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RETENTION MODIFIED SOLID-LIQUID EQUILIBRIUM

A modified solid-liquid equilibrium (sle) is proposed and applied to characterize the equilibrium between the solid and the liquid phases existing in industrial crystallisers.*

The retention factor, which provides the basis for the calculation of the sle, is defined and an experimental technique for its determination is presented. An example is given for the binary system 1,8-cineole/ α -pinene.*

1 — INTRODUCTION

The development of continuous column crystallisation and its application to the processing of essential oils required the study of the solid-liquid equilibrium (sle) for the systems experimented. This study led to some new concepts relating the equilibrium to the separability of those systems.

The thermodynamic sle for crystals and liquid under equilibrium, as determined by conventional laboratory techniques, does not reproduce what happens in industrial crystallisers: in fact, the actual equilibrium is achieved between a liquid phase, identical to the liquid in the sle, and a solid phase composed of crystals and retained liquid, adherent and included [1]. We will designate this as the «retention modified solid-liquid equilibrium» (sle*). This concept, applicable to mixed crystals and eutectic systems, is developed here for the latter and applied to the 1,8-cineole/ α -pinene binary.

2 — RETENTION FACTOR

The retention factor, G , measures the amount of liquid retained by the crystals in a slurry and is defined by

$$G = \frac{m_l}{m_l + m_c} \quad (1)$$

where m_c is the mass of crystals and m_l is the mass of retained liquid.

Consider a binary eutectic system A + B with no solid solubility (fig. 1). The cooling of a solution with a content in A higher than that of the eutectic point (E_A , mass fraction) will produce, when the temperature reaches T_w , a liquid (y_A , mass fraction of A) in equilibrium with a solid phase, made up from pure crystals of A ($x_A = 1$) and included and adherent liquid.

As a first approximation we consider this retained liquid to be identical to the final liquid phase. Although this is not accurate for the included liquid, it is a reasonable working hypothesis for the conditions in a continuous crystallisation column, where the recrystallisation occurring along the equipment ensures the renewal of the retained liquid. So the average composition of this solid phase, x_A^* , the mass fraction of A, is

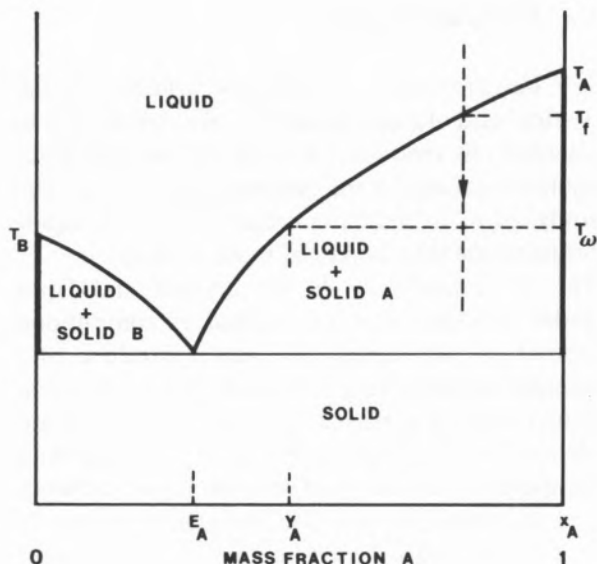


Fig. 1
Freezing of a binary eutectic system

$$x_A^* = \frac{y_A \cdot m_l + m_c}{m_l + m_c} \quad (2)$$

and from Eq. (1)

$$m_l = \frac{G}{1 - G} \cdot m_c \quad (3)$$

therefore

$$x_A^* = 1 - G(1 - y_A) \quad (E_A < y_A \leq 1) \quad (4)$$

Given G and the sle, the sle* for the A field may be calculated from y_A values, between E_A and 1. Similarly the modified solidus for the B field is

$$x_B^* = 1 - G(1 - y_B) \quad (E_B < y_B \leq 1) \quad (5)$$

or

$$x_A^* = G y_A \quad (0 \leq y_A < E_A) \quad (6)$$

At the eutectic point, the liquid and crystals have the same composition and so does the solid phase. The diagram x_A^* vs y_A (fig. 2) has a discontinuity at the eutectic point: for the A field, the diagram is a straight line of slope G starting from the (1,1) point; for the B field, it is also a straight line, of the same slope, ending at the (0,0) point. The discontinuity represents the impossibility of total separation of pure A and B.

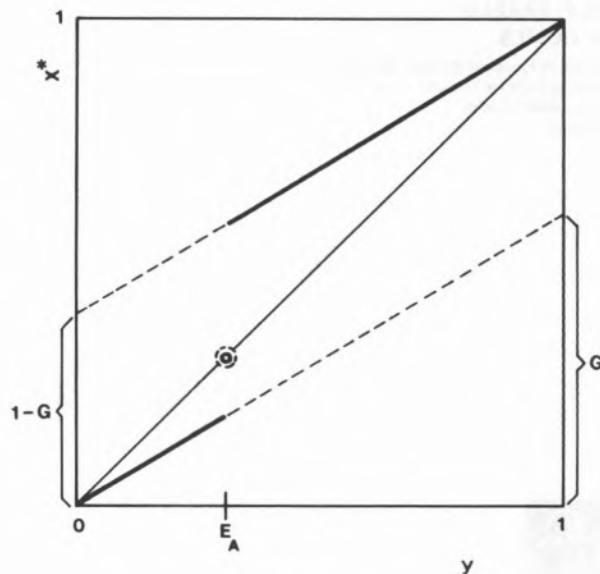


Fig. 2
 x^*/y diagram for an eutectic system

3 — EXPERIMENTAL

3.1 — SLE

The heating curve technique allows for the determination of the liquidus line by the simultaneous reading of temperature and observation of the melting solid: the end of the melting is taken as the disappearance of turbidity caused by minute solid particles suspended in the liquid.

The determination is made on a quickly frozen sample thus producing a homogeneous distribution of the components [2]. The 6 cm³ sample contained in double-wall glass cell is slowly heated (0.1 K/min) in a thermostated bath with precise temperature control and strong agitation. The temperature is measured by a Ni-Cr/Ni-Al thermocouple referred to the melting ice, and registered on a Phillips PM 8100.

The freezing curve technique allows for the determination of the liquidus line: freezing shows up as a peak on the temperature-time diagram; the solidus is difficult to detect. The equipment is similar to the one described above, including a freezing thermostated bath. For very low temperatures we used adequate cryogenic mixtures. The results are quite reproducible, but deviate several degrees Celsius from the actual liquidus, because Miers super-solubility curves are obtained [3].

As there has been some criticism about the reliability of these methods we used a technique of our own to determine under microscopic observation, the liquidus and solidus lines. Under a slow cooling of the microscope stage the commencement of freezing is observed when very small crystals appear. Under heating of a quickly frozen sample, we determine the solidus as the melting begins on the intersection of crystallisation planes with different orientations. We use a modified Leitz microscope where the usual stage was replaced by a thermostated one. The recirculating alcohol is refrigerated by a Hectofrig Flow Cooler CA 3. The microscope stage can be electrically heated by means of a voltage controller. A water-vapour free environment is usually created around the stage, by circulating cold nitrogen. The liquidus is highly reproducible and confirms the results obtained by the heating curves, the solidus being fairly visualized [4].

For 1,8-cineole/ α -pinene sle determination, we used

1,8-cineole : eucaliptole «codex», with a minimum content of 99,9%, its main impurity being α -pinene.

α -pinene : BDH, AnalaR with a minimum content of 99%.

The liquidus and solidus lines show an eutectic system with no solid solubility (fig. 3 a).

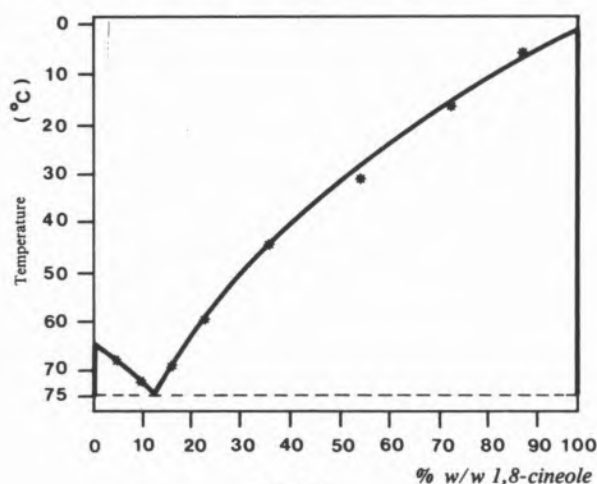


Fig. 3a)

SLE for the 1,8-cineole/ α -pinene binary

3.2 — RETENTION FACTOR

Determination of the retention factor requires the characterisation of a solid phase in contact with a

liquid and the measurement of the relative masses of the phases and retained liquid. This requires the separation of those phases at constant temperature which is the procedure's major difficulty, when working below 273 K.

To ensure the highest efficiency in separation we used vacuum filtration. The retention factor determination started by growing crystals in a stirred crystalliser located in a thermostated space, which also enclosed the vacuum filtration equipment, so that the system was filtered at constant temperature. The compositions were obtained by G.L.C. on the solid and liquid phases separated by filtration.

For the eutectic system 1,8-cineole/ α -pinene the crystallisation and filtration temperatures were below 273 K and as low as 241 K; the 1,8-cineole content in the mother liquor ranged from 55 to 90%.

4 — RESULTS AND DISCUSSION

The retention factor, G , was obtained from Eq. (4)

$$G = \frac{1 - x^*}{1 - y}$$

and it was not found to be temperature sensitive nor could we find any definite correlation between the magnitude of G and the mother liquor concentration. The average value of G was 0.062 ± 0.001 .

If A refers to 1,8-cineole, $E_A = 0.13$ (w/w) and assuming a constant value of $G = 0.062$

$$\begin{aligned} 0.13 < y_A \leq 1 & \quad x_A^* = 0.938 + 0.052 y_A \\ 0 \leq y_A < 0.13 & \quad x_A^* = 0.062 y_A \end{aligned}$$

The modified solid-liquid equilibrium is represented in fig. 3 b.

This work, which has been confined to a specific eutectic system, is now being extended to a range of systems. Meanwhile, this effect has already been found, by the authors, to be of general occurrence and independent of the solid-liquid equilibrium type. The large difference between the extreme retention factors encountered, claims for better understanding of the phenomenon, one possible explanation relying on the crystal habit. As a matter of fact, low retention factors, less than 10%, were found for scattered, almost spherical particles;

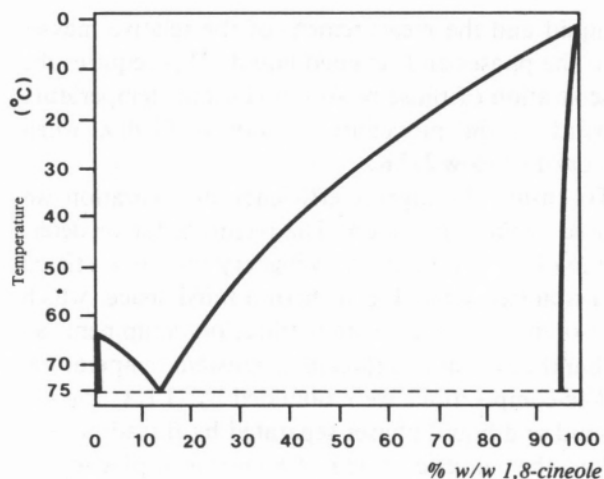


Fig. 3b)
SLE* for the 1,8-cineole/ α -pinene binary

larger factors, up to 30%, were found for needle shape crystals, with dendritic growth.

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REFERENCES

- [1] H. SCHILDKNECHT, J. BREITER, *Chemiker Zeitung*, **94**, n.º 1,3 (1970).
- [2] H. VAN WIJK, W. SMIT, *Anal. Chim. Acta*, **23**, 545-551 -551; (1960); *ibid.*, **24**, 41-45 (1961).
- [3] J.W. MULLIN, «Crystallisation», 2nd ed., Butterworths, London.
- [4] M.F. FARELO, PhD thesis, IST, Lisboa, 1979.

RESUMO

Equilíbrio Sólido-Líquido Modificado

Estabelece-se o conceito de equilíbrio sólido-líquido modificado, *esl**, para caracterizar as fases sólida e líquida efectivamente presentes no processamento industrial por cristalização. Para caracterizar e calcular o *esl**, define-se a taxa de retenção e apresenta-se uma técnica experimental para a sua determinação. Exemplifica-se com o sistema binário 1,8-cineol/ α -pineno.