CSEM's
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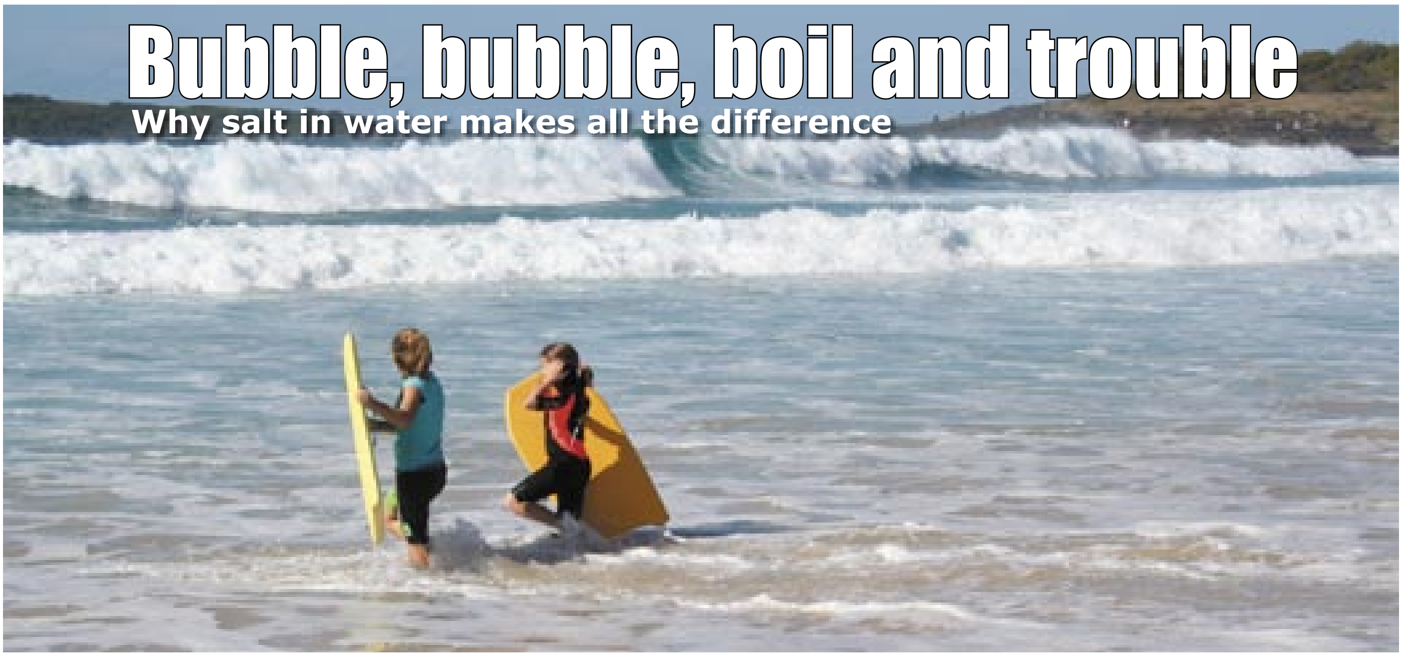

Bubble, bubble, boil and trouble

Why salt in water makes all the difference

Colloid scientists at Applied Maths are measuring how dissolved salts are affecting bubble coalescence. The scientists believe the data they are collecting will be critical for testing theories on how air/solvent interfaces operate. This in turn may transform many industrial processes connected with soft matter systems (for example, emulsions, gels and colloids). Indeed, this understanding might also revolutionise biology as we know it.

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"Anyone who has taken a dip in the Australian surf will have observed, and maybe marvelled at, the clean white foam produced by a breaking wave," says Dr Vince Craig. "It's a bright effervescent mix that persists for some five to 10 seconds and then it's gone. What most people don't realise is that the behaviour of this foam, the size of the bubbles and their persistence, is largely governed by the salt in the water. If there was no salt in those waves, the foam would look completely different!"

Dr Craig is based in the Department of Applied Maths, and he has long been fascinated by the effect that salt has on bubble behaviour. Indeed, the more he's worked in the area, the more he's convinced that what we can learn from this behaviour is basic to fundamental processes that drive all biology as well as having valuable applications to many industries.

"It's often said that all life depends on water," explains Dr Craig. "But we think there's a much stronger statement you can make, and that is that all life depends on salty water".

Low salt and high salt

"If you have water with low salt, that is water with a low concentration of salt, all the interactions between the particles are very simple," says Dr Craig. "The dissolved salt exists as ions that can be described as just a simple charge. The forces at work are long range and repulsive, and nothing much complicated can happen.

"However, if you increase the salt concentrations the electrostatics are screened, the forces become much shorter ranged and they become much more complicated because different salts do different things. So, you suddenly have these specific ion effects and this opens up an enormously rich complexity of what can happen. Unfortunately this is something that is not really addressed in the scientific literature.

"The golden theory in this area is known as the DLVO theory, the letters standing for the theoreticians that came up with it. It was developed more than 50 years ago, and it describes how two particles interact if they have a low charge in a low concentration of salt at large distances. The theory works very well in these situations but many situations are not like that, they've got higher charges or a lot more salt and the surfaces interact in other ways. However what people try to do is fit their data with the DLVO theory and then add something else to explain the difference. What's wrong is the theory to begin with. It simply doesn't apply to high salt conditions.

"There's a lot of data in biology, for example, that reveals that by adding a different salt or a different concentration of the same salt you can produce a very different outcome

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but there's no real theory to explain why this is so.

"Researchers like Barry Ninham, Applied Maths' founding professor, have championed the importance of this problem for many years but it's a really difficult challenge. And one of the limitations faced by theoreticians is that they don't have a lot of experimental data to test their theories with.

Measuring bubble coalescence

Which is where measuring the effect of different salts on bubble coalescence comes in. It's a study that several colloid scientists at Applied Maths have been grappling with over many years. At the moment, Christine Henry is the researcher at the lab bench making the measurements.

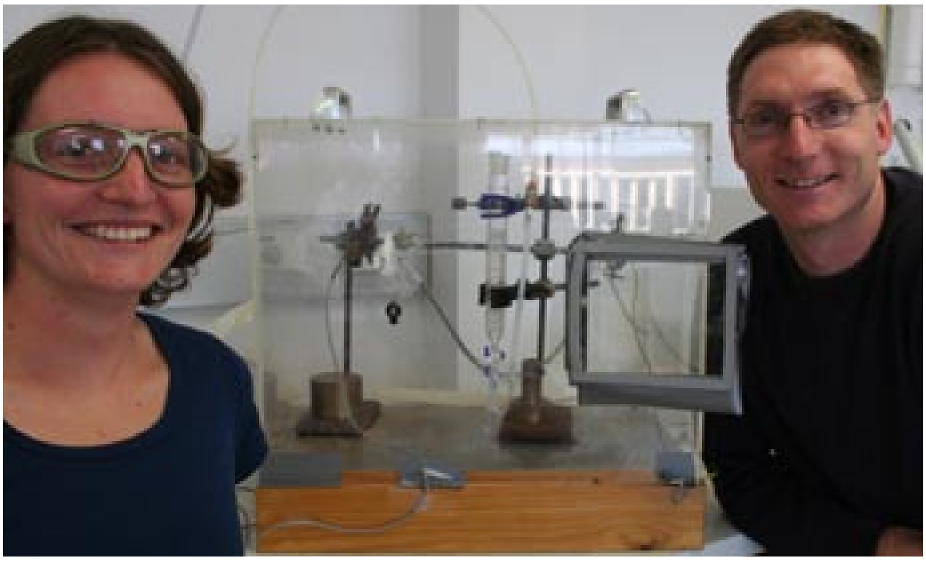
"It's been known for a long time that dissolved salts will affect how bubbles coalesce in water," says Ms Henry. "The salt in the water is in some way stopping the bubbles from melding or coalescing together as they do in pure water.

"The presence of the salt ions in the water is keeping the bubbles separate, making them stable for a longer time. But it's not just any salt that causes this effect, because some salts have no effect and nobody understands why that is and why some behave differently to others."

To measure the effect of different salt solutions (and the same salt solutions at different concentrations), Ms Henry creates bubbles by feeding nitrogen through a glass frit (a porous disc made of closely packed particles) placed at the bottom of a glass tube filled with the salt solution.

"We shine a laser beam through the bubbles as they move up the column. The beam is collected by a photodiode detector on the other side of the column and the light signal is converted into a voltage. So, in effect, we're measuring the turbidity of the solution. If you have a lot of small bubbles the laser light is scattered more and the signal coming through to the photodiode detector is lower. If the bubbles are coalescing then we have fewer and larger bubbles, less light scattering, and we get a higher signal coming through.

"We're measuring dynamic collisions of bubbles over time and taking an average. It's a simple, reproducible method that works well, and it's



Christine Henry and Vince Craig with the apparatus for measuring bubble coalescence. "With bubble coalescence we see really rich complex behaviour from a very simple system," says Dr Craig.

been used by previous investigators, including Vince Craig, Barry Ninham and Ric Pashley, to measure the effect of single salts in solution on bubble coalescence. I'm extending these studies by studying mixtures of salts and the effect of salts in non-aqueous systems."

Different ions, different effects

"The traditional view of colloid science and surface chemistry has been that you just look at ions as point charges and it doesn't really matter what types of ions they are," says Ms Henry. "However, our research is demonstrating that it does matter what ions are present. We're seeing that the size and the symmetry of the ion makes a difference on bubble coalescence, and this understanding has wide repercussions.

"Our results are demonstrating that looking at the ions as real bodies, with a size and a polarisation and so on, means that we can get much more accurate information about what's happening at the interface of a liquid and gas or a liquid and a solid. Indeed, this seems to control a lot of the behaviour down at that very fine scale.

"While this is providing us with some clues about the behaviour of bubbles, which has some important applications in itself, possibly the more important aspect of this research lies in understanding how the different salt solutions interact with various proteins and membranes in biological systems. For example, anywhere in the human body the salt concentrations in the cells are high enough to see these effects and it matters which ions are present. You can see different effects depending whether you have sodium versus potassium as an ion or chloride versus bromide."

Simple systems, complex behaviour

"With bubble coalescence we see really rich complex behaviour where different salts do very different things," says Dr Craig. "For example, nitrate and chlorate have opposite effects on bubble coalescence but those ions are so similar. The chlorate and the nitrate ion is almost exactly the same shape with similar bond lengths; you just change the nitrogen for chlorine. However, one inhibits bubble coalescence and the other has no effect whatsoever. So, what's the difference? It must be due to the slight change in the ion, or what it does at the interface.

"And bubbles offer us about the simplest system you can possibly imagine – you've basically got air, water and salt. So, here's an opportunity where you can provide some really high quality data with which the theoreticians can use to test their theories in a simple system; a system that is more accessible than say a really complex protein system in a cell. And we're also measuring the surface tension of these systems.

"Christine's work has shown that we can explain all the bubble coalescence behaviour by the behaviour of ions at the air water interface. We can categorise all the different ions using a set of combining rules. So, for simple electrolytes, one electrolyte at a time, we can predict what all of them will do with no exceptions. And then, with the mixed electrolyte measurements that Christine has done, we showed that with another level of knowledge on top of those rules we can now predict what any salt solution will do, and it's based on an understanding of how these ions behave at the interface. We don't understand it well but we have a basic understanding of what's happening.

Beyond water

"So, how does this relate back to all life on Earth?" asks Dr Craig. "Well, for all the complex stuff that happens in our cells you need to understand and be able to describe what the ions do at interfaces. Unfortunately, at the moment it's too complicated to describe this in the complex environment inside a cell but we have this lovely simple model system represented by the bubble interface where we do have some level of understanding.

"Christine is starting to bridge that gap because the problem is that a protein doesn't look like water or air, it looks more like an oil. Consequently, Christine is starting to do bubble coalescence in non aqueous systems. This is a bit tricky because you've got to have an oil that will dissolve lots of different salts. So, now we're looking at how bubble coalescence behaves in all these non aqueous systems, and we're looking for how the ions behave in these systems which is a crude model of a protein or a membrane.

"We have some tantalising results so far. Christine has shown that salts can inhibit bubble coalescence in these systems, and we know that in some cases the ion assignments, whether they inhibit coalescence or not, are different to their assignments in water but we haven't got enough data yet to say whether there is a set of combining rules that can be applied.

"So, all the questions that we've thrown up can now be investigated in this parallel system which will throw up a lot more information, plus we're looking at investigating other solvent systems in due course."

Bubbles and industry

The applications of this work are still many years off and it's difficult to know exactly what they'll be though Dr Craig points out there are many industrial processes beyond soft matter systems (see Ions and industry) that depend directly on interactions with bubbles.

"There are a many areas where there are applications involving bubbles in a simple sense," comments Dr Craig. "There are lots of chemical engineering situations where they want mass transfer, so they have a gas bubbling up through a solvent. They need to know what the bubble size is and they need to keep it small. Many of these systems involve high salt concentrations in their solutions. So this work is directly informing such processes. With Christine's latest work we can say if they wrote down the recipe of how much salt they've got in the solution we can tell them what will foam and what won't."

"I guess the most obvious application would be froth flotation in the mining industry," observes Ms Henry. "This involves passing bubbles through a liquid containing the ore as fine particles. The mineral goes to the surface of those bubbles where it is scraped off and collected. These systems usually involve solutions with high concentrations of salts, so any information about keeping the bubbles small, which keeps the surface area large, would probably be an advantage to engineers managing these systems."

"Another area is in electrochemistry when they're doing electroplating or working with fuel cells they're creating bubbles on surfaces. These systems also have a lot of electrolytes in the solutions and they need to know how these bubbles will behave. The bubbles often drive convection current so if they're coalescing or not their size will be different and that behaviour will change."

High salt may rewrite biology

The effects of specific ions at air water interfaces is such a fundamental property that Dr Craig believes a better theoretical framework for what's happening has the potential to rewrite biology.

"I'm a colloid scientist," he says. "From my point of view, all of biology is really a form of colloid science. Colloid science is about surfactants and polymers in solution, and surfaces interacting. And that's basically what every living creature is – it's surfactants, lipids that make up our membranes, polymers which are proteins in solution; and these systems are doing wonderfully complex things. Therefore, from a colloid science point of view, when our knowledge gets to a high enough level we should be able to describe the biological machine.

"How do two cells come together or how does a cell split apart? All of this must be governed by colloidal principles though we're a very long way off understanding it. And the first thing we have to understand is how surfaces and surface forces

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Ions and industry

The importance of ions at interfaces is not just a problem for biologists, it's also basic to any industry working with soft matter systems. Soft matter describes a broad suite of materials that are not runny like a liquid or hard like a solid, they lie somewhere in between and include everything from shampoo and toothpastes right through to gels.

"Many soft matter systems go through vast changes when you change the electrolyte in them," says Dr Craig. "But, at the moment, there's no real theory to explain why this is happening. It's all done empirically, a trial and error approach.

"So, if we can understand how ions behave at different interfaces we can inform many industrial processes as well. For example, if someone wants to design a better gelling agent then they should be able to understand which ions will behave in which way with which surfaces.

"At the moment there's not a single soft matter system where they can predict this from first principles. What they do is start by applying their experience with a similar system which they understand through empirical studies. Then they modify that. Sometimes it works, sometimes they're surprised because something completely different happens for which they have no theory.

"It's a huge problem in formulation science because people really want to control the flow properties of the product their manufacturing. For example, they might have a food product and if one of its ingredients changes just a little bit the whole flow properties of that product may change. Or it might be a very expensive cosmetic, and people aren't willing to pay for it if its runny, they want it to be beautiful and smooth and it might be a very small change that leads to a dramatic change in properties – not all the time but in some cases.

"Though, it has to be said, it isn't always an electrolyte that's responsible for an observed change in properties but it is known that if you change the electrolyte you can get very dramatic differences and the current theories don't really cope with that. And that's because they simply don't explain the effects of different salts."

Next generation ceramics

Building tomorrow's dielectric resonator materials at RSC

Many of the information and communication technologies that have transformed the modern world have been built on the back of advanced materials. Consider the connection between ceramic dielectric resonators and the explosive growth of wireless telecommunications.

"The development of ceramic dielectric resonators with large dielectric constants and low dielectric losses at microwave frequencies has revolutionised the wireless telecommunications industry," claims Professor Ray Withers, Head of the Solid State Inorganic Chemistry Group at the Research School of Chemistry. "These materials have dramatically reduced the size and cost of filters and oscillators in a wide range of systems including cellular mobile phones, radar systems and global positioning systems.

"This, in turn, has lead to renewed interest in developing even better dielectric materials. Advanced oxide ceramics for use as dielectric resonators at RF/microwave frequencies are critical elements in these systems The global market for these ceramics was on the order of $400 million in 2002."

In response to this growing need, Professor Withers and colleague Dr Yun Liu are currently engaged in a five year ARC-sponsored hunt for the next generation of advanced dielectric ceramics. They believe that the commercial competitiveness of these materials depends on developing new dielectric ceramics that out perform existing materials in three key areas.

"First, the new dielectric ceramics need to be environmentally sensitive and cost effective," says Professor Withers. "Next, they must maintain high performance, and by that I mean they must have a moderate to high dielectric constant, low dielectric losses as well as a near-zero temperature coefficient of resonant frequency. And finally, their dielectric constants should be electric and/or magnetic field tunable while maintaining good performance."

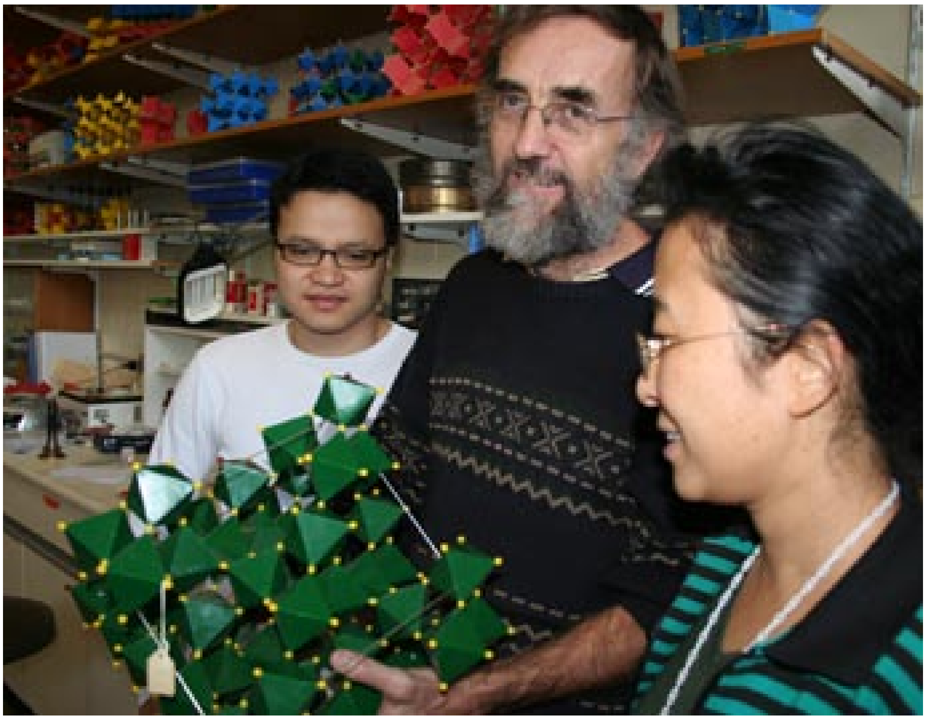
Tunable dielectric ceramics are something akin to the Holy Grail in this area. They promise to revolutionize RF/microwave electronics by consolidating components operating at different frequencies into the one electric field tunable component. Tunable devices are highly desirable for wireless equipment because they will save board space, enhance performance and battery life, and reduce cost. Their availability is expected to lead to new designs in tunable filters, phase shifters, tunable resonators, electrically steerable antennas and matching networks.

Fire up the furnace: another ceramic sample is prepared in the synthesis lab of the Solid State Inorganic Chemistry Group at RSC.

However, while the goals are clear, achieving them require a full understanding of the crystal chemistry of potential dielectric ceramic materials because the devil is in the detail of the crystal structure.

"There are three parameters crucial to the usefulness of new dielectric ceramics as resonators and filters for wireless communications," explains Professor Withers. "You need a high permittivity (enabling miniaturization), low dielectric losses at microwave frequencies (enabling sharper signals, narrower bandwidths and lower insertion losses) and an extremely low temperature coefficient of resonant frequency (eliminating temperature-dependent frequency drift). Unfortunately, the simultaneous optimisation of all three parameters is extremely difficult and rules out the use of most conventional, very high dielectric constant materials such as ferroelectrics.

"Dielectric ceramics that have been found to meet these criteria to a sufficient extent to be used commercially to date almost invariably involve either octahedrally co-ordinated early d^0 transition metal ions such as Ti^{4+}, Ta^{5+}, Nb^{5+}, W^{6+} and/or lone pair containing cations such as Pb^{2+} and Bi^{3+} etc, that are susceptible to moving off-centre either statically or dynamically in a co-operative fashion and hence capable of giving



Professor Ray Withers (centre) with a model showing the crystal lattice of pyrochlore, one of the materials being analysed and modified in the quest for the next generation of dielectric resonators. "We're particularly interested in understanding how you get dipole moments with these crystals," says Professor Withers.

On his left is PhD student Nguyen Hai Binh while Dr Yun Liu stands on his right.

rise to high permittivity.

"The search for improved dielectric ceramics necessarily involves an understanding and control of the chemical and other forces that produce polar behaviour in crystalline materials. We're seeking to understand and control the local crystal chemistry responsible for polar behaviour in these materials, and we're examining a carefully targetted range of primarily octahedral, corner-connected framework structures containing d^0 early transition metal ions. In particular this includes titanates, niobates, tungstates and/or mixtures thereof. These include complex cubic perovskites, hexagonal perovskites, Ln-doped bismuth layer structured ferroelectrics and pyrochlores. We're also systematically investigating the dependence of the associated microwave dielectric properties upon dopant composition, synthesis conditions and annealing atmospheres."

But the search for improved dielectrics goes beyond just understanding the structure and function of any particular ceramic. It's also about taking into account a range of factors such as the toxicity and the cost of different ceramic ingredients and the ability to make a ceramic-based device at a temperature that allows for cheaper processing.

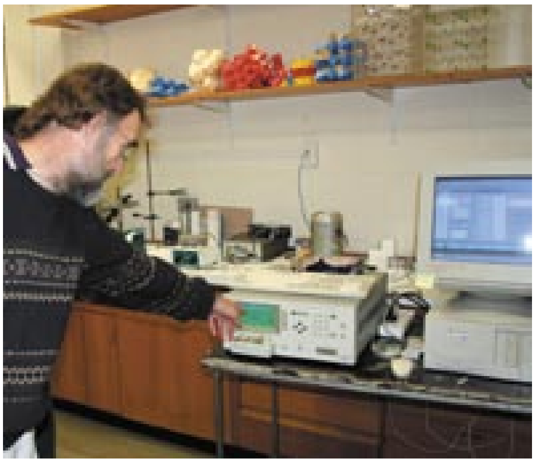
"It's not just about creating the best functional material," says Professor Withers. "It's also about using ingredients that are suitable for industry. Mobile phone base station receivers, for example, are made out of the triple perovskites barium magnesium tantalate and barium zinc tantalate. These are excellent materials but the price of tantalum, a relatively scarce element, has gone up an order of magnitude in the last decade so those materials are now getting very expensive. Currently there's a push to look at niolates which have very similar chemical properties but are 10 to 20 times cheaper. Then there's the problem with toxic lead in some relaxor ferroelectrics. Again, we're looking at more suitable ingredients.

Dr Yun Liu mounts a substrate on the spin coater. The spin coater is used to create thin layers (of around half a micrometre thickness) by dropping solutions of the material created through a sol gel process onto the substrate.

"But industry also want materials that you can produce at relatively low temperatures in order that it can be co-fired with silver or copper alloy electrodes, which means no higher than around 900-1000°C. The big push at the moment is to make what they call low temperature co-fired ceramics or LTCCs. Most of the oxide dielectric ceramics used currently require sintering temperatures of above 1350°C, which is way too high."

Once they have identified, synthesised and analysed the more promising materials for dielectric resonators the researchers will then move into the second stage of the project which is more at the applied end of the spectrum and involves nano-assembly techniques and the optimisation of dielectric properties for high performance devices.

"This stage is necessarily more concerned with processing and its effects upon dielectric properties," explains Professor Withers. "We aim to make both 0-3 and 2-2 nano-assembled composite dielectric devices using both bulk ceramics as well as thin films of dielectric materials chosen on the basis of the results obtained from the first stage of this project. The aim is to design and develop novel tunable dielectric composites with relatively low loss, high dielectric constant and high temperature-stability. We plan to exploit potential applications in micro planar tunable RF/microwave devices and/or high-density capacitors."



Professor Withers with the LCR meter used to measure the capacitance of sample materials in order to determine their dielectric constant and dielectric loss.

The aims of the investigation are quite ambitious in that they go well beyond materials chemistry and into the realm of materials engineering.

"Our investigation will bring together the fundamental materials chemistry expertise as well as the materials science processing expertise needed to develop practical microwave dielectric materials and devices," says Professor Withers.

"Fundamental understanding of the local crystal chemistry as well as of the longer range nano-structure/short range ordering of relaxor materials is essential in order to rationally search for component dielectric materials with better properties than those that are currently available. Likewise, the subsequent processing of such materials into appropriate thin film or ceramic composite forms enables the optimisation of desired dielectric behaviour."

Professor Withers and Dr Liu bring a suite of complementary skills to the investigation. Professor Withers has many years experience unpicking crystal structure using diffuse electron diffraction and a broad range of other analytical techniques (such as XRD and neutron diffraction) while Dr Liu has considerable expertise in thin film processing, sol-gel synthesis and device fabrication.

"This is an important field in which Australia needs to stay in contact with," says Professor Withers. "Wireless communication is simply becoming too important to ignore, and expertise in microwave and RF frequency devices and the materials that drive them is something the nation should be investing in."

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behave when you have a large amount of salt involved because all these complex processes operate in, and indeed depend upon, this environment.

"At this time colloid science makes few useful predictions for biology, and that's because all of biology exists in this high salt regime. So, it's a wonderful challenge for colloid scientists to create valid theories that work at these high salt concentrations and an inevitable outcome of that will be massive advances in the field of biology because this framework provides a blueprint for all biology.

"At the moment, however, it's a bit sad because biology is a form of colloid science that we, as colloid scientists, don't have much to contribute to. I see this bubble coalescence work as making some important experimental advances that will be a great tool for the theoreticians to test a lot of what they're doing. Because if a surface forces theory can't explain our simple bubble system then it's unlikely to provide much value in explaining a much more complicated protein and membrane system."

An ocean of interest

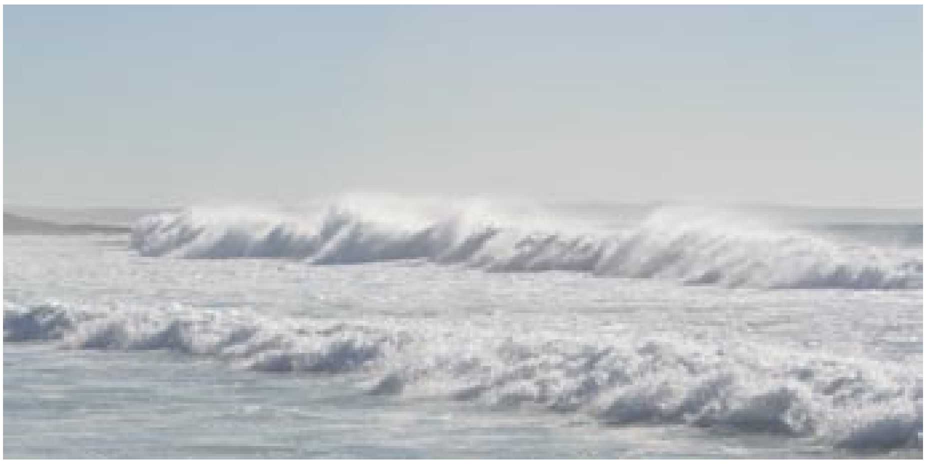
"The science of ions and interfaces has languished somewhat in recent years," laments Dr Craig. "That's in part because I don't think people understood how the challenge might be approached. However, more recently, this whole area seems to be taking off, and one of the reasons for this is a growing interest in global ocean atmosphere chemistry.

"In the sea, bubbles are created by wave action and these bubbles rise to the surface where they burst. And when that happens they throw out particles of salt into the atmosphere. How much of each ion that they throw out depends on how the ions are situated at the interface. And these ions, such as chloride, when released into the atmosphere can have dramatic effects at a global scale.

"Given the growing interest in global chemistry and climate change some of the world's best minds are now attempting to model ions and interfaces and it's the data we're producing that they'll be using to test their theories with."

High salt and the origin of life

And just to underline how critical salt



Chemicals thrown out into the atmosphere via bubbles have a significant impact on global atmospheric chemistry.

is to the processes of life on Earth, Dr Craig is happy to throw in a few observations on what this means for the history of life.

"There's an evolutionary aspect to this as well," he explains. "We're saying that complex interactions can't take place unless you've got a lot of salt. If we accept that life probably started in the ocean then it gives you a time limit as to when it was possible for life to take off – the oceans first needed to build up their salt levels to some critical level.

"And flowing on from this, I'm currently looking for someone to help me search the literature to survey what salt levels are found in all living creatures to find out what's the lowest salt level any creature can live with. I'm even prepared to speculate on what that level might be, around 0.1 molar salt concentration. That's where the threshold lies for the inhibition of bubble coalescence. We're not sure why it applies to bubbles but I have a feeling that this is also the minimum level needed to sustain complexity. If you don't find any living creatures with cells less than 0.1 molar of salt then you've got to start thinking that complexity is really dependent on salt levels. I'd love it if the biologists were to take this up.

"Look, this concept of complexity requiring high salt is a big idea and I'd love to engage biologists and other researchers with any interest in this field. It'd be great, for example, if some biologists were to read this and say 'this is a mad idea, I'm going to prove this guy wrong' and then engage with these ideas and attack this problem from a different direction. At the end of the day, that's what exciting science is all about.

"Life needs salty water, and a lot of salt. And that's why all living creatures carry around in their cells quite a lot of salt. If they didn't need it, it wouldn't be there."

So, next time you're down on the coast watching the surf bubble and froth, take a second to consider that you're observing a process that depends on high levels of dissolved salt and that your very existence might also depend on those same processes.

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PS: As Materials Monthly *is the newsletter of the CSEM, it's pleasing to note that Christine Henry, whose research is featured in this story, was a CSEM Prize winner in 2004 for her honours research on nanorheology.*

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