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THE INFLUENCE OF SPECIFIC ION EFFECTS ON THE DIFFUSIVITY OF LONG-CHAIN
PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)

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THE INFLUENCE OF SPECIFIC ION EFFECTS ON THE DIFFUSIVITY OF LONG-CHAIN
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BY THE COMMITTEE CONSISTING OF

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DEDICATION

*This dissertation is dedicated to my biggest supporter through these early years of my career,
Emma.*

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TABLE OF CONTENTS

LIST OF TABLES	viii
LIST OF FIGURES	ix
ABSTRACT	xiii
Chapter 1. Introduction.....	1
1.1. Introduction to per- and polyfluoroalkyl substances (PFAS)	1
1.2. Current technology for the removal of PFAS from water	3
1.3. Design Principles of Foam Fractionation Columns	5
1.4. Prior Work	7
1.5. Research Objectives and Hypothesis	9
Chapter 2. Literature Review	12
2.1. Transport and Thermodynamics of Electrolytes	12
2.1.1. Debye–Hückel Theory	12
2.2.1. The Mean Spherical Approximation.....	17
2.3.1. The Nexus of Transport and Thermodynamics of Electrolytes	18
2.2. Diffusion of PFOA and PFOS in Literature	21
2.3. Aggregation Behavior and Speciation of PFAS	22
2.4. Research Gaps.....	26
Chapter 3. Materials and Methods.....	27
3.1. Materials and Sample Preparation	27
3.2. Surface Tension	28
3.3. ¹⁹ F NMR.....	28
3.4. Small-angle X-ray Scattering.....	29
3.5. Conductometry.....	29
3.5.1. Conductometry Measurements	29
3.5.2. Modeling Conductivity with the Mean Spherical Approximation	30
3.6. ¹⁹ F DOSY-NMR	34
3.7. Modeling Thermodynamic Non-idealities with the Mean Spherical Approximation ..	35
Chapter 4. Results and Discussion.....	39
4.1. Specific Ion Effects on Surface Tension.....	39
4.2. Speciation and Solubility Detected with ¹⁹ F NMR.....	41
4.3. Aggregation Detection with SAXS.....	48
4.4. Interpreting Speciation with Conductometry	48

4.5.	Specific Ion Effects on Self-Diffusion.....	52
4.6.	Modeling Fickian Diffusion.....	58
Chapter 5.	Conclusions and Future Work.....	61
5.1.	Summary	61
5.2.	Suggested Future Work.....	62
References	63	
Appendix	77	
	Appendix A. Supporting Figures for Materials and Methods.....	77
	Appendix B. Supporting Figures for Results and Discussion	82

LIST OF TABLES

Table 1-1. Common equations that are utilized to predict the activity coefficients of single, strong electrolytes. The approximation of Güntelberg (101), which contains no adjustable parameters, can be used with caution for solutions containing more than one salt (100). $\gamma_{\pm}$ is the mean ion activity coefficient and γ_i is the activity coefficient of ion i . $A = 1.8246 \times 10^6(\epsilon T)^{-\frac{3}{2}}$ and $B = 50.29 \times 10^8(\epsilon T)^{-\frac{1}{2}}$ where ϵ is the dielectric constant and T is temperature. $I = 12C_i z_i^2$ where C_i and z_i are the molarity and charge of ion i (73,100). a_i and b_i are adjustable parameters. Davies (68) supposed that the adjustable parameter, b , in the approximation by Guggenheim (102) could be set equal to 0.3 for all ions, which serves the purpose of making fair predictions in the absence of experimental data..... 13

Table 2-1. Common equations that are utilized to predict the activity coefficients of single, strong electrolytes. The approximation of Güntelberg (1), which contains no adjustable parameters, can be used with caution for solutions containing more than one salt (2). $\gamma_{\pm}$ is the geometric mean activity coefficient of a salt and γ_i is the activity coefficient of ion i . $A = 1.8246 \times 10^6(\epsilon T)^{-\frac{3}{2}}$ and $B = 50.29 \times 10^8(\epsilon T)^{-\frac{1}{2}}$ where ϵ is the dielectric constant and T is temperature. $I = \frac{1}{2} \sum C_i z_i^2$ where C_i and z_i are the molarity and charge of ion i (2,3). a_i and b_i are adjustable parameters. Davies (4) supposed that b_i in the approximation by Guggenheim (5) could be set equal to 0.3 for all ions, which serves the purpose of making fair predictions in the absence of experimental data.13

Table 0-2. pK_a values of PFOA and the corresponding measurement method. Reproduced from reproduced from Balasurya et al. (6).25

Table 0-1. A sample matrix of the PFOA samples studied with ^{19}F NMR. ^aThe concentration of dissolved PFOA if no precipitation occurred.43

Table 0-2. A sample matrix of the KPFOS samples studied with ^{19}F NMR. ^aThe concentration of dissolved KPFOS if no precipitation occurred. ^bMaximum concentration of BaCl_2 . ^cMaximum concentration of NaCl , KCl , and MgCl_2 . ^dMaximum concentration of LiCl and CaCl_245

Table 0-3. Infinite dilution diffusivities for all the species comprising the ^{19}F DOSY-NMR samples. PFO^- and PFOS^- diffusivities at infinite dilution are from the conductivity data collected in this study. All other values were taken from (3).57

Table A-1. Refit parameters for $r^{(0)}$, $\sigma^{(1)}$, and R . AARD values are given for the Lewis-Randall (molality) scale mean ionic activity and osmotic coefficients.82

LIST OF FIGURES

Figure 1-1. Structures of perfluorooctanoic acid and potassium perfluorooctanesulfonate.	1
Figure 1-2. An air-water interfacial boundary in the presence and absence of surfactant. The increased size of the arrow in the leftmost image is to highlight the directionally dependent H-bonding at the surface. Dotted arrows are to represent transient H-bonds, as the average number of H-bonds per water molecule is between 3 and 4 (4).	2
Figure 1-3. Schematic depiction of a foam fractionation column.....	4
Figure 2-1. Bilayer, vesicular, and disklike micelles formed in a 1 wt% PFNA solution (left) and a 90 mM NH ₄ PFO solution with 150 mM NH ₄ Cl as the supporting electrolyte (right) (126).	24
Figure 4-1. Room temperature equilibrium surface tension of 100 ppm PFOA + 0.1 M supporting electrolyte solutions. Error bars represent the standard deviation of 2 replicates. ρ represents the radial charge density of the cation of the supporting electrolyte and was taken from (7). Lines are to group the different series, mono- and divalent cations, together and guide the eye.	39
Figure 4-2. Room temperature equilibrium surface tension of 50 ppm KPFOS + 0.1 M supporting electrolyte solutions. Error bars represent the standard deviation of 2 replicates. ρ represents the radial charge density of the cation of the supporting electrolyte and was taken from (7). Lines are to group the different series, mono- and divalent cations, together and guide the eye.	40
Figure 4-3. 1D ¹⁹ F NMR spectra of PFOA with peak assignments. Temperature was 25 °C.....	42
Figure 4-4. Changes in solubility of PFOA in response to supporting electrolyte concentration and species. Concentration is represented with reduced concentration, C_R . The black line represents where no precipitation occurred with the gray bar representing the statistical error from qNMR. Error bars represent the standard deviation of 2 replicates. Temperature was 25 °C for all samples.	44
Figure 4-5. Changes in solubility of KPFOS in response to supporting electrolyte concentration and species. Concentration is represented with reduced concentration, C_R . The black line represents where no precipitation occurred with the gray bar representing the statistical error from qNMR. Error bars represent the standard deviation of 2 replicates. Only one replicate was performed for BaCl ₂ . Temperature was 25 °C for all samples.	45
Figure 4-6. 1D ¹⁹ F NMR spectra of KPFOS with peak assignments. Peaks that have not been assigned are boxed. Temperature was 25 °C.	46
Figure 4-7. 1D scattering profile of 600 ppm KPFOS. Temperature was 25 °C.	48

Figure 4-8. A plot of Ostwald's dilution law for PFOA. The intercept is the inverse of the limiting molar conductivity of PFOA.	49
Figure 4-9. Extrapolation of the limiting molar conductivity of dilute solutions of KPFOS.	50
Figure 4-10. Application of the MSA transport model to PFOA. The line shown is the best fit with the fitting variable being the apparent equilibrium constant of PFOA. The corresponding pK_a value was 0.69.	51
Figure 4-11. Application of the MSA transport model to KPFOS. The lines shown are MSA transport model predictions corresponding to the scenarios in which KPFOS is a strong electrolyte and weak electrolyte.	52
Figure 4-12. Dependence of D^* on concentration of PFOA. Data from this study is compared to that of Gauthier and Mabury (2024) (8). Error bars represent the standard deviation of 2 replicates. Temperature was 25 °C.	53
Figure 4-13. Dependence of D^* on concentration of KPFOS. Data from this study is compared to that of Gauthier and Mabury (2024) (8). Data from (8) was for the acidic form of PFOS rather than KPFOS. Error bars represent the standard deviation of 2 replicates. Temperature was 25 °C.	54
Figure 4-14. Dependence of D^* of PFOA on concentration and species of supporting electrolyte. Error bars represent the standard deviation of 2 replicates. Temperature was 25 °C. Lines are to help guide the eye. PFOA concentration was allowed to change from 1000 ppm from precipitation.	55
Figure 4-15. Dependence of D^* of KPFOS on concentration and species of supporting electrolyte. Error bars represent the standard deviation of 2 replicates. Temperature was 25 °C. Lines are to help guide the eye. KPFOS concentration was allowed to change from 270 ppm from precipitation.	56
Figure 4-16. A comparison of Fickian diffusion coefficients measured via bubble pressure tensiometry with predictions from the generalized Hartley-Crank model developed by Lieast et al. (9,10). Data was originally reported in our work (11).	59
Figure 4-17. A comparison of Fickian diffusion coefficients measured via bubble pressure tensiometry with predictions from the generalized Hartley-Crank model developed by Lieast et al. (9,10). Data was originally reported in our work (11).	60
Figure A-1. Variation of pendant drop volume for 100 ppm PFOA trials 1 and 2.	77
Figure A-2. Extrapolation of dynamic surface tension data (100 ppm PFOA trial 1) to obtain equilibrium surface tension values using the long time Ward-Tordai model (equation 6).	77

Figure A-3. Time-dependent conductivity measurements to show the dilution of KPFOS from 575 ppm to 550 ppm. Values were recorded immediately following the addition of water to the sample.78

Figure A-4. The BIMSA model predictions of mean ionic activity coefficients on the Lewis-Randall scale (molality basis) and osmotic coefficients for lithium salts after refitting to $\gamma_{\pm}$ (LR). Data were taken from Robinson and Stokes (3). Molarity to molality scale conversions were performed with density data taken from (12).78

Figure A-5. The BIMSA model predictions of mean ionic activity coefficients on the Lewis-Randall scale (molality basis) and osmotic coefficients for sodium salts after refitting to $\gamma_{\pm}$ (LR). Data were taken from Robinson and Stokes (3). Molarity to molality scale conversions were performed with density data taken from (12).79

Figure A-6. The BIMSA model predictions of mean ionic activity coefficients on the Lewis-Randall scale (molality basis) and osmotic coefficients for potassium salts after refitting to $\gamma_{\pm}$ (LR). Data were taken from Robinson and Stokes (3). Molarity to molality scale conversions were performed with density data taken from (12).79

Figure A-7. The BIMSA model predictions of mean ionic activity coefficients on the Lewis-Randall scale (molality basis) and osmotic coefficients for magnesium salts after refitting to $\gamma_{\pm}$ (LR). Data were taken from Robinson and Stokes (3). Molarity to molality scale conversions were performed with density data taken from (12).80

Figure A-8. The BIMSA model predictions of mean ionic activity coefficients on the Lewis-Randall scale (molality basis) and osmotic coefficients for calcium salts after refitting to $\gamma_{\pm}$ (LR). Data were taken from Robinson and Stokes (3). Molarity to molality scale conversions were performed with density data taken from (12).80

Figure A-9. Experimental conductivity data for acetic acid along with the predicted molar conductivity from the MSA transport model (Equation 16). Two sets of experimental data from literature (13,14) and experimental data collected in this study are shown. Two replicate measurements were performed Limiting ionic molar conductivity values were taken from (3) and used within Equation 15 to calculate D_i^0 of the acetate ion and H^+ . The ionic radii of H^+ was taken from (15) and the ionic radii of the acetate ion was deduced by solving the Stokes-Einstein equation for the hydrodynamic radius. K_a used in the calculation of α was taken from (13). ...83

Figure A-10. Sigmoidal fitting of differential specific conductance to determine the CMC of SDS. The sigmoidal equation takes the form $\frac{d\kappa}{dc} = \frac{(\bar{y}_{max} - \bar{y}_{min})}{1 + \exp(1 + ([SDS] - CMC))} + \bar{y}_{min}$ where $\bar{y}_{max}$ is the average of the highest magnitude differential conductance values and $\bar{y}_{min}$ the average of the lowest magnitude differential conductance values. The CMC determined from the fitting was 8.248 mM.84

Figure A-11. Experimental conductometry SDS data collected in this study alongside MSA transport predictions with the degree of ionization of the micelles as a fitting variable. The

number of replicate experiments performed was 2. α_{mic} converged to 0.357 with an AARD of 0.922%.85

Figure A-12. Experimental conductometry SDS data collected in this study with linear trendlines for the two concentration regions, above and below the CMC. The slope after the CMC divided by the pre-CMC slope was found to be 0.322.86

ABSTRACT

Decades of use of per- and polyfluoroalkyl substances (PFAS) have resulted in contamination spanning the globe. Accumulation of PFAS within the environment and biota has raised concerns over their toxicity. A number of studies revealing health effects related to elevated PFAS exposure have been performed. Despite current efforts to enact more phase outs for PFAS in non-essential cases, their chemical stability will prevent the cycle of uptake and reemission into the environment for decades to come. Foam fractionation is a technique that can be used to remove PFAS from water. Some work has been done in identifying and systematically studying important physicochemical properties of PFAS, but diffusivity has not been as well represented in the prior studies. Additionally, the widespread nature of PFAS contamination necessitates further research regarding the physicochemical interactions within diverse aquatic environments, including diffusivity. The goal herein is to not only study the effect of not only charge, but also ion identity on diffusivity. Several other physicochemical characteristics are investigated, such as surface tension, solubility limits, and speciation. Modeling approaches that are novel in their application to PFAS are used in the study of speciation and aggregation. The key findings of the study were indicative that Hofmeister-like series emerge when close contact is made between anionic PFAS and cations. Different species-specific phenomena are present in the case of diffusivity, which highlights an area where trends that do not explicitly follow Hofmeister-ordering necessitate other explanations.

Chapter 1. Introduction

1.1. Introduction to per- and polyfluoroalkyl substances (PFAS)

Per- and polyfluoroalkyl substances (PFAS) are defined by the OECD as fluorinated substances that contain at least 1 fully fluorinated methyl or methylene moiety that is not halogenated. This definition encompasses approximately 24 million species, including a subclass comprised of surface-active agents (16). Fluorinated surface-active agents, or surfactants, are generally classified by the length of their hydrophobic chain with seven or more carbons being referred to as long-chain. Two of the most common long-chain fluorosurfactants are perfluorooctanoic acid (PFOA) and the potassium salt of perfluorooctanesulfonic acid (KPFOS) (17,18). The structures of PFOA and KPFOS have been depicted in **Figure 1-1**.

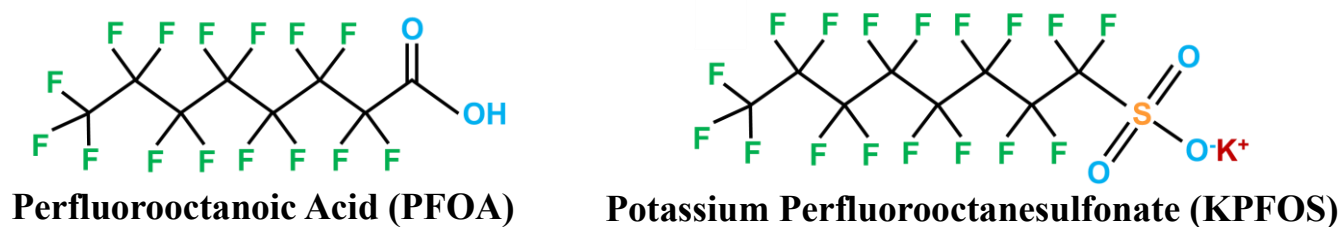


Figure 1-1. Structures of perfluorooctanoic acid and potassium perfluorooctanesulfonate.

Surfactants tend to adsorb onto interfaces, such as the air-water interface, due to their amphiphilic nature. The process of adsorption lowers the energy per area, better known as interfacial or surface tension, of an interface by replacing the solvent molecules at the phase boundary. Solvent molecules at an interface between immiscible phases can otherwise only interact favorably with their side-to-side and bulk neighbors which is the origin of surface tension (19). In **Figure 1-2**, an air-water interface has been depicted with and without surfactant present.

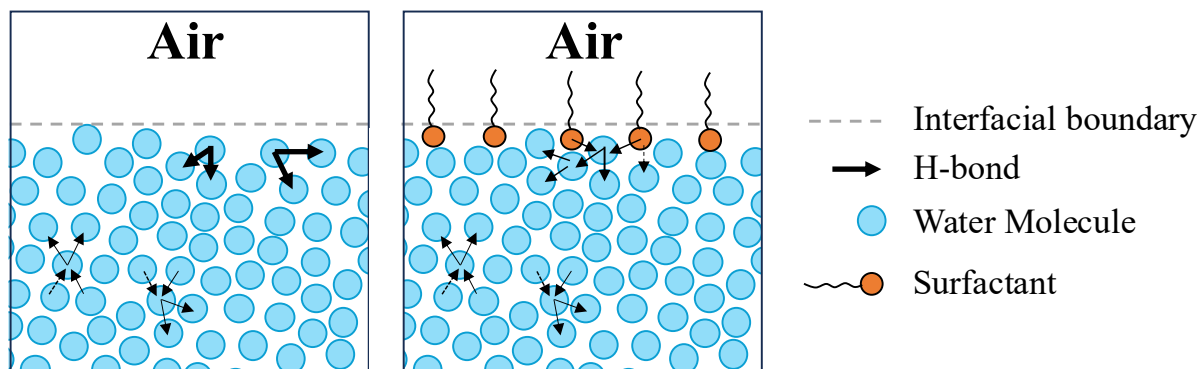


Figure 1-2. An air-water interfacial boundary in the presence and absence of surfactant. The increased size of the arrow in the leftmost image is to highlight the directionally dependent H-bonding at the surface. Dotted arrows are to represent transient H-bonds, as the average number of H-bonds per water molecule is between 3 and 4 (19).

Long-chain fluorosurfactants are particularly potent at lowering interfacial tension by comparison to their hydrocarbon analogues owing to the highly hydro- and oleophobic perfluoroalkyl chain (17,20). This remarkable ability paired with the strength of the C-F bond has led to a wide array of uses for surface-active PFAS, including as detergents, spreading agents, emulsifiers, foaming agents, medical imaging aids, etc. (17,21–23). While the unique properties of PFAS prove useful in many applications, their resistance to degradation coupled with widespread use have led to accumulation in both the environment and biota (24–28). KPFOS, PFOA, and their respective salts were some of the earliest PFAS to fall under scrutiny which led to their distinction as persistent organic pollutants (POPs) in 2009 and 2019, respectively (29,30). Despite this action leading to decreases in the production volume as well as subsequent phase-outs of KPFOS and PFOA several years ago both compounds are detectable in many matrices across the globe currently (31,32). This is cause for enormous concern because it has been demonstrated by many authors that PFAS are toxic to humans and wildlife. Animal-based studies have demonstrated that chronic exposure to PFAS results in immunotoxicity and carcinogenicity (33,34). Studies on humans have linked a number of adverse health effects such

as reproductive harm, endocrine disruption, ulcerative colitis, hypertension, high cholesterol, and increased risk of cancer to elevated PFAS exposure (35–38).

1.2. Current technology for the removal of PFAS from water

Municipal and other conventional wastewater treatment methods are not effective in removing PFAS from water. Long-chain PFAS generally remain chemically unaltered as they pass through waste treatment while precursor species, such as 6:2-fluorotelomersulfonic acid (6:2-FTS), may degrade into short-chain PFAS (39–41). Several technologies have emerged as candidates in remediating PFAS by separation, destruction, or a combination of the prior. The most widely utilized methods to separate PFAS from water are adsorption to granular activated carbon (GAC) and anionic exchange resin (42). GAC is low cost by comparison to anionic exchange resins, although the latter has been demonstrated to have a higher removal efficiency for PFOA and PFOS (42–46). However, it is difficult to reliably regenerate GAC and anionic exchange resins without the use of solvents, such as methanol, ethanol, or acetone. Even with the utilization of non-aqueous solvents, 100% recovery of solid sorbents is often not achieved which necessitates safe disposal of the spent adsorbent (42,47–49). Membrane filtration has demonstrated high removal efficiencies for long- and short-chain PFAS but also faces several challenges. Reverse osmosis (RO) and nanofiltration (NF) are susceptible to fouling and require high energy demand to generate pressure gradients, especially for RO (50,51). It is essential to close the loop of repeated capture and re-emission of PFAS by destructive methods, such as advanced oxidation processes (AOPs), thermal decomposition, and biodegradation (52). Yet, the efficiency of destructive methods is dependent on the concentration of the feed stream which drives the need for the development of separative methods (53).

Foam fractionation has been considered as a promising candidate to address the need to remove surface-active PFAS from water for several years (54–57). The separation principle of foam fractionation at the surface-level is quite simple. Gas is first sparged through the aqueous matrix containing surfactant. The surfactant adsorbs to the air-water interfaces and are convectively carried out of the liquid pool by the upward motion of the bubbles. Foam or bubbly liquid enriched in surfactant is subsequently collected from the upper section of the column. The fraction from the bottom of the column is more lean in surfactant concentration (58,59). A simple depiction of a foam fractionation column is presented in **Figure 1-3**.

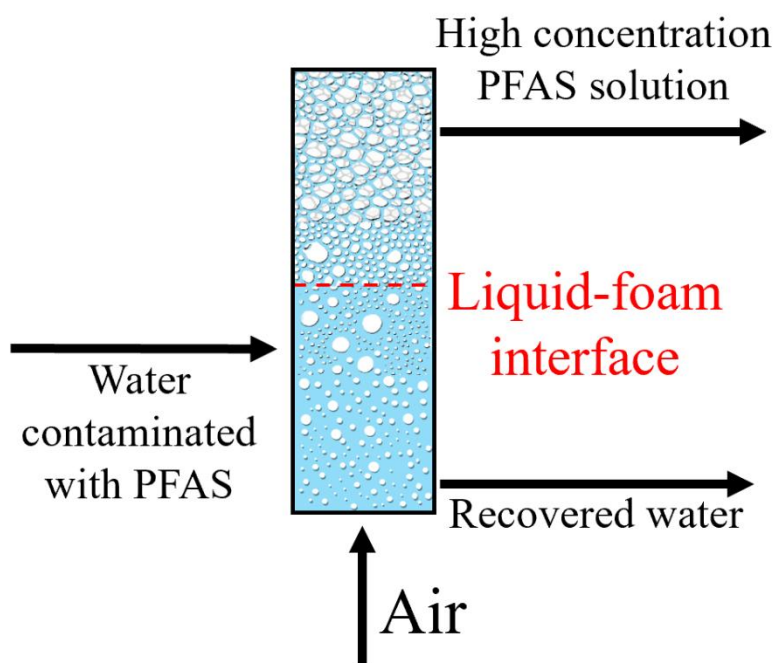


Figure 1-3. Schematic depiction of a foam fractionation column.

Foam fractionation has been demonstrated by several studies to efficiently remove long-chain PFAS from water. McCleaf et al. showcased removal efficiencies of approximately 99% for PFOA and PFOS from contaminated municipal water with a pilot scale foam fractionation column that was fed concentrate from an NF membrane (55). Smith et al. reported removal efficiencies of approximately 95% for PFOA and PFOS in a pilot-scale unit treating landfill

leachate (57). McCleaf et al. and Smith et al. observed lower removal efficiencies for short-chain surface-active PFAS, such as perfluorobutanesulfonic acid (PFBS), by comparison to PFOA and PFOS due to lower hydrophobicity (55,57). However, McCleaf et al. were able to enhance the removal of short-chain PFAS with the addition of a cationic cosurfactant (55).

1.3. Design Principles of Foam Fractionation Columns

There are several important physical properties needed for the design of a foam fractionation column. These properties are most easily highlighted by design equations that are subsequently presented (60). Take first that adsorption in the liquid pool is under consideration. Equation 1 is the quantity of PFAS being captured by the bubbles per time, which is

$$N = k_L A_i (C_\infty - C_i) \quad (1)$$

where N is mass flowrate, k_L is the overall mass transfer coefficient, A_i is the surface area of the bubbles, C_∞ is the bulk PFAS concentration, and C_i is the PFAS concentration in the subsurface layer of water near the air-water interface. k_L in the liquid pool can be calculated by considering local equilibrium between the sublayer and bubble surfaces with adsorption from the sublayer to the interface being instantaneous. Wakao and Kaguei found that, for flow around a bed of closely packed solid spheres with Re less than 3000, k_L is

$$k_L = \frac{(2 + 1.1Re^{0.6}Sc^{1/3})D_{AB}}{d} \quad (2)$$

where Re is the Reynolds number, Sc is the Schmidt number, d is the sphere diameter, and D_{AB} is the Fickian diffusion coefficient (61). The Schmidt and Reynolds numbers are defined respectively by Equations 3 and 4

$$Re = \frac{\rho_f V d}{\mu} \quad (3)$$

$$Sc = \frac{\eta}{\rho_f D_{AB}} \quad (4)$$

where ρ_f is liquid density, η is dynamic viscosity, and V is the absolute slip velocity between the bubbles and the liquid. If the bubbles are not closely packed, expressions similar to Equation 2 that were developed by Frössling and Levich can be considered for Re greater than 1 and less than 1, respectively (62,63).

Modeling mass transfer in the foam is a more complicated matter. One approach is to use Equation 2 under the assumption that the bubbles in the foam are spherical, but a more conservative design would instead consider a time dependent model for surfactant adsorption. This is because adsorption in the foam does not benefit greatly from convective flow since the slip velocity between the air and liquid in the films is relatively slow (60). It is also possible to capture more complex behavior, such as dampened diffusion of ionic surfactants to the interface due to formation of an electric double layer (64–67). If it is assumed that the interfaces within the foam are stationary surfaces due to low slip velocity, then one may utilize the Ward-Tordai model to describe adsorption as a kinetic process. Equations 5 and 6 are different forms of the Ward-Tordai model, the former given for short time scales (on the order of milliseconds) and the latter for long time scales (56,68). Equation 5 is

$$\gamma - \gamma_0 = -2CRT \left(\frac{D_{AB}t}{\pi} \right)^{0.5} \quad (5)$$

where t is time, γ is the surface tension at time t , γ_0 is the initial surface tension which in this case is that of pure water, C is the bulk concentration of surfactant, R is the gas constant, T is temperature, and D_{AB} is the Fickian diffusion coefficient. Equation 6 is

$$\gamma - \gamma_{eq} = \frac{2RT\Gamma_m^2}{C} \left(\frac{1}{\pi D_{eff}t} \right)^{0.5} \quad (6)$$

where γ_{eq} is the surface tension at equilibrium, Γ_m is the maximum surface excess, and D_{eff} is the effective diffusion coefficient. Equations 5 and 6 were developed for nonionic surfactants but ionic effects are explicitly accounted for in more sophisticated models (64–67). More attention is given to the treatment of ionic surface-active PFAS within Equation 5 in the next section.

Beyond the relationships presented in Equations 2 through 6, there are other connections between the physical characteristics of the aqueous solution in the liquid pool and foam to the operating variables of a foam fractionation column. One example is the influence of surface tension, nozzle diameter, and gas flowrate on the bubble size produced in the column (69,70) although a full length discussion is outside the scope of this work. Nonetheless, it is apparent that several physical properties are of importance in the study of foam fractionation for the removal of PFAS from water.

1.4. Prior Work

Our group has conducted several prior investigations regarding physicochemical characteristics of long- and short-chain PFAS; PFOA, KPFOS, and KPFBS (11,71,72). To briefly recap, the primary properties that were examined were; dynamic and equilibrium surface tension; maximum surface excess; storage and loss moduli of the air-water interface saturated with PFAS; and the Fickian diffusion coefficients. The influence of the presence of two salts, NaCl and CaCl₂, on these properties was explored in the more recent studies (11,72).

The most recent of our publications estimated the Fickian diffusion coefficient, D_{AB} , by analyzing dynamic surface tension data measured over short time scales with bubble pressure tensiometry via Equation 5 (11). This is currently, to the best of our knowledge, the first time that the diffusivity of PFOA, KPFOS, and KPFBS were measured by utilizing bubble pressure tensiometry. It is apparent from the results that diffusivity varies by several orders of magnitude

with bulk surfactant concentration for PFOA, KPFOS, and KPFBS. Moreover, increasing the concentration of supporting electrolyte, NaCl or CaCl₂, altered the diffusivity of PFOA and KPFOS by one order of magnitude. The diffusivity of KPFBS at constant bulk surfactant concentration was increased by more than 2 orders of magnitude with increasing CaCl₂ concentration (11).

If the results presented in (11) are taken at face value, the implication would be that diffusivity is one of the most important physical properties to consider when designing a foam fractionation column for PFAS remediation. A change in solution composition would have a large impact on k_L and thereby greatly alter mass flux. This is especially the case for aqueous matrices that contain electrolytes, even in small quantities. Still, it is not clear solely from the results in (11) whether the observed D_{AB} values have a phenomenological origin.

It was suggested in our work that the short time scale Ward-Tordai model cannot adequately capture diffusion characteristics unless all assumptions hold for the surfactant concentrations being examined (11,73,74). To clearly state these assumptions, the first is that diffusion must be controlled by transfer of surfactant from the bulk to the subsurface. By consequence, there must not be an energy barrier present for movement of surfactant from the subsurface to the interface (68,74). The second assumption is that the bulk concentration of surfactant is effectively constant with time (68). Two examples are given to consider where each assumption may not hold. If the bulk concentration of surfactant is sufficiently low at the beginning of the experiment, then the bulk concentration may be depleted as adsorption to the bubble surface occurs. In the case of an ionic surfactant the formation of an electric double layer at the interface can occur. This could hinder the movement of surfactant from the subsurface to the interface via coulombic interactions. These coulombic interactions would pose an energetic

barrier for adsorption of surfactant from the subsurface to the interface (60,64–67). A counter argument for both cases is that the time scale of less than 40 milliseconds, which was used in the analysis of the dynamic surface tension data, is not long enough to deplete the bulk concentration or cause a significant buildup of charge at the interface. The distinction between whether the assumptions hold or not requires a rigorous evaluation. Beyond the assumptions of the model, association of surfactant monomers could also play a role. As surfactant concentration increases, dimerization occurring below the critical micelle concentration (CMC) could cause an apparent decrease in diffusivity due to a larger hydrodynamic drag being exerted on larger species.

Furthermore, the influence of electrolytes in our prior studies were only investigated on the basis of valency and concentration (11,72). It has been established for decades that physicochemical behavior of ions within aqueous systems is dictated not only by charge and concentration, but also by size (3–5,7,75–84). These phenomena, which can occur in non-aqueous systems as well, have been coined as specific ion effects (SIE) (77,85). SIE are not only exclusive to monoatomic ions, but also polyatomic ions, including ionic surfactants. As pointed out by other authors, the identity of the headgroup for a given ionic surfactant can cause SIE to manifest (86–88). It is therefore of great interest to consider how different surfactant functional groups, such as carboxylate and sulfonate, as well as the identity of supporting electrolytes influence diffusivity.

1.5. Research Objectives and Hypothesis

Discussion in the previous section has brought to light where further investigation is warranted. In this study, the hypothesis is that specific ion effects influence the diffusivity of PFAS not only due to the identity of the ionic headgroup of the surfactant but also that of the supporting electrolyte. The corresponding objective is to quantify the influence of SIE on the diffusivity of

PFAS species with different headgroups as well as differing species of supporting electrolytes. The PFAS selected for this purpose are PFOA and KPFOS and the supporting electrolytes considered herein are LiCl, NaCl, KCl, MgCl₂, and CaCl₂. While the identity of all ions within the system is important when describing SIE (77) the choice was made to study only chloride salts as supporting electrolytes to primarily target SIE related to the identity of the cation.

It has now been thoroughly established that the findings in our prior study on diffusivity of KPFOS, PFOA, and KPFBS (11) are dependent on the strength of the assumptions of the short time scale Ward-Tordai model. To qualify those results, the second objective is to model D_{AB} with ionic effects included and to draw a comparison with the bubble pressure tensiometry results.

In addition, it is necessary to evaluate the possibility that sub-CMC association of surfactant monomers causes changes in the diffusion characteristics of PFOA and KPFOS. The possibility of weak electrolyte behavior cannot be ruled out, so changes in the degree of ionization of the surfactant anions with solution composition must also be investigated. Therefore, the third and final objective is to determine the speciation and aggregation state of PFOA and KPFOS within the electrolyte systems of interest.

To address the objectives, several experimental and modeling approaches are utilized. Self-diffusion coefficients of PFOA and KPFOS in the presence and absence of LiCl, NaCl, KCl, MgCl₂, and CaCl₂ are measured with fluorine NMR diffusion-ordered spectroscopy (¹⁹F DOSY-NMR). The potential for aggregation behavior or changes in the speciation of PFOA and KPFOS are investigated by conductometry, small-angle X-ray scattering (SAXS), and fluorine NMR (¹⁹F NMR). By utilizing conductometry measurements coupled with modeling approaches developed

by other authors (89–95), a robust model for the Fickian diffusivity that accounts for ion identity and concentration can be established (11).

Chapter 2. Literature Review

2.1. Transport and Thermodynamics of Electrolytes

Solutions containing electrolytes have been studied systematically for approximately 200 years (80,96,97). By consequence, there is an extensive body of work describing both the transport and thermodynamics of electrolytes. The result of decades of development in the field has led to different theoretical treatments which are capable of predicting transport and thermodynamic properties of ions (15,81,92,98–106). The reader is encouraged to consult more extensive reviews that compare these approaches (103,107,108) but two of the primary theories are discussed herein, the first of which is Debye–Hückel theory.

2.1.1. Debye–Hückel Theory

Debye–Hückel theory was developed on the basis that ions can be treated as point charges embedded within a dielectric medium, although a minimum distance between ions is considered such that overlap does not occur (81,108). A linearized form of the Poisson-Boltzmann equation is used to relate the electric potential of ions to their local charge density, which is consequence of the neighboring ions of opposite charge (81,108). By using this framework, the extended Debye–Hückel equation was established. After assuming the denominator would approach unity at infinite dilution, the Debye–Hückel limiting law was drawn from the extended Debye–Hückel equation. These models predict the thermodynamic nonideality in the form of activity coefficients for strong electrolytes (3,81). However, without explicit inclusion of the interaction with the solvent, ion activity only decreases from unity with increasing concentration (3). Several authors made modifications to the extended Debye–Hückel equation to account for ion

activity increasing as higher concentrations are approached. These approximations and the corresponding authors have been listed in **Table 2-1** in the style of Morgan and Stumm (2).

Table 2-1. Common equations that are utilized to predict the activity coefficients of single, strong electrolytes. The approximation of Güntelberg (1), which contains no adjustable parameters, can be used with caution for solutions containing more than one salt (2). $\gamma_{\pm}$ is the geometric mean activity coefficient of a salt and γ_i is the activity coefficient of ion i . $A = 1.8246 \times 10^6 (\epsilon T)^{-\frac{3}{2}}$ and $B = 50.29 \times 10^8 (\epsilon T)^{-\frac{1}{2}}$ where ϵ is the dielectric constant and T is temperature. $I = \frac{1}{2} \sum C_i z_i^2$ where C_i and z_i are the molarity and charge of ion i (2,3). a_i and b_i are adjustable parameters. Davies (4) supposed that b_i in the approximation by Guggenheim (5) could be set equal to 0.3 for all ions, which serves the purpose of making fair predictions in the absence of experimental data.

Approximation	Equation	Approximate Applicability [Ionic Strength (M)]
Debye–Hückel Limiting Law (81)	$\log \gamma_{\pm} = -A z_1 z_2 \sqrt{I}$	< 0.005
Extended Debye–Hückel (81)	$\log \gamma_{\pm} = -\frac{A z_1 z_2 \sqrt{I}}{1 + B a_i \sqrt{I}}$	< 0.1
Güntelberg (1)	$\log \gamma_{\pm} = -\frac{A z_1 z_2 \sqrt{I}}{1 + \sqrt{I}}$	< 0.1
Guggenheim (5)	$\log \gamma_{\pm} = -\frac{A z_1 z_2 \sqrt{I}}{1 + \sqrt{I}} + b_i I$	< 0.1
Davies (4)	$\log \gamma_{\pm} = -\frac{A z_1 z_2 \sqrt{I}}{1 + \sqrt{I}} + 0.3I$	< 0.5
Truesdell-Jones (WATEQ Debye–Hückel) (83)	$\log \gamma_i = -\frac{A z_1 z_2 \sqrt{I}}{1 + B a_i \sqrt{I}} + b_i I$	< 1.0

Of the approximations listed above, the most successful in predicting activity coefficients of single, strong electrolytes is Truesdell-Jones. Success of Truesdell-Jones is owed to the presence of 2 empirically fit parameters that are specific to a given ion (3,83).

Conductivity of an electrolyte solution is inherently tied not only to concentration but also the fundamental properties, such as charge and diffusivity, of the constituent ions that are present. This observation was empirically made by several scientist during the 19th century (96,109–111), but it was the Debye–Hückel theory that made the first non-empirical approaches to describing the conductance of ionic solutions possible. This was done by way of an extension of the Debye–Hückel theory made by Onsager. The extension henceforth became the Debye–Hückel-Onsager (DHO) theory (15,112,113). DHO theory would then be utilized by Onsager (112,113) to correct the empiricism formulated by Kohlrausch (109) to what is known widely as the DHO limiting law. The DHO limiting law is

$$\frac{\kappa}{c} \equiv \Lambda = \Lambda^o - (A + B\Lambda^o)\sqrt{c} \quad (7)$$

where; κ is specific conductance; c is concentration; Λ is molar conductivity; Λ^o is limiting molar conductivity; A is a constant involving the valence of the ions, dielectric constant, and temperature; and B is a constant involving the valence of the ions, dielectric constant, temperature, and viscosity. Equation 7 is valid only in highly dilute solutions which lead to its distinction as a limiting law (3). It was Kohlrausch, however, that determined that the limiting molar conductivity of a salt is comprised of that of its constituent ions. This is formally written as

$$\Lambda^o = v_+\lambda_+^o + v_-\lambda_-^o \quad (8)$$

where v_+ and v_- are the stoichiometric coefficients of the cation and anion, respectively. λ_+^o and λ_-^o are the limiting ionic molar conductivities of the cation and anion, respectively. Equation 8 is therefore called Kohlrausch's law of independent migration (109).

Ostwald was the first to relate the conductivity of weak electrolytes to their degree of ionization under the assumption of ideal behavior of the ions (111). Starting from the equilibrium constant, in this case for a weak acid, in an ideal solution

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (9)$$

where K_a is the equilibrium constant, $[H^+]$ is the hydronium concentration, $[A^-]$ is the anion concentration, and $[HA]$ is the concentration of the associating acid. Rearrangement yields

$$K_a = \frac{c\alpha^2}{1 - \alpha} \quad (10)$$

where α is the degree of ionization and c is the total concentration of the acid. Given that

$$\alpha = \frac{\Lambda}{\Lambda^o} \quad (11)$$

the familiar form can be found

$$\frac{1}{\Lambda} = \frac{1}{\Lambda^o} + \frac{\Lambda}{(\Lambda^o)^2} \frac{c}{K_a} \quad (12)$$

which is referred to as Ostwald's dilution law (111). An extension for the case of associating electrolytes that accounts for non-ideality would later be made by Fuoss and Kraus within the DHO framework (114).

One of the newest developments with the DHO theory is the development of a model by Boroujeni et al. to describe the conductivity of complex mixtures of salts (15). The form of the model, which was first suggested by Onsager and Kim (115) and thereafter utilized by several other authors (92,101,102) prior to Boroujeni et al., is

$$\kappa = \frac{e^2}{k_B T} \sum_{i=1}^N \rho_i D_i^o z_i^2 \left(1 + \frac{\delta v_i}{v_i^o} \right) \left(1 + \frac{\delta k_i}{k_i} \right) \quad (13)$$

where e is the elementary charge constant, k_B is the Boltzmann constant, T is temperature, ρ_i is the number density of ion i , D_i^o is the diffusion coefficient at infinite dilution of ion i , and z_i is the charge of ion i . $\frac{\delta v_i}{v_i^o}$ and $\frac{\delta k_i}{k_i}$ are the electrophoretic and relaxation corrections, respectively (15). The electrophoretic correction accounts for the hydrodynamic hinderance caused by the counterflow of the solvent and surrounding ionic atmosphere. The relaxation correction accounts for the opposing electrostatic force produced when that ionic atmosphere becomes distorted and lags behind the moving ion. These correction terms can be calculated with the DHO theory. More discussion of the corrective terms will be given subsequently in chapter 3, but for now it suffices to mention the dependencies of each.

$$\frac{\delta v_i}{v_i^o} = \frac{\delta v_i}{v_i^o}(\mu, T, \varepsilon, c_i, z_i, D_i^o, \sigma_{ij})$$

and

$$\frac{\delta k_i}{k_i} = \frac{\delta k_i}{k_i}(T, \varepsilon, c_i, z_i, D_i^o, \sigma_{ij})$$

where σ_{ij} is the distance of closest approach for ions i and j . σ_{ij} is found simply by

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (14)$$

Values of σ_i depend on the ion under consideration and were taken by Boroujeni et al as the crystallographic diameters reported by Marcus (15,116). The only variable left that requires further explanation is D_i^o . It is due to Nernst that the connection can be drawn between the limiting ionic molar conductivity and the mobility of ions at infinite dilution (110). The diffusivity of an ion at infinite dilution is

$$D_i^o = \left(\frac{RT}{F^2}\right) \left(\frac{\lambda_i^o}{z_i^2}\right) \quad (15)$$

where F is Faraday's constant.

It is now apparent that the model only relies on a few values which can readily be retrieved from literature (3,116) making it predictive in nature since no adjustable parameters are required (15). Also, as mentioned by Boroujeni et al., a simple modification of Equation 13 to include the degree of ionization could be made in order to predict the conductivity of weak electrolytes (15). Specific conductance would then be

$$\kappa = \frac{e^2}{k_B T} \sum_{i=1}^N \rho_i \alpha_i D_i^o z_i^2 \left(1 + \frac{\delta v_i}{v_i^o}\right) \left(1 + \frac{\delta k_i}{k_i}\right) \quad (16)$$

where α_i is the degree of ionization of species i . Including the degree of ionization allows for one to model systems where ion pairing occurs, making it a tool that has the potential to obtain equilibrium constants from data fitting (15). However, this aspect of the model is not novel. Other authors have used similar forms of Equation 13 to study systems where ion pairing occurs, including micellar systems. In these investigations the other theoretical framework of interest, the mean spherical approximation, was employed to solve for the correction terms (89,90).

2.2.1. The Mean Spherical Approximation

Treatment of ions with the mean spherical approximation (MSA) is that of charged hard spheres imbedded in a dielectric continuum (92,100,104,108). Owing to the explicit inclusion of the finite volume occupied by the ions, it is also possible to determine Helmholtz energy of an electrolyte system (108). Subsequently, the MSA can be utilized for the purpose of predicting the activity coefficients of ions as demonstrated by Simonin et al. (93–95). As for the transport model that predicts conductivity, success in modeling complex mixtures has been demonstrated by several authors (89,90,92). It is worth mention that the DHO-based model presented in Boroujeni et al. made improvements in the ability of conductivity predictions to be made for higher concentrations of electrolytes compared to prior work with the same framework

(115,117). But by comparison, the MSA generally can make more accurate conductivity and activity predictions across a wider concentration range owing to better treatment of ion-ion and ion-solvent correlations (117,118). Given these considerations, the approach used herein to model conductivity and activity is the mean spherical approximation. Details of the routine used to assess the primary calculations of the MSA, both for activity coefficients and conductivity, will be discussed in Chapter 3.

2.3.1. The Nexus of Transport and Thermodynamics of Electrolytes

Discussion within this section has thus far dealt with the topics of thermodynamics and transport of ions separately. However, the two coincide (3). A formal statement of this crossover for a single strong electrolyte diffusing through a solvent is known as the Nernst-Hartley relation (119) which is

$$D_{AB} = D_{AB}^o \left(1 + \frac{d \ln \gamma_{\pm}}{d \ln c} \right) \quad (17)$$

where

$$D_{AB}^o = \frac{RT(v_1 + v_2)}{F^2 v_1 |z_1|} \frac{\lambda_1^o \lambda_2^o}{(\lambda_1^o + \lambda_2^o)} \quad (18)$$

with D_{AB}^o representing the diffusivity at infinite dilution of a salt (110). Effects related to concentration are introduced in Equation 17 through the thermodynamic correction term, but Onsager and Fuoss introduced concentration corrections to the kinetic contribution, D_{AB}^o (98). The result is

$$D_{AB} = (D_{AB}^o + \Delta_1 + \Delta_2) \left(1 + \frac{d \ln \gamma_{\pm}}{d \ln c} \right) \quad (19)$$

where Δ_1 and Δ_2 are the first and second order electrophoretic correction terms which carry the same physical depiction described in **Section 2.1.1**. Diffusing ions described with Equations 17 and 19 are essentially treated as moving through a stationary solvent that imposes friction on

ions. This limits the application of Equations 17 and 19 to dilute solutions, less than around 20 mM (3). Stokes and Agar extended the Nernst-Hartley relation to more concentration solutions where the motion of the solvent with the ions becomes more pronounced due to hydration (3). Leaist, Curtis, and Al-Dhaher generalized this model in order to extend its use to the case of mixtures of electrolytes (9,10). Diffusivity of salt species i is related to the presence of salt species k by

$$D_{ik} = D'_{ik} - c_i \left[\sum_{q=1}^N V'_q D'_{qk} + c'_o V_o D'_o \left(\frac{\partial \ln f_o}{\partial c_k} \right)_{c_{p \neq k}} \right] \quad (20)$$

where c_i is molarity scale concentration of species i , V'_q is the partial molar volume of the hydrated electrolyte, V_o is the partial molar volume of water, D'_o is the diffusion coefficient of free water, and c_k is the molal scale concentration of species k . D'_{ik} is the “pure” diffusion coefficient given by

$$D'_{ik} = RT \sum_{q=1}^N L'_{iq} \left[\left(\frac{\partial \ln f_q}{\partial c_k} \right)_{c_{p \neq k}} + h_q \left(\frac{\partial \ln f_o}{\partial c_k} \right) \right] \quad (21)$$

where f_i is the molal scale activity of species i . f_i is given simply by

$$f_i = c_i \gamma_i \quad (22)$$

considering the molal concentration scale. $\mathbf{L}'$ is the finite-concentration electrolyte mobility matrix, which is defined as

$$\mathbf{L}' = \frac{1}{\eta_r} [\mathbf{v}^T (\mathbf{l}^o)^{-1} \mathbf{v}]^{-1} \quad (23)$$

with

$$\eta_r = \frac{\eta}{\eta_o} \quad (24)$$

where η_r is relative viscosity, η_o is the viscosity of the pure solvent, and η is the viscosity of the mixture. $\mathbf{v}$ is the ionic stoichiometric coefficient matrix with $\mathbf{v}^T$ being the corresponding transpose. $\mathbf{l}^o$ is an N by N diagonal matrix comprised of ionic mobility coefficients (10). The corresponding components are of the form

$$l_{ss}^o = \frac{c_s D_s^o}{RT \eta_r} \quad (25)$$

c'_o in Equation 20 is the concentration of unbound water, and is related to the salt concentration by

$$c'_o = c_o - \sum_{i=1}^N h_i c_i \quad (26)$$

with c_o being the total concentration of water, h_i representing the number of water molecules bound to salt species i , and c_i the concentration of salt species i .

Equation 20 gives one the ability to model Fickian diffusivities within aqueous systems containing more than 1 salt (3,9,10). Leaist et al. were able to model three ternary systems with fair accuracy; $\text{CaCl}_2 + \text{HCl} + \text{H}_2\text{O}$, $\text{MgCl}_2 + \text{NaCl} + \text{H}_2\text{O}$, and $\text{SrCl}_2 + \text{NaCl} + \text{H}_2\text{O}$ (9,10). Additionally, it is useful in the study of SIE that Equation 20 combines ion-specific properties, including ionic charge and mobility at infinite dilution, with solution-dependent effects arising from electrolyte hydration, viscosity, and thermodynamic nonideality. A major strength lies in the ability to separately access the quantities D_{11} , D_{12} , and D_{22} . The main difficulty encountered is that ion and solvent activity are required, but prior sections established that one of applications of the MSA serves this purpose well (93–95,108).

2.2. Diffusion of PFOA and PFOS in Literature

Despite the extensive body of work on the matter of diffusing electrolytes established by many authors across several decades, no ionic PFAS have been examined under this lens to the best of our knowledge. A likely cause is the striking lack of relevant thermodynamic data, such as osmotic coefficients, for even the most studied PFAS species (120). Another cause is certainly that the routine required to evaluate the diffusivity of ionic PFAS is cumbersome. Nonetheless, there are several studies that have made observations on the diffusion coefficients of PFOA and KPFOA in water. A majority measured self-diffusion coefficients rather than Fickian diffusion coefficients. For ease of discussion, the Fickian diffusivity will maintain the symbol D_{AB} whereas the self-diffusion coefficient will take on the symbol D^* .

Schaefer et al. used the capillary method of Cussler to measure room temperature D_{AB} for several PFAS in water, including PFOA and PFOS. Reported quantities for D_{AB} of PFOA and PFOS were $0.49 \pm 0.09 \times 10^{-5}$ and $0.54 \pm 0.04 \times 10^{-5}$ cm²/s, both within synthetic groundwater (121). Schaefer et al. stated that the result for PFOA was corroborated by an earlier study in which Nordstierna et al. found with NMR that the D^* of NaPFO at room temperature is $0.437 \pm 0.009 \times 10^{-5}$ cm²/s at a concentration of 10 mM in pure water (122). Ning et al. similarly found that D^* was $0.504 \pm 0.001 \times 10^{-5}$ cm²/s for PFOA at a concentration of 1000 mg/L (123). Schaefer et al. were the only authors of those mentioned to attempt to rationalize the results by modeling D_{AB} . The Wilke-Chang Equation was employed but did not adequately describe the data as remarked by the authors (121).

Gauthier and Mabury recently performed an investigation of D^* for 47 PFAS species, including PFOA and PFOS, using ¹⁹F DOSY-NMR (8). Findings of the study indicated that D^* of PFOA and PFOS vary appreciably with concentration, notably increasing in an exponential

fashion at higher concentrations. The increase in D^* is especially apparent above a surfactant concentration of 6 mM. This conflicts with the findings of Nordstierna et al. who observed only a small difference in D^* of NaPFO at concentrations of 10 and 20 mM (122). Also, D^* for 10 and 20 mM NaPFO that were measured by Nordstierna et al. (122) were much closer to the values of D^* found at highly dilute concentrations by Gauthier and Mabury (8). Gauthier and Mabury mentioned that the increase in diffusivity appears to occur as the CMC is approached, but a similar trend to PFOA and PFOS was shown for perfluorobutanoic acid (PFBA) which was well below its CMC in the observed range. One might speculate that a possible reason for the disagreement between (8) and (122) is the use of a 50 mM phosphate buffer in all samples which was meant to control pH (8). Another noteworthy result of Gauthier and Mabury is the change observed in D^* for PFOS and perfluoropentanoic acid (PFPeA) with NaCl concentration. D^* decreased for PFOS and PFPeA by approximately one order of magnitude going from 0 to 5% by weight NaCl at constant surfactant concentration. These observations were attributed simply to “ionic effects” by the authors (8).

2.3. Aggregation Behavior and Speciation of PFAS

Emphasis in this study is placed on diffusivity, but it is important to evaluate whether the diffusing species are in monomeric form or aggregated. Another consideration is that the association state of the monomer with its counterion can also influence diffusion (3).

Aggregation behavior of several surface-active PFAS, including the salts of PFOA and PFOS, have been studied by many authors (122,124–138). One of the most important metrics to describe the aggregation of surface-active PFAS, and all surfactants in general, is the critical micelle concentration (CMC). When the bulk concentration of surfactant exceeds the CMC the excess monomers spontaneously form micelles. CMCs are readily measured with several

methods. Surface tension measurements in our prior work allowed for us to determine the CMC of several surfactant plus supporting electrolyte systems by interpolating the concentration at which equilibrium surface tension no longer decreases with increasing surfactant concentration (11,71). The CMC can be observed by conductometry as well. Specific conductance of ionic surfactants increases with concentration, showcasing a constant linear slope until the CMC is reached. Above the CMC, the slope is lower than in the sub-CMC region owing to the lower mobility of micelles compared to their constituent monomers (139). Data measured above and below the CMC can be used to interpolate the CMC. Kancharla et al. showcased the dependence of the CMC of NH_4PFO on the concentration of urea utilizing conductometry (137). Tamaki et al. in a similar fashion compared the CMC of 5 salts of perfluorohexanesulfonic acid (PFHxS). The general trend observed was that the CMC decreased as the radial charge density of the cation decreased (133).

There are also many different shapes that micelles can take on (140). Micellar morphology depends on multiple factors, including the size and shape of the surfactant, temperature, surfactant concentration, and supporting electrolyte concentration/species. The array of morphologies is best demonstrated by Wang et al. who studied PFAS micelles with CryoTEM (130). Two select PFAS of interest, perfluorononanoic acid (PFNA) and the ammonium salt of PFOA (NH_4PFO), are shown in **Figure 2-1**.

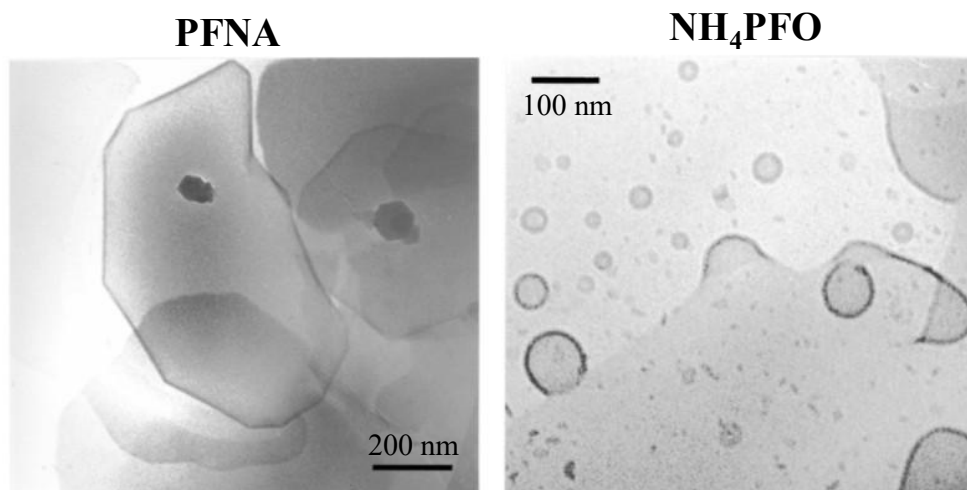


Figure 2-1. Bilayer, vesicular, and disklike micelles formed in a 1 wt% PFNA solution (left) and a 90 mM NH_4PFO solution with 150 mM NH_4Cl as the supporting electrolyte (right) (130).

Micelle shape and size can also be determined with small-angle X-ray scattering (SAXS) or small-angle neutron scattering (SANS). Several authors have used small-angle neutron and/or small-angle X-ray scattering on systems of the salts of PFOA and PFOS (124–126,131,138). Boden et al. used SAXS to describe how NH_4PFO transitions from spatially ordered disklike micelles to a lamellar phase arranged into regularly spaced layers upon decreasing temperature (131). Sanga et al. used SAXS to study the effect of the counterion on micellar morphology of PFOA. Mg^{2+} was found to induce the formation of long, cylindrical micelles whereas the micelles formed in the presence of Li^+ , Na^+ , and NH_4^+ were smaller by comparison (141). Inada et al. studied the structure of PFOS micelles with SAXS and SANS. The findings were that PFOS forms spherical core-shell micelles in water that have a radius of $18 \pm 3 \text{ \AA}$ with the core containing 10% water by volume (126). Unlike PFOS, Kancharla et al. along with several other authors treat the micellar cores of NH_4PFO and the cesium salt of PFOA (CsPFO) as being free of water (124,125,138).

Now onto discussion of the speciation of PFOA and PFOS. Acidic behavior of PFOA has been investigated by several authors (6,142–149). **Table 2-2**, which was reproduced from

Balasuryia et al. (6), encompasses the measurement techniques and the corresponding pK_a values measured for PFOA.

Table 2-2. pK_a values of PFOA and the corresponding measurement method. Reproduced from reproduced from Balasuryia et al. (6).

Study	pK_a of PFOA	Method
Balasuryia et al. (2025) (6)	-0.27±0.18	^{19}F NMR
López-Fontán et al. (2005) (147)	1.306	Conductometry
Musegades et al. (2024) (148)	2.2	Surface Tension
Burns et al. (2008) (143)	3.8	Potentiometry
Vierke et al. (2013) (149)	0.5	Vapor Phase Measurement
Cheng et al. (2009) (144)	<1.0	ESI-MS
Brace et al. (1962) (142)	2.8	Differential Refractometry
Igarashi et al. (1992) (146)	1.01	Phase Separation
Kim et al. (2020) (145)	0.96	Vapor Phase Measurement

Overall, measured pK_a values of PFOA range from -0.27 to 3.8 with the median being 1.01.

According to most authors, the implication is that PFOA is nearly completely ionized at most pH values. Yan et al. performed conductometry experiments on KPFOS that showcased a strong linear dependence of specific conductance on concentration which implies no association between K^+ and PFOS^- (150). The possibility of dimer formation should also be investigated. Cheng et al. found evidence of dimers mediated by proton-bridging for PFOA whereas PFOS was not found to dimerize (144).

2.4. Research Gaps

Review of available literature has revealed that Fickian diffusion characteristics PFOA and PFOS have not been adequately described. Some authors studied the effect of supporting electrolyte composition on diffusivity but either did not systematically approach the effect or did not offer up a satisfactory explanation (8,121). No attempts to model D_{AB} of any PFOA or PFOS salt as single components, let alone in mixtures with other electrolytes, using Equations 19 and 20 have been made to the best of the author's knowledge. It is necessary to take account for how speciation or aggregation could influence the diffusivity of PFOA and KPFOS, especially in sub-CMC concentrations because they are more environmentally relevant (8). Several studies have already made important conclusions regarding the micellization behavior of the salts of PFOA and PFOS but less have investigated the possibility of dimerization. Electrolyte effects on the diffusivity of PFOA and PFOS are also poorly understood, especially through the lens of ion identity, which is important because natural waters across the globe vary widely in composition (2). Addressing these research gaps are essential to adequately describe, or better yet predict, D_{AB} for PFOA and PFOS.

Chapter 3. Materials and Methods

3.1. Materials and Sample Preparation

KPFOS (heptadecafluorooctanesulfonic acid potassium salt, purity $\geq 98.0\%$, CAS: 2795-39-3) and PFOA (perfluorooctanoic acid, purity 95%, CAS: 335-67-1), sodium dodecyl sulfate (SDS) (purity $\geq 99.0\%$, CAS: 151-21-3), potassium chloride (KCl) (purity $\geq 99.5\%$, CAS: 7447-40-7), and lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$) (purity $\geq 99.0\%$, CAS: 1310-66-3) were purchased from Sigma-Aldrich. Sodium chloride (NaCl) was purchased from Fisher BioReagents (purity $\geq 99.0\%$, CAS: 7647-14-5). Calcium chloride (CaCl_2) (purity 97%, CAS: 10043-52-4), magnesium chloride (MgCl_2) (pure, CAS: 7786-30-3), and deuterium oxide (D_2O) (99.8 atom % D, CAS: 7789-20-0) were purchased from Thermo Scientific. Barium chloride dihydrate ($\text{BaCl}_2\cdot 2\text{H}_2\text{O}$) (purity $\geq 99.0\%$, CAS: 10326-27-9) and acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) (glacial, purity $\geq 99.0\%$, CAS: 64-19-7) were purchased from Alfa Aesar. Lithium chloride (LiCl) (purity 99.0%, CAS: 7447-41-8) was purchased from Acros Organics. LiCl , NaCl , KCl , MgCl_2 , and CaCl_2 were dried under vacuum at 80 °C for 24 hours before use. All other chemicals were used as received without further purification.

All solutions were prepared in ultrapure deionized water having a resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$ or higher from a Millipore Direct-Q® 3 Remote Water Purification System. One liter stock samples of 3000 ppm PFOA and 600 ppm KPFOS were prepared in polypropylene reagent bottles and stirred for at least 72 hours before use. Subsequent dilutions from these stock solutions were used to prepare lower concentration PFOA or KPFOS samples. After dilution, if necessitated, the appropriate amount of supporting electrolyte was added directly and stirred for at least 30 minutes prior to measurement.

10% D₂O by volume was incorporated into all NMR samples as the lock solvent. 0.01 M LiOH·H₂O was used in one set of samples to shift the pH of PFOA solutions to investigate the relationship between diffusivity and degree of ionization.

200 mM acetic acid and 82 mM SDS solutions were prepared in volumetric flasks and stirred for 24 hours prior to conductometry measurements.

3.2. Surface Tension

An optical tensiometer (Attension KSV Instruments, Biolin Scientific, Finland) was employed to measure dynamic surface tension. The droplet was contained within a quartz cuvette that was partially filled with deionized water and sealed with ParaFilm®. This was done to prevent evaporation of the droplets under observation from occurring. Droplet volumes as a function of time for both 100 ppm PFOA trials can be seen in **Figure A-1** in **Appendix A**. The results show that droplet volumes did not vary significantly through the duration of the measurement.

Measurements were taken over the course of 1 hour and data was subsequently extrapolated to equilibrium with Equation 6 as described in our prior work (11). An example is shown in **Figure A-2** in **Appendix A**. Each sample composition was subjected to a minimum of two replicate tests to ensure the accuracy and reliability of the results.

3.3. ¹⁹F NMR

¹⁹F NMR spectra were acquired on a 500 MHz JEOL ECZL NMR instrument equipped with a 5 mm gradient inverse broadband Royal probe tuned to 470.5 MHz for fluorine. Temperature of the probe was held constant at 25 °C and 10 minutes of dwell time was allocated to allow for thermal equilibration of the sample. ¹⁹F NMR spectra were recorded with a single pulse excitation having a width of 4.7895 μs (45° flip angle). 16 scans were performed with a repetition rate of 4.203 s where 3.203 s were used for acquisition and 1 s for the relaxation delay.

MestReNova was used to analyze all spectra. Baseline correction was performed with Bernstein polynomials and phasing was manually corrected. The qNMR add-in was utilized to determine analyte concentration with conversion coefficients calculated from the average of 3 known concentration samples of PFOA (1500, 2000, and 2500 ppm PFOA) and KPFOS (300, 400, and 500 ppm KPFOS) with 2 repetitions at each concentration.

3.4. Small-angle X-ray Scattering

Samples were loaded via syringe into quartz capillaries with a nominal diameter of 1.5 mm and wall thickness of 0.01 mm (Charles Supper Company, Natick, MA, USA) before being sealed closed with epoxy. All solutions listed in **Tables 4-1** and **4-2** (barring the KPFOS and BaCl₂ mixtures) were examined with synchrotron X-ray scattering at Argonne National Lab. Exposure time was 500 ms. 2-D scattering profiles were azimuthal integrated to obtain 1-D scattering patterns.

3.5. Conductometry

3.5.1. Conductometry Measurements

Conductivity measurements were made on a Fisherbrand™ accumet™ XL200 Benchtop pH/Conductivity meter. The probe utilized was a Fisherbrand™ accumet™ temperature-compensated two-cell conductivity probe (cat. No. 13-620-200) with a cell constant of 1 cm⁻¹. The ideal range of this probe is 10 – 2000 μS/cm and measurements were made only within this range when possible. Standard solutions having conductivity values of 84 μS/cm and 1413 μS/cm were purchased from Environmental Express and used for calibration. All measurements were made with 2 repetitions at each concentration.

After the initial measurement of a concentrated sample, serial dilutions were made to reach the desired analyte concentrations. 60 seconds were allotted for the solutions to mix after

the diluting solution was added with continuous stirring used for the entire experiment duration. This was assumed to be enough time for samples to equilibrate based on a time-dependent trial observing the conductivity of KPFOS after dilution of a concentrated sample (see **Figure A-3** in **Appendix A**).

3.5.2. Modeling Conductivity with the Mean Spherical Approximation

Data collected from conductometry were utilized to study the aggregation or speciation of PFOA and KPFOS. The general approach used was fitting of equilibrium constants that dictate α_i in Equation 16 (repeated here for clarity)

$$\kappa = \frac{e^2}{k_B T} \sum_{i=1}^N \rho_i \alpha_i D_i^o z_i^2 \left(1 + \frac{\delta v_i}{v_i^o} \right) \left(1 + \frac{\delta k_i}{k_i} \right) \quad (16)$$

with all quantities except α_i being known. This is the same approach used by Durand-Vidal et al. in the study of sub-CMC aggregation occurring in alkaline ion decanoate solutions (89). Major Equations utilized in the calculations are the same as those presented by Roger et al. (92) and will be recounted herein, sparing some details.

δv_i is the electrophoretic correction to the velocity of species i and v_i^o is the velocity of species i within the externally applied electric field E

$$v_i^o = \frac{z_i e E D_i^o}{k_B T} \quad (27)$$

k_i is the electric force acting on species i and is simply

$$k_i = z_i e E \quad (28)$$

$\frac{\delta k_i}{k_i}$ can be found with

$$\frac{\delta k_i}{k_i} = -\frac{\kappa^2 e_k^2}{3} \sum_{p=1}^s \chi_k^p \sum_{j=1}^s \sum_{i=1}^s \frac{t_j \chi_j^p \mu_i (e_i \omega_i - e_j \omega_j)}{e_i e_j (\omega_i + \omega_j)} \frac{\sinh(\kappa \sqrt{q_p} \sigma_{ij})}{\kappa \sqrt{q_p} \sigma_{ij}} \left[\int_{\sigma_{ij}}^{\infty} r \exp(-\kappa \sqrt{q_p} \sigma_{ij}) h_{ij}^o dr \right] \quad (29)$$

where the distance of closest approach between two ions is

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (30)$$

and

$$\omega_i = \frac{D_i^o}{k_B T} \quad (31)$$

κ is the inverse Debye screening length, given by

$$\kappa = \sqrt{\sum_l \frac{\rho_l e_l^2}{\varepsilon_0 \varepsilon_r k_B T}} \quad (32)$$

with e_l being the charge of species l . The relative ionic strength is

$$\mu_i = \frac{\rho_i e_i^2}{\sum_{j=1}^s \rho_j e_j^2} \quad (33)$$

and the mean mobility at infinite dilution is

$$\bar{\omega} = \sum_{j=1}^s \mu_j \omega_j \quad (34)$$

with the transport number at infinite dilution being

$$t_j = \frac{\mu_j \omega_j}{\bar{\omega}} \quad (35)$$

q_p is given by

$$q_p = \sum_{i=1}^s \frac{\bar{\omega} t_i}{\omega_i + \alpha_p} \quad (36)$$

and χ_k^p given by

$$\chi_k^p = \frac{N_p \omega_k}{\omega_k^2 - \alpha_p^2} \quad (37)$$

where

$$\frac{1}{N_p^2} = \sum_{i=1}^s \frac{t_i \omega_i^2}{(\omega_i^2 - \alpha_p^2)^2} \quad (38)$$

α is a root within Equation 39, which has s roots

$$-2\bar{\omega}\alpha \sum_{i=1}^s \frac{t_i}{\omega_k^2 - \alpha^2} = 0 \quad (39)$$

that are bounded accordingly to

$$0 = \alpha_1^2 < \omega_1^2 < \alpha_2^2 < \dots < \alpha_s^2 < \omega_s^2 \quad (40)$$

The integral in Equation 29 can be approximated by

$$\int_{\sigma_{ij}}^{\infty} r \exp(-\kappa\sqrt{q_p}\sigma_{ij}) h_{ij}^{\circ} dr \approx -\frac{e_i e_j \kappa \sqrt{q_p} \sigma_{ij} \exp(-\kappa\sqrt{q_p}\sigma_{ij})}{4\pi\epsilon_0\epsilon_r k_B T [\kappa^2 q_p + 2\Gamma\kappa\sqrt{q_p} + 2\Gamma^2 - 2\Gamma^2 Y]} \quad (40)$$

where

$$Y = \frac{\sum_m^s \frac{\rho_m z_m^2}{(1 + \Gamma\sigma_m)^2} \exp(-\kappa\sqrt{q_p}\sigma_m)}{\sum_m^s \frac{\rho_m z_m^2}{(1 + \Gamma\sigma_m)^2}} \quad (41)$$

Now, turning to the electrophoretic correction,

$$\delta v_i = -\frac{eE}{3\pi\eta_o} \left(\mathcal{V}_i + \frac{\pi}{4} \sum_j \rho_j z_j \sigma_j^2 - \frac{\pi}{6} \sum_j \rho_j \sigma_j^3 \mathcal{V}_j \right) \quad (42)$$

where

$$\mathcal{V}_i = \frac{\Gamma z_i}{1 + \Gamma\sigma_i} + \frac{\pi}{2\Delta} \frac{P_n \sigma_i}{1 + \Gamma\sigma_i} \quad (43)$$

with Γ given by

$$4\Gamma^2 = \frac{e^2}{\varepsilon k_B T} \sum_{i=1}^s \rho_i \left(\frac{z_i - \frac{\pi}{2\Delta} P_n \sigma_i^2}{1 + \Gamma \sigma_i} \right)^2 \quad (44)$$

with P_n , Ω , and Δ given by Equations 45, 46, and 47 respectively

$$P_n = \frac{1}{\Omega} \sum_{k=1}^s \frac{\rho_k \sigma_k z_k}{1 + \Gamma \sigma_k} \quad (45)$$

$$\Omega = 1 + \frac{\pi}{2\Delta} \sum_{k=1}^s \frac{\rho_k \sigma_k^3}{1 + \Gamma \sigma_k} \quad (46)$$

$$\Delta = 1 - \frac{\pi}{6} \sum_{k=1}^s \rho_k \sigma_k^3 \quad (47)$$

The model encompassed by Equations 16 and 27-47 will be referred to for the remainder of the work as the MSA transport model for clarity. Primary inputs to the MSA transport model are charge (z_i), number densities (ρ_i), diffusion coefficients at infinite dilution (D_i^o), and ionic diameters σ_i . D_i^o was determined with Equation 15 with the limiting ionic molar conductivity values given by Robinson and Stokes for H^+ , Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , the acetate ion, the benzoate ion, and Cl^- (3). Limiting ionic molar conductivity values were measured for species relevant to this study, which were the PFO-, PFOS-, the dodecyl sulfate ion. For these species, the most consistent treatment of the diameter is to use the Stokes-Einstein equation

$$D_i^o = \frac{k_B T}{6\pi\eta r_h} \quad (48)$$

where the hydrodynamic radius (r_h) is half of the ionic diameter. Diameters for the acetate and benzoate ions were found in the same way. Radii for the remaining species were taken from Boroujeni et al. (15).

3.6. ^{19}F DOSY-NMR

^{19}F DOSY-NMR spectra were acquired on the same instrument detailed in **Section 3.3**. The pulse sequence selected was the bipolar pulse pair stimulated echo. The pulsed-field gradient strength was arrayed from 10 to 280 mT/m in 16 steps. Pulse gradient time and diffusion time were set to 2 and 200 ms, respectively. 90° pulse width was $9.579\ \mu\text{s}$ with a relaxation delay of 1 s and acquisition time of 3.165 s. 16 scans were used at each gradient strength for all PFOA samples. 16 scans were used for KPFOS samples with supporting electrolyte concentrations less than 50 mM. 32 scans were used for KPFOS samples with supporting electrolyte concentrations greater than or equal to 50 mM. Data were analyzed to deduce D^* using the Stejskal–Tanner equation within MestReNova. The Stejskal–Tanner equation (151) is

$$I = I_o e^{-D^* \gamma^2 g^2 \delta^2 (\Delta - \frac{\delta}{3})} \quad (49)$$

with I_o representing the signal intensity at zero gradient strength, γ representing the gyromagnetic ratio of the fluorine nuclei, g representing the gradient strength, δ representing the diffusion gradient length, and Δ representing the diffusion time.

3.7. Modeling Thermodynamic Non-idealities with the Mean Spherical Approximation

Simonin et al. developed the BIMSA model in a series of three publications (93–95). The extent of the discussion is lengthy, and so only essential features of the model are discussed. Anions are treated as having a constant diameter which is equal to that of their crystallographic diameters. Hard sphere diameters of cations are considered to decrease with salt concentration since amount of water available to hydrate the ions becomes scarce as salt concentrations increase. This is reflected by

$$\sigma = \sigma^{(0)} + \sigma^{(1)}C_s \quad (50)$$

where $\sigma^{(0)}$ is the cation diameter at infinite dilution, $\sigma^{(1)}$ is the salt-specific size decay parameter, and C_s is the concentration of salt species s . In this way, the specificity of $\sigma^{(1)}$ for each given salt incorporates hydration of the anion species indirectly. Permittivity is also treated as decreasing with increasing salt concentration by

$$\varepsilon = \frac{\varepsilon_0}{1 + RC_s} \quad (51)$$

where ε_0 is the permittivity of pure water and R is the permittivity decay parameter specific to a given salt. The electrostatic interaction strength is characterized by the Bjerrum length, which is

$$\lambda = \frac{\beta e^2}{4\pi\varepsilon_0\varepsilon_r} \quad (52)$$

with $\beta = 1/(k_B T)$. The reduced charge of species i is

$$z'_i = \frac{z_i - \eta\sigma_i^2}{1 + \Gamma\sigma_i} \quad (53)$$

with η being

$$\eta = \frac{\pi}{2\Delta} P_n \quad (54)$$

where variables have the same meaning as in **Section 3.5.2** and the screening parameter (Γ) is given by Equation 44. For a non-associating electrolyte

$$\frac{\Gamma}{\pi\lambda} = \sum_i \rho_i (z'_i)^2 \quad (55)$$

Electrostatic internal-energy density is

$$\beta\Delta E_o^{MSA} = -\lambda \sum_i \rho_i z_i \frac{\Gamma z_i + \eta \sigma_i}{1 + \Gamma \sigma_i} \quad (56)$$

By summing the electrostatic internal-energy density, the screening contribution, and the Carnahan-Starling hard sphere contribution

$$\beta\Delta A = \beta\Delta E_o^{MSA} + \frac{\Gamma^3}{3\pi} + \beta\Delta A^{HS} \quad (57)$$

the excess Helmholtz free energy is found. The result allows for the calculation of activity coefficients by

$$\ln \gamma_i = \left(\frac{\partial \beta\Delta A}{\partial \rho_i} \right)_{T, \rho_{j \neq i}} \quad (58)$$

as well as excess osmotic coefficients

$$\Delta\phi = \rho_t \left[\frac{\partial}{\partial \rho_t} \left(\frac{\partial \beta\Delta A}{\partial \rho_t} \right) \right]_{x_i} \quad (59)$$

and the osmotic coefficient is simply

$$\phi = 1 + \Delta\phi \quad (60)$$

In this way, the departure from ideal behavior for ion species in mixture can be explicitly predicted. Additionally, association can be accounted for by modification of Equation 57 (94).

As for the overall input parameters that are used, they are charge (z_i), number densities (ρ_i),

ionic diameters (σ_i), cation size decay parameters ($\sigma^{(1)}$) permittivity decay parameters (R), and thermodynamic equilibrium constants (K_a). Reasonable assumptions must be made in this situation regarding $\sigma^{(1)}$ and R since, to the authors knowledge, no studies have determined the experimental activity or osmotic coefficients of PFOA or KPFOS. It is assumed herein that $\sigma^{(1)}$ and R are both zero for PFOA and KPFOS. It is not expected that this will greatly impact the efficacy of the results since PFOA and KPFOS are relatively dilute in any given sample (on the order of 1 mM). This additionally means that cross terms corresponding to σ are also taken to be zero, but Simonin explicitly demonstrated that this also has a minimal impact on the efficacy of the results (93).

In the first paper (95) of the series, Simonin demonstrated that the model was capable of predicting activity coefficients with high accuracy. The second (93) and third (94) papers shifted focus to predicting osmotic coefficients and thus those data were used for the fit of $\sigma^{(1)}$ and R . Predictions made for the activity coefficients were noticeably worsened comparatively to paper 1 owing to the fit of osmotic coefficients (95). However, the osmotic coefficients predicted with parameters in the first paper (95) are much better in agreement with available experimental data (3) than the activity coefficients predicting using osmotic coefficient fit parameters. Since this was the case, it was selected to refit the activity coefficient data from Robinson and Stokes (3) corresponding to the lithium, sodium, potassium, magnesium, and calcium salts presented in the second paper (93). The refit was performed with the same stipulations described by Simonin and coworkers. Thermodynamic consistency is enforced between salts with the same cation and different anion by imposing that $\sigma^{(0)}$ must be a constant for a given cation. Results from the refit are graphically shown in **Figures A-4 through A-8 in Appendix A. Table A-1 in Appendix A** shows the refit parameters utilized herein for subsequent calculations as well as the absolute

average relative deviation between the model predictions and experimental data for activity and osmotic coefficients.

Chapter 4. Results and Discussion

4.1. Specific Ion Effects on Surface Tension

It is first useful to utilize dynamic surface tension measurements to reconcile the role that SIE play in the diffusion of PFOA and KPFOS. Keeping the concentration of both surfactant and supporting electrolyte constant, but changing the species of supporting electrolyte, a reverse Hofmeister series (80) emerges for PFOA.

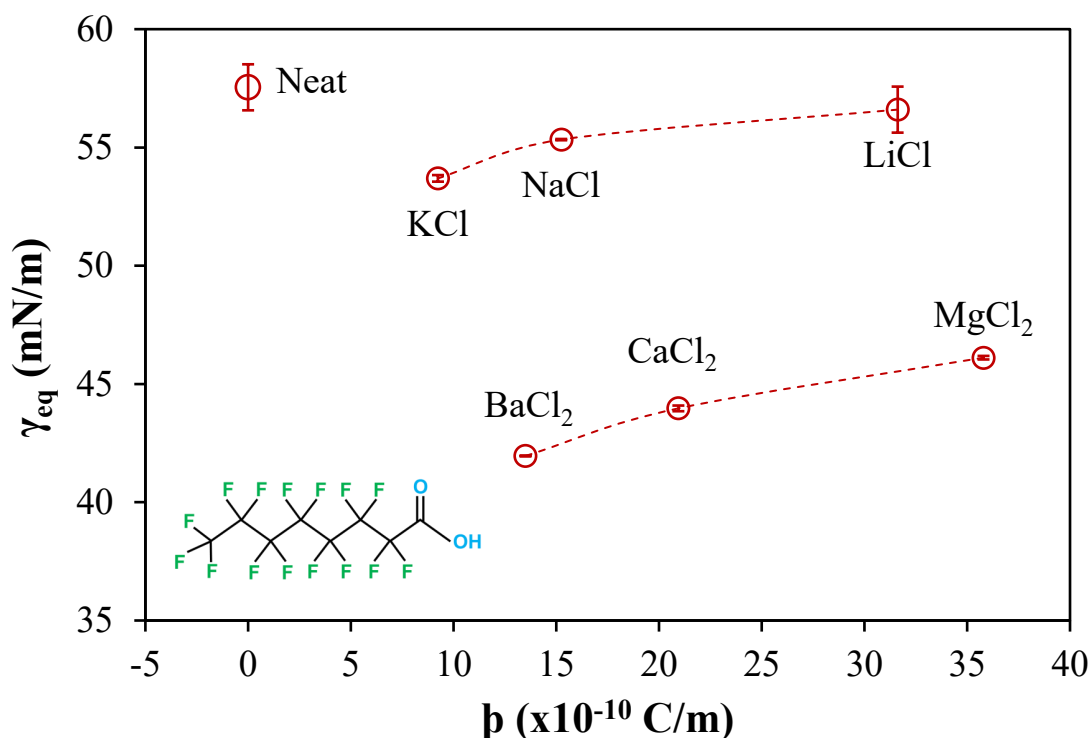


Figure 4-1. Room temperature equilibrium surface tension of 100 ppm PFOA + 0.1 M supporting electrolyte solutions. Error bars represent the standard deviation of 2 replicates. p represents the radial charge density of the cation of the supporting electrolyte and was taken from (7). Lines are to group the different series, mono- and divalent cations, together and guide the eye.

In all cases, the addition of supporting electrolyte lowers the equilibrium surface tension of PFOA. Charge screening at the interface is most likely responsible since the effect cannot be ascribed to a concentration gradient of the supporting electrolyte since its concentration is high in

all cases. The mono- and divalent electrolyte series are separated by a little over 10 mN/m due to the higher ionic strength of the divalent supporting electrolytes which increases hydrophobicity or rather induces “salting out” of PFOA. Beyond this, the radial charge density of the cation also clearly plays a role. The presence of charge diffuse cations, such as K^+ and Ba^{2+} , results in a lower surface tension at equilibrium compared to charge dense cations, such as Li^+ and Mg^{2+} . One plausible explanation for this trend is that charge diffuse cations have a similar affinity for water to that of the carboxylate group of PFOA. Collins remarks that ions with similar affinities for water are able to more easily form ion pairs (76). Although the carboxylate headgroup is sterically compact, its radial charge density may be reduced by the electron-withdrawing effect of the perfluoroalkyl chain (152). This would account for the better pairing of PFO^- with charge diffuse cations by comparison to charge dense cations.

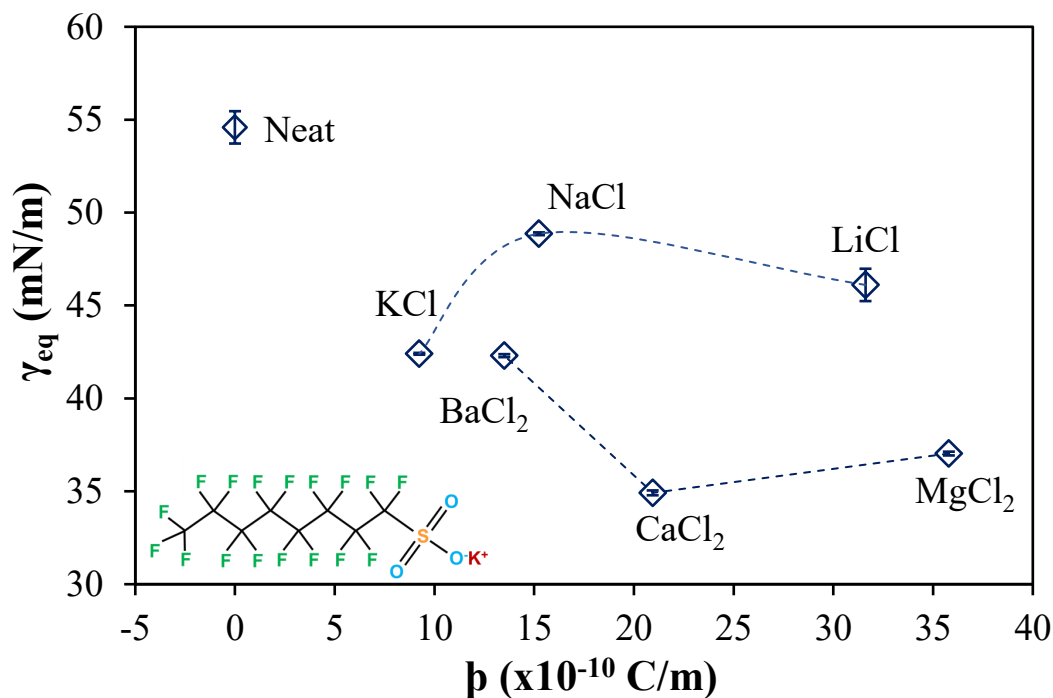


Figure 4-2. Room temperature equilibrium surface tension of 50 ppm KPFOS + 0.1 M supporting electrolyte solutions. Error bars represent the standard deviation of 2 replicates. ρ represents the radial charge density of the cation of the supporting electrolyte and was taken from (7). Lines are to group the different series, mono- and divalent cations, together and guide the eye.

General observations regarding the presence of electrolytes inducing charge screening as well as the higher ionic strength of the divalent salts inducing salting out are the same for KPFOS. But in contrast to the distinct Hofmeister series showcased by PFOA, the same series was not found for KPFOS. Most notably, the highest equilibrium surface tension in each series is observed with the presence of sodium or barium chloride. Interestingly, it appears that this coincides with the relatively similar radial charge densities of 13.50 and 15.24×10^{10} C/m (7) for Ba^{2+} and Na^+ , respectively.

An explanation based on radial charge density of the cations would not suffice to describe the trend in equilibrium surface tension for KPFOS, so an alternative is offered based on solubility. It is possible then that the sulfonate group in KPFOS has a similar affinity for water to sodium and barium which causes precipitation to occur. This would act to increase the equilibrium surface tension as some of the surfactant in the bulk solution is lost to precipitation. Direct observation of precipitates was made for the sample of 50 ppm KPFOS with 0.1 M BaCl_2 as supporting electrolyte. Precipitates were not visible to the eye for 50 ppm KPFOS with 0.1 M NaCl but warranted further investigation with a method capable of deducing changes in solubility. Fluorine NMR suits this purpose well.

4.2. Speciation and Solubility Detected with ^{19}F NMR

To further investigate SIE trends related to solubility ^{19}F NMR paired with quantitative NMR (qNMR) analysis were used. Spectral intensity in NMR is directly proportional to the concentration of nuclides present in the sample. Inasmuch, samples with known analyte concentration can be used to determine a conversion factor that relates intensity to concentration. Equation 61 showcases the relationship

$$C_i = CCF \frac{I_A}{N} \quad (61)$$

where C_i is the unknown concentration of analyte i , CCF is the concentration conversion factor, I_A is the absolute integral of the peak, and N is the number of nuclides in the peak.

Discussion will first focus on PFOA. The ^{19}F NMR spectra of PFOA at a concentration of 2500 ppm is shown in **Figure 4-3**.

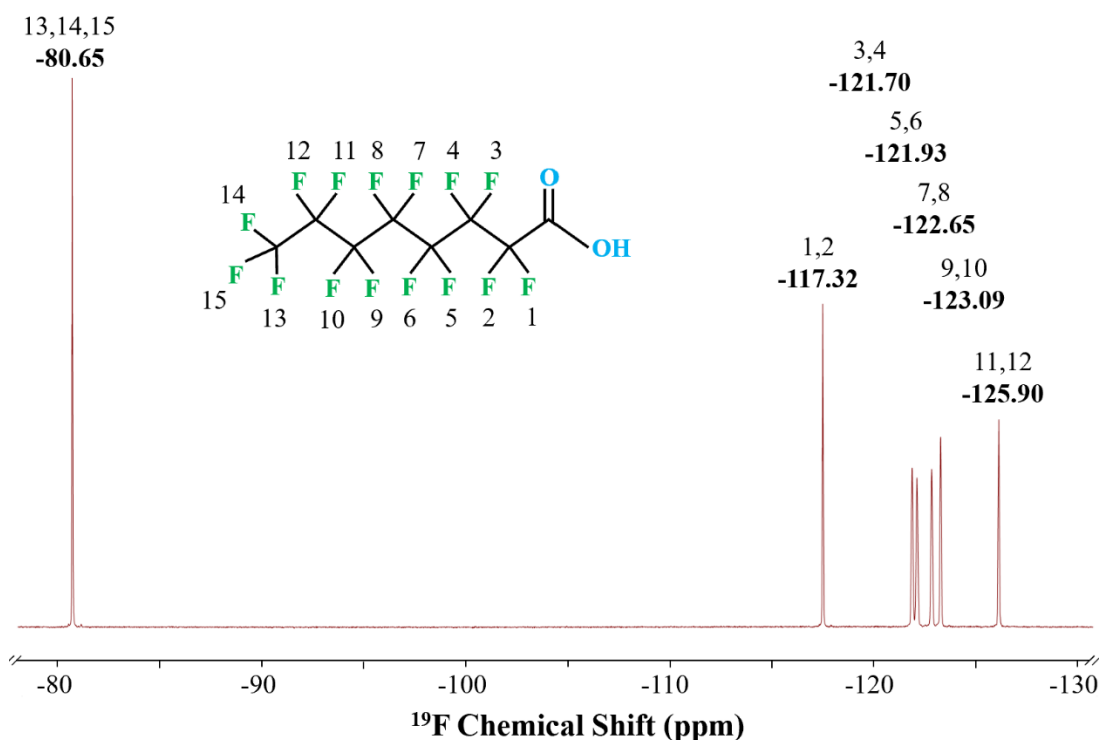


Figure 4-3. 1D ^{19}F NMR spectra of PFOA with peak assignments. Temperature was 25 °C.

Peak positions in **Figure 4-3** agree well with those that were found in prior studies (8,123).

Fluorines located on the terminal carbon in the fluorinated tail at a chemical shift of -80.65 have a noticeably more intense resonance compared to the upfield groups. For qNMR, the CF_3 - group was selected for integration since it has the highest intensity and can therefore be used for the most accurate measurement of PFOA concentration. Similarly, the CF_3 - group with a chemical shift of -80.64 was used for qNMR analysis of KPFOS solutions.

Careful preparation was required to ensure that precipitates were not incorporated into the NMR samples. A stock solution of 3000 ppm PFOA was diluted with water to prepare samples

at a concentration of 1111 ppm PFOA. Supporting electrolyte was then added directly and the solution was subsequently stirred for a minimum of 30 minutes. This time was given to allow precipitates to nucleate and sink to the bottom of the reagent bottle. Solution was then drawn from the top of the container and added into an NMR tube along with D₂O. A syringe filter was not utilized in this case as other authors have demonstrated that adsorption of PFAS to the filters can significantly impact experimental results (153,154). The final PFOA concentration was 1000 ppm in the NMR tubes if no precipitation had occurred. **Table 4-1** encompasses all of the PFOA samples that were studied with ¹⁹F NMR.

Table 4-1. A sample matrix of the PFOA samples studied with ¹⁹F NMR. ^aThe concentration of dissolved PFOA if no precipitation occurred.

Concentration of PFOA (ppm)	Supporting Electrolyte	Supporting Electrolyte Concentration (M)
100 500 1000 1500 2000 2500	None	0
1000 ^a	LiCl NaCl KCl MgCl ₂ CaCl ₂	0.001 0.0025 0.005 0.01 0.05 0.1 0.25 0.5

Results of the qNMR analysis on the changes in solubility of PFOA due to the presence of a supporting electrolyte are presented in **Figure 4-4**. Concentration was reported as reduced concentration, which is

$$C_R = \frac{C_s}{C_o} \quad (62)$$

with C_s representing the concentration of surfactant in the sample and C_o representing the initial concentration of PFOA before precipitation occurred (C_o was 1000 ppm for all PFOA samples).

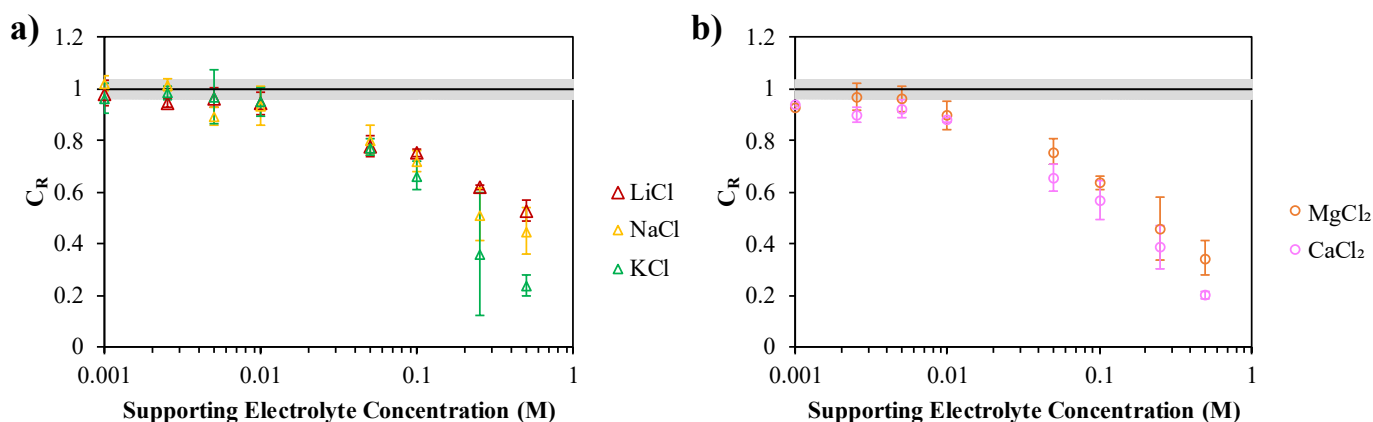


Figure 4-4. Changes in solubility of PFOA in response to supporting electrolyte concentration and species.

Concentration is represented with reduced concentration, C_r . The black line represents where no precipitation occurred with the gray bar representing the statistical error from qNMR. Error bars represent the standard deviation of 2 replicates. Temperature was 25 °C for all samples.

Given the error associated with the measurement, the onset of precipitation of PFOA begins for LiCl, NaCl, and KCl at approximately 10 mM supporting electrolyte concentration. The onset is at 5 mM for MgCl₂ and CaCl₂. Similar to the surface tension results in **Section 4.1**, there is a Hofmeister-like series that emerges in the extent of precipitation. On the basis of hydration, one may be led to believe that the charge dense ions, such as Li⁺ and Mg²⁺, that are more hydrated than their charge-diffuse counterparts (93) (see **Table A-1** in **Appendix A**) should salt out PFOA. Salting out would occur if the water was mostly occupied by the cation of the supporting electrolyte. This is seemingly a reasonable depiction since the average distance of separation between neighboring ions for monovalent electrolytes at the highest concentration used herein is approximately 11.8 Å⁻¹ (3). However, charge-diffuse cations decrease the solubility limit of PFOA to a greater extent than the charge-dense ions. Collin's law of matching water affinities can be used to rationalize the trend (76). The charge-diffuse cations are more readily able to pair

with PFO^- as a result of overlapping affinities for water. An examination of the results for KPFOS are now made to qualify this claim.

Table 4-2 encompasses the KPFOS samples that were studied with ^{19}F NMR.

Table 4-2. A sample matrix of the KPFOS samples studied with ^{19}F NMR. ^aThe concentration of dissolved KPFOS if no precipitation occurred. ^bMaximum concentration of BaCl_2 . ^cMaximum concentration of NaCl , KCl , and MgCl_2 . ^dMaximum concentration of LiCl and CaCl_2 .

Concentration of KPFOS (ppm)	Supporting Electrolyte	Supporting Electrolyte Concentration (M)
100 200 270 300 400 500	None	0
270 ^a	LiCl NaCl KCl MgCl ₂ CaCl ₂ BaCl ₂	0.001 0.0025 0.005 0.01 ^b 0.05 ^c 0.1 ^d

Results showing the change in solubility of KPFOS as a function of supporting electrolyte concentration and species are shown in **Figure 4-5**.

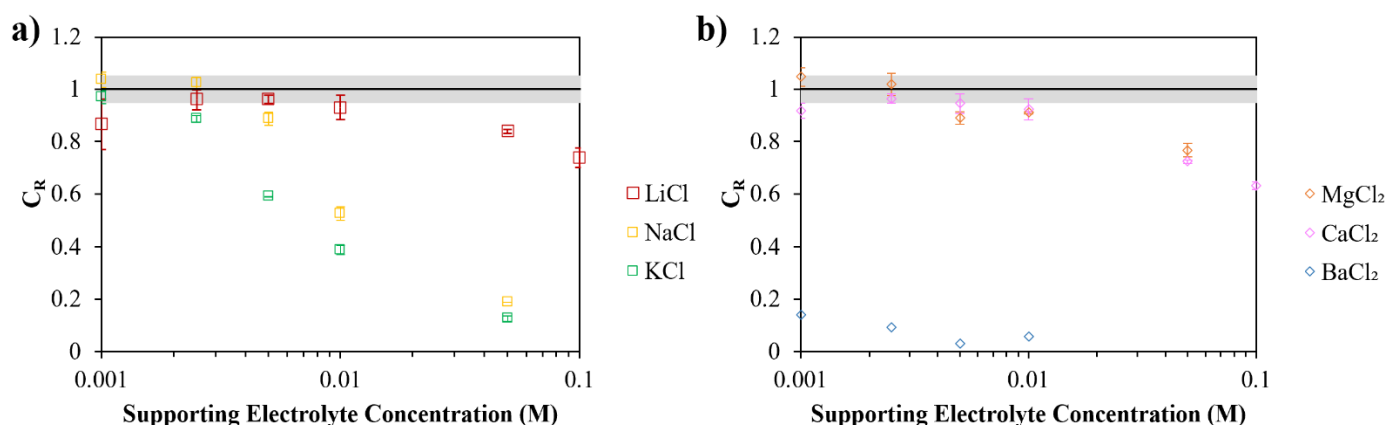


Figure 4-5. Changes in solubility of KPFOS in response to supporting electrolyte concentration and species. Concentration is represented with reduced concentration, C_R . The black line represents where no precipitation occurred with the gray bar representing the statistical error from qNMR. Error bars represent the standard deviation of 2 replicates. Only one replicate was performed for BaCl_2 . Temperature was 25 °C for all samples.

The solubility of KPFOS is markedly lowered in the presence of BaCl₂, even in highly dilute solutions. Furthermore, the solubility of KPFOS in 0.05 M NaCl is approximately 50 ppm and expected to be lower with 0.1 M NaCl. Earlier speculation that the maxima in equilibrium surface tension with sodium and barium chloride were the consequence of precipitation are now confirmed quantitatively. Trends observed for KPFOS related to the identity of the supporting salt bolster the claim that matching water affinity (76) of the ions controls solubility as opposed to salting out. This is most clearly demonstrated by the steep decline in the solubility of KPFOS in the presence of Ba²⁺ which is loosely hydrated by comparison to Mg²⁺ and Ca²⁺ (93).

In all ¹⁹F NMR spectra generated for PFOA solutions the only peaks present correspond to the fluorinated tail group. There are some additional peaks that appear in the spectra for KPFOS, however.

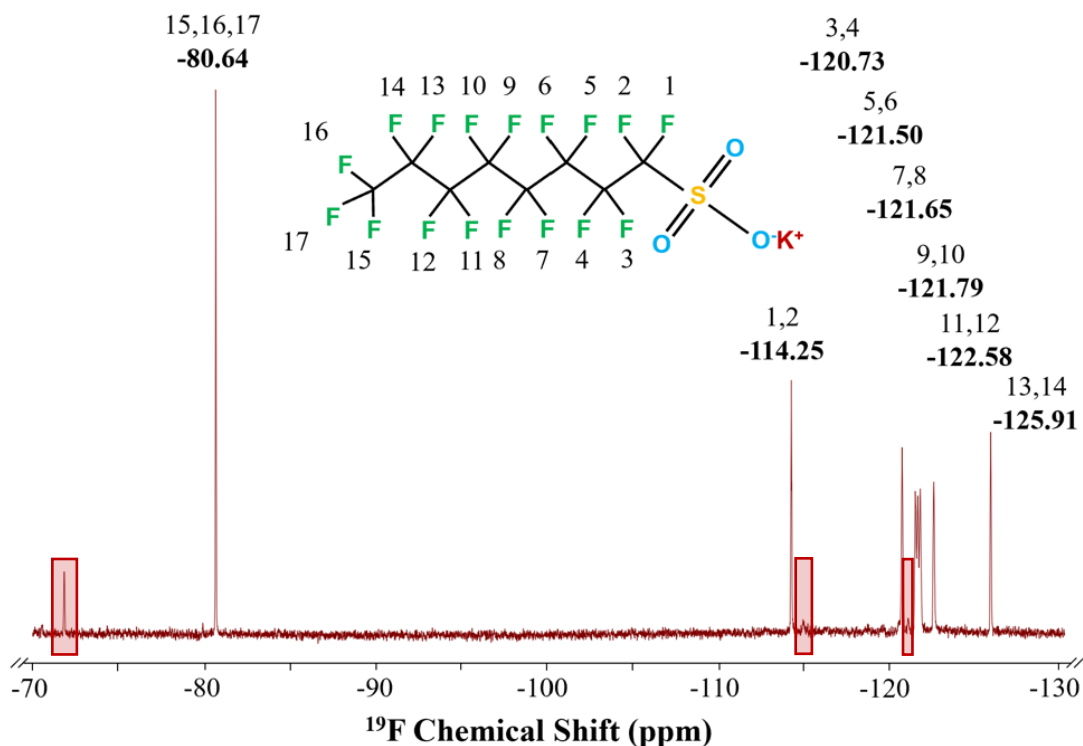


Figure 4-6. 1D ¹⁹F NMR spectra of KPFOS with peak assignments. Peaks that have not been assigned are boxed. Temperature was 25 °C.

3 unassigned peaks can be observed in a majority of the KPFOS ^{19}F NMR spectra. Intensity of the 3 peaks changes with the concentration of KPFOS but the peak with a chemical shift of -71.78 did not appear to respond as profoundly as KPFOS to the presence of supporting electrolytes. Because no further purification was performed on the KPFOS it is likely that at least one of the peaks is the result of residual impurities, but the peaks positioned at -114.43 and -121.10 are harder to discern as impurities. Micellization results in upfield shifts of monomeric peaks (155). Dimerization via cation bridging (144) also cannot be ruled out yet. The subsequent section addresses micellization as a possibility.

4.3. Aggregation Detection with SAXS

In the interest of determining if any of the solutions listed in **Tables 4-1** and **4-2** (barring the KPFOS and BaCl₂ mixtures) are micellar, synchrotron small-angle X-ray scattering was performed at Argonne National Laboratory's Advanced Photon Source. After background subtraction was performed, all spectra were either over-subtracted, or intensity did not depend on the scattering vector. The background subtracted spectra for 600 ppm KPFOS is shown in **Figure 4-7**.

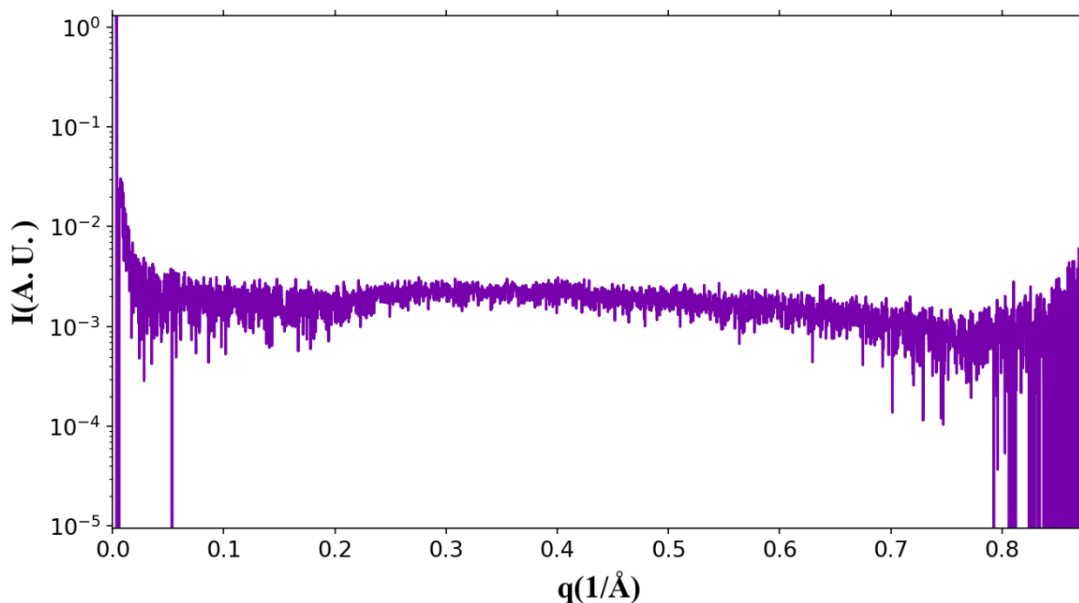


Figure 4-7. 1D scattering profile of 600 ppm KPFOS. Temperature was 25 °C.

The conclusion drawn was that none of the solutions examined are micellar.

4.4. Interpreting Speciation with Conductometry

Since the presence of micelles in the solutions being examined was ruled via SAXS, it must now be determined if dimerization occurs in any of the PFOA or KPFOS systems studied herein. Conductometry coupled with the MSA transport theory has been shown as a capable tool for studying such systems (89,90). The general procedure to examine systems that contain

associating or aggregating species is shown for two model species, acetic acid and sodium dodecyl sulfate, in **Appendix B**.

Perhaps the most important value to obtain for an electrolyte in conductometric studies is limiting molar conductivity. Given insight into the behavior of PFOA as a weak acid from literature, the limiting molar conductivity can be retrieved with Ostwald dilution law. **Figure 4-8** is the plot of the inverse molar conductivity with specific conductance for PFOA.

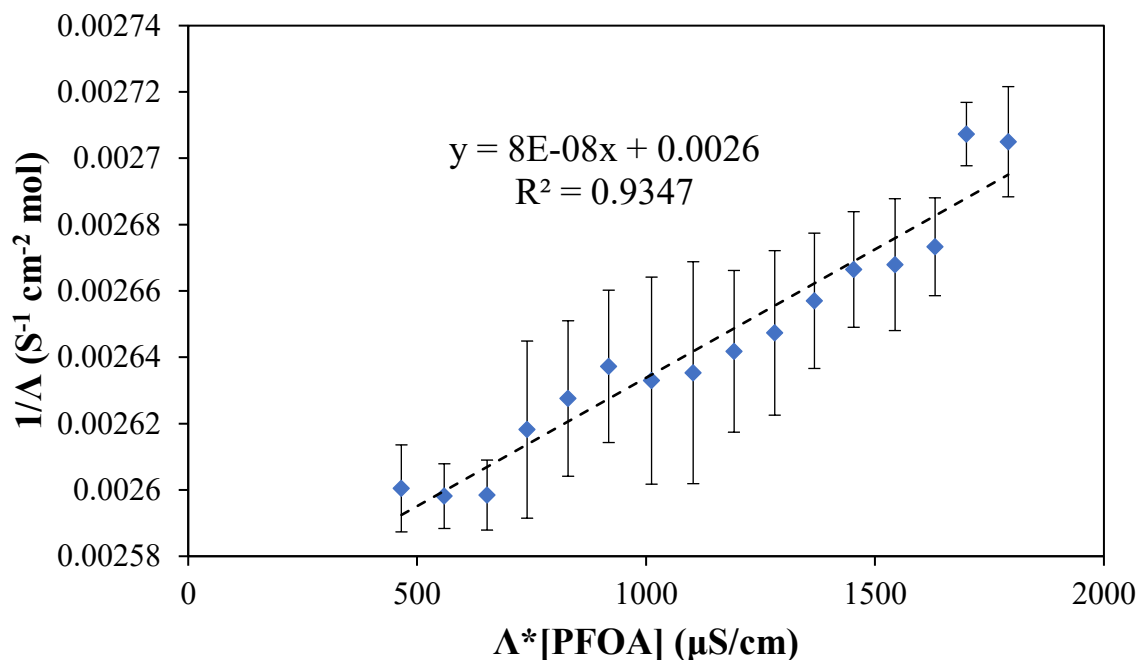


Figure 4-8. A plot of Ostwald's dilution law for PFOA. The intercept is the inverse of the limiting molar conductivity of PFOA.

A different treatment is needed for KPFOS. One can instead obtain the limiting molar conductance by extrapolation of molar conductivity to infinite dilution. The result is shown in **Figure 4-9**.

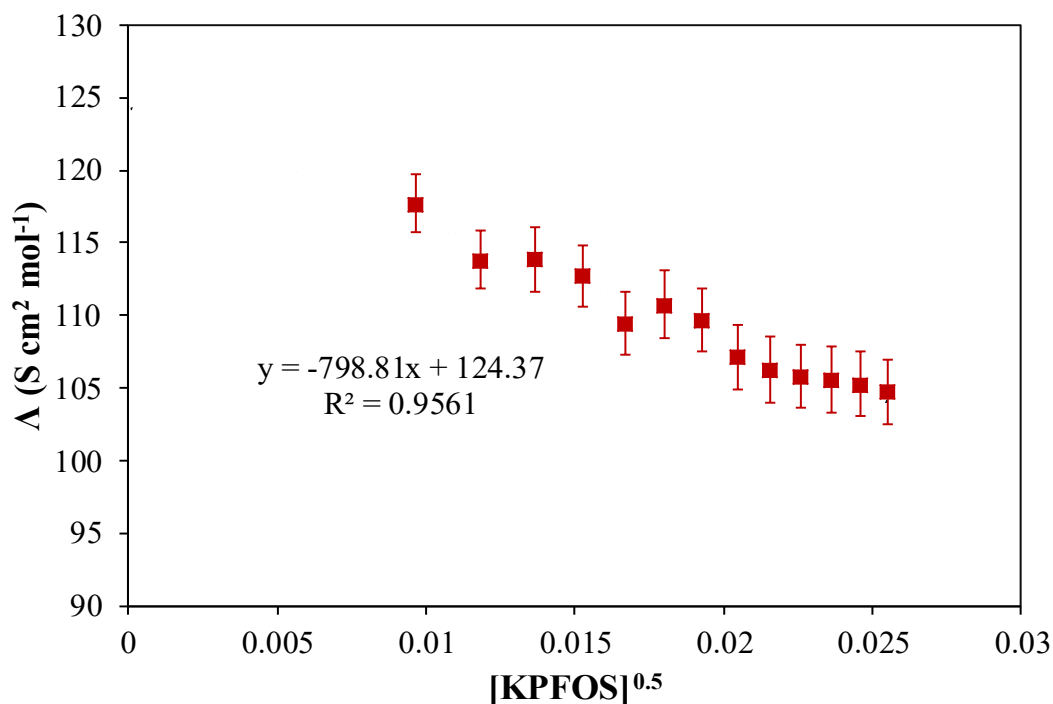


Figure 4-9. Extrapolation of the limiting molar conductivity of dilute solutions of KPFOS.

There are two subsequent values of interest that can be determined from limiting molar conductance. The first is the diffusivity at infinite dilution (D_i^o) with Equation 15. The second is the ionic radii (r_i) which is found from Equation 48 having obtained D_i^o . Subsequent calculations can then be done with these values in the MSA transport model to study speciation. It is worth mentioning that values of r_i obtained for polyatomic ions by the Stokes-Einstein equation are rather small but are self-consistent within the framework of the MSA model as mentioned by other authors (90). Application of the MSA transport model is shown for PFOA in **Figure 4-10**.

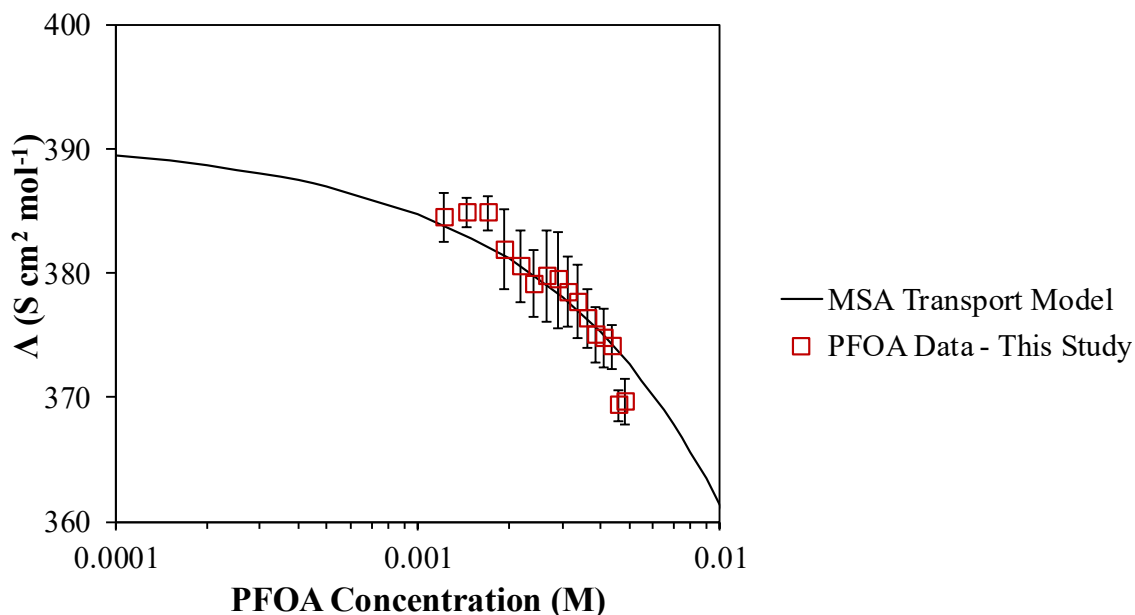


Figure 4-10. Application of the MSA transport model to PFOA. The line shown is the best fit with the fitting variable being the apparent equilibrium constant of PFOA. The corresponding pK_a value was 0.69.

From the fitting of the MSA transport model to the apparent equilibrium constant of PFOA, a pK_a value of 0.69 was obtained. An attempt was made to determine the thermodynamic equilibrium constant of PFOA from extrapolation of apparent K_a values at differing ionic strengths to infinite dilution (13). For this reason, several conductivity measurements were made on mixtures of PFOA and supporting electrolytes. Upon fitting of this data, it was apparent that a systematic error occurred since all experimental conductivity values were approximately 50 $\mu\text{S}/\text{cm}$ higher than that of the model, even considering the degree of ionization equal to 1. Nonetheless, the results in Figure 4-10 are at least telling of the physicochemical profile of PFOA as a weak acid with no evidence found for the formation of dimers.

Difficulty was also found in the interpretation of the results from the fitting for KPFOS. Two different versions of the MSA transport model, corresponding to weak and strong electrolytes, are plotted against the molar conductivity data for KPFOS in **Figure 4-11**.

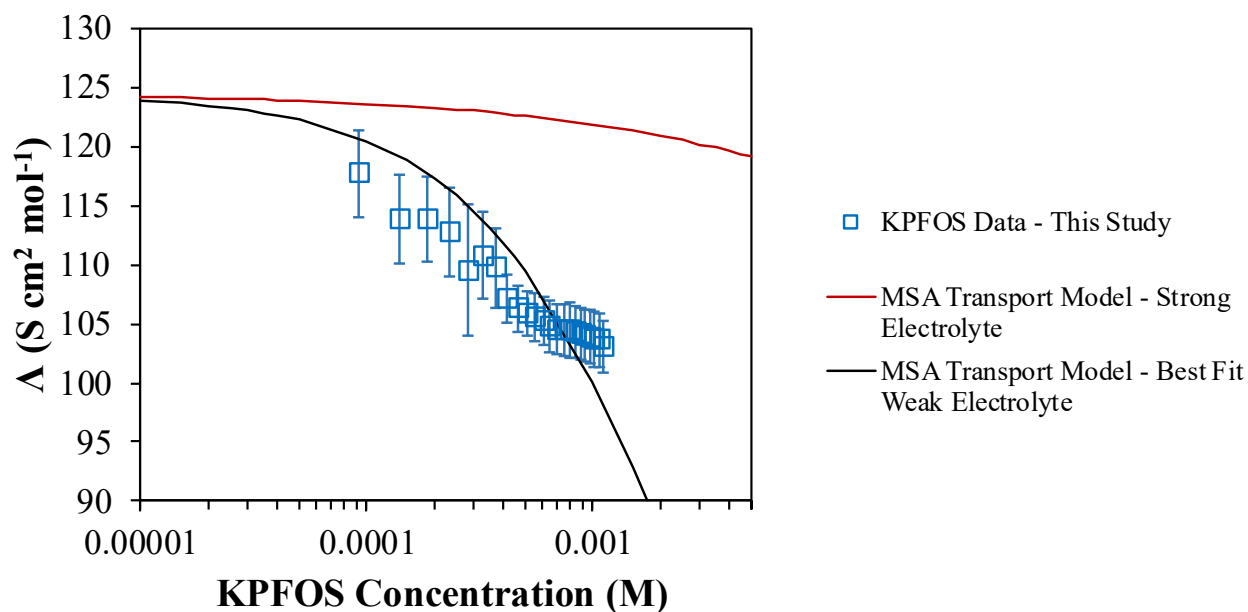


Figure 4-11. Application of the MSA transport model to KPFOS. The lines shown are MSA transport model predictions corresponding to the scenarios in which KPFOS is a strong electrolyte and weak electrolyte.

A lack of goodness-of-fit is indicative that KPFOS does not behave simply as a strong or weak electrolyte. The inflection of molar conductivity upward at high concentrations is most often observed in micellar systems past the CMC (89). At this point in the study, it has already been made apparent with X-ray scattering that none of the systems studied herein are micellar in nature. Additionally, the Krafft point temperature of KPFOS has been reported to be 80 °C (133). In an effort to better understand whether dimerization was occurring, a simple equilibrium condition of PFOS^- interchanging with its charged dimeric form, 2PFOS^{2-} , was also attempted to fit to the experimental data, but without success. This observation has not been made in the available literature to the best of the author's knowledge.

4.5. Specific Ion Effects on Self-Diffusion

The influence of specific ion effects on the self-diffusivity of PFOA and KPFOS was quantified with ^{19}F DOSY-NMR. Selection of which resonance to use for measurement of D^* was done so

based on statistical significance. Similar to the qNMR analysis in **Section 4.2**, it was found that the CF₃- moiety of PFOA and KPFOS was the most suitable in this regard. Dependence of D^* on PFOA concentration is examined in **Figure 4-12**.

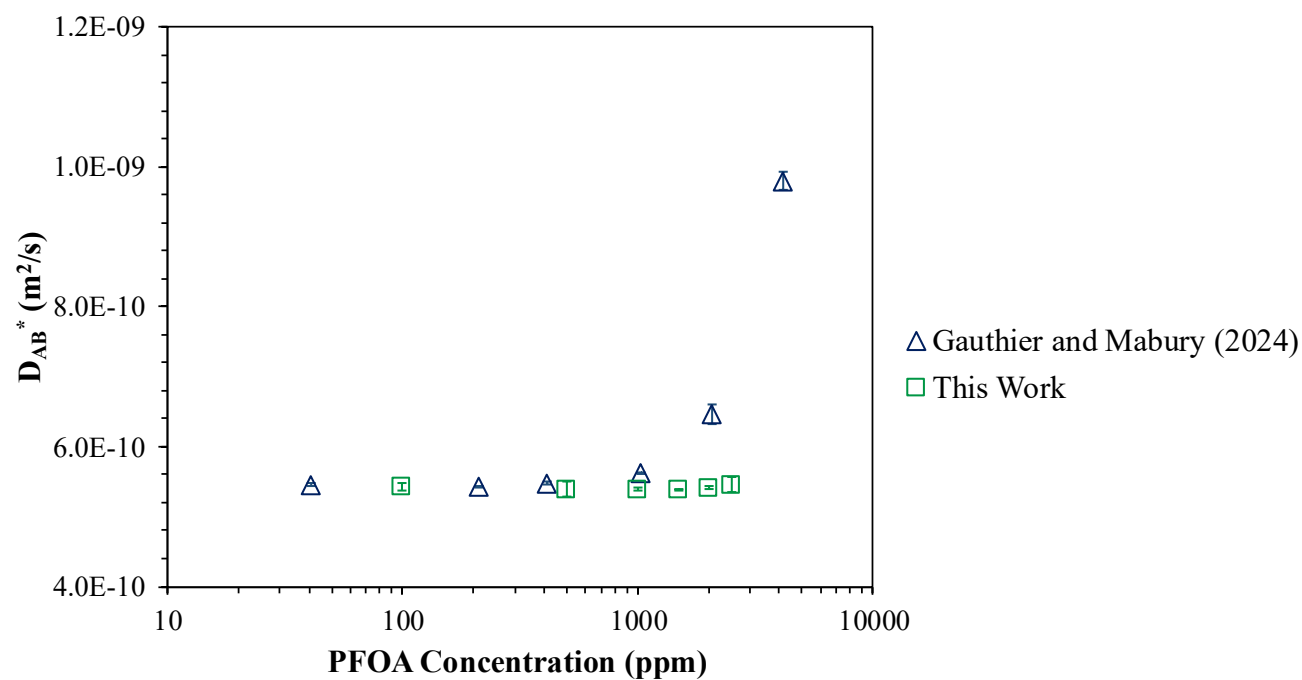


Figure 4-12. Dependence of D^* on concentration of PFOA. Data from this study is compared to that of Gauthier and Mabury (2024) (8). Error bars represent the standard deviation of 2 replicates. Temperature was 25 °C.

and **Figure 4-13** shows the dependence of D^* on concentration for KPFOS.

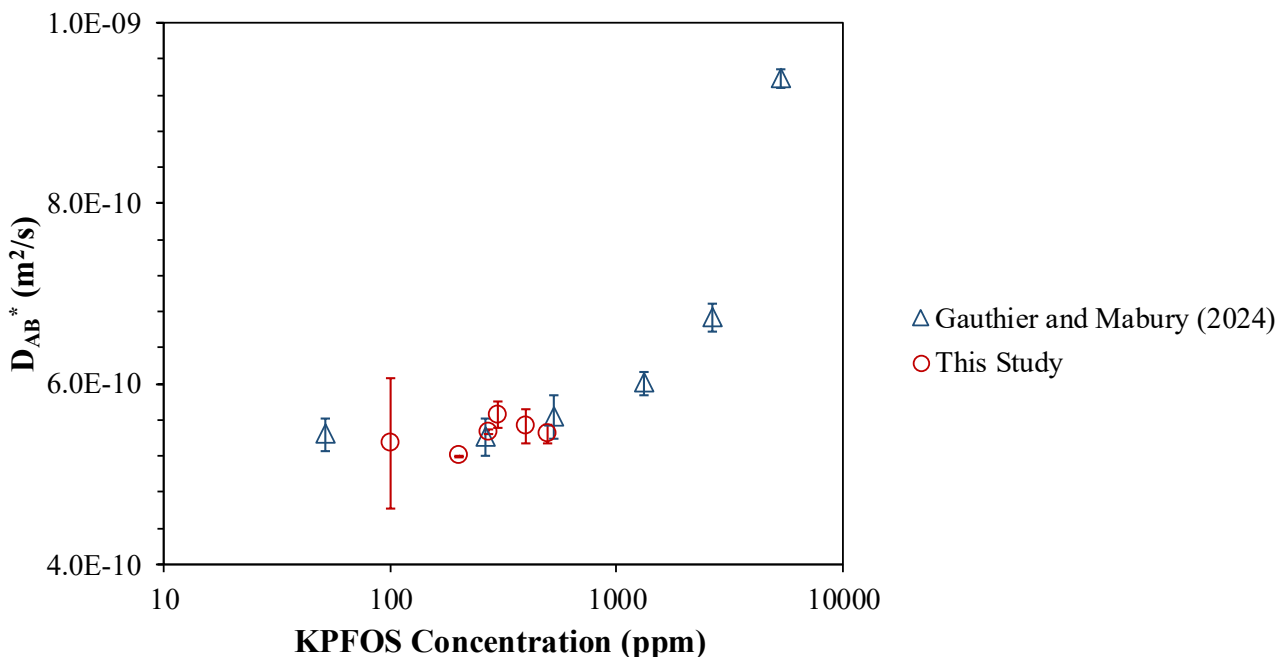


Figure 4-13. Dependence of D^* on concentration of KPFOS. Data from this study is compared to that of Gauthier and Mabury (2024) (8). Data from (8) was for the the acidic form of PFOS rather than KPFOS. Error bars represent the standard deviation of 2 replicates. Temperature was 25 °C.

D^* values at low concentrations of PFOA are within experimental agreement between this study and (8) but a differing trend is observed at higher concentrations. The same is true of KPFOS, but some caution is needed in the comparison since Gauthier and Mabury utilized the acidic form of PFOS rather than KPFOS. Discussion in the **Literature Review Section** already pointed out that Nordstierna et al. (122) similarly did not observe D^* change significantly with concentration for NaPFO. The marked increase in D^* at high concentrations may be due to the author's use of a pH buffer in all samples, but more investigation is necessitated to make that claim definitively.

Surfactant and salt concentrations utilized were the same as those reported in **Tables 4-1** and **4-2**. However, in some cases, the obtained values of D^* were not statistically viable. High concentrations of supporting electrolyte not only can cause line-broadening (8) but were also demonstrated to decrease solubility considerably in some cases in **Section 4.2**. One outcome was that all solutions of KPFOS with BaCl₂ could not be analyzed to determine D^* . Attention will be

drawn to other such cases as they appear. **Figure 4-14** shows the variation of D^* with supporting electrolyte species and concentration for PFOA.

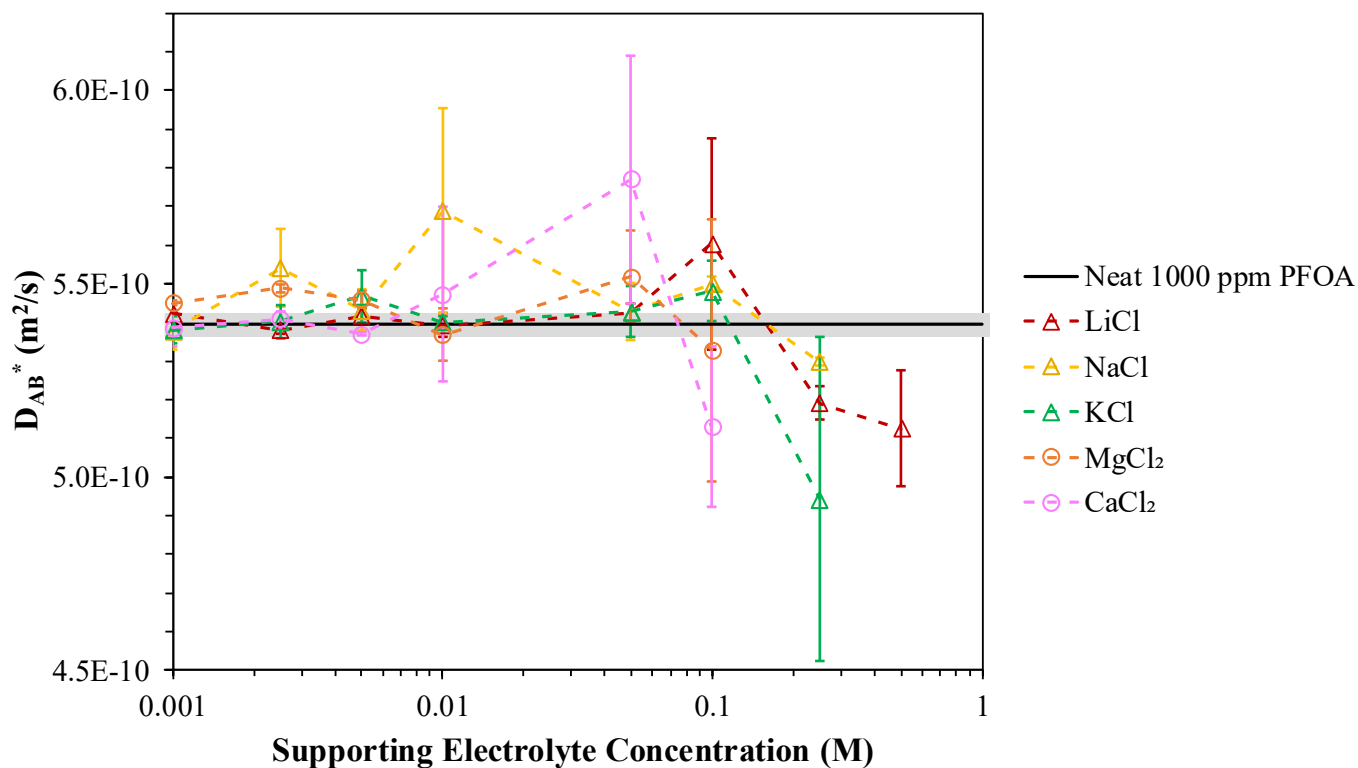


Figure 4-14. Dependence of D^* of PFOA on concentration and species of supporting electrolyte. Error bars represent the standard deviation of 2 replicates. Temperature was 25 °C. Lines are to help guide the eye. PFOA concentration was allowed to change from 1000 ppm from precipitation.

At a supporting electrolyte concentration of 5 mM and below, there is little change in D^* , except for a small increase with the presence of MgCl_2 . At a supporting electrolyte concentration of 10 mM and above, D^* appears to increase modestly but is followed quickly by sharp declines as 100 mM is approached. **Figure 4-15** shows the variation of D^* with supporting electrolyte species and concentration for KPFOS.

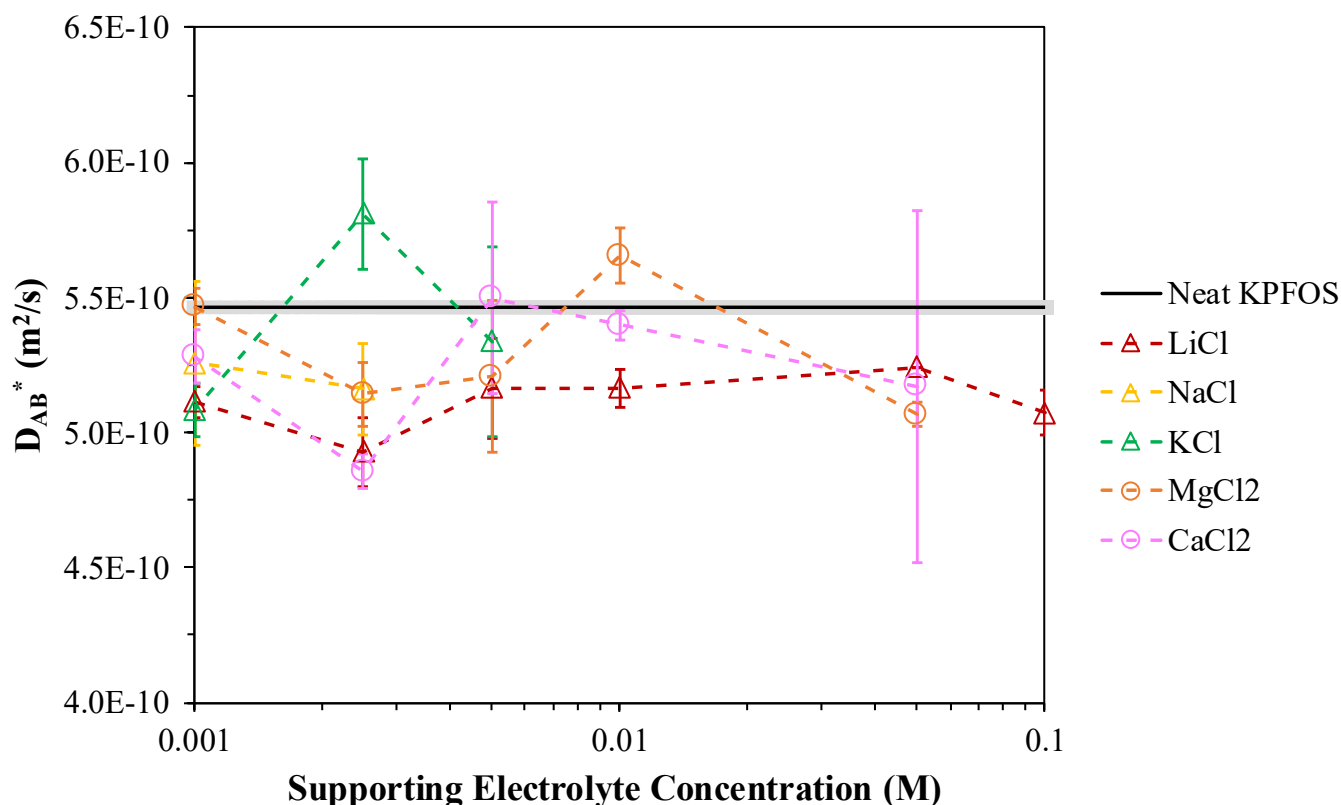


Figure 4-15. Dependence of D^* of KPFOS on concentration and species of supporting electrolyte. Error bars represent the standard deviation of 2 replicates. Temperature was 25 °C. Lines are to help guide the eye. KPFOS concentration was allowed to change from 270 ppm from precipitation.

Trends in D^* are more easily discernable for KPFOS. Introduction of small amounts of LiCl, NaCl, MgCl₂, and CaCl₂ all similarly cause a decrease in D^* before a slight increase is observed near the onset of insolubility. KCl was observed to increase the diffusivity of KPFOS at a concentration of 2.5 mM followed by a decline when solubility of KPFOS decreased. KCl and NaCl data sets had to be truncated due to poor intensity at higher field strengths.

The surface tension and solubility data showcased much more easily discernable trends owing to one primary mechanism whereas multiple effects are competing in the case of D^* . Nonetheless, it is clear that the net effect witnessed in mixtures of ions is that the speed of slower ions is increased whereas highly mobile ions are slowed down (9). It is useful to consider the relative rate at which the ions present in these systems move in the absence of any other ions.

The diffusion coefficients at infinite dilution for all species of interest have been listed in **Table 4-3**.

Table 4-3. Infinite dilution diffusivities for all the species comprising the ^{19}F DOSY-NMR samples. PFO^- and PFOS^- diffusivities at infinite dilution are from the conductivity data collected in this study, which were found to quantitatively agree with values evaluated from conductometry data of other authors within experimental error (147,156). All other values were taken from (3)

Species	$D_i^0 (\text{m}^2 \text{s}^{-1}) \times 10^9$
H^+	9.314
Cl^-	2.033
K^+	1.957
PFOS^-	1.355
Na^+	1.334
PFO^-	1.102
Li^+	1.028
Ca^{2+}	0.792
Mg^{2+}	0.706

Take first that the proton is the exception in this explanation owing to its ability to traverse the solution with the hopping mechanism rather than by Brownian motion (3). It is apparent that PFOS^- should intrinsically diffuse faster not only due to its high mobility, but also that it's K^+ counter ion is highly mobile. Mixtures of KPFOS and KCl have the highest overall diffusive potential which explains the peak value observed in **Figure 4-15**. It is also noteworthy that all the other supporting electrolytes would only serve to dampen the diffusivity of PFOS^- , which is seen occurring most prominently at concentrations of 2.5 mM. Changes in D^* for PFO^- with solution composition are not as remarkable likely due to the placement of PFO^- in the midrange

of mobilities. For both PFOS⁻ and PFO⁻ it appears that the onset of precipitation serves to decrease D^* . It becomes more important at these higher supporting electrolyte concentrations to consider that the viscosity of the solution is changing. However, low solubilities coupled with high line-broadening make the statistical significance of D^* not sufficiently high enough to allow for a thorough examination in this range.

4.6. Modeling Fickian Diffusion

As described in Section 2.3.1, Lieast et al. developed a predictive model for determination of Fickian diffusion coefficients in ternary electrolyte systems (9,10). Fundamentally, the model combines limiting ionic diffusivities with activity-derived thermodynamic factors from the model of Simonin (93–95), viscosity, hydration, and volume-flow corrections. Owing to rigorous treatment, this model can be utilized as a rational to check whether the assumptions made in the short time Ward-Tordai model are applicable to systems containing ionic surfactants. Only PFOA is examined under this lens. Some assumptions about the nature of PFOA are made to employ the model, which include that the surfactant is in low enough concentration as to not affect the density and permittivity of water and that it is entirely ionized. Also, PFO⁻ is treated as constant diameter ion rather than being assigned a size decay parameter that is a function of concentration. The number of hydrating waters for each salt under investigation is required by the model and for PFOA was assumed to be equal to that of NH₄PFO which has 11 hydrating waters (157). Changes in solution density and viscosity were taken to only arise from the presence of the supporting electrolyte. Density data was taken from (12) and Dole-Jones parameters were taken from (158–160). Since the primary equations of the model were already recounted from (9,10) in **Section 2.3.1**, and having stated the necessary assumptions, the results of Figure 4-16 may be discussed.

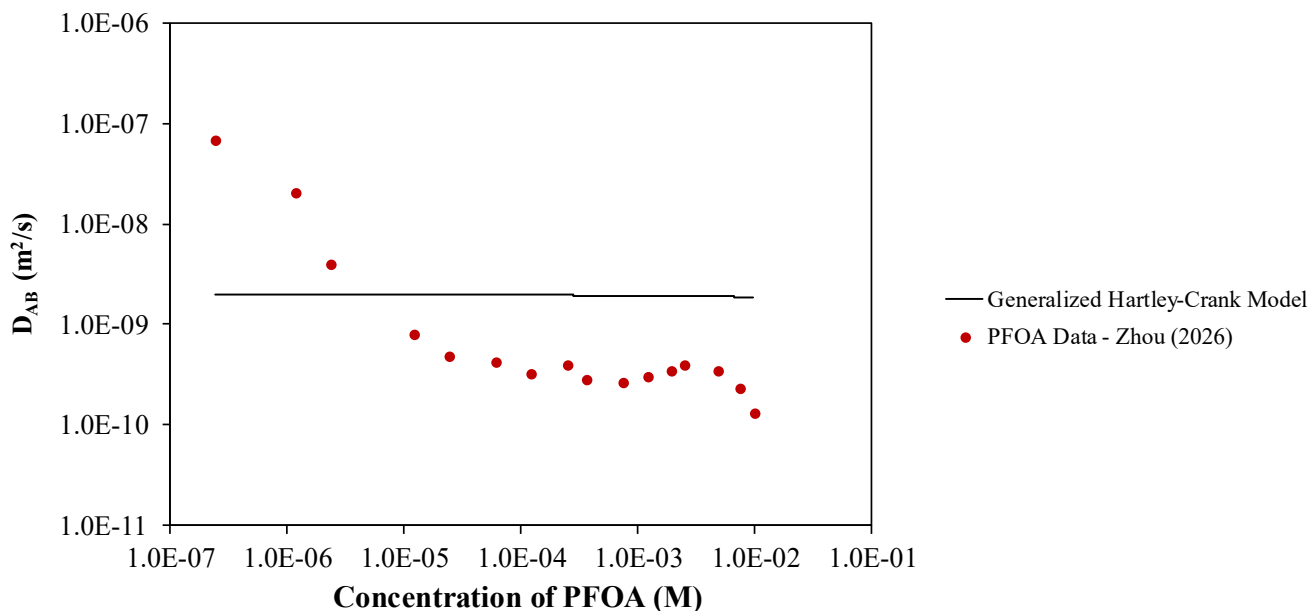


Figure 4-16. A comparison of Fickian diffusion coefficients measured via bubble pressure tensiometry with predictions from the generalized Hartley-Crank model developed by Lieast et al. (9,10). Data was originally reported in our work (11).

The apparent diffusion coefficients obtained from bubble pressure tensiometry decreased sharply with increasing PFOA concentration at the dilute end of the investigated range before reaching a comparatively stable region at intermediate concentrations. The exceptionally large coefficients obtained at the lowest concentrations are unlikely to represent corresponding increases in the intrinsic Fickian diffusivity, because the dilute-limit coefficient is expected to approach a finite value, which is predicted by the model. The decrease in diffusivity observed in the highest concentrations likewise are likely not representative of a change in the intrinsic Fickian diffusivity. A case where supporting electrolytes are present is considered in **Figure 4-17**.

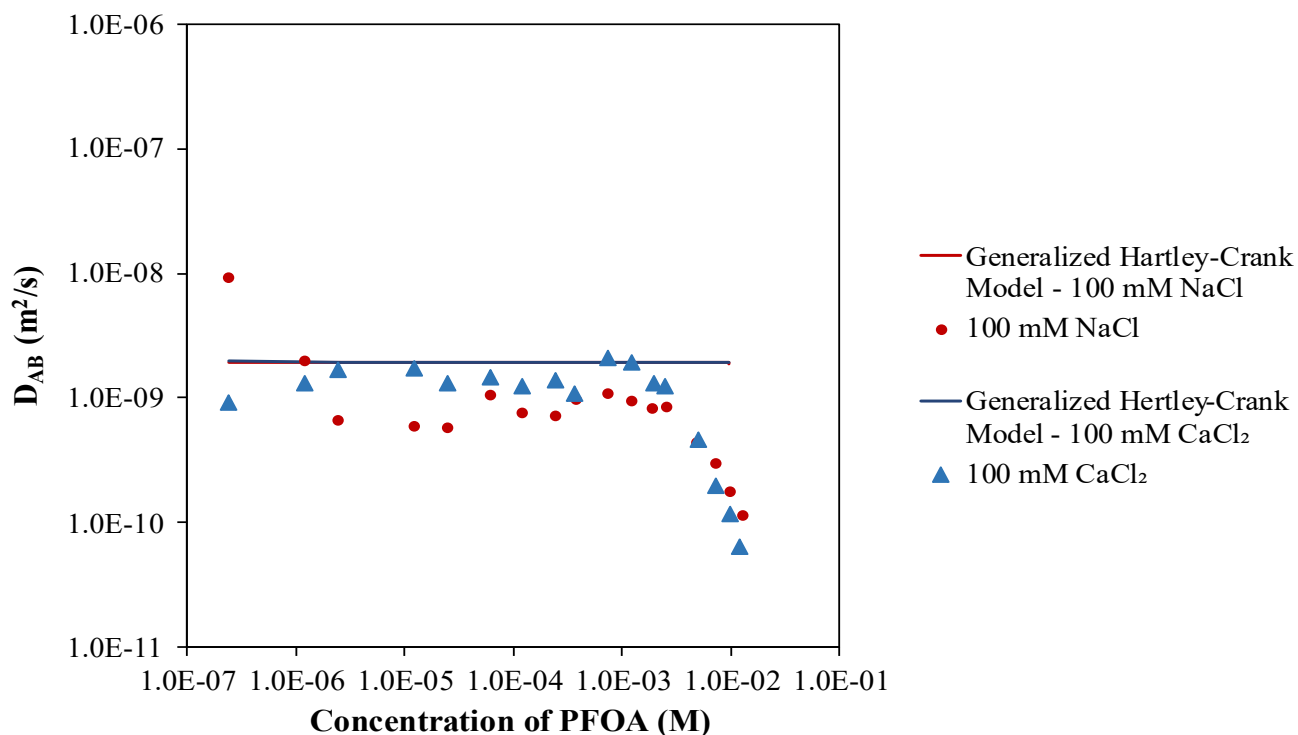


Figure 4-17. A comparison of Fickian diffusion coefficients measured via bubble pressure tensiometry with predictions from the generalized Hartley-Crank model developed by Lieast et al. (9,10). Data was originally reported in our work (11).

For both NaCl and CaCl_2 the onset of the decline in D_{AB} occurs at a lower surfactant concentration. This may be evident of the formation of an electric double layer near the interface which imposes an additional energetic barrier for adsorption (60,64–67). It is owing to the Generalized Hartley-Crank model that more confidence is placed in these claims, but it is uncertain if it can be taken as absolute in its predictions.

Chapter 5. Conclusions and Future Work

5.1. Summary

This research explores specific ion effects on the diffusivity and other properties of interest for two long-chain PFAS, perfluorooctanoic acid (PFOA) and potassium perfluorooctanesulfonate (KPFOS). Based on the surface tension and solubility data collected, it was apparent that Hofmeister trends can emerge for situations in which there is close contact between cations and anions. However, a case was found where the Hofmeister series is not followed, which was the interaction of cations with the sulfonate group of PFOS^- . For both PFOA and KPFOS, the experimental observations were explained on the basis of matching water affinities that stipulates ions with similar charge densities are better able to form contact pairs.

Modeling of conductivity with the mean spherical approximation was not successful in the study of the aggregation behavior of KPFOS. It was apparent from X-ray scattering that no micellar solutions were investigated during the course of the experiments, but the interpretation is that KPFOS likely undergoes self-association at appreciable concentrations that is mediated by the presence of divalent ion impurities. Although success was not had in describing the phenomena, it is the first time that self-association of KPFOS has been systematically approached to the best of the author's knowledge.

Self-diffusivity was found to be intrinsically tied to the limiting ionic molar conductivity of the species within the system being considered. The PFOS^- ion has higher mobility than the PFO^- ion. A corresponding observation was the diffusion of KPFOS seemed to be more profoundly dependent on composition of the solution than PFOA.

5.2. Suggested Future Work

This study focused only on long-chain PFAS whereas the study of short-chain PFAS could yield more fruitful observations in some instances, such as diffusion in highly saline samples. In this way, effects related to competition for hydration could be better understood. It is also apparent that KPFOS shows a more complicated association equilibria than that of PFOA. This in of itself deserves more attention, especially owing to the somewhat unique appearance of the molar conductance curve. Trends relating to water affinity of the ions investigated herein are likely to also effect micellization which could be investigated with higher concentrations of surfactant in the presence of supporting electrolytes via SAXS.

It was also made apparent from the lack of available literature data that thermodynamic quantities that are relevant to modeling ionic PFAS, such as osmotic coefficients, should be made. Wider access to these quantities can unlock many different possible areas of study, such as micellization modeling.

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Appendix

Appendix A. Supporting Figures for Materials and Methods

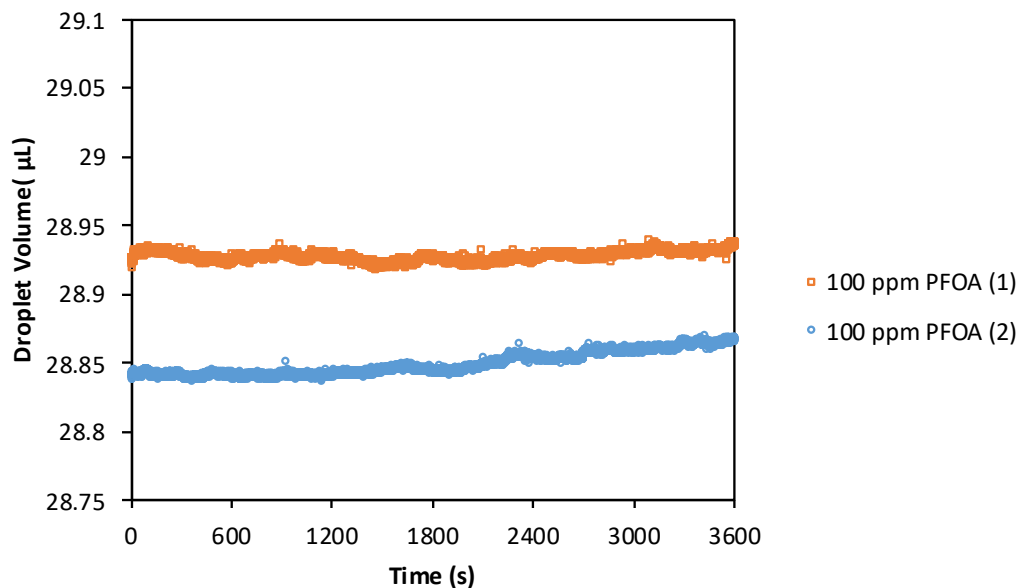


Figure A-1. Variation of pendant drop volume for 100 ppm PFOA trials 1 and 2.

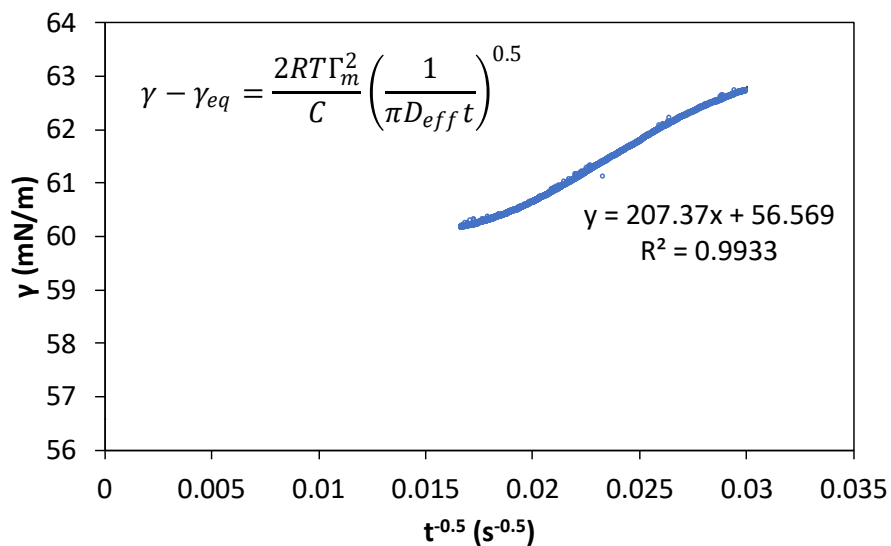


Figure A-2. Extrapolation of dynamic surface tension data (100 ppm PFOA trial 1) to obtain equilibrium surface tension values using the long time Ward-Tordai model (equation 6).

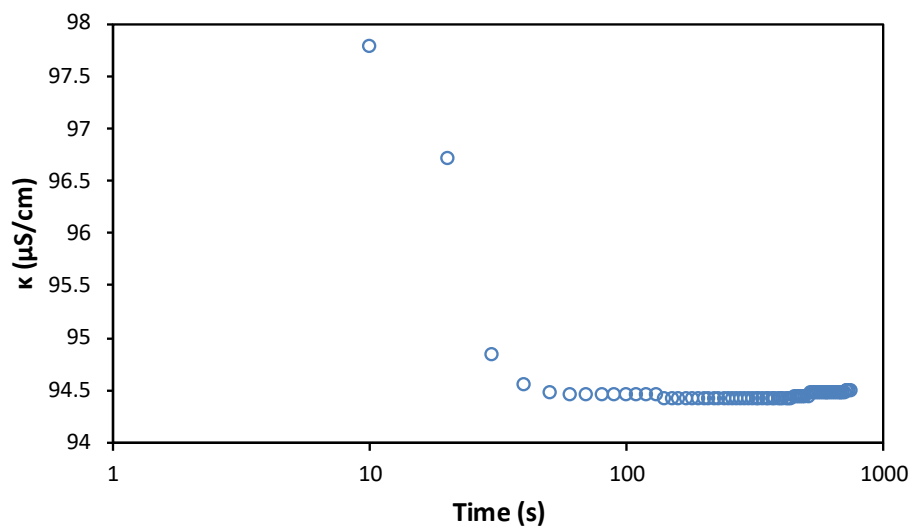


Figure A-3. Time-dependent conductivity measurements to show the dilution of KPFOS from 575 ppm to 550 ppm. Values were recorded immediately following the addition of water to the sample.

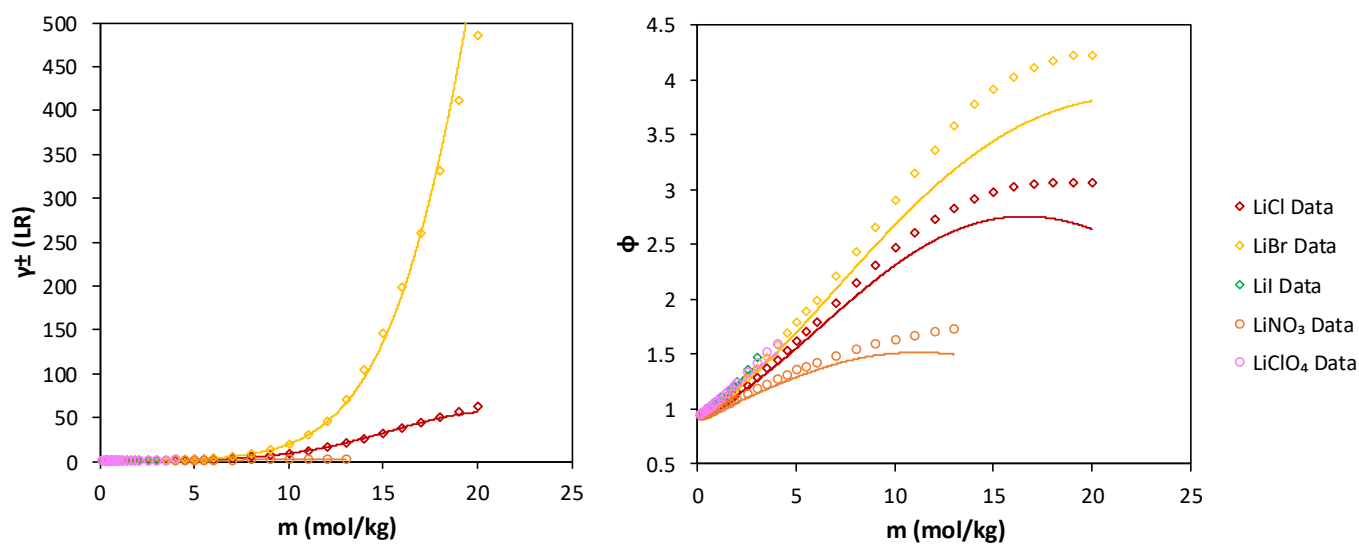


Figure A-4. The BIMSA model predictions of mean ionic activity coefficients on the Lewis-Randall scale (molality basis) and osmotic coefficients for lithium salts after refitting to $\gamma_{\pm}$ (LR). Data were taken from Robinson and Stokes (3). Molarity to molality scale conversions were performed with density data taken from (12).

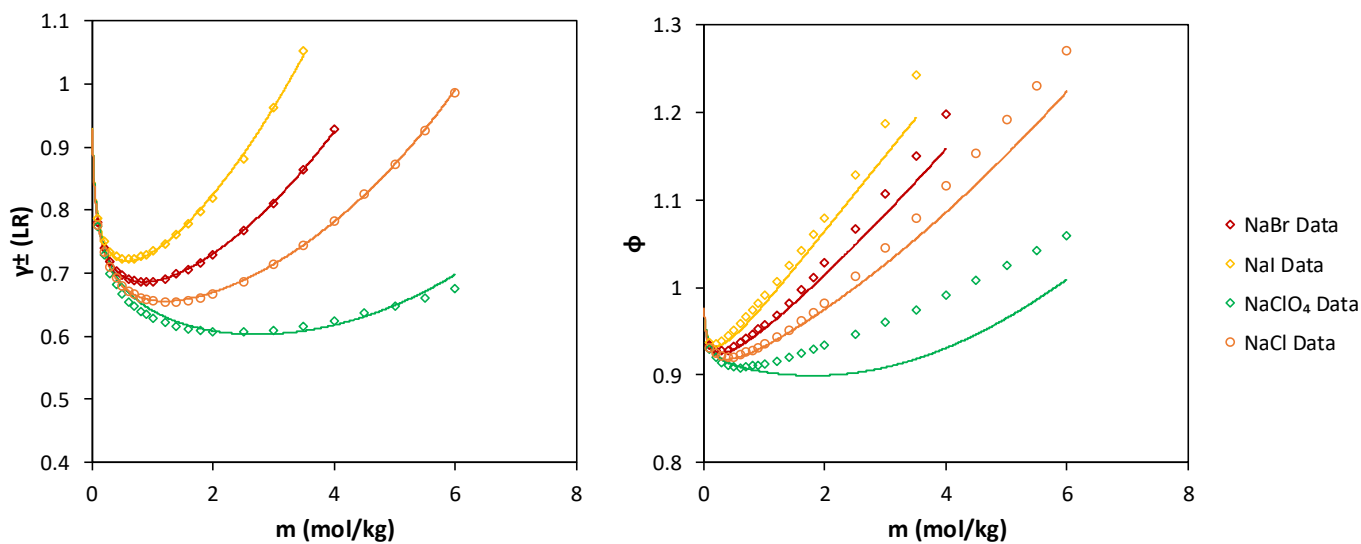


Figure A-5. The BIMSA model predictions of mean ionic activity coefficients on the Lewis-Randall scale (molality basis) and osmotic coefficients for sodium salts after refitting to $\gamma_{\pm}$ (LR). Data were taken from Robinson and Stokes (3). Molarity to molality scale conversions were performed with density data taken from (12).

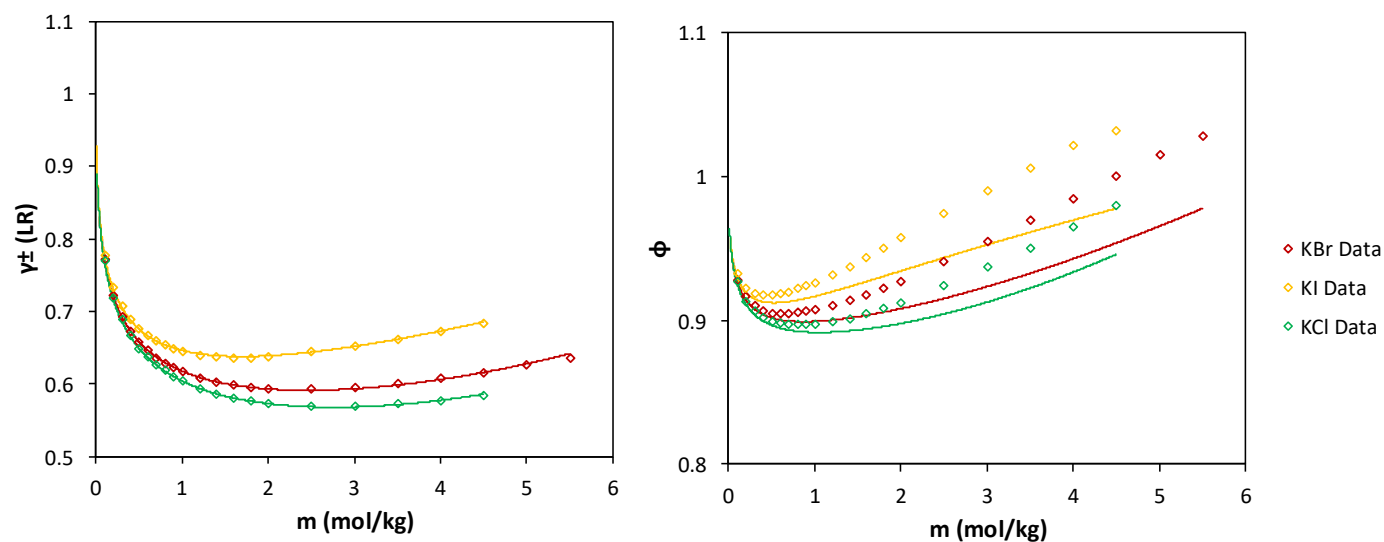


Figure A-6. The BIMSA model predictions of mean ionic activity coefficients on the Lewis-Randall scale (molality basis) and osmotic coefficients for potassium salts after refitting to $\gamma_{\pm}$ (LR). Data were taken from Robinson and Stokes (3). Molarity to molality scale conversions were performed with density data taken from (12).

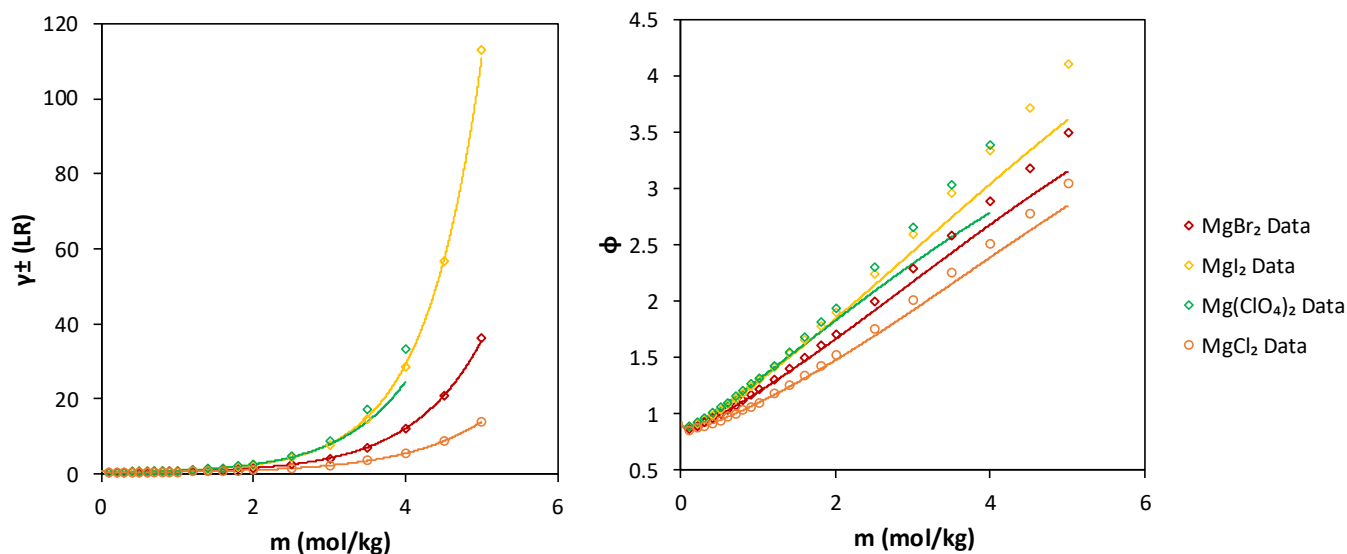


Figure A-7. The BIMS model predictions of mean ionic activity coefficients on the Lewis-Randall scale (molality basis) and osmotic coefficients for magnesium salts after refitting to $\gamma_{\pm}$ (LR). Data were taken from Robinson and Stokes (3). Molarity to molality scale conversions were performed with density data taken from (12).

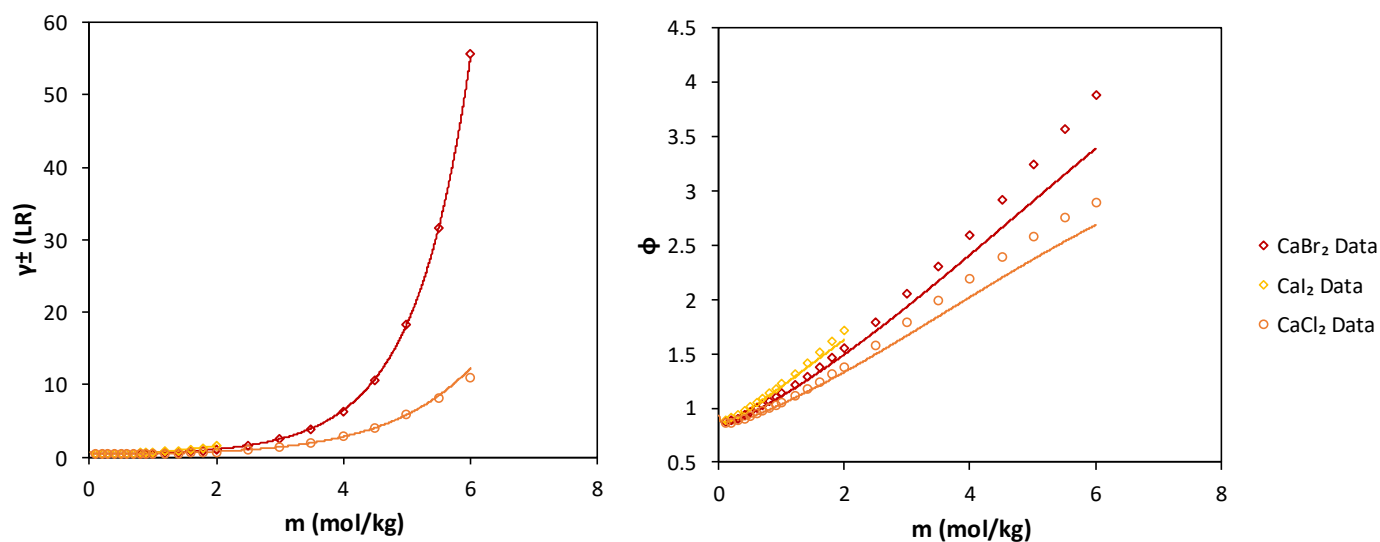


Figure A-8. The BIMS model predictions of mean ionic activity coefficients on the Lewis-Randall scale (molality basis) and osmotic coefficients for calcium salts after refitting to $\gamma_{\pm}$ (LR). Data were taken from Robinson and Stokes (3). Molarity to molality scale conversions were performed with density data taken from (12).

Table A-1. Refit parameters for $r^{(0)}$, $\sigma^{(1)}$, and R . AARD values are given for the Lewis-Randall (molality) scale mean ionic activity and osmotic coefficients.

Salt	Cation Radius at Infinite Dilution (Å)	Anion Radius (Å)	Cation $\sigma^{(1)}$ (Å L/mol)	R (L/mol)	AARD $\gamma_{\pm}$ (LR) (%)	AARD ϕ (LR) (%)
LiCl	2.688	1.81	-0.0911	0.1537	1.6	4.0
LiBr	2.688	1.95	-0.0970	0.1492	3.1	4.7
LiI	2.688	2.16	-0.1504	0.1138	1.1	1.0
LiNO ₃	2.688	1.7	-0.0957	0.1460	1.0	3.5
LiClO ₄	2.688	2.265	-0.1389	0.1706	0.2	1.7
NaBr	1.975	1.95	-0.0401	0.07186	0.1	0.9
NaI	1.975	2.16	-0.0700	0.05863	0.3	1.2
NaClO ₄	1.975	2.265	-0.0494	0.19723	1.4	2.7
NaCl	1.975	1.81	-0.0273	0.08177	0.2	1.2
KBr	1.700	1.95	-0.01968	0.08062	0.2	1.8
KI	1.700	2.16	-0.06300	0.07884	0.2	1.8
KCl	1.700	1.81	-0.005405	0.07471	0.1	1.2
MgBr ₂	3.348	1.95	-0.2482	0.05050	0.4	3.0
MgI ₂	3.348	2.16	-0.2927	0.03110	1.3	3.4
Mg(ClO ₄) ₂	3.348	2.265	-0.3448	0.02361	1.2	2.0
MgCl ₂	3.348	1.81	-0.2201	0.09558	1.0	2.2
CaBr ₂	3.167	1.95	-0.1927	0.07130	0.6	3.9
CaI ₂	3.167	2.16	-0.2816	0.03772	0.5	1.8
CaCl ₂	3.167	1.81	-0.1883	0.09543	2.0	3.1

Appendix B. Supporting Figures for Results and Discussion

The degree of ionization of a weak acid is related to its equilibrium constant (K_a) and total concentration (c). Equation 10 is recalled

$$K_a = \frac{c\alpha^2}{1 - \alpha} \quad (10)$$

which can be rearranged to find

$$\alpha = \frac{-K_a + \sqrt{K_a^2 + 4cK_a}}{2c}$$

with the assumption of ideal behavior. Recalling Equation 16

$$\kappa = \frac{e^2}{k_B T} \sum_{i=1}^N \rho_i \alpha_i D_i^o z_i^2 \left(1 + \frac{\delta v_i}{v_i^o}\right) \left(1 + \frac{\delta k_i}{k_i}\right) \quad (16)$$

where equation 63 can be inserted in place of α_i . All information other than K_a is either specified for a given experimental condition, can be readily obtained from literature, or can be measured.

This allows for the fitting of experimental conductometry data by minimization of residuals.

Figure 4-8 shows three sets of data, two taken from literature (13,14) and the third measured herein, along with the MSA transport model curve.

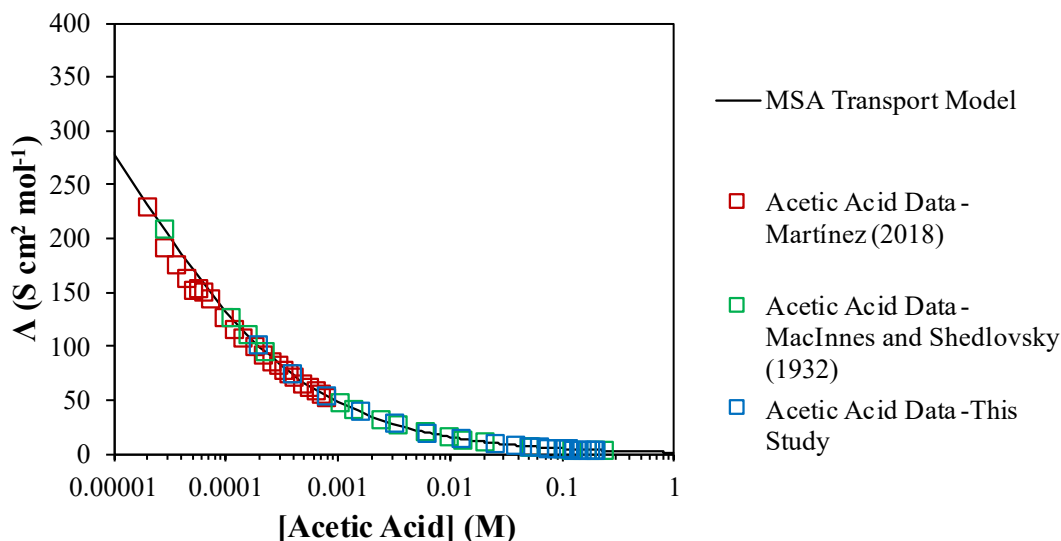


Figure A-9. Experimental conductivity data for acetic acid along with the predicted molar conductivity from the MSA transport model (Equation 16). Two sets of experimental data from literature (13,14) and experimental data collected in this study are shown. Two replicate measurements were performed Limiting ionic molar conductivity values were taken from (3) and used within Equation 15 to calculate D_i^0 of the acetate ion and H^+ . The ionic radii of H^+ was taken from (15) and the ionic radii of the acetate ion was deduced by solving the Stokes-Einstein equation for the hydrodynamic radius. K_a used in the calculation of α was taken from (13).

AARD values are used to assess the quality of the MSA predictions. The AARD can be obtained from

$$AARD(\%) = \frac{100}{N} \sum_{k=1}^N \frac{|\Lambda_{cal} - \Lambda_{exp}|}{\Lambda_{exp}}$$

with N representing the number of data points, Λ_{cal} representing the molar conductivity from the MSA transport model prediction, and Λ_{exp} representing the experimental molar conductivity.

The AARD values obtained for MacInnes and Shedlovsky, Martinez, and this study were 1.65%, 4.62%, and 5.25%, respectively.

Conductivity of sodium dodecyl sulfate (SDS) above and below the CMC was modeled with the MSA. In addition to charge, concentration, ionic radii, and diffusivity at infinite dilution the CMC and mass balances are needed for micellar systems. The CMC for SDS was deduced from a sigmoidal fitting of differential specific conductance as suggested by Sugihara et al.

(139). The sigmoidal fitting is shown in **Figure A-10** which resulted in a CMC value of 8.248 mM.

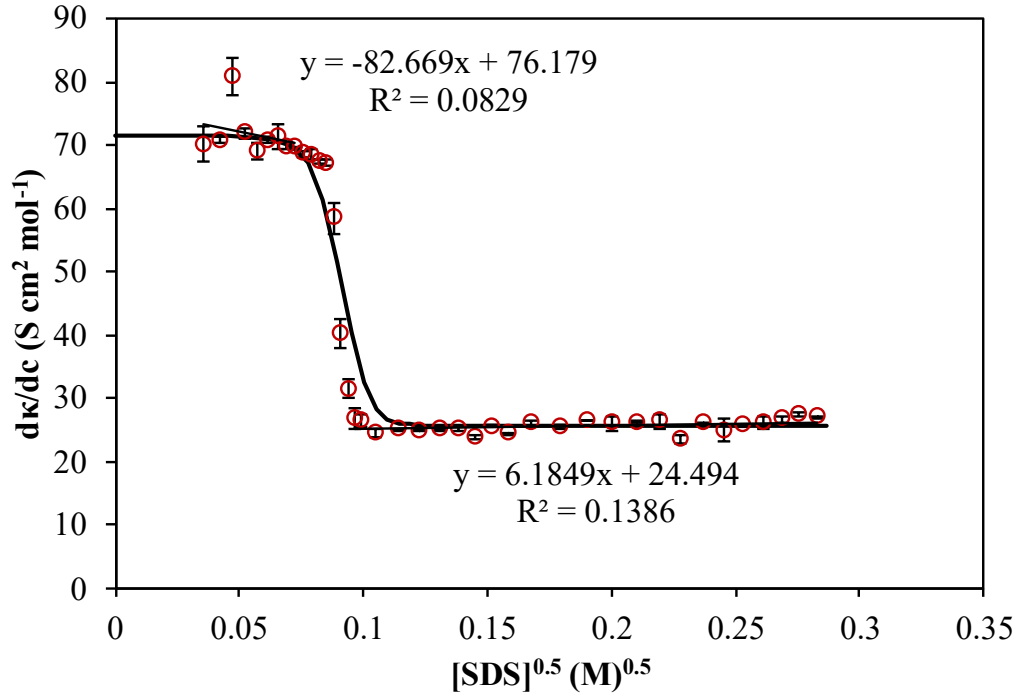


Figure A-10. Sigmoidal fitting of differential specific conductance to determine the CMC of SDS. The sigmoidal equation takes the form $\frac{d\kappa}{dc} = \frac{(\bar{y}_{max} - \bar{y}_{min})}{1 + \exp(1 + ([SDS] - CMC))} + \bar{y}_{min}$ where $\bar{y}_{max}$ is the average of the highest magnitude differential conductance values and $\bar{y}_{min}$ the average of the lowest magnitude differential conductance values. The CMC determined from the fitting was 8.248 mM.

Literature values for the CMC of SDS agree well with the obtained value (161,162). SDS micelles are considered to grow in size with increasing concentration accordingly to the empirical equation of Bales et al. (163)

$$N_{agg} = 49.5 \left[\frac{\alpha_{mic}[SDS] + (1 - \alpha_{mic})CMC}{CMC} \right]^{0.25}$$

where N_{agg} represents the micellar aggregation number and α_{mic} is the degree of ionization of the micelles. Diffusivity at infinite dilution of the micelles is taken to change with the aggregation number. The charge of the micelle is found by

$$z_{mic} = -\alpha_{mic}N_{agg}$$

Then, the concentration of micelles is

$$[Micelles] = \frac{[SDS] - CMC}{N_{agg}}$$

and the Na^+ concentration is found by

$$[Na^+] = CMC + z_{mic}[Micelles]$$

The fitting variable selected was α_{mic} given that all other information is available. The resulting plot is of the experimental data collected in this study and the MSA transport model prediction is shown in **Figure A-11**.

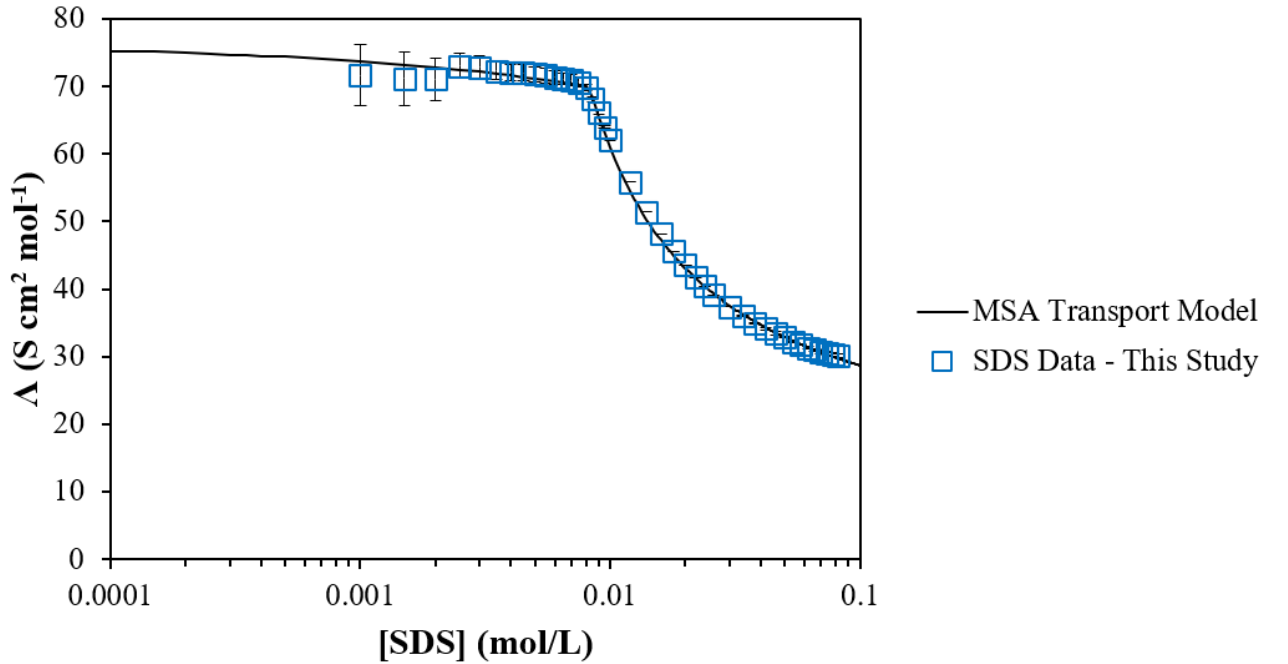


Figure A-11. Experimental conductometry SDS data collected in this study alongside MSA transport predictions with the degree of ionization of the micelles as a fitting variable. The number of replicate experiments performed was 2. α_{mic} converged to 0.357 with an AARD of 0.922%.

Of course, α_{mic} can also be experimentally determined with conductometry by taking the ratio of the two slopes in the plot of specific conductance as a function of concentration. This plot is shown in **Figure A-12**.

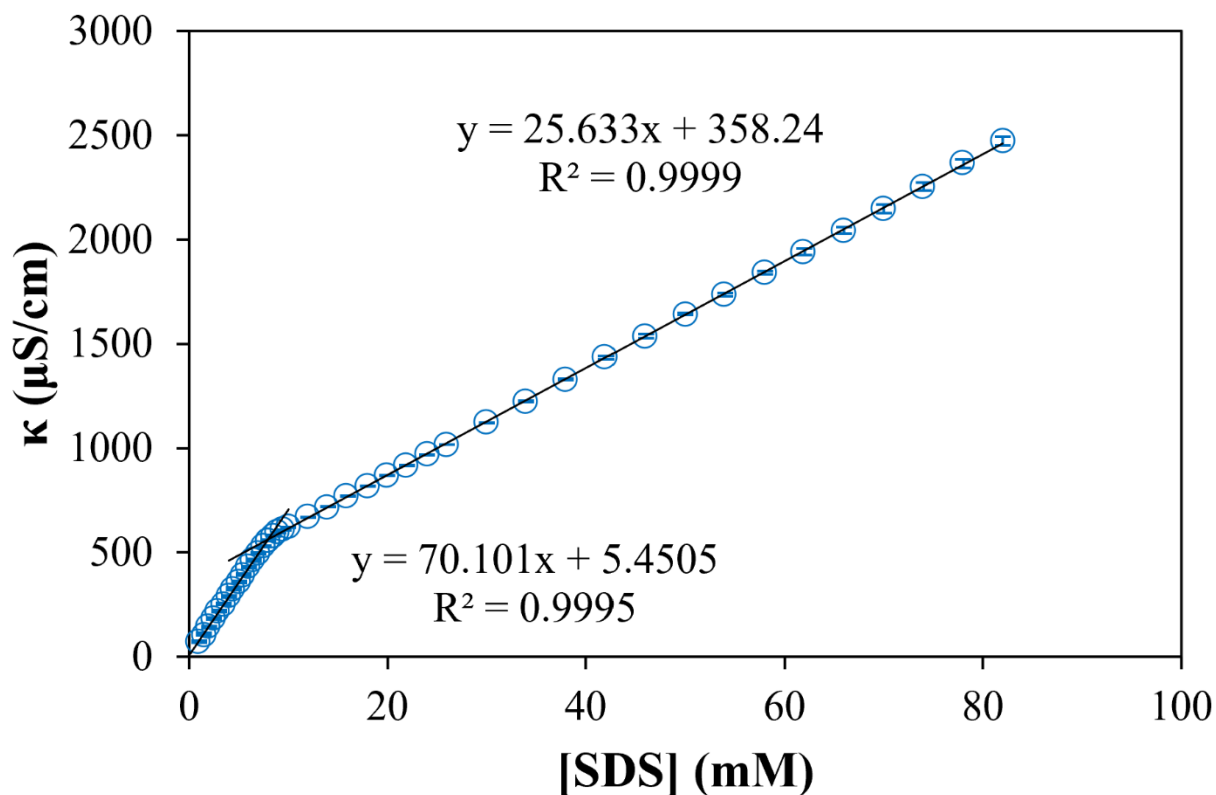


Figure A-12. Experimental conductometry SDS data collected in this study with linear trendlines for the two concentration regions, above and below the CMC. The slope after the CMC divided by the preCMC slope was found to be 0.322.

The values obtained for the degree of ionization of the micelles by fitting of the MSA transport model and by direct calculation from the experimental data are closely in agreement. This strongly suggests that the MSA transport model (coupled with the correct mass balances) captures the essential physicochemical characteristics of the system.