

LIQUID-SOLID PHASE TRANSFORMATION OF POTASSIUM IODIDE AQUEOUS SOLUTIONS OF DIFFERENT CONCENTRATIONS HELD INSIDE A POROUS MATERIAL

M. Lemerrier¹, M. Brun² and J. F. Quinson³

¹INSTITUT NATIONAL DES SCIENCES APPLIQUEES, 69622 VILLEURBANNE CEDEX, FRANCE

²ECOLE CENTRALE DE LYON, 69131 ECULLY CEDEX, FRANCE

³UNIVERSITE CLAUDE BERNARD - LYON I, LABORATOIRE DE CHIMIE APPLIQUEE ET DE GENIE CHIMIQUE, URA CNRS 417, 43 BOULEVARD DU 11EME NOVEMBRE 1918, 69622 VILLEURBANNE CEDEX, FRANCE

Calorimetric analysis shows a succession of transformations inside and outside the pores, whose characteristics depend on the concentration of the solution and the amount of porous body present.

For a given porous body, whatever the initial concentration of the solution, the capillary condensate concentration evolves systematically, during cooling, towards the eutectic concentration even if the initial salt concentration is higher than the eutectic one. It should be noted that this phenomenon indicates migration outside the pores of water or potassium iodide according to the initial concentration.

For various samples whose pore size is decreasing, successive solidification of divided water and eutectic occurs at decreasing temperatures. The freezing temperature depression of water in divided KI solutions does not seem to be a function of the salt concentration but is dependent mainly on the division effect. A nearly linear relationship between pore radius and the reciprocal of temperature depression may experimentally be established for divided eutectic.

Keywords: calorimetric analysis, liquid-solid phase transformation, porous materials

Introduction

The predictability of solidification of a fluid held inside a porous body is important in various fields such as freezing of soils, foodstuff, biological materials.

Liquid-solid transformations of divided pure substances have been widely studied [1-9].

For a pure substance and under particular experimental conditions, certain authors [9] have shown that the triple point temperature of the capillary condensate is lowered in relation to the pore radius.

When cooling a solution, concentration and division effects will occur simultaneously.

In the case where the porous medium is connected to a large amount of dilute solution, previous papers [11, 12] have shown that the capillary condensate evolves towards the eutectic concentration.

The purpose of the present work is in one hand to generalize the preceding results to solutions whose concentration is higher than the eutectic one, in the other hand to consider the case where the eutectic quantity is insufficient to saturate the porous material. In this aim, the ratio of salt and porous material amounts is controlled.

Solidification temperature depression of a capillary condensate: theoretical background

When a porous material is entirely saturated by a condensate, a unique correspondence exists between the freezing temperature and the curvature of the liquid-solid interface. The lowering of this temperature, T , obtained by combining Laplace and Gibbs-Duhem is then:

$$T - T_0 = \Delta T = - \int_T^{T_0} \frac{d(\gamma_{ls} C_{ls})}{\Delta S_m} \quad (1)$$

where T_0 is the normal solidification temperature, ΔS_m the volume transition entropy of the liquid phase. C_{ls} and γ_{ls} are respectively the main curvature and the surface tension of the liquid-solid interface.

The solidification in a capillary can proceed either by a progressive penetration of liquid-solid meniscus, formed initially at the outlet of the pore at the normal solidification temperature, or by a classical mechanism of nucleation.

For any mechanism envisaged, the curvature of the solid-liquid interface is spherical at the beginning of solidification, and :

$$C_{ls} = \frac{2}{R_n} = \frac{2}{R - t} \quad (2)$$

where R_n is the curvature radius of the solid-liquid interface, R the pore radius; t is the thickness of the condensate layer adhering to the pore walls and which is not affected by the state change.

By introducing condition (2) in the theoretical Eq. (1), the following expression is obtained:

$$\frac{1}{\Delta T} = \frac{\overline{\Delta S_m}(T)}{2\gamma_s(T)}(R-t) \quad (3)$$

where $\overline{\Delta S_m}(T)$ is the average value of the volume entropy of transition in the temperature range $T-T_0$.

It may be noted that the value of the abscissa at the origin corresponds to the thickness t .

Experimental procedure

Calorimetric analysis is a technique that is very suitable to study the phase transition of a condensate held inside and outside the pores.

The analysis of a potassium iodide solution that thoroughly saturates a porous material is performed by using a Mettler DSC 30 differential scanning calorimetry.

Porous materials

Textural characteristics of the porous materials used, determined by water thermoporometry [13], are shown in Table 1, where R_{\max} is the pore radius corresponding to the maximum of the pore size distribution curve and V the total porous volume per gram of porous material.

Table 1

Type	SiO ₂	SiO ₂	SiO ₂	Al ₂ O ₃	SiO ₂
R_{\max}/nm	3.3	6.9	9.6	11.1	25.4
$V/\text{mm}^3 \text{g}^{-1}$	230	520	530	490	640

Sample preparation

During cooling of a KI solution divided inside a porous material, it has already been shown [11] that the capillary condensate concentration evolves towards the eutectic one.

The weight $m_{\text{KI sat}}$ (mg) of potassium iodide necessary to fill the porous volume $v_p(\text{mm}^3)$ of a sample with eutectic is given by the equation:

$$m_{\text{KI sat}} = v_p \rho_{\text{EUT}} X_{\text{EUT}} \quad (4)$$

where X_{EUT} is the eutectic mass fraction, ρ_{EUT} the eutectic volumic weight (mg/mm^3) and $v_p(\text{mm}^3)$ is equal to $m_p \times V \times 10^{-3}$; $m_p(\text{mg})$ and $V(\text{mm}^3/\text{g})$ are re-

spectively the weight of porous material used and the total porous volume per gram of porous material.

By varying both the weight of solution m_{sol} , and its initial concentration X , the weight of salt in solution m_{KI} can be adjusted according the relationship:

$$m_{\text{KI}} = m_{\text{sol}} X \quad (5)$$

Phase transition of a KI aqueous solution able to saturate the porous sample with the eutectic

This case occurs when $m_{\text{KI}} \geq m_{\text{KI sat}}$

Analysis of DSC curves

As solid phases (ice and crystalline KI) are completely immiscible, three types of DSC curves, represented in Fig. 1, can be observed during a continuous cooling.

a) Case where $X = X_{\text{EUT}}$ (0.52)

The eutectic solution has the same behaviour as a pure compound. So only two peaks 2 and 3 are observed. Peak 2 characterizes the crystallization of eutectic solution outside the pores after a variable supercooling of a few degrees. Peak 3 characterizes the equilibrium liquid-solid transformation of eutectic solution inside the pores; the spreading of the curve is a function of the pore radius distribution.

b) Case where $X < X_{\text{EUT}}$

Three peaks (1, 2 and 3) are observed.

Peak 1 represents the supercooling breakdown of excess water followed by progressive ice deposition. As a result salt concentration in the solution increases as temperature is lowered.

When this concentration becomes the eutectic one, the crystallization of bulk solution occurs and gives peak 2.

Finally peak 3 characterizes the liquid-solid change of the divided solution: its temperature allows to assume that the concentration inside the pores has increased to reach a value very close to the eutectic one.

c) Case where $X > X_{\text{EUT}}$

In the same way, three peaks (4, 2, 3) are still observed.

Peak 4, which appears first, corresponds to KI deposition outside the pores with supersaturation and then progressive dilution of solution.

When the eutectic concentration is reached, the bulk solution crystallizes (peak 2)

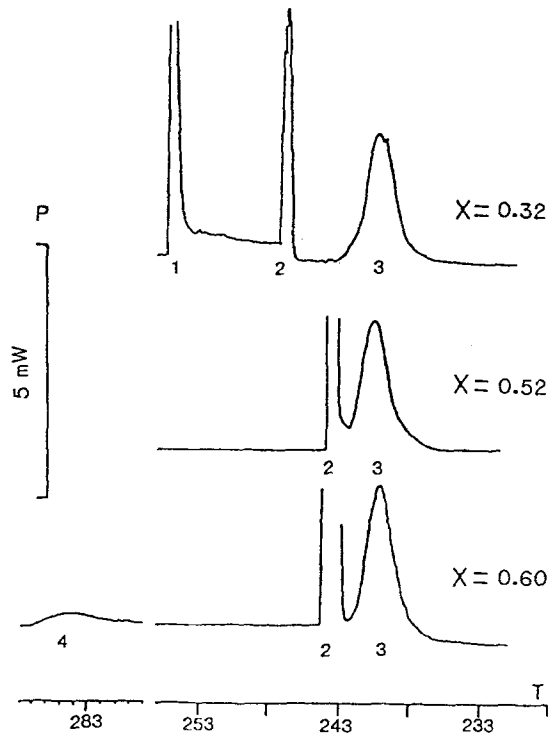


Fig. 1 DSC curves during cooling of KI solutions saturating a porous material

Peak 3 is due to crystallization inside the pores of a solution which still seems to be close to eutectic as its position is experimentally identical to that of peak 3 obtained in the case where $X = X_{EUT}$.

Peak analysis has been confirmed by:

- heating samples: reverse equilibrium transformation occurs.
- using only bulk solution: only peaks 1, 2, 4 can be observed.
- varying the amount and mean pore size of porous body: peak 3 only is modified.

During cooling, the inside the pores liquid concentration evolves towards the eutectic one whatever the initial concentration of solution. If $X < X_{EUT}$, water migrates out of pores, crystallizes outside, is replaced by a solution of increasing concentration. If $X > X_{EUT}$, KI migrates out of pores, crystallizes outside, is replaced by a solution of decreasing concentration.

Division effect

a) Case $X = X_{EUT}$

The temperature depression ΔT of the solution held inside different porous materials has been determined.

The curve $\Delta T^{-1} = f(R)$ obtained is given in Fig. 2. This curve can be considered to be a straight line as already noted [12]. According to Eq. (3), this observation seems to indicate that the volumic transition entropy and surface tension vary with the temperature in the same way.

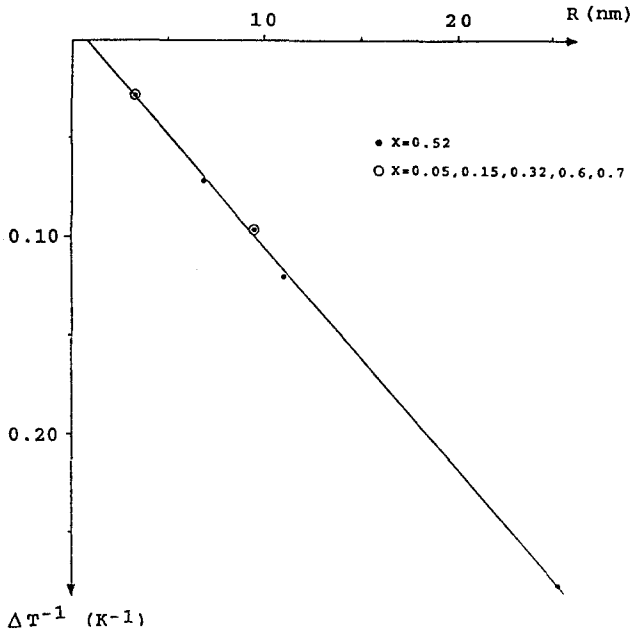


Fig. 2 Curve representing the relation between the reciprocal solidification temperature depression and pore radius, for a KI solution saturating a porous material

Its abscissa at the origin, which corresponds to the thickness t is nearly equal to 0.8 nm. This value is identical to that determined by Brun *et al.* [8] in the case of pure water. This result confirms that the layer which does not change in state is free of solute, and is in good agreement with Litvan's assertion [10].

b) Case $X \neq X_{EUT}$

For a given porous material ($R_{\max} = 9.6$ nm), Table 2 gives ΔT vs. concentration X .

Estimating accuracy of ± 0.2 K on the temperature measurement, it may be considered that ΔT has nearly the same value whatever that of X . This result confirms that the capillary condensate evolves systematically towards the eutectic concentration irrespective initial salt concentration.

Table 2

X	0.05	0.15	0.32	0.52	0.60	0.70
$\Delta T / K$	10.5	10.5	10.4	10.3	10.2	10.2

Phase transition of a KI aqueous solution. Unable to saturate the porous sample with the eutectic

This case occurs when $m_{KI} < m_{KI_{sat}}$

Description of DSC curves

During cooling, the DSC curve shows three peaks (Fig. 3).

Peak 1 is due to an ice deposit that progressively increases with the quantity of the excess solution. So when the temperature is lowered, the salt concentration of solution increases. Ice deposit stops at the T_S temperature (peak end) corresponding to an X_S solute concentration lower than the eutectic one.

Peaks 2 and 3 characterize the capillary condensate since their areas are function of the amount of porous body used.

Ice deposit starts again (peak 2) at the mouth of the largest pores at a T_{SP} temperature for which the solution still has the concentration X_S . Then salt concentration increases again as temperature is lowered.

Peak 3 occurs when the eutectic salt concentration is reached.

These assumptions are confirmed by the relative increase in peak 3 and decrease in peak 2 when the amount of salt used is increased.

Calculation of X_S

From the successive steps proposed to describe the solidification of KI solutions unable to saturate the pores with eutectic, it is possible to calculate X_S .

Using a weight m_{sol} of solution whose salt concentration is X , the quantity m_{EUT} and volume v_{EUT} of eutectic solution that can be obtained are calculated by the relations:

$$m_{EUT} = \frac{X m_{sol}}{X_{EUT}} \quad \text{and} \quad v_{EUT} = \frac{X m_{sol}}{X_{EUT} \rho_{EUT}}$$

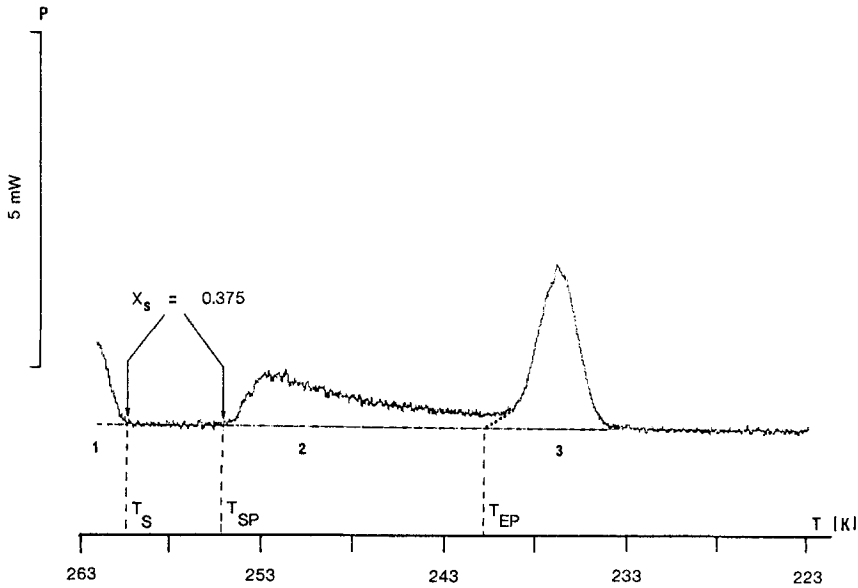


Fig. 3 DSC curves during cooling of a KI solution saturating a porous material

In these conditions, the water volume held inside the pores unfilled by the eutectic condensate is : $v_w = v_p - v_{EUT}$

and its weight: $m_w = \rho_w (v_p - v_{EUT})$

So the X_s concentration is deduced from the expression:

$$X_s = \frac{m_{KI}}{m_w + m_{EUT}} = \frac{X m_{sol}}{\rho_w \left\{ v_p - \frac{X m_{sol}}{X_{EUT} \rho_{EUT}} \right\} + \frac{X m_{sol}}{X_{EUT}}} \quad (6)$$

Concentration effect

The equilibrium temperature T_s between bulk ice and solution of calculated concentration X_s has been determined for samples unsaturated with the eutectic condensate.

In order that the temperature T_s should be an equilibrium temperature, the following experimental procedure has been used:

- firstly the sample is cooled until supercooling breakdown of bulk water occurs
- then the sample is heated until the bulk ice partially melts
- finally a second cooling is performed while the solution is in equilibrium with bulk ice.

The curve Σ (Fig. 4) representing $T_S=(X_S)$ characterizes the temperature depression ΔT_1 of the freezing point of water due to the potassium iodide solute for a bulk solution; this curve is in good agreement with the equilibrium diagram given by the literature [12] for the binary H₂O–KI system.

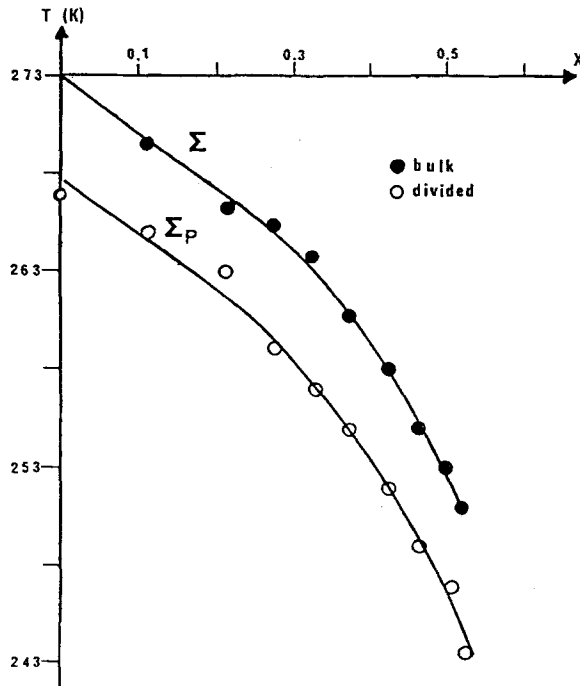


Fig. 4 Equilibrium curves between ice and KI liquid solution saturating a porous material

The freezing temperature T_{SP} of water held inside the largest pores ($R=10$ nm) of a given porous material ($R_{max}=9.6$ nm) has been measured for different values of X_S : the curve Σ_p (Fig. 4) representing $T_{SP} = f(X_S)$ is the freezing curve of water for a divided solution.

As Σ_p is nearly parallel to Σ , it may be concluded that the freezing temperature depression $\Delta T_2=T_S-T_{SP}$, of water in divided KI solution does not seem to be a function of the salt concentration but is dependent on mainly the division effect.

More generally freezing temperature depression of water, as a solvent of a divided solution, results from two cumulative and thoroughly independent effects, division and concentration :

$$\Delta T = \Delta T_1 + \Delta T_2$$

Phase diagram

For a given diameter, the freezing curve Σ_p , of water as a solvent of a binary solution held inside a porous material, has been determined (Fig. 4). Unfortunately, mainly because of the small value of the enthalpy of dissolution of KI in water, it has not been possible to observe the second branch of the liquidus curve, i.e. the solubility curve Γ_p of KI.

Nevertheless, as the effect of division is to lower equilibrium temperatures, Γ_p is located below the solubility curve Γ of KI in bulk water.

The branches Σ_p and Γ_p intersect at E_p , the eutectic point for the solution inside the pores. Its abscissa X_{E_p} should not be, in principle, equal to that of E , the eutectic point for the bulk solution. However this difference $X_{EUT} - X_{E_p}$ is apparently slight as it is not experimentally observed. In any case the schematic H_2O -KI phase diagram drawn in Fig. 5, with X_{E_p} taken equal to X_{EUT} , is compatible with the various peaks observed earlier. The evolution of the solution during a continuous cooling, is also plotted in Fig. 5 for the various cases studied.

a) case $X = X_{EUT} = 0.52$

Temperature is lowered from point A to point E without phase change. At point E, eutectic solution crystallizes outside the pores (Fig. 1; peak 2); then the remaining eutectic solution, located inside the pores is cooled from E to E_p where it crystallizes (Fig. 1, peak 3).

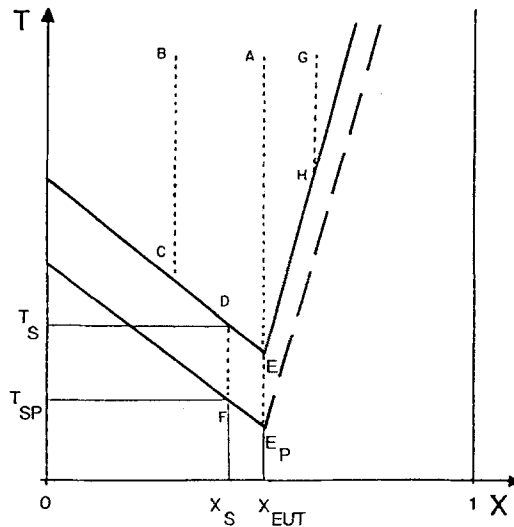


Fig. 5 Schematic phase diagram of the bulk and divided binary systems H_2O -KI and evolution of the solution during a continuous cooling

b) case $X < X_{\text{EUT}}$ and $m_{\text{KI}} < m_{\text{KI sat}}$

Ice only crystallizes outside the pores (Fig. 3, peak 1) from *C* to *D*. From *D* to *F* the solution remaining inside the pores is simply cooled. Ice starts to crystallize again inside the pores at point *F* (Fig. 3, start of peak 2) and finally, at E_p , eutectic solution crystallizes inside the pores (Fig. 3, peak 3).

c) case $X < X_{\text{EUT}}$ and $m_{\text{KI}} > m_{\text{KI sat}}$

As the salt quantity is sufficient to fill the pores with the eutectic solution, ice crystallizes outside the pores from *C* to *E* (Fig. 1, peak 1); at *E*, eutectic crystallizes outside the pores (Fig. 1, peak 2); then the remaining eutectic inside the pores solution crystallizes at E_p (Fig. 1, peak 3) in the same way as in case a.

d) case $X > X_E$ (and sufficient amount of solution)

The solution outside the pores crystallizes in two stages; progressive KI deposit from *H* to *E* (Fig. 1, peak 4), then eutectic deposit at *E* (Fig. 1, peak 3). Then the eutectic solution inside the pores evolves as in case a.

Conclusion

The freezing temperature depression of water as a solvent of a KI divided solution is nearly the same whatever the salt concentrations: this shows that the concentration has only a secondary effect in comparison with the division effect.

During cooling, according to the initial salt concentration, the migration outside the pores of solute or solvent occurs so that the capillary condensate always evolves towards the eutectic composition.

For a porous material thoroughly saturated by the eutectic, the freezing point temperature of capillary condensate varies as a function of pore radius as in the case of pure liquid.

When the amount of potassium iodide inside the solution is not able to saturate the sample with the eutectic, ice appears in the biggest pores and eutectic in the others.

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Zusammenfassung — Kalorimetrische Analyse zeigt eine Reihe von Umwandlungen inner- und außerhalb von Poren, wobei die Charakteristik der Umformungen von der Konzentration der Lösung sowie von der Menge des anwesenden porösen Körpers abhängt. Bei einem gegebenen porösen Körper verändert sich die Konzentration des Kapillarkondensates unabhängig von der Ausgangskonzentration systematisch immer in Richtung der eutektischen Konzentration, auch wenn die Salzkonzentration zu Beginn über der eutektischen Konzentration liegt. Man muß bemerken, daß diese Erscheinung je nach Ausgangskonzentration auf Migration von Wasser oder Kaliumjodid außerhalb der Poren hinweist.

Für verschiedene Proben mit abnehmender Porengröße findet bei sinkender Temperatur ein nacheinanderfolgendes Erstarren von getrenntem Wasser und Eutektikum statt. Die Gefrierpunktserniedrigung von Wasser in derartig getrennten KI-Lösungen scheint nicht eine Funktion der Salzkonzentration zu sein sondern hauptsächlich vom Separierungseffekt abzuhängen. Für unterteilte Eutektika konnte ein annähernd linearer Zusammenhang zwischen dem Porenradius und dem Reziproken der Temperaturerniedrigung festgestellt werden.