Aveyard and Saleem (1976) for n-dodecane. This indicates that the chain size of the hydrocarbon is not so important for interfacial tension, while the conformation makes a considerable difference, as already mentioned comparing Figures 4 and 5.

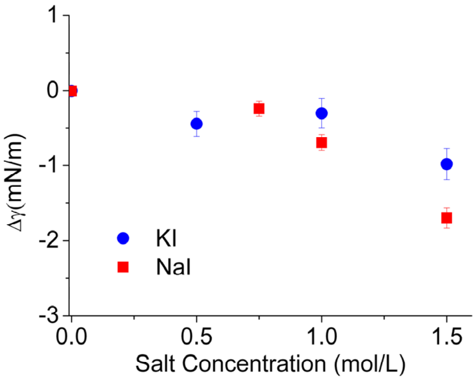

Figure 7: Excess interfacial tension (Δγ) for n-heptane interacting with 2 iodide electrolytes: NaI (squares) and KI (circles),as a function of salt concentration.

In Figure 8 we study the influence of the cation on the decrease of surface tension provided by acetate salts interacting with n-heptane. We note that calcium acetate enhances the effect of decreasing the interfacial tension. This was expected because, in fact, the concentration of acetate ion is the double for $Ca(Ac)_2$. However, even multiplying the concentration by the factor of 2, the curve for the calcium salt would still fall under the curve for the sodium salt. This means that there is an additional effect provided by the cation and possibly Ca^{2+} is more attracted to the interface than Na^+ in these systems. In order to check if this is also true for other salts, we show in Figure 9 the comparison between NaCl and $CaCl_2$. We can see that this is not the case for chloride ions. According to Figure 9, $CaCl_2$ is more efficient at increasing the interfacial tension of n-heptane/water than NaCl. This is intriguing because it suggests that Ca^{2+} is repelled by the interface in this system.

A simple explanation of this apparent contradiction is: the acetate ions are attracted to the interface, imparting a negative charge to it. This negatively charged interface attracts Ca^{2+} ions, which enhances the surfactant effect of acetate. Nevertheless, Cl^- is repelled by the interface, contributing to keep Ca^{2+} away. The excess interfacial tension for $CuCl_2$ is just a little lower than that for $CaCl_2$. So the series in this case is: $CaCl_2$ > $MgCl_2$ > $CuCl_2$ > NaCl.

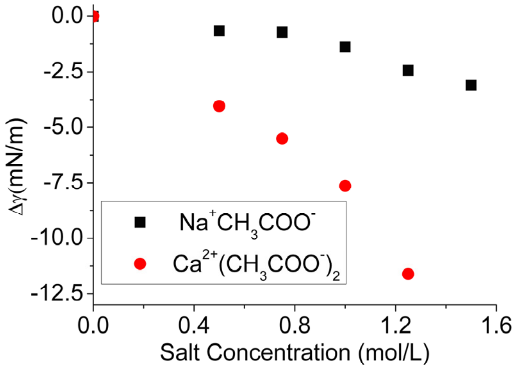

Figure 8: Excess interfacial tension (Δγ) for n-heptane interacting with 2 acetate electrolytes: $NaCH_3COO$ (squares) and $Ca(CH_3COO)_2$ (circles), as a function of salt concentration.

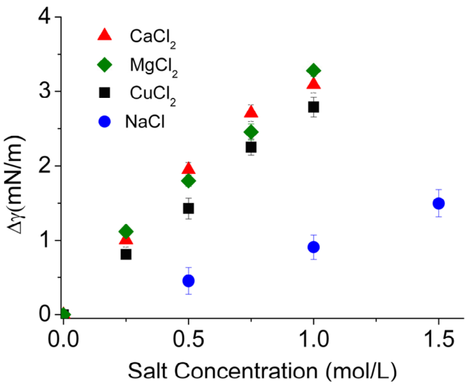

Figure 9: Excess interfacial tension (Δγ) for n-heptane interacting with 4 different chloride electrolytes: NaCl (circles), $CuCl_2$ (squares), $MgCl_2$ (diamonds) and $CaCl_2$ (triangles), as a function of salt concentration.

CONCLUSION

We studied the excess interfacial tension for two different hydrocarbons – cyclohexane and n-heptane – interacting with different electrolyte solutions. Based on the results presented, one can conclude that, for moderate concentrations, ion specific effects on the excess interfacial tensions of these systems are considerable. The results also suggest that ion specificity for electrolytes against the hydrocarbons studied is more pronounced than for air/water systems. We speculate that this difference could be explained by involving the cavity potential of the ions in the discussion. Also, the differences between the results for cyclohexane and n-heptane show that the conformation of the hydrocarbon plays an important role in this study.

ACKNOWLEDGEMENTS

The authors thank the Brazilian agencies CAPES and CNPq, and the National Institute of Oil and Gas (INOG) for supporting this project. We are also thankful to Dr. Drew Parsons for fruitful discussions about the results obtained. Finally, we would like to thank the referees who contributed to improving the quality of this paper.

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