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PURIFICATION OF ε-CAPROLACTAM BY CRYSTALLIZATION

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Purification of ε-caprolactam by crystallization from trichloroethylene has been experimentally studied. Physical properties of the caprolactam-trichloroethylene system and its relevant crystallization characteristics were determined. Evaporative crystallization realized in an air-lift type of crystallizer was selected as the best mode of crystallization. Bench-scale model of such crystallizer of 16 l volume was constructed and its performance with the studied system was tested. Based on the data obtained from the model crystallization experiments a full-scale crystallizer of 100 m^3 volume was designed, built and successfully put into operation.

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Introduction

ε-Caprolactam (hereinafter called CAP) is used for production of synthetic fibres and various plastic materials. The quality of these products strongly depends on the CAP purity, mainly on a content of impurities which can be oxidized by $KMnO_4$ and the basic substances in both volatile and free form. In order to meet the ever-increasing demands on CAP purity, different methods of purification are employed, such as solvent extraction, crystallization from aqueous solution or melt, and chemical purification. These processes, however, must be followed by further extensive purification by e.g. multistage vacuum distillation [1].

Crystallization of CAP from some organic solvents, namely toluene and trichloroethylene (hereinafter called TRI) exhibits a better purifying effect than crystallization from water. Therefore, these solvents constitute promising media for CAP crystallization that would enable reduction of downstream purifying operations to a minimum.

This contribution describes the development of caprolactam crystallization from trichloroethylene on a bench-scale later scaled-up to a production unit with an annual capacity exceeding 20000 tons.

Physical Properties of Phases

ε-caprolactam - $C_8H_{11}ON$ - m.p. 69.9 °C, solid phase density 1120 kg m^{-3}
trichloroethylene - C_2HCl_3 - b.p. 86.7 °C, density and viscosity 1461 kg m^{-3} and 0.55 mPa s, respectively.

Solubility of CAP in water-free TRI was determined by the last crystal method [2], see Table I.

Tab. I Solubility of caprolactam in trichlorethylene

Temperature, T °C	Solubility, p wt.%	Temperature, T °C	Solubility, p wt.%
0	28	30	46
5	29.8	40	56.1
10	32.7	48.5	66
20	38.3	55.5	76

These data fitted to the solubility equation [3] by the least square method yielded

$$\log x = -47.5140 + \frac{1545.8471}{T} + 16.9696 \log T \qquad (1)$$

where x is the mole fraction of CAP in the saturated solution in TRI and T is the absolute temperature in K.

Density, ń, and viscosity, ç, of undersaturated solutions of CAP in TRI were determined by the pycnometric method [4] and the Höppler viscometer (a falling ball), respectively. Experimental data for 30, 40 and 50 °C were fitted by the least square method to expressions

$$\rho = Ac + B \tag{2}$$

$$\eta = C10^{(cD)} \tag{3}$$

here p is the solute concentration expressed in wt.% and A through D are adjustable constants. The calculated constants of Eqs (2) and (3) for density expressed in kg m^{-3} and viscosity in Pa s together with the concentration range over which these expressions are valid, are listed in Table II.

Tab. II Parameters of Eqs (2) and (3)

Temperature, °C	$-A$	$B\times10^{-3}$	$C\times10^{4}$	$D\times10^{2}$	Validity wt.%
30	4.2483	1.44	5.875	1.618	33 – 47
40	4.0245	1.425	4.842	1.662	28 – 57
50	3.592	1.397	2.871	1.862	50 – 68

The vapour pressure over saturated water-free solutions of CAP in TRI determined with the isoteniscope is given in Table III. It can be approximated within the temperature range from 25 to 40 °C by the Raoult law

$$p_i = p_i^0 x_i \tag{4}$$

where p_i and p_i^0 is the saturated vapour pressure over solution and pure solvent, respectively and x_i is the solvent mole fraction in the solution. The saturated vapour pressure of pure solvent (TRI) within the studied temperature range is expressed by

$$\log p_i^0 = 10.09881 - \frac{1822.28}{T} \tag{5}$$

where T is temperature in Kelvin, obtained by correlating the data reported in Ref. [4]

The metastable zone width of CAP solution in TRI, ΔT_{max}, was measured by the polythermal method [6] at cooling rate $(-dT/dt)$ = 3, 5 and 20 K h^{-1} for solutions saturated at three different temperatures T_{nas}. The apparent nucleation order, n, was evaluated by correlating the experimental data according to [6]

$$\log \Delta T_{\max} = E + \frac{1}{n} \log \left[-\frac{dT}{dt} \right] \tag{6}$$

where E is the adjustable constant, see Table IV.

The enthalpy of CAP crystallization from its TRI solution was estimated as −112.1 kJ kg^{-1} at 25 °C based on the molar differential dissolution enthalpies 103.73 and 107.32 kJ kg^{-1} determined calorimetrically for 5.7072 and 6.0244 molal solution, respectively.

Tab. IV Maximum undercooling and apparent nucleation order of caprolactam solution in trichloroethylene

T_{nas}	ΔT_{max}, °C			n
	$(-dT/dt)$ = 2, K h^{-1}	$(-dT/dt)$ = 5, K h^{-1}	$(-dT/dt)$ = 20, K h^{-1}	
30	1.08	1.72	3.44	1.99
48.4	3.37	5.2	10.04	2.11
64.2	3.21	4.98	9.66	2.09

Crystallization

Selection of Crystallization Mode

Crystallization affected by indirect cooling proved to be unsuitable for the studied system due to the fast development of encrustation on the heat exchange surface, which prevented efficient heat transfer. Encrustations were formed even at a temperature difference of 1 °C between the cooling surface and the solution bulk. Moreover, following from the material balance, a certain amount of solvent must be removed from solution during crystallization in order to achieve a satisfactory crystallizer production rate. Since CAP dissolved in TRI slowly decomposes at temperatures over 50 °C, evaporation should be preferably carried out under reduced pressure for reducing operational temperature.

Furthermore, CAP crystals float on its saturated TRI solution due to their lower density. A thick layer of crystals formed at the liquid surface adversely affects the evaporation rate that must be somehow enhanced. Bubbling an inert gas through the crystallizing system results in a substantial increase of the liquid-gas interfacial area and thus enhances evaporation. Therefore, an air-lift crystallizer of vacuum type [7] represents a suitable equipment for crystallizing CAP from its solution in TRI.

Bench-Scale Equipment

A bench-scale air-lift vacuum crystallizer of 16 l working volume consisted of a metallic cylinder (150 mm diameter, 1120 mm length) with conical bottom. A cylindrical draught tube, 90 mm in diameter and 760 mm in length, was concentrically fixed in the crystallizer starting 120 mm above its bottom and ending 40 mm under the liquid level. Filtered ambient air was sparged at a fixed rate into the crystallizer through a perforated sparge ring of 80 mm diameter situated inside the draught tube 500 mm under the liquid level. Feed solution was continuously introduced by suction with a controlled rate through an inlet tube penetrating axially through the crystallizer bottom and reaching 30 mm into the draught tube. Crystal suspension was continuously overflowing from the liquid level through an outlet tube of 20 mm diameter surrounded by a small pocket into a collecting flask. A lid containing thermometers, the sparger and a vapor outlet tube tightly closed the crystallizer. The whole system worked at underpressure. Auxiliary circuits, such as condensation of TRI from vapors, vacuum generation, inert gas purification etc. are not described.

Temperature was measured in an annulus near the upper and lower edge of the draught tube. Underpressure prevailing in the system was continuously monitored and kept at a constant level during each experiment.

Weight and volume of suspension leaving the crystallizer for a certain time were determined. CAP crystals were separated, dried in a thin layer under an infra heater and weighed. From these data magma density (m_c) and the crystallizer specific production rate (dm_c/dt) were calculated. Crystal size distribution (CSD) was determined by sieve analysis carried out for 15 min.

Crystallization Model Experiments

Conditions under which crystallization model experiments were performed, specifically experiment duration, rate of solution and gas dosing into the crystallizer, prevailing pressure, temperature of feed solution t_S, and gas, t_I, introduced into the equipment and temperature of suspension leaving crystallizer, t_{susp}, are listed in

Table V.

Results of experiments, i.e. the mean crystal size, L_{av}, density, m_c expressed in kg of CAP crystals contained in 1 kg of mother solution and the crystallizer production rate, dm_c/dt, expressed as kg of crystalline CAP produced from 1 m^3 of the crystallizer working volume per 1 hour, together with the separation intensity, SI, defined as the mass of equivalent 1 mm crystals produced in 1 m^3 of crystallizer volume in 1 hour [8], ie.

$$SI = L_{av}[\text{mm}]\frac{dm_c}{dt}[\text{kg m}^{-3}\text{ h}^{-1}] \qquad (7)$$

Tab. V Conditions of crystallization model experiments

Experiment No	1	2	3	4	5	6
Duration, h	32	35	21	30	21	25
Solution dosing, $l\,h^{-1}$	6	6	6	6	4	4
Gas dosing, $l\,min^{-1}$	4.2	4.2	8	32.5	2.7	2.7
Pressure, kPa	15.16	13.3	14.9	14.23	13.96	14.23
c(CAP), wt.%	44.8	44.2	43.5	44.3	44.4	44
c(w), wt.%	0.25	0.34	n	0.45	0.36	0.38
t_S, °C	47	47	49.5	49	49	49
t_i, °C	23	22	22	22	21.5	21
t_{susp}, °C	29	26.5	24.2	29.2	26	25.5

n - not determined, c(CAP) and c(w) - concentration of CAP and water in the feed solution of CAP in TRI, respectively

Tab. VI Results of crystallization experiments

No	L_{av}, mm	m_c, kg kg^{-1} soln.	dm_c/dt, kg m^{-3} h^{-1}	SI
1	0.75	0.212	62.5	47
2	0.85	0.172	56.25	48
3	0.75	0.25	75	56
4	1	0.067	26.87	27
5	0.95	0.176	37.5	36
6	1.02	0.163	36.25	37

are reported in Table VI.

Experimental values given in Table VI fitted by the least square method gave the equation [2]

$$L_{av}^{(1+3g/n)} = 3Bm_c^{(1-cg/n)}\left(\frac{dm_c}{dt}\right)^{(g/n-1)} \tag{8}$$

where g represents the crystal growth order and B is the system constant yielded

$$L_{av} = 2.942m_c^{-0.0355}\left(\frac{dm_c}{dt}\right)^{-0.332} \tag{9}$$

Comparing Eqs (8) and (9) gives $g/n = 0.668$ and $c = 1.55$. Combining these results with the nucleation order (see Table IV) gives the crystal growth order $g = 1.3$.

From Eq. (7) it transpires that the mean size of CAP crystals produced in the model continuous air-lift crystallizer is a function of both magma density and the crystallizer specific production rate. The dependence on the crystallizer production rate is substantially more pronounced than that on the magma density.

The crystallizer operated satisfactorily without any major failure. The suspension mixing induced by gas sparging was sufficient as signified by identical temperature at the upper and lower draught tube edge, similar CSD of solid phase in suspension leaving and remaining in crystallizer and virtually no vertical size separation of crystals along the crystallizer length. Encrustation was occasionally formed on the inner walls of the crystallizer above the liquid level, especially when a "fountain" caused by a high gas flow appeared on the liquid surface. Scales never developed both on the crystallizer walls under the liquid level and inner or outer surface of the draught-tube. However, the outlet tube and surrounding pocket were prone to encrusting that sometimes resulted in a complete blockage of the outlet.

Crystal purity

Purification efficacy of CAP crystallization from TRI was evaluated based on two crystallization runs performed with an industrial solution containing all usual impurities. From each run 9 suspension samples, each of 2 l volume, were processed as follows: crystals were separated either by vacuum filtration using a Büchner funnel or a filtration centrifuge, dried and dissolved in distilled water to form 50 wt.% solution. Absorbance of this solution and filtrate adjusted to 50 wt.% concentration was determined with a spectrophotometer at 290 nm wavelength in

a 10 cm cuvette. Range of experimental absorbance values of both CAP solution and corresponding filtrate are given in Table VII.

In general, the higher the filtrate absorbance, the higher the absorbance of the corresponding crystals solution. The purity of crystalline CAP increased, i.e. absorbance of its solution decreased, if CAP crystals separated from suspension were re-suspended in 50 wt.% solution of pure CAP in TRI and then separated by vacuum filtration. The absorbance of their aqueous solution varied in the range (1.2, 3.6) compared to the absorbance range (10, 46) of untreated crystals solution.

Tab. VII Experimental absorbance values

Separation	Absorbance		Run
	Solution	Filtrate	
centrifuge	1.6 – 4.8	127 – 172	I
filtration	3.6 – 12.4	177 – 1025	II
filtration	10 – 46	177 – 1025	II

CAP purified by crystallization must be further processed in order to get the final pure product. This procedure was simulated in the laboratory as follows: 10 wt.% of water was added to a wet crystalline CAP (containing about 5 wt.% of TRI) separated by filtration from the suspension leaving the crystallizer. After removing the solvents present by vacuum distillation at 100 °C, 0.5 wt.% of NaOH in the form of 25 wt.% aqueous solution was added and thereafter water thus introduced into the system was removed by vacuum distillation at 100 °C. 80% of the resulting CAP melt was distilled off at 150 °C and pressure 1 kPa. Aqueous solution containing 50 wt.% of this distillate exhibited the absorbance of 0.15, acidity of 6×10^{-3} mmol kg^{-1} and the permanganate number 24 000 sec. Purity of the end product thus obtained considerably surpassed the quality of CAP purified by crystallization from water [9].

Parameters of Full-Scale Crystallizer

Based on the experimental results obtained a suitable full scale crystallizer and its process parameters were specified as follows:

(i) The full scale crystallizer should be of the "air-lift" type operating under vacuum.

(ii) Walls of crystallizer above the liquid level should be equipped with a heating device for occasional removal of the encrustation formed. Inner crystallizer walls should be polished.

(iii) The optimum working temperature from the view-point of evaporation is 50 °C since the partial pressure of TRI over a saturated solution reaches maximum as follows from Eq. (4) where x_i and p_i^0 are calculated from Eqs (1) and (5). However, the solution saturated at this temperature is both too concentrated (approx. 68 wt.%) and too viscous (approx. 5 mPa s). Therefore, a working temperature of around 30 °C is preferred though the partial pressure of TRI over the saturated solution is about 25% lower than at 50 °C, but the saturation concentration and solution viscosity is only 46 wt.% and 3 mPa s, respectively.

(iv) Evaporation rate of TRI must be enhanced by an additional stream of gas introduced into the draught tube.

(v) An operating pressure of the crystallizer should be around 6 kPa.

(vi) Crystallizer should operate under conditions ensuring magma density around 20 wt.% of solid CAP and production rate about 50 kg of crystals from 1 m^3 per hour. Under these conditions an expected mean crystal size is 1 mm.

(vii) A certain amount of solution must be continuously withdrawn from the crystallizer in order to maintain constant impurity content in the solution at an acceptable level (equivalent to absorbance of 50 wt.% solution, being around 1000).

(viii) Crystals should be separated from the mother liquor using a centrifuge and, after separation, washed with pure solution of CAP in TRI. Thereafter this product is subjected to further purification.

Conclusion

A full scale crystallizer of 100 m^3 volume was designed and constructed according to criteria specified above. During trial period of this equipment, several unforeseen technical problems arose, mostly concerning an insufficient mixing intensity and suspension outlet encrusting. These were, however, successfully solved through minor modifications of the original design. The crystallizer was later brought to the full production capacity of about 20 000 t per year, producing CAP of expected purity.

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