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Evaporation of water from agitated freezing slurries at low pressure

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Abstract

In an absorptive vacuum freezing process, water evaporates from the freezing solution and condenses on a cold salt solution. Given sufficient condensing capacity, the evaporation rate will be controlled by the freezing solution vapor pressure. The size of the condensing equipment which matches a given evaporation system can be estimated using rate measurements made with low vapor pressure freezing solutions.

Keywords: Evaporation; Freezing; Triple point

1. Introduction

A few studies of vacuum freezing (VF) processes to separate solvent from solutions, especially water from seawater [1–3], have been reported. The Office of Saline Water's interest in freeze concentration for sea and brackish water desalination was due to its potential low-energy consumption. The principal attraction of applying freeze concentration to food liquids is its capability for concentrating heat-sensitive mixtures without damaging them. Concentration by VF avoids the localized sub-cooling encountered in indirect freezing.

VF is driven by evaporation of water at or below the triple point pressure of the agitated solution. Since this pressure is 0.61 kPa (4.58 mm Hg) or lower, an agitated, low-vacuum vessel is required. The advantage, which offsets the cost of the low pressure

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compared to the more usual indirect freeze concentration method is that the freezing slurry is chilled uniformly, without a stationary interface between the coolant and the freezing slurry. Stationary interfaces required constant, costly removal of ice or special interface treatment to keep the ice from reducing heat transfer to the coolant.

The limited rate at which water can evaporate from the agitated freezing slurry limits the undercooling to a very small valve. Furthermore, the coldest part of the agitated slurry cannot be much colder than the average temperature. The inherently uniform and controlled chilling produces the largest ice crystal sizes consistent with the liquid composition and ice particle residence time in the freezer. Larger crystals are preferred since they are easier to separate from the liquid.

There are two components of a VF system: the vapor removal unit to keep the slurry at or below its triple point and a freezing/evaporation unit to keep ice particles suspended with a fluid slurry/vapor interface. An economical system will have the freezer and vapor removal units of nearly the same capacity; both are expensive, and an arbitrary overdesign in the absence of good design information is to be avoided. Designs for seawater desalination plants with freezing vapor pressures around 0.48 kPa (3.6 mm HG) have too little vapor removal capacity for the VF of higher triple-pressure solutions such as brackish water and food and agricultural liquids. In principle, a balance between the size of evaporation and condensation units could be calculated from existing correlations, but the hydrodynamics are not standard for either the condensation or evaporation surfaces. Although the mass flow rate of water vapor can be measured, the evaporating surface has not as yet been characterized well enough to model its significant features.

Condensation on a flowing cold NaCl solution was found to be an inexpensive water vapor removal method; however, the low operating pressures, below 611 Pa (4.58 mm Hg), make the effectiveness of this method dependent on keeping the fraction of non-condensable gas in the vapor phase low. Air introduced with the feed and from equipment leaks will accumulate near the condensing interface unless removed by a mechanical pump downstream from the condenser.

At steady state the rate of water evaporation is equal to the sum of condensation and pumping rates:

$$(\mathrm{d}m/\mathrm{d}t)_{\mathrm{evap}} = (\mathrm{d}m/\mathrm{d}t)_{\mathrm{abs}} + \mathrm{pumpingrate} \qquad (1)$$

Absorption is the usual term to describe the transfer of water from vapor to the (absorbent) solution under conditions where dilution of solute in the flowing solution controls water vapor condensation. However, for best condensation rates, the heat of condensation should be removed as rapidly as possible. Therefore, most condensers chill the absorbent through the vessel walls while the vapor condenses on the inner film surface, and the effects of heat and mass transfer are combined. In our experiments heat transfer was the major rate-limiting factor, as evidenced by little effect of absorbent concentration (above about 9% salt) on condensation rate. To simplify terminology we identify the salt solution on which the vapor condenses as the absorbent.

2. Theory

Several models of evaporation have been proposed. One of the earliest argued that the vaporization energy of a molecule is equal to the energy required to create a molecular size hole in the liquid. Although the energy for creating a molecular hole in the liquid can be calculated from intermolecular potential models of varying complexity, the information is not important for water, especially at low temperatures, where there is very little energy needed for cavity formation [4].

A more up-to-date evaporation model has two steps: movement of the molecules to the vapor/liquid interface, and expansion to vapor density. An analysis by Agrawal and Menon relates latent heat and surface tension of water [5]. They showed that an energy per unit mass required to move water from the bulk to the vapor interface can be calculated from the measured surface tension. This can be added to the energy required to expand water from the liquid to the vapor density at saturation pressure. The ratio of this energy sum over the latent heat varies from 6.8 near the freezing point to 6.2 at the normal boiling point. At the freezing point the energy needed to move water to the vapor interface (58 cal/g) is nearly twice the work of expansion (30 cal/g). As temperature rises, surface creation energy decreases monotonically while the expansion work increases to a maximum (47 cal/g), around 220°C.

Released from freezing sites, water molecules and their latent heat move from the liquid side to the vapor side of the liquid/vapor interface. The lower pressure created by vapor condensation downstream drives this movement. Freezing and the associated heat release occurs at the (ice) crystal's surface. In some views of associating liquids and solutions [6,7], special modules such as those at external and/or internal interfaces of a liquid body are necessarily related by structuring of the intervening bulk liquid. Thus one might expect some coordination between events at the freezing ice surfaces and the vapor interface.

It has been shown [8] that the evaporation rate, *ER*, depends on the difference between a calculated, characteristic liquid pressure, P_s, and the measured vapor pressure over the solution (well above the interface), P_v:

$$ER = f_1(P_s - P_v) \tag{2}$$

Similarly we consider that condensation rate, *CR*, depends on the difference between the measured vapor pressure, P_v, and a characteristic absorbent vapor pressure, P_a:

$$CR = f_2(P_v - P_a) \tag{3}$$

These equations are strictly formal, since when used to model the VF process, P_s and P_a are average values over the liquid surfaces. Their accurate measurement for nonequilibrium, high flux conditions would be difficult. The equations do show the underlying assumptions behind the expectation that for a given plant design there will be a freezer vapor pressure and an absorber vapor pressure for which the process can be carried out with a balance between the water removal and freezing units.

At the balance pressure, $ER \cong CR$, and P_v for the system could be determined implicitly from Eqs. (2) and (3). The balancing pressure determined at one set of conditions can then be used to predict the optimum relative size of the DFC units (with a given triple-point pressure). The absorbent pressure is strictly determined by the condenser design since transfer through the absorbent film is controlled by the area and thickness of the flowing film. Because its the more costly unit, DFC sizing begins by determining the smallest acceptable freezer size. The condenser size which best matches the agitated freezer for the range of pressures needed to concentrate a given feed can be determined if the relative size of the units is known.

3. Experimental

The agitated freezer/condenser is contained in a single vacuum shell, as shown in Fig. 1. The shell consists of two sections: the top is a condenser 127 cm high and the bottom is a freezer 66 cm high. The cylindrical sections are 61 cm in diameter with hemispherical ends.

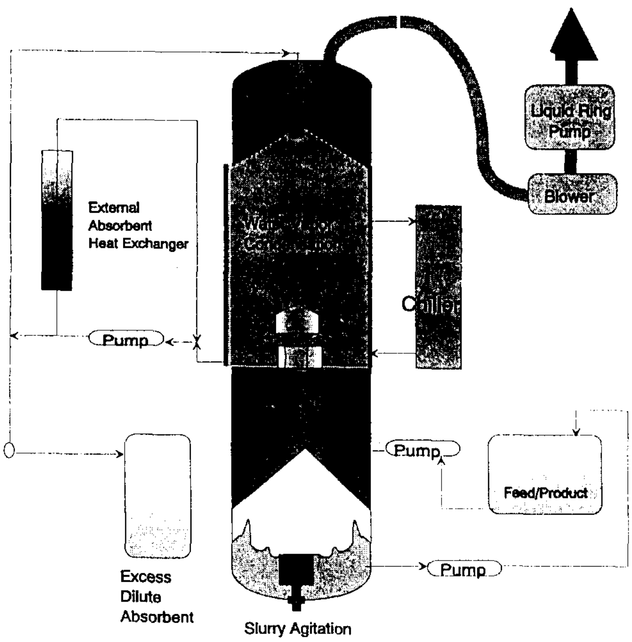

Fig. 1. Agitated freezer/condenser in a single vacuum shell.

The condenser contains spray heads for introduction of NaCl solution absorbent against the wall 76 cm above the bottom of the section. The absorbent drains along a vertical shell wall surface of approximately 1.5 M^2. An automatic level control drains solution when water vapor absorption exceeds the original charge of 43 l. Drained absorbent was continuously weighed and condensation rate calculated from the drained weight measurements. All measurements including temperature, pressure, and flow rate were automatically logged at 20 s intervals.

Refrigerated methanol was pumped through the absorbent chilling coils which enclosed the section of absorbent shell contacting the falling absorbent film. Inlet and outlet temperatures and flow rate were measured, allowing calculation of the heat flow from absorbent to the methanol. An auxiliary refrigerant-cooled heat exchanger connected to the absorbent recirculation loop served to prepare a recycle absorbent of the desired temperature. Net heat flow to the absorbent was calculated from the measured flow rate; and inlet and out temperatures and absorbent concentration were calculated from refractive index measurements of periodic absorbent samples. Absorbent concentrations between samples were interpolated using the continuously measured drainage rate. Total heat flow due to water vapor condensation is the sum of the heat flow to the methanol and the net heat flow to the absorbent.

Because pressures required for freeze concentration are so low, water vapor absorption equipment developed for air dehumidification and cooling is not effective. Air and other noncondensable gas entering the vapor space between the freezing slurry and absorbent will be pushed to the absorbent surface by the water vapor flow impeding water vapor condensation. A combined blower/liquid ring pump is used to remove approximately 150 cfm of mainly water vapor, but more importantly, air from the absorption section, through an outlet at the top. To maintain the low pressure required, a chilled salt solution is recirculated through the liquid ring pump as sealant. Sealant chilling (3.5 kW) is needed to maintain an absorption pressure of 545 Pa (4.1 T). Pumped water vapor removal, about 0.2 kg/s (determined directly by weight loss from the freezer without absorbent flow) [10], is negligible in the context of Eq. (1), so the rate of evaporation from the freezer is only slightly greater than the condensation rate on the recirculating absorbent.

The lower freezer contains inlets, outlets, a viewing port and connections for pressure gauges and thermocouples. Two vertical baffles (7.6×23 cm high) are attached to the wall on a diameter of 5.1 cm from the agitator, which is centered in the bottom of the tank. The agitator is a 15 cm high, 16 cm diameter, fluted cylinder driven through a shaft seal from below. The four flutes (or channels) rotate 90° from the top to bottom. This type of agitation was determined to be more vigorous than turbine blades or propellers and more effective in keeping the ice pumpable and swept from the walls. Dilute solutions freeze quite rapidly at the triple point and will adhere to smooth vertical surfaces if the surfaces are not vigorously rinsed. An agitation range of 200-500 rpm can be used, with a throughput of 180-820 kg/h. At agitation rates below 200 rpm, ice visibly adheres to the freezer walls and agitator.

The freezer is connected at the inlet and outlet to progressing cavity pumps which convey fluid through — and seal — the freezer. Both pumping rates are metered and the feed rate controlled by the pressure difference between the absorbent section and the bottom of the freezer. This control method permits the fluid mass in the freezer to be maintained near 45 kg.

4. Analysis of results

Pressure differences based on measurements of P_v and estimates of P_a and P_s from equilibrium calculations based on temperature and concentrations measurements are small. But they show which liquid is closer to equilibrium with the vapor phase (and accordingly has less effect on rates of transfer). The difference between P_v and P_a decreases as the water vapor removal capacity nears the evaporation capacity. With undersized absorption equipment and dilute freezing solutions (with higher equilibrium pressure and evaporation rate potential), P_v will be controlled by the absorbent and condensing conditions, whereas with more concentrated freezing solutions, P_v will approach the equilibrium absorbent pressure, P_a, and be controlled by the freezing solution.

Fig. 2 shows the effect of auxiliary chiller use on the difference between P_a and P_v. Reducing condensation capacity by eliminating the auxiliary chilling reduces the pressure difference. The data were modelled with RS1 least squares fitting procedures. Extrapolating the auxiliary chilled line of Fig. 2 to the maximum possible system pressure, the triple point of water indicates an absorbent concentration of 28% NaCl would be needed (above the maximum solubility) to condense water vapor at the rate the freezing solution can evaporate. Fig. 3, which shows the dependence of condensation rate on the shell coolant flow rate, indicates that above about 1000 kg/h condensation is insensitive to shell cooling. To increase condensation capacity beyond the 7-8 kg/h plateau indicated in the figure, it is necessary to increase the absorbent/vapor contact surface by enlarging the absorber or to improve the ability of the absorbent film to transfer heat. This is usually achieved by thinning the film and/or increasing turbulence in the absorbent film by increasing the absorber height.

A related graph of the operating domain, Fig. 4, shows the variation of mass transfer between liquid phases with P_v. Freezer residence time clearly affects the rates of evaporation and condensation. This is possibly due to an enhancement of the ice freezing rate by particles. The two residence times, 0.1 and 0.22 h, shown in Fig. 4 correspond to measured slurry ice contents of 10.7 (±1) and 27.1 (±4) wt%, respectively. The runs shown in Fig. 4 took 4-5 h.

5. Discussion

Extrapolation of the measurements at 2-3 wt% NaCl to pure water indicates that our freezer could evaporate about 21 kg/h from an agitated slurry with an unagitated vapor interface of 0.3 M^2. The rate per unit of unagitated surface, 19 $g/s/M^2$, is surprisingly close to evaporation rates reported by Shiloh and Siderman [1] for an unbroken slurry surface, about 20 $g/s/M^2$. This suggests there is little effective surface increase as a result of fairly vigorous agitation. The maximum rate of evaporation from a freezing slurry is certainly below a rate that can be calculated from a simple theoretical

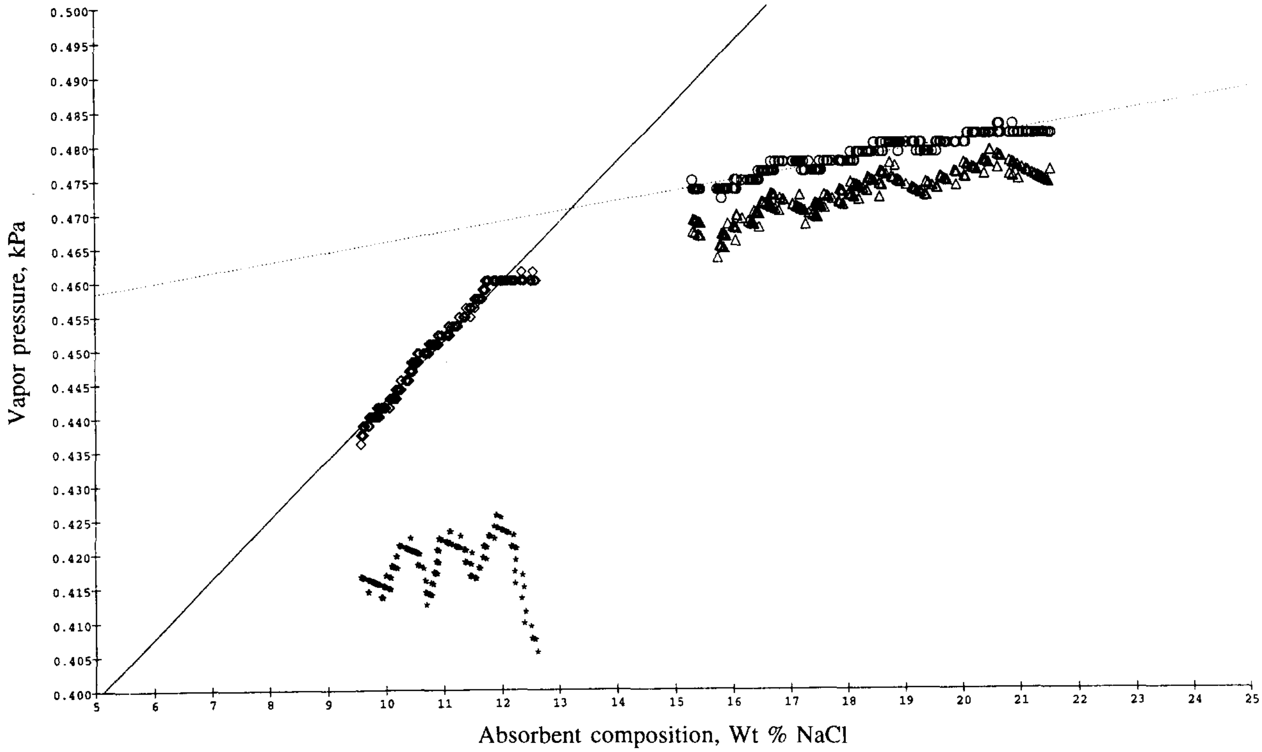

Fig. 2. Vapor pressure of absorbent. ○, measured pressure, no auxiliary chilling; ...., 0.4510+.001478x; Δ, equilibrium absolute pressure, no auxiliary chilling; ◇, measured pressure, auxiliary chilling; —, 0.355+.00869x; *, equilibrium absolute pressure, auxiliary chilling.

basis. This is the rate at which evaporation from a condensate covered surface is impeded by collisions between evaporating and vapor molecules [6]. An estimate of this value is 700 g/s/M^2 (500 lb/h/ft^2). Clearly, it is not only the interfacial area but also its kinetic energy that controls evaporation rate; unfortunately neither can be easily measured.

How is energy transported in an agitated slurry between the freezing and evaporating sites? The minimum discrete amount of energy needed to evaporate water molecules would seem to be hard to generate in a freezing solution from random liquid molecule motions. Is it plausible that the energy released by freezing — also in discrete quantities — is preserved during movement to the evaporation sites? Restriction of evaporation to the slurry/vapor interface has recently [10] been given a thermodynamic basis, showing that the energy to evaporate a liquid molecule is essentially the interfacial calculated from the energy surface area and surface tension. It has been demonstrated some time ago that the triple-point liquid/vapor interface is not diffuse, and an estimate of the interface thickness of water at the triple point, ~5 A, based on estimates of the surface tension-isothermal compressibility product, is approximately the size of a single molecule [11].

Intermolecular energy concentrates on the more attractive side of an interface between phases. A thin liquid film between a solid and vapor will tend to be divided to match the differing boundary phases. Water adjacent to a freezing ice particle, which is not freezing to the surface, must, at least temporarily, absorb the energy given up by the water which is

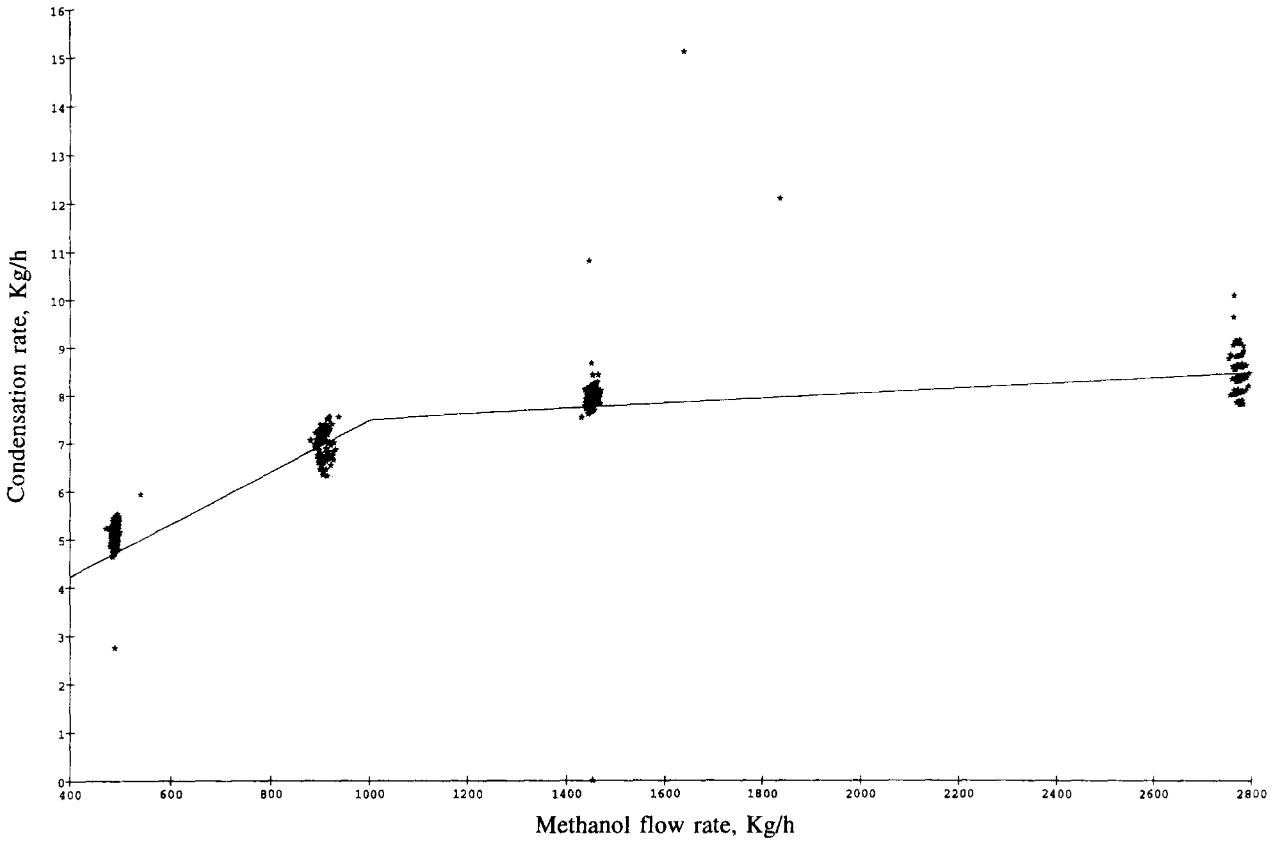

Fig. 3. Condensation rate dependence on shell coolant flow rate. $4.51+.00297x - .00244(|x-1005|)$.

freezing and attaching to the ice particle. The adjacent water is therefore less connected with and warmer than the bulk liquid further from the freezing surface. This water should be readily evaporated if the particle and the water around it are close enough to the interface. It would be less likely for energy to move from the freezing-sites distant from the interface through the triple-point temperature bulk fluid to the interface. Since the energy required to move liquid water to the interface (58 cal/g) is about 3/4 of the heat of fusion at the freezing temperature, little of the energy released at the freezing site would be expected to migrate by diffusion to the vapor interface as an energy entity. An extended transfer route would require that the minimum energy needed for evaporation accumulate at the vapor interface by thermal fluctuations from heat resident in the supercooled bulk liquid. The validity of this model of the VF process is not completely academic since ice purity will be affected by the thickness of the liquid films on ice particles. Solute will be trapped on the freezing surfaces by evaporation of very thin films where insufficient time elapses during the freezing and evaporation for it to diffuse out of the film. Controlling the thickness of the films, possibly by agitation, may thus be necessary for concentration of some solutions by VF. Ozawa and Kinosita [12] calculated the self-diffusion coefficient for water in a thin layer on a freezing surface and show that the mobility of water molecules within the layer are much less than within the bulk liquid.

Processes can be postulated which maintain

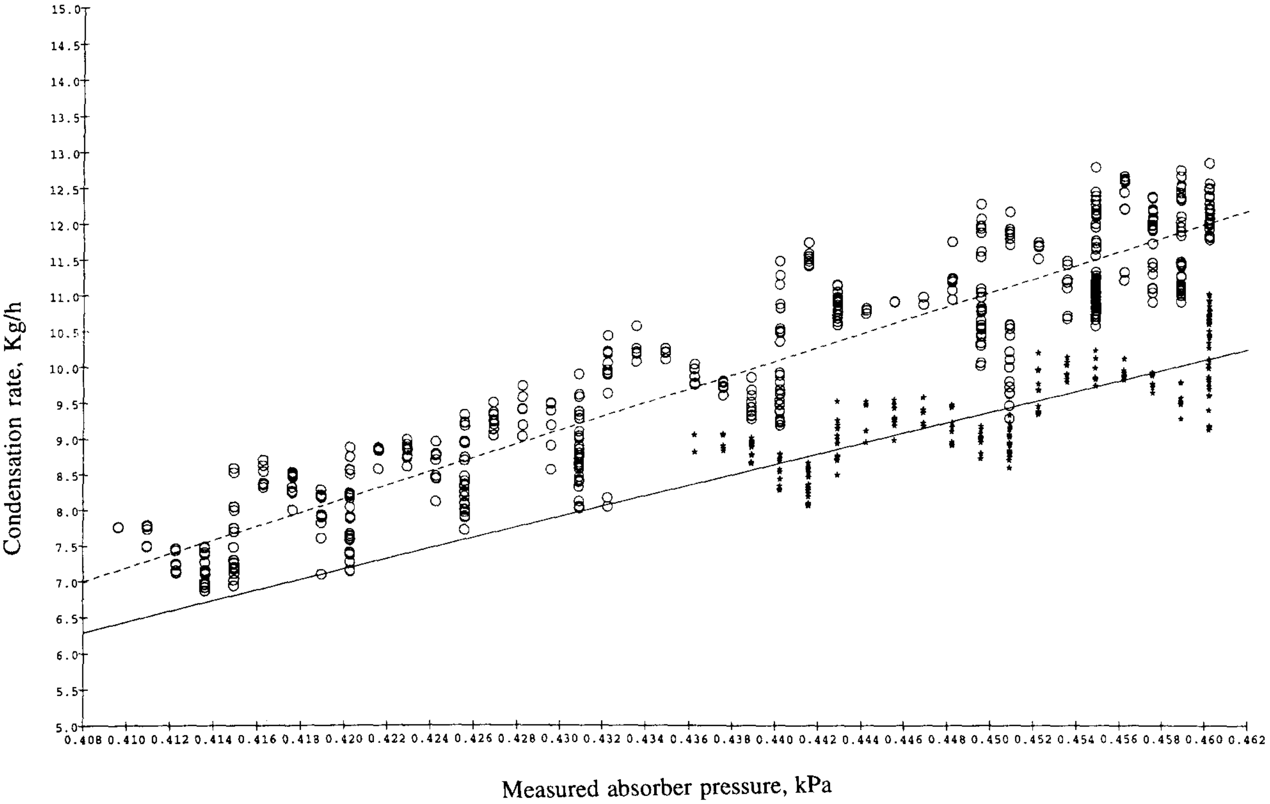

Fig. 4. Mass transfer rate, evaporation-limiting conditions. *, freezer residual time=0.1 h; ——, $73.32x-23.62$, SD=.32; ○, freezer residual time=.22 h; ---, $96.2x-32.2$, SD=.59.

the discrete quantities of energy released from the freezing sites during transport to the interface without evoking transport on ice particles. The formation of clusters in liquids and solutions have been proposed to account for features of supercooling or supersaturation [13,14]. Evidence for discrete ice-like clusters in liquid water of about 20 A at normal freezing temperatures has been reported [13]. A convincing argument has recently been published [15], which postulates the existence of cluster-like structures in liquid water. The basis for the postulate is good agreement of experimental heat capacities with a model which includes a contribution from the vibrational energy to maintain an equilibrium between the structures. Given the existence of clusters in a freezing slurry, and assuming something like the non-statistical approach to (unagitated) solutions [16,17] is applicable, one might predict a dynamic force network in the slurry which clusters at points of intersection and matter preferentially transported along channels of clustering sites between the ice particles and the liquid/vapor interface. The clustering sites in the agitated slurry are, in the proposed view, analogous to solutes in a solution, with temperature driving the organization rather than surface tension. In the solution case, interfacial molecules most influence solution ordering, correspondingly, in the slurry; the most influential clusters are those at the vapor interface.

6. Conclusions

In this study we determined the pressure and evaporation rate from a freezing NaCl solution, which at more dilute concentration depends on water vapor removal (by condensation on a chilled flowing aqueous NaCl film), under conditions where the freezing rate is constrained by the vapor pressure of the freezing solution. By extending the trend of increased condensation capacity with increased pressure to the dilute solution limit of feed composition (solute-free water), the maximum possible vapor removal capacity or the experimental unit was estimated.

The water vapor removal capacity for a particular application can be estimated using the measurements and method described using published composition vs. pressure data or methods such as those of Cisternas and Lam (electrolytes) [18], Chen (sugars, salts and acids) [19], Archer [20] or Thurmond and Brass [21] (NaCl), or Bromley (sea salt solutions) [22]. Study of the evaporation from an agitated freezing slurry, where the rates are dependent on transport processes within the slurry, can provide information about heat and mass transport in liquids between known bounding phases.

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