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Novel Applications of Non Hofmeister Ion Specificity in Bubble Interactions

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ABSTRACT

The ion specificity of bubble-bubble interactions in water remains unexplained. Whatever their valence all ion pairs either completely inhibit bubble coalescence or have no effect whatever. The phenomenon appears unrelated to Hofmeister specificity. Salts which inhibit coalescence enable the formation of a high density bubble column evaporator (BCE). If hot gas bubbles are injected into the bubble column evaporator at a significantly higher temperature than the water, the hot bubble surfaces can be used to produce thermal effects in dissolved and dispersed solutes. These two properties can be exploited for a wide range of applications. Among these, high temperature aqueous reactions catalyzed at low solution temperatures, measurement of enthalpies of vaporization of concentrated salt solutions, wastewater treatments by sterilization and de-watering and desalination are a few.

1. Introduction

The most familiar ion specific phenomena are embodied in the term of Hofmeister effects. The "normal" Hofmeister series are sometimes reversed or have different permutations and various permutations. Classical theories of physical chemistry cannot explain Hofmeister effects. However as the articles in this journal will show, new theory is beginning to pin down their origin [1-5].

It is not necessary to rehearse them further. We are concerned here with another kind of ion specific effect. Like Hofmeister effects it is universal and without explanation after 40 or more years. Nonetheless, it admits of an astonishing variety of applications. We illustrate these with particular novel applications of the bubble column evaporator (BCE) to more efficient and cost effective water treatment.

1. Background to the BCE

When a gas is passed through a sinter into a column of water the bubbles fuse as they ascend. The column stays relatively clear with large (~cm) ascending bubbles. If salts are added in the column solution, such as NaCl, over a narrow concentration range of around 0.15 m, physiological concentration, the bubbles no longer fuse. The column forms a dense opaque mass of finer bubbles. For a wide variety of salts, the phenomenon occurs at roughly the same Debye length, but for a different set of salts no bubble coalescence inhibition occurs, the column stays clear up to the highest soluble concentration. More astonishing is the fact that there is a simple rule that predicts which salts or mixtures of salts exhibit the phenomenon or not [6••]. There are no known exceptions. A similar effect occurs with sugar isomers. This phenomenon is not affected by gas types [6••, 7, 8].

A second unexplained phenomenon that we will exploit occurs in tandem. If the injected bubble forming gas is heated above the column solution temperature then a nanometer-region close to the bubble surface appears to be extremely hot and turbulent. Aqueous reactions that normally require high temperature can be performed at much lower solution temperatures. The bubbles are macroscopic for the effects to occur and we have no explanation. These two phenomena open up a range of novel applications in what has come to be termed a bubble column evaporator (or BCE).

2. Applications of the BCE

We summarize a diverse range of recent works in what follows. A suitably designed water/aqueous solution gas bubble column has been used recently for a surprisingly large range of processes. All are based on the properties of electrolyte and other solute solutions in inhibiting bubble coalescence, and on inhomogeneous temperature discontinuities.

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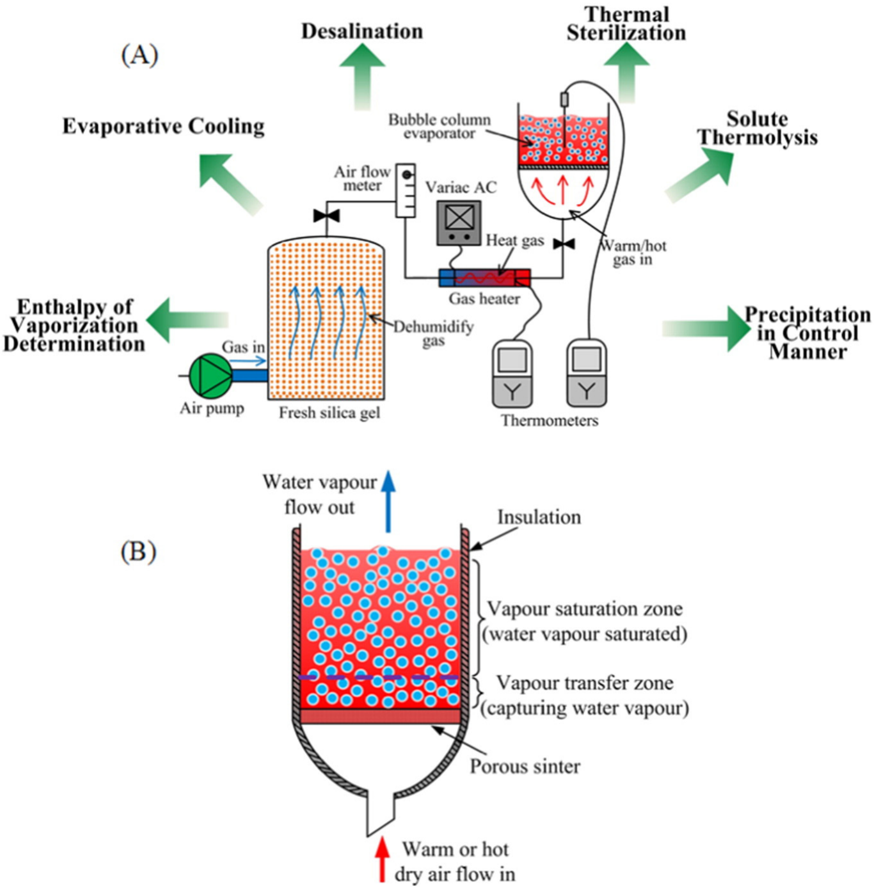

Fig. 1. Schematic diagram of the BCE system. (A) Different applications of the BCE system; (B) Schematic diagram of the bubble column in a BCE system.

Among several applications the bubble evaporation process (see Fig. 1(A)) has been used to:

1) develop a new method for the precise determination of enthalpies of vaporization (ΔH_{vap}) of concentrated salt solutions [9, 10];
2) as an evaporative cooling system [11••];
3) as a sub-boiling thermal desalination unit [12, 13];
4) for sub-boiling thermal sterilization [14•, 15•, 16•];
5) for low temperature thermal decomposition of different solutes in aqueous solution [17••];
6) for the inhibition of particle precipitation from supersaturated solutions [18].

In addition to these methods, a bubble column condenser designed to exploit the thermal properties of bubble-bubble interactions has also been studied for the production of high quality water as condensate [19-21].

Each of these novel applications can be very useful in wide ranging industrial practices. As a specific illustrative example, we discuss in detail its application to wastewater treatment.

The use of the BCE for these applications such as wastewater treatment is predicated on the observation that a continuous flow of hot, dry bubbles of about 1-3mm diameter rise quickly in an aqueous column. Bubbles rapidly absorb water vapour and transfers heat for vaporization rather than into the solution [10]. For instance, with a continuous inlet air flow at 150°C pumped into the bubble column, the temperature of the water or salt solution in the bubble column of the BCE does not go beyond 45°C during the process. This is essentially due to the high enthalpy of vaporization of water. This temperature reduction is independent of air flow rate and bubble size.

A (thermodynamic) theory has been developed to explain these results, which is based simply on the steady state thermal balance created as new, warm bubbles enter the column and evaporate precisely that amount of water equivalent to the thermal energy supplied by the bubble to the (cooler) column [11••]. The technical details for the BCE are available [14•, 15•, 17••].

The steady state thermal energy balance within a BCE, containing salt solutions, as illustrated in Fig. 1(B), can be used to explain the process whereby the heat supplied from the entering warm bubbles (per unit volume of dry gas) is balanced by the heat required for vaporization, to reach the equilibrium water vapor pressure within these bubbles.

3. The thermodynamic equilibrium in the BCE

This principle is based on the steady state volumetric balance within a bubble column, which has been used for the determination of the enthalpy of vaporization (ΔH_{vap}) of concentrated salt solutions [9-11••], and is described by the following Eq. (1):

$$[\Delta T \times C_p(T_e)] + \Delta P = \rho_v(T_e) \times \Delta H_{vap}(T_e) \quad (1)$$

Here, (in units of $J \cdot m^{-3}$), $C_p(T_e)$ is the specific heat per unit volume of the gas flowing into the bubble column at constant pressure; T_e is the steady state temperature near the top of the column; ρ_v is the water vapour density at T_e, which can be calculated from the water vapour pressure of salt solutions at the steady state temperature, using the ideal gas equation; ΔT is the temperature difference between the gas entering and leaving the column; ΔP is the hydrostatic differential pressure between the gas inlet into the sinter and atmospheric pressure at the top of the column. This represents the work done by the gas flowing into the base of the column until it is released from the solution.