

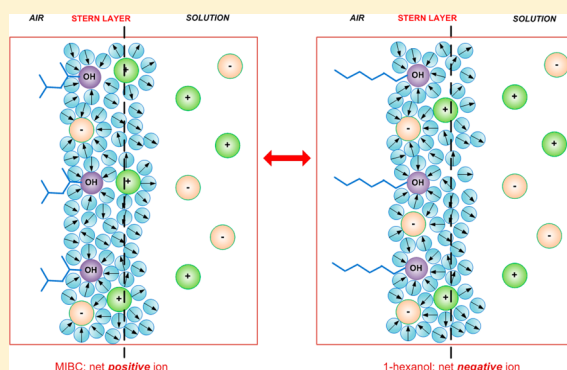
Surface Potential of a 1-Hexanol Solution: Comparison with Methyl Isobutyl Carbinol

Cuong V. Nguyen,[†] Chi M. Phan,^{*,†} Ha M. Ang,[†] Hiromichi Nakahara,[‡] Osamu Shibata,[‡] and Yoshiaki Moroi[‡]

[†]Department of Chemical Engineering, Curtin University, Perth, Western Australia 6845, Australia

[‡]Department of Biophysical Chemistry, Faculty of Pharmaceutical Sciences, Nagasaki International University, Sasebo, Nagasaki 859-3298, Japan

ABSTRACT: Alcohols have an amphiphilic characteristic and are employed in industrial processes to enhance interfacial properties. In this study, the change in surface potential (ΔV) and surface tension of 1-hexanol were measured on the subsurface of electrolyte solutions (NaCl at 0.02, 0.2, and 2 M). The results were fitted by a newly proposed model, which includes the influence of electrolytes and surface concentration of surfactant at the air–water interface. The findings were compared to those of a previous study on methyl isobutyl carbinol (MIBC). Most significantly, the modeling results showed opposite behaviors between the two systems: adsorbed MIBC enhances the presence of cations, whereas adsorbed 1-hexanol enhances the presence of anions. The difference highlights the significance of the molecular structure on the arrangement at the air/water interface.



INTRODUCTION

Surface-active agents are widely used in many chemical processes, including foaming, emulsification, floatation, wetting, and coating, which can be found in the mineral, food, and pharmaceutical industries.^{1,2} The interfacial properties of surfactant solutions play a critical role in the efficiency of various industrial processes and lead to a large number of experimental and theoretical investigations in the field.^{3–5} Despite these studies, interfacial adsorption remains not well-defined. One of the measurable properties of the adsorption layer is the change in surface potential (ΔV),⁶ which influences the double-layer charge, the disjoining pressure, thin-film stabilization, and foaminess.⁷

There are a number of proposed models for surface potential at the air/water interface.^{8–10} However, most of these models focus on ionic surfactants relating to the interfacial adsorption of their counterions. Moreover, these models require multiple parameters, which cannot be verified independently, to describe the experiment data.

Recently, the influence of methyl isobutyl carbinol (MIBC) on the air/water interfacial potential has been quantified using a newly proposed model, with only two independent parameters.¹¹ Sodium chloride (NaCl) was added to determine the concentration of electrolytes and reduce the degree of freedom of the model. The modeling results indicated a small charge at the Stern layer. In spite of the neutral charge, MIBC has a positive effect on the surface potential by disrupting/reorienting water molecules.^{9,12}

The influence of the molecular structure of alcohols on surface behavior has been studied by tensiometry.^{13,14} These studies revealed that the linear isomers had stronger interfacial activities despite the lower water solubility than the corresponding branched isomers. Recent research on the effect of the tail structure, i.e., different lengths, on the surface potential was carried out with ionic surfactants.¹² Surprisingly, the length of the tail impacted the locations of the average centers of positive and negative charges, which leads to a discrepant increase in the surface potential.

In the present study, surface adsorption of 1-hexanol (an isomer of MIBC) from the aqueous solutions with NaCl is investigated by surface tensiometry (γ) and surface potential (ΔV). The main motivation is to identify any difference in surface properties, which makes MIBC a more effective frother than 1-hexanol in mineral floatation.

THEORETICAL MODEL

A new model for nonionic surfactants was proposed for alcohols (shown in Figure 1). The change in surface potential is given by¹¹

Received: March 19, 2013

Revised: May 23, 2013

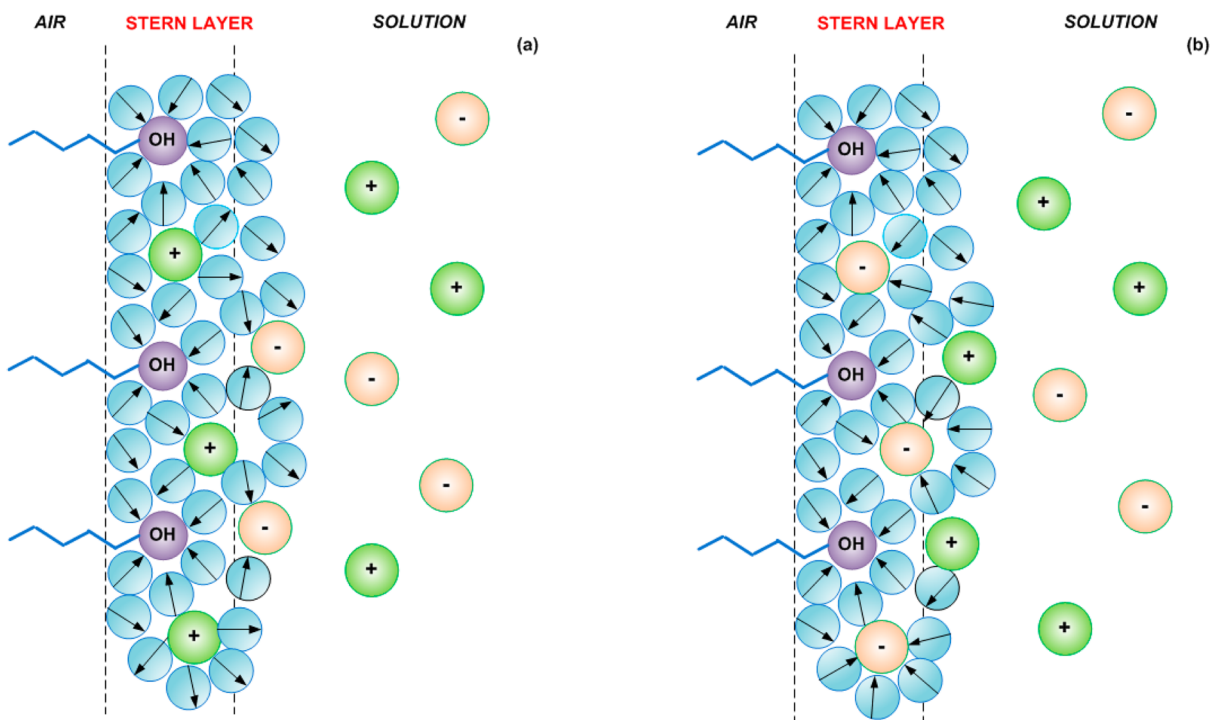


Figure 1. Schematic representation for 1-hexanol: (a) $\alpha > 0$, (b) $\alpha < 0$.

$$\Delta V = \Gamma_a \beta + \frac{2k_B T}{e} \operatorname{arcsinh} \left(\frac{\alpha e N_A \Gamma_a}{\sqrt{(8 \times 10^3) c_{\text{cation}} N_A \epsilon \epsilon_0 k_B T}} \right) \quad (1)$$

where N_A is the Avogadro constant, Γ_a is the surface concentration of alcohol, k_B is the Boltzmann constant, T is the temperature, e is the charge of one electron, c_{cation} is the effective cation concentration, which is also equal to the anion concentration in the bulk, and ϵ and ϵ_0 are the dielectric constant and the permittivity of a vacuum, respectively.

In the case of strong electrolyte solutions, eq 1 has two free parameters, α and β , which depend on the physical properties of the system. As derived previously, β is defined as¹¹

$$\beta = N_A \left[\frac{\mu^t}{\epsilon_a \epsilon_0} + \alpha e \frac{\lambda_s}{\epsilon_s \epsilon_0} \right] \quad (2)$$

where μ^t is the total normal dipole moment per alcohol molecule, ϵ_a and ϵ_s are dielectric permittivities of the adsorbed layer and the Stern layer, respectively, and λ_s is the thickness of the Stern layer.

In the model, α can be considered as an “effective charge” of the hydroxyl group, which is related to the surface charge at the boundary between the diffuse layer and the Stern layer, σ . This surface charge density is given as¹⁵

$$\sigma = e N_A (\Gamma_{\text{cation}} - \Gamma_{\text{anion}}) \quad (3)$$

where Γ_{cation} and Γ_{anion} are the surface concentrations of adsorbed ions at the interface due to the adsorption of alcohol.

The net charge, $\Gamma_{\text{ion}} = \Gamma_{\text{cation}} - \Gamma_{\text{anion}}$, can be either negative or positive. Within the Stern layer arrangement, the headgroup of the alcohol is assumed to be thermodynamically balanced by a certain number of ions, and therefore

$$\Gamma_{\text{ion}} = \alpha \Gamma_a \quad (4)$$

Summarily, α represents the net ion adsorbed due to the balance with alcohols. It is well-accepted that anions and cations are not adsorbed equally at the interface.^{16–18} Typically, the anions are more enhanced at the water surface.¹⁹ The relative adsorption between anions and cations depends on their interaction with the water interfacial layer. Since the adsorbed alcohols disrupt the water arrangement, it is expected that adsorbed alcohols affect the relative ionic adsorption. In Figure 1, two scenarios are presented: (a) $\alpha > 0$ (cations get closer to the interface than anions) and (b) $\alpha < 0$ (anions get closer to the interface than cations).

The surface excess of alcohol is determined by a combination between the surface tension and Langmuir isotherm:²

$$c_b = \frac{1}{K} \left(\frac{\Gamma_a}{\Gamma_m - \Gamma_a} \right) \quad (5)$$

where c_b is the bulk concentration of the alcohol solution and K and Γ_m are adsorption constants, which can be found by fitting the surface tension to the Szyszkowski equation:²

$$\gamma_0 - \gamma_a = -RT \Gamma_m \ln(1 + K c_b) \quad (6)$$

where γ_0 and γ_a are the surface tension of alcohol-free (pure solvent or supporting solute) and alcohol solutions, respectively.

In applying eq 5, the Gibbs energy of supporting electrolyte adsorption is assumed to be independent of alcohol adsorption as proposed by Karraker and Radke.¹⁰ One critical aspect of the modeling framework, eq 1, is that the degree of freedom is 2. Consequently, the model has to be applied to two different sets of experimental data, i.e., two different ion concentrations, simultaneously.¹¹

EXPERIMENT

Materials. Both 1-hexanol ($\geq 99\%$) and sodium chloride ($\geq 99.5\%$) purchased from Sigma-Aldrich were used without

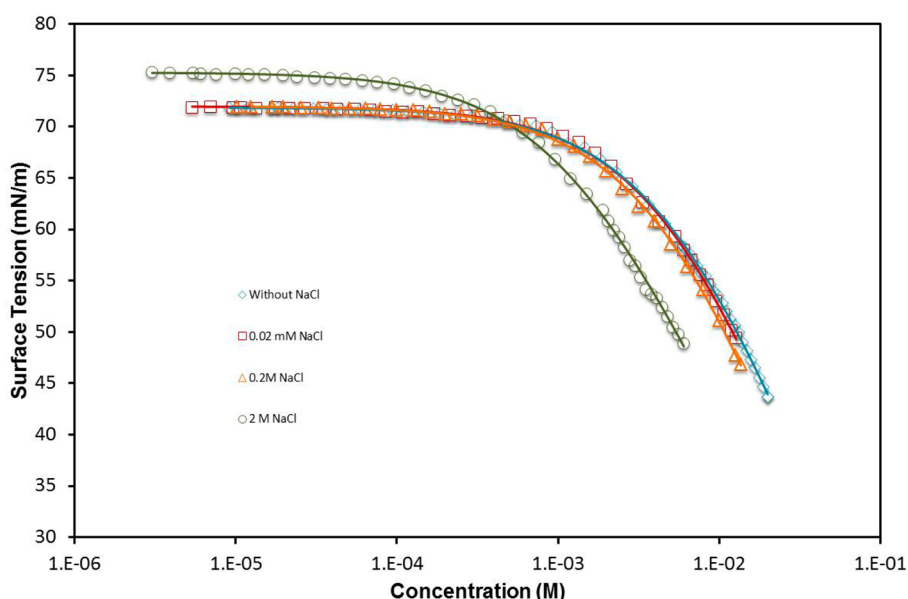


Figure 2. Surface tension of 1-hexanol with and without NaCl (dots, experimental data; lines, modeled prediction).

further purification. Water was obtained by using a Milli-Q system, which consists of a prefilter, a carbon cartridge, two mixed-bed ion exchange cartridges, and an ultrafiltration cartridge, to produce pure water. All glassware, plastic bottles, and apparatuses used in the experiments were carefully cleaned and dried.

Surface Tension (γ). A tensiometer, KSV Sigma 701 (KSV Instrument Ltd., Finland), coupled with an automatic micro-disperser employing the Wilhelmy plate method²⁰ was used for equilibrium surface tension measurement. The instrument was calibrated against pure water before measurements were made. The surfactant concentration was increased gradually by dispersing stock solution into the measurement cell. The software automatically determined the surface tension as a function of the bulk concentration. The Wilhelmy plate is made of platinum with a perimeter of 39.4 mm. Before each measurement, the plate was flushed with pure ethanol and water and then heated over a Bunsen burner for a few seconds to remove contamination. All the measurements were conducted at a room temperature of 298 K.

Surface Potential (ΔV). The surface potential of 1-hexanol solutions was determined relative to the surface potential of the pure supporting electrolyte (0.02, 0.2, and 2 M NaCl) using an ionizing ²⁴¹Am electrode. The details of surface potential measurement have been described elsewhere.^{6,12,21}

RESULTS

Surface Tension. The surface tensions (γ) of 1-hexanol in water and NaCl solutions are depicted in Figure 2. The experimental data were fitted to eq 5 by the least-squares method, using K and Γ_m as adjustable parameters. The fitting procedure was done with Solver (in Microsoft Excel).

The standard deviation (δ_γ) in Table 1 was calculated using

$$\delta_\gamma = \sqrt{\frac{\sum (\gamma_{\text{exptl}} - \gamma_{\text{modeled}})^2}{n}} \quad (7)$$

where n is the number of experimental data, which is greater than 30 for all experiments used in this investigation. Since the automatic microdispenser could accurately produce wide ranges

Table 1. Adsorption Isotherm Constants for 1-Hexanol

solution	K (M^{-1})		Γ_m (10^6 mol/ m^2)		δ_γ (mN/m)
	this study	lit.	this study	lit.	
water	173.2	178 ^a	7.53	7.4, ^b 7.6 ^a	0.17
0.02 M NaCl	164.4		8.10		0.23
0.2 M NaCl	186.5		8.06		0.20
2 M NaCl	800.7		6.11		0.25

^aLavi and Marmur.²² ^bComley et al.²³

of concentrations, the apparatus provided more measurements and consequently improved the accuracy of modeling. It is noted that the standard deviations for all measurements in this study were smaller than 0.3 mN/m, which is much smaller than the accepted thresholds.²⁴ Moreover, the best fitted values of K and Γ_m are consistent with other data in the literature.

It should be noted that 1-hexanol and MIBC had similar trends in surface tension. The data for pure water and a low concentration of NaCl almost overlap. However, this changed significantly with increasing concentration of NaCl. The behavior of K and Γ_m in different salinities is similar to the modeling results of MIBC in NaCl and SDS in NaCl²⁴ as well.

Surface Potential. The surface potential of 1-hexanol in 0.02, 0.2, and 2 M sodium chloride solutions is plotted in Figure 3. Due to the low solubility of 1-hexanol in 2 M NaCl solution, the surface potential data were measured up to a concentration of 1 mM. The increment of the surface potential with the 1-hexanol concentration was gradual and nonlinear, which is in contrast to the results for cationic and anionic surfactants.⁶ Consequently, the simplified model,⁹ which indicated the linear influence of the concentration on the surface potential, could not be applied. It should be noted that ΔV was referenced to the respective NaCl solutions without alcohol.

As α and β in eq 1 are independent of the NaCl concentration, the model was fitted against the data at both concentrations simultaneously (using the least-squares method with Polymath). It should be noted that the best fitted values of α and β were independent of the initial guesses (with an overall standard deviation of 7.5 mV). The third data set, i.e., 0.2 M

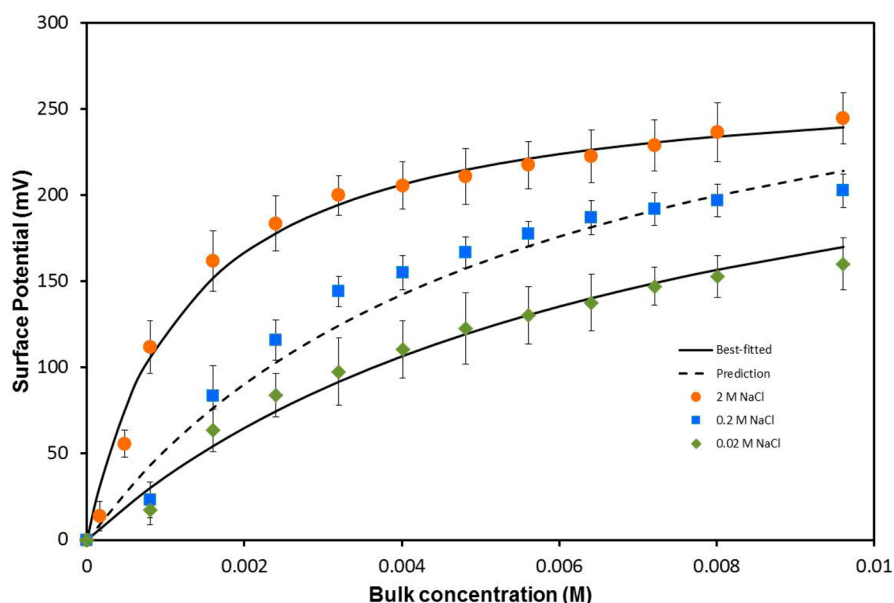


Figure 3. Surface potential of 1-hexanol on the NaCl aqueous solutions (points, experimental data; lines, modeled predictions). The best fitted values of the parameters are reported in Table 2.

NaCl, was used for modeled verification only (broken line in Figure 3). As shown in Figure 3, the model fits the data very well.

Most strikingly, the best fitted parameters (Table 2) show a contrast in the values of α between 1-hexanol and MIBC: a

Table 2. Best Fitted Adsorption Parameters for MIBC and 1-Hexanol

param	MIBC (previous study)	95% confidence interval	1-hexanol (this study)	95% confidence interval
α	0.043	0.008	−0.047	0.010
β (10^4 (V m ²)/mol)	3.30	0.10	4.57	0.12

change from positive to negative, albeit small in magnitude. The negative value of α for 1-hexanol indicates that the *net* charge is negative (i.e., there are more anions at the Stern layer than cations). The results indicate a structural change between the two systems. On the other hand, the best fitted value of β remains within the physically feasible range.¹¹

To confirm the opposite charges at the Stern layer, the 95% confidence intervals²⁵ of the fitting parameters were calculated for both systems (Table 2). In spite of the large variation for α ($\sim 20\%$), the 95% confidence intervals remain on the opposite sides: positive for MIBC and negative for 1-hexanol. Figure 4 shows the surface potential at the air–water interface as a function of the surface excesses. Since arcsinh is an odd and monotonic function, the sign of α determines the relative position between the 2 and 0.02 M curves. A negative value of

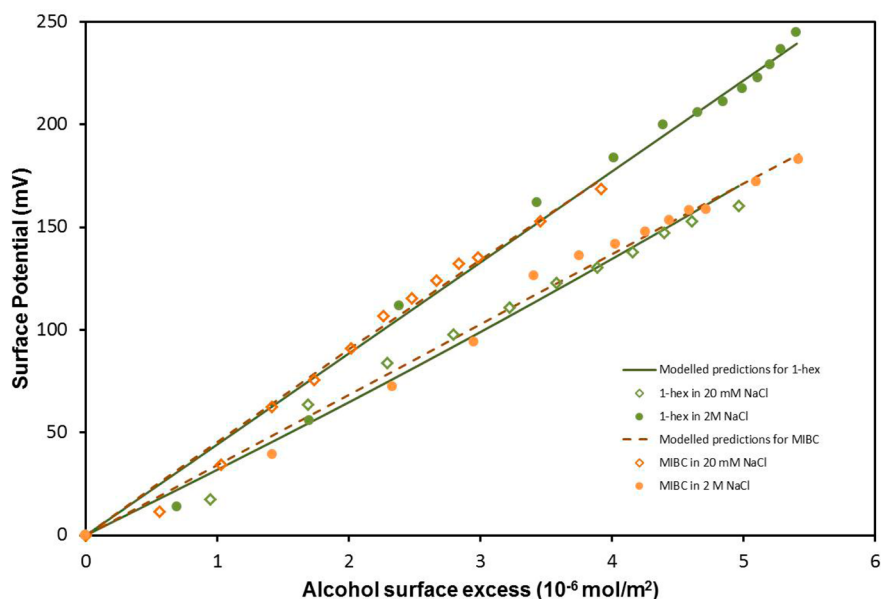


Figure 4. Comparison between 1-hexanol and MIBC.

α means the 2 M curve is above the 0.02 M curve, as seen with 1-hexanol. In contrast, a positive α means the 2 M curve is below the 0.02 M curve, as with MIBC. If $\alpha = 0$, eq 1 results in the same line for both the 2 and 0.02 M curves. The confidence intervals in Table 2 and relative positions in Figure 4 confirm the opposite signs of α between the two alcohols.

DISCUSSION

For NaCl in water, it has been accepted^{17,18,26,27} that the anion locates closer to the interface than the cation. The exact nature of anion enhancement is not clear due to experimental difficulties. Nevertheless, molecular simulations have provided some useful insights. For instance, a well-ordered dual-layer structure has been proposed for the air/water interface.^{28,29} The water interfacial arrangement can have a strong influence on hydrated ions in the bulk.³⁰ Simulations with different ionic systems at the air/water interface also presented ordered arrangements of ions near the interface.^{16,27}

With adsorbed alcohols, the ion arrangement near the interface should be altered dramatically. Previously, an investigation of 1-butanol at the electrolyte solution interface,³¹ which is particularly important for atmospheric chemistry, has revealed an interesting change in terms of the anion/cation ratio. The X-ray photoelectron spectroscopy (XPS) experimental results indicated that adsorbed 1-butanol decreased the Γ^-/K^+ ratio in “the region of the liquid interface”. The XPS data could not confirm which ion is higher: the reported Γ^-/K^+ ratio was either smaller or greater than 1, depending on the 1-butanol concentration and photoelectron kinetic energy. However, the accompanied simulation of 1-butanol in 5 M NaI solution was able to quantify the average number of alcohol molecules directly interacting with ions over 1 ns (tabulated in Table 1³¹). The data show that 1-butanol contacts with more anions than cations. Applying these numbers to eq 4, one can easily calculate the average ionic charge per 1-butanol molecule. Remarkably, the magnitude of these numbers (from -0.038 to -0.004) is comparable to our calculated α , i.e., -0.047 , for 1-hexanol in NaCl.

The results in this study indicated that adsorbed 1-hexanol still enhanced the anions (as with 1-butanol). Adsorbed MIBC, in contrast, enhanced the cations. This contrast can be explained by considering the spatial distribution around the hydroxyl group. It is generally perceived that the headgroup of the alcohol (hydroxyl) is negatively charged¹¹ and consequently attracts cations. However, the alpha-carbon should be positively charged. If the whole group (alpha-carbon and hydroxyl) is located inside the water phase, anions can penetrate into the space between the alcohol and interface due to Coulombic attraction with the alpha-carbon. For straight alcohols, such as 1-butanol and 1-hexanol, this leads to a net negative charge. For MIBC, however, the two hydrocarbon branches occupy the space surrounding the alpha-carbon and reduce the available space for anions. Consequently, less anion can penetrate in, and the layer is positively charged.

Although the net charge of the interfacial layer is relatively small, $\sim 10^{-8}$ mol of electrons/m², the structural change (sign of α) might have a profound impact on the selectivity of the mineral particles adsorbing to the air/water interface. Consequently, this could be the main reason for superior flotation performance of MIBC over 1-hexanol.³²

It is also noteworthy that the model apparently overestimates the surface potential at low alcohol concentrations (in Figures 3 and 4). A possible explanation is that the adsorbed alcohols

may be too far apart at these concentrations to have an effective interaction with the ions (the net ionic charge is <5% of that of adsorbed alcohol).

There are two theoretical developments to investigate the ion enhancement at the interface: polarizable force fields¹⁶ and hydrated cations.³³ The absolute values, or the change, of α from this study can provide much needed evidence to verify these theories. On the other hand, molecular simulations might be able to verify, or otherwise, our hypothesis about anion distribution around alcohols.

CONCLUSIONS

The surface potential (ΔV) and surface tension (γ) of 1-hexanol were measured in electrolyte solution at three concentrations: 0.02, 0.2, and 2 M NaCl. Similar to the other isomer, methyl isobutyl carbinol, the surface potential gradually increased with increasing 1-hexanol concentration. The proposed model for alcohols was applied successfully.

The best fitted values of two fitting parameters indicated opposite behavior between 1-hexanol and MIBC: adsorbed MIBC molecules enhance the presence of cations, whereas 1-hexanol molecules enhance the presence of anions. The structural change might be the underlying reason for superior flotation performance of MIBC over 1-hexanol. To quantify the influence of the molecular structure on the interfacial adsorption and the presence of ions near the adsorption layer, further study on the molecular arrangement at the interface is recommended.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Chang, C. H.; Franses, E. I. *Colloids Surf., A* **1995**, *100*, 1–45.
- (2) Eastoe, J.; Dalton, J. *Adv. Colloid Interface Sci.* **2000**, *85* (2–3), 103–144.
- (3) Moorkanikara, S. N.; Blankschtein, D. *Langmuir* **2010**, *26* (24), 18728–18733.
- (4) Jódar-Reyes, A. B.; Lyklema, J.; Leermakers, F. A. M. *Langmuir* **2008**, *24* (13), 6496–6503.
- (5) Rideg, N. A.; Darvas, M.; Varga, I.; Jedlovsky, P. *Langmuir* **2012**, *28* (42), 14944–14953.
- (6) Nakahara, H.; Shibata, O.; Moroi, Y. *J. Phys. Chem. B* **2011**, *115* (29), 9077–9086.
- (7) Wang, L.; Yoon, R.-H. *Int. J. Miner. Process.* **2008**, *85* (4), 101–110.
- (8) Karakashev, S.; Nguyen, A.; Miller, J., Equilibrium Adsorption of Surfactants at the Gas–Liquid Interface. In *Interfacial Processes and Molecular Aggregation of Surfactants*, Narayanan, R., Ed.; Springer: Berlin, Heidelberg, 2008; Vol. 218, pp 25–55.
- (9) Warszyński, P.; Barzyk, W.; Lunkenheimer, K.; Fruhner, H. J. *Phys. Chem. B* **1998**, *102* (52), 10948–10957.
- (10) Karraker, K. A.; Radke, C. J. *Adv. Colloid Interface Sci.* **2002**, *96* (1–3), 231–264.
- (11) Phan, C. M.; Nakahara, H.; Shibata, O.; Moroi, Y.; Le, T. N.; Ang, H. M. *J. Phys. Chem. B* **2012**, *116* (3), 980–986.
- (12) Nakahara, H.; Shibata, O.; Rusdi, M.; Moroi, Y. *J. Phys. Chem. C* **2008**, *112* (16), 6398–6403.
- (13) Le, T. N.; Phan, C. M.; Ang, H. M. *Asia-Pac. J. Chem. Eng.* **2012**, *7* (2), 250–255.
- (14) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; John Wiley & Sons: Hoboken, NJ, 2003.

- (15) Yeskie, M. A.; Harwell, J. H. *J. Phys. Chem.* **1988**, *92* (8), 2346–2352.
- (16) Jungwirth, P.; Tobias, D. J. *Chem. Rev.* **2005**, *106* (4), 1259–1281.
- (17) D'Auria, R.; Tobias, D. J. *J. Phys. Chem. A* **2009**, *113* (26), 7286–7293.
- (18) Yang, L.; Fan, Y.; Gao, Y. Q. *J. Phys. Chem. B* **2011**, *115* (43), 12456–12465.
- (19) Ghosal, S.; Hemminger, J. C.; Bluhm, H.; Mun, B. S.; Hebenstreit, E. L. D.; Ketteler, G.; Ogletree, D. F.; Requejo, F. G.; Salmeron, M. *Science* **2005**, *307* (5709), 563–566.
- (20) Barnes, G.; Gentle, I. *Interfacial Science: An Introduction*; Oxford University Press: Oxford, U.K, 2005.
- (21) Nakahara, H.; Shibata, O.; Moroi, Y. *Langmuir* **2005**, *21* (20), 9020–9022.
- (22) Lavi, P.; Marmur, A. J. *Colloid Interface Sci.* **2000**, *230* (1), 107–113.
- (23) Comley, B. A.; Harris, P. J.; Bradshaw, D. J.; Harris, M. C. *Int. J. Miner. Process.* **2002**, *64* (2–3), 81–100.
- (24) Prosser, A. J.; Franses, E. I. *Colloids Surf., A* **2001**, *178* (1–3), 1–40.
- (25) Walpole, R. E.; Myers, R. H.; Myers, S. L.; Ye, K. *Probability & Statistics for Engineers & Scientists*, 9th ed.; Pearson Education: Boston, MA, 2011.
- (26) Jungwirth, P.; Tobias, D. J. *J. Phys. Chem. B* **2001**, *105* (43), 10468–10472.
- (27) Jungwirth, P.; Tobias, D. J. *J. Phys. Chem. B* **2002**, *106* (25), 6361–6373.
- (28) Yuet, P. K.; Blankschtein, D. J. *J. Phys. Chem. B* **2010**, *114* (43), 13786–13795.
- (29) Fan, Y.; Chen, X.; Yang, L.; Cremer, P. S.; Gao, Y. Q. *J. Phys. Chem. B* **2009**, *113* (34), 11672–11679.
- (30) Beck, T. L. *Chem. Phys. Lett.* **2013**, *561–562* (0), 1–13.
- (31) Krisch, M. J.; D'Auria, R.; Brown, M. A.; Tobias, D. J.; Hemminger, C.; Ammann, M.; Starr, D. E.; Bluhm, H. *J. Phys. Chem. C* **2007**, *111* (36), 13497–13509.
- (32) Crozier, R. D.; Klimpel, R. R. *Miner. Process. Extr. Metall. Rev.* **1989**, *5* (1–4), 257–279.
- (33) Levin, Y.; dos Santos, A. P.; Diehl, A. *Phys. Rev. Lett.* **2009**, *103* (25), 257802.