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研究課題名（和文）Freezing-based desalination: A molecular approach to understanding and optimisation.

研究課題名（英文）Freezing-based desalination: A molecular approach to understanding and optimisation.

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研究成果の概要（和文）：気候の変化と世界人口の増加により世界中の水供給に対する欲求が高まっている。問題は世界に十分な水がないということではなく、そのほとんどが不純物と混ざり合っていることである。したがって、海水の純水抽出（脱塩）は社会にとって長い間関心を集めており、淡水化によって得られた世界の水供給量は増加している。しかしこれは大量のエネルギーを必要とするという難点がある。
本研究では、氷が凍結すると不純物を排除する傾向があることを利用して、氷結に基づく脱塩を検討する。これを行うためには、水-不純物混合物の熱物性的特性を理解することが重要である。研究の結果は不純物の分子構造の知識に基づいてその熱物性的特性を予測する。

研究成果の概要（英文）：With a changing climate and increasing world population, the pressure on water supplies around the world is increasing. The problem is not that there is insufficient water in the world, but rather that most of it is mixed with impurities. Extracting pure-water from the sea (“desalination”) has therefore been of long interest to society, and the amount of the world’s water supply obtained through desalination is increasing. One difficulty however is that this requires a large amount of energy.
This research considers freezing-based desalination, using the fact that freezing water takes relatively little energy, and that ice tends to reject impurities as it freezes. To do this, understanding the thermo-physical properties of water-impurity mixtures is crucial. These properties originate on the nano-scale, and a novel result of this work is the ability to predict such properties based only on knowledge of the molecular structure of the impurity.

研究分野：　機械工学

キーワード：　Desalination　Nano-scale　Simulation　Freezing

１．研究開始当初の背景

With a changing climate and increasing world population, the pressure on water supplies around the world is increasing. 70% of the world's surface is covered by water and 95% of all water in the world is contained in oceans. Therefore, the problem is not that there is insufficient water, but rather that most of it is mixed with impurities.

Extracting pure-water from the sea has therefore been of long interest to society, and the percentage of the world's water supply obtained through desalination continues to increase. 1st-generation thermal methods (essentially boiling the water) used to be the primary way to extract pure water from salt water, however this is very energy-intensive and is typically only economical when utilising heat generated by another mechanism (for example, utilising waste-heat from power-plants).

The 2nd-generation method is membrane-based desalination (essentially filtering the impurities) and while this is also fairly energy-intensive, it is less-so than thermal methods, and the number of installed membrane desalination plants has overtaken thermal desalination plants in recent years.

The high cost of membrane desalination still limits its application to rich countries, and therefore advances in desalination technology are still required. This research considers a new "3rd-generation" approach: taking advantage of the fact that ice tends to reject impurities as water freezes. A freezing/thawing approach could conceivably be more efficient than boiling techniques due to the lower latent heat required to initiate phase-change, while avoiding the technical complexity associated with fabrication of membranes for membrane-based desalination.

２．研究の目的

The successful realisation of freezing-based desalination will require optimum design to minimise energy requirements and maximise efficiency. For this reason, it is important to understand how liquids transport heat away and flow under pressure. While these are macro-scale observables, they originate on the nano-scale, and therefore a molecular approach to the study of such phenomena is of interest. This can pose a challenge for experiment, and hence molecular simulation can make an important contribution in this area. Consequently, the aim of this research is to take advantage of the detailed insight provided by molecular simulation to elucidate liquid properties related to freezing desalination.

Furthermore, the development of machine-learning related statistical techniques is continuing, having recently found application in nano-scale optimisation problems; particularly related to solid material properties. This research aims to make use of such novel techniques to gain new insight into the properties of liquids.

３．研究の方法

As described in the previous section, the small time and length scales involved makes experimental study of the nano-scale origins of such thermo-physical properties challenging. Therefore, we apply nano-scale computer simulation in the form of Molecular Dynamics (MD) simulation. The open-source MD package GROMACS is utilised to run the calculations. This software is chosen partly because of its ability to utilise GPGPU acceleration and therefore shorten calculation times. Calculation of thermal conductivity employs the equilibrium-based Green-Kubo method, while viscosity calculation utilises periodic non-equilibrium forcing. Statistical analysis is performed using regression coupled with L1-norm regularisation; this relatively-recent statistical technique allows determination of the principle factors underlying each thermo-physical property. In this work, such properties are related to molecular structure in an effort to obtain general relations between the molecular structure of the impurity and subsequent effects on the properties of water. This in turn permits prediction of thermo-physical properties based only on knowledge of molecular structure.

４．研究成果

The influence of a glycol-water mixture on the thermo-physical properties of water is considered. Such a mixture is of interest from a freezing perspective because it has a peculiar freezing property; namely a very low eutectic point (ie, low mixture freezing temperature). Furthermore, it strikes a balance between simplicity and complexity, being a small molecule while retaining multiple degrees of freedom in terms of structure.

Research focussed in particular on two important thermo-physical properties for freezing desalination: thermal conductivity,

which is key for the transport of latent heat away from the freezing surface, and viscosity, which plays a key role in the energy required for pumping of liquid around the desalination system

Firstly, the sensitivity of both thermo-physical properties to change in molecular structure of the impurity was mapped out (figure 1).

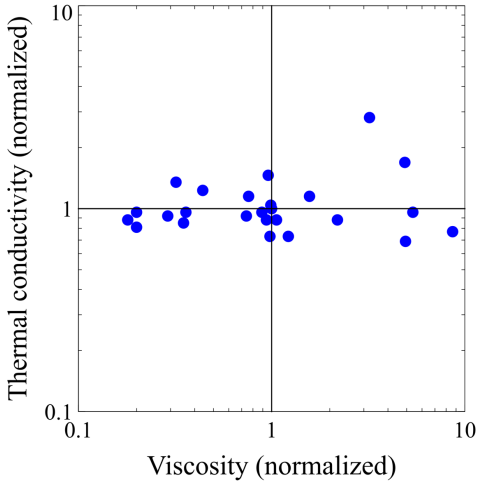

Figure 1: Relation of thermal conductivity to viscosity with impurities of different molecular structures.

This demonstrates how viscosity is far more sensitive to structure than thermal conductivity, and suggests that although the ability to transport latent heat away from the freezing surface may be controlled to some extent by the nature of the impurities in the liquid, a more likely route to energy efficiency may be the control of viscosity of the system.

A novel aspect of this work was to combine L1-norm regularised regression analysis with molecular structure information and related thermo-physical property information. This analysis method permitted identification of the principle relations between bond-lengths of the glycol molecule and the thermo-physical properties of the mixture as a whole. While it is not possible in real-life to minutely adjust the lengths of bonds, the aim of this analysis method was to derive a general relation between the structure and the thermo-physical properties, and demonstrate, for the first time, the ability to predict the properties of a liquid from the structure of the impurity in water. For the case of a water-glycol mixture, the thermal conductivity and viscosity were determined to follow the following equations respectively:

$$k = 0.69 - 0.13(CC)(CO)^2 - 0.06(CC)(CH)(q)$$

$$\mu = 26.0 + 51.4(OH)^3 + 11.1(CC)^2(CO) - 2.0(OH)(CC)(q) - 85.0(OH)$$

where terms such as (CO) refer to deviation in bond-length (in this example, the Carbon-Oxygen bond-length) from the original values for glycol and (q) represents a charge-distribution factor. The accuracy of these equations in predicting the properties of water with the impurity is highlighted in figure 2 where good agreement between predicted and measured properties can be observed.

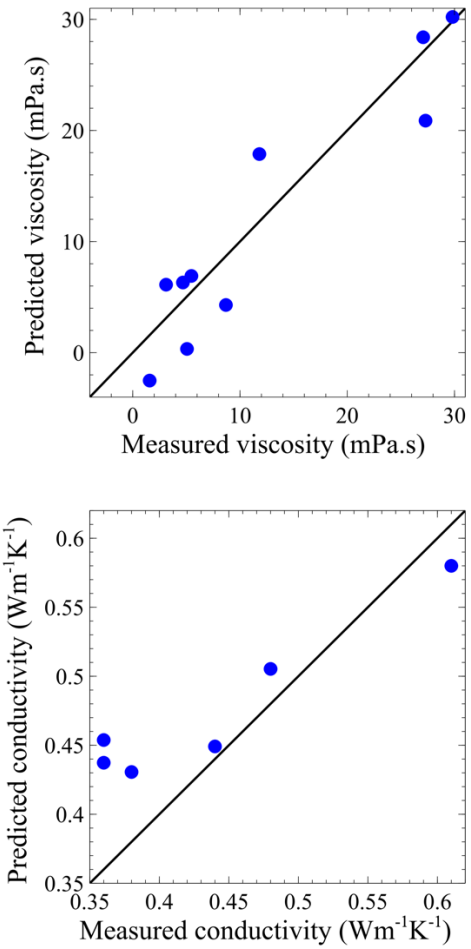

Figure 2: Prediction of change in viscosity (top) and thermal conductivity (bottom), based only with knowledge of change in molecular structure of the impurity.

In conclusion, a new method of predicting the influence of impurities on key freezing-related thermo-physical properties of water mixtures was developed and demonstrated with a model system. We combined statistical regularisation with molecular

structure information and quantitative simulation of thermo-physical properties. This work is expected to set a new direction for the estimation of liquid properties, and contribute to the development and optimisation of freezing-based desalination systems.

５．主な発表論文等
〔雑誌論文〕（計　　1 件）

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〔図書〕（計　0 件）

〔産業財産権〕

○出願状況（計　　0 件）

○取得状況（計　　0 件）

〔その他〕
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