THE INFLUENCE OF AMMONIUM SULPHATE ON THE DISTRIBUTION OF CAPROLACTAM IN THE WATER/TRICHLORO ETHYLENE SYSTEM

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When manufacturing caprolactam, the sulphuric acid—caprolactam mixture formed in the Beckmann rearrangement is neutralized with aqueous ammonia. Two immiscible phases result, the one is a nearly saturated aqueous solution of ammonium sulphate (37—40 %) with about 0.7 % caprolactam content ("sulphate-brine"), and the other ("lactam-oil"), is an aqueous solution of caprolactam containing up to 68 % caprolactam and about 0.2 % ammonium sulphate. For purification, the concentrated aqueous caprolactam solution is extracted with an organic solvent, *e. g.* trichloro ethylene.

The distribution of caprolactam between trichloro ethylene and water is especially in small concentrations [1] strongly in favour of water, therefore, to achieve good yields, a rather substantial quantity of the solvent has to be used: the volume ratio of trichloro ethylene to water is 3 : 1.

As it is known that inorganic salts tend to turn the distribution of organic substances between water and solvent, in favour of the solvent, it seemed likely that the distribution conditions in the extraction medium might be improved by the admixture of ammonium sulphate received in the process of neutralization. Additionally, the 0.7 % residual caprolactam content of the sulphate-brine could thus be recovered. To follow up this idea it became necessary to investigate, and to measure, the distribution pattern of the quaternary system caprolactam/water/ammonium sulphate/trichloro ethylene. Data referring to the ternary systems caprolactam/trichloro ethylene/water, and caprolactam/ammonium sulphate/water were known, partly from our previous investigations [1], and partly from the work of Czechoslovakian colleagues [2].

In the system caprolactam/ammonium sulphate/water (Fig. 1) water must actually be regarded as the "distributive" component, for it is the increase in the quantity of water present that brings about the emergence of a critical plait-point (K) for the otherwise immiscible aqueous solutions of the caprolactam, and of the ammonium sulphate. A particularly interesting feature of this system is that caprolactam solutions having a greater concentration than 72 %, are in equilibrium with solid ammonium sulphate and not with its aqueous solutions. According to the findings of the Czechoslovakian authors, within the range of 30° C to 50° C the course of the saturation curves does not change appreciably with temperature. Our measurements at 45° C have shown that the greatest part of that curve coincides with the saturation isotherm for 20° C, but near the point D, for instance, the solubility of the ammonium sulphate increases by about 1 %. A similar phenomenon was also observed near the point F. Our data referring to the equilibrium curves and tie-lines of the system caprolactam/ammonium sulphate/water, and somewhat more detailed than those *loc. cit.*, are presented in Fig. 1 and Table 1.

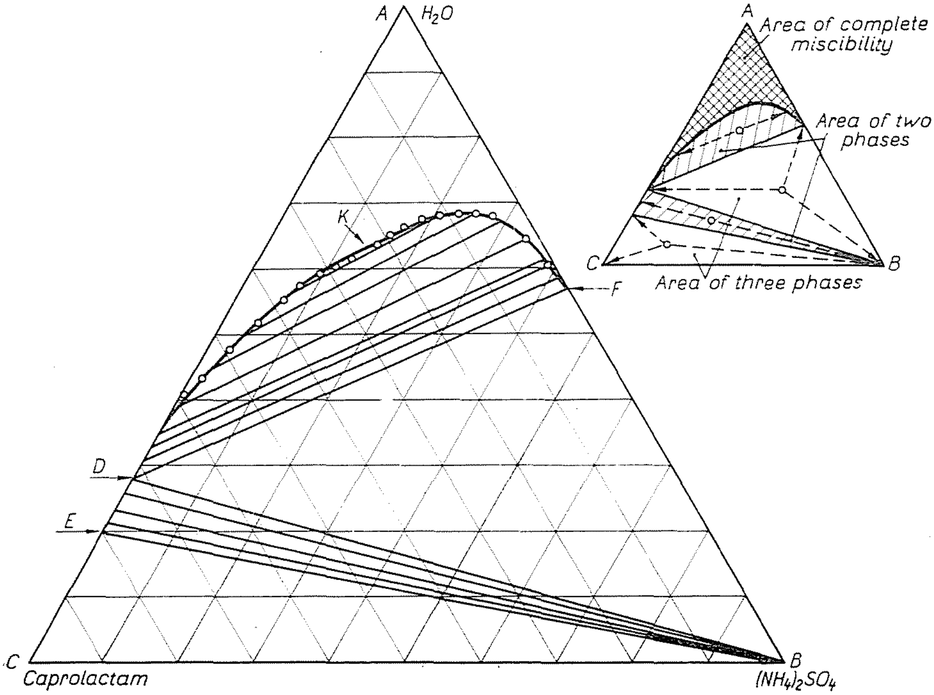

Fig. 1. The system ammonium sulphate/caprolactam/water at 20° C

Owing to difficulties in the analyses, on the one hand, and to difficulties of presentation, on the other, the data for the quaternary system ammonium sulphate/water/trichloro ethylene/caprolactam were gathered by measurements in the practically-significant two-phase ranges only. Thus, no investigation was made of ranges where, beside the trichloro ethylene phase, *e. g.* two aqueous phases, or solid ammonium sulphate, were evident. To facilitate both measurements and presentation, it was assumed that the trichloro ethylene phase does not dissolve ammonium sulphate, nor does the aqueous phase dissolve trichloro ethylene. Based partly on preliminary measurements,

Table 1

Equilibrium data of the system ammonium sulphate/caprolactam/water, at 20 °C

a) Saturation isotherm

% weight								
Caprolactam	Ammon. sulph.	Water	Caprolactam	Ammon. sulph.	Water	Caprolactam	Ammon. sulph.	Water
0	41.2	58.8	16.7	17.2	66.1	38.5	6.5	55.0
0.92	38.8	60.3	19.4	15.6	65.0	43.6	4.7	51.7
1.74	33.7	64.5	21.9	14.3	63.8	49.2	3.2	47.6
4.32	27.8	67.9	24.0	13.1	62.9	54.8	1.65	43.6
6.50	25.3	68.2	26.6	11.8	61.7	63.7	0.20	36.1
8.80	22.9	68.3	29.0	10.6	60.4	66.6	0.04	33.4
11.2	20.8	68.0	31.5	9.3	59.2	72.0	solid	28.0
13.8	18.9	67.3	35.0	7.8	57.2		$(NH_4)_2SO_4$	

b) Tie-lines

Caprolactam phase			Ammonium sulphate phase		
Caprolactam	Ammon. sulph.	Water	Caprolactam	Ammon. sulph.	Water
69.5	0	30.5	0.6	40.0	59.4
67.5	0	32.5	0.7	38.8	60.5
65.0	0.2	34.8	0.9	37.9	61.2
60.5	0.5	39.0	1.6	34.0	64.4
53.5	2.0	44.5	3.0	29.8	67.2
46.8	3.7	49.5	6.0	25.6	68.4
43.5	4.7	51.8	9.0	22.8	68.2
36.5	7.3	56.2	11.2	20.8	68.0

partly on exactly measured data [1] of the system trichloro ethylene/ /water/caprolactam, both these assumptions appear to be justified. Therefore, the aqueous solution of ammonium sulphate has been regarded as a uniform homogeneous solvent which can be characterized by its ammonium sulphate: :water ratio; accordingly, within a given series of measurements, this ratio was kept constant and only the caprolactam contents had been varied.

Four series of measurements were made with aqueous ammonium sulphate solutions having, respectively, a 5, 10, 20, and 30 % initial ammonium sulphate concentration, *i. e.* with ammonium sulphate: water weight ratios of 0.0527, 0.111, 0.250, and 0.429. Within each series of measurements the caprolactam concentration was increased till a third phase appeared, generally an aqueous solution rich in ammonium sulphate. As the whole of the saturation isotherm has not been determined, and since in aqueous solutions tie-lines have been plotted up to only 30, 18, 11, and 3.3 %, respectively, of caprolactam contents, and in trichloro ethylene solutions up to only 14, 16, 26, and 34 %, respectively, it seemed superfluous to present our data in a triangular plot. The distribution coefficient $\left(k = \frac{y}{x}\right.$, where y is the concentration of caprolactam in the trichloro ethylene phase, and x is the concentration of caprolactam in the aqueous phase$\left.\right)$ steadily increases with an increase of the ammonium sulphate : water ratio, between 0.111 and 0.250 it is higher than 1.0 (Fig. 5, Tables 2/I, II, III, IV). If these data are presented in the *Hand*-co-ordinate system [3], nearly straight lines result (Fig. 4). If the distribution coefficient is not constant, *i. e.* the plot in the x/y co-ordinate system is not a straight line, then it is customary to use the *Hand*-co-ordinates which take into account the mutual solubility of the solvents. In this system the weight ratio of the solute and the solvent which gives the bulk of the phase, to the extract $\left(\frac{y}{b}\right)$, respectively to the raffinate phase $\left(\frac{x}{a}\right)$, is represented.

In a logarithmic system this representation usually results in a straight line.

Thus:

$$\log \frac{y}{b} = \log \left(\frac{y}{b}\right)_{\frac{x}{a}=1} + n \log \frac{x}{a}$$

$$\frac{y}{b} = a \left(\frac{x}{a}\right)^n .$$

In the case of the problem dealt with in this paper it was assumed that the ammonium sulphate + water phase does not dissolve trichloro ethylene at all, consequently, that $a = 100 - x$; but no great error is introduced in assuming the same for the trichloro ethylene phase, *i. e.* that the quantity of dissolved water therein is negligible. At least, in our previous experiments [1] even in the case of pure water the uptake of water by the trichloro ethylene phase increased to more than 1 % only, if its caprolactam content was higher than 15 %.

So, in the present instance the formulas

$$\log \frac{y}{100 - y} \quad \text{and} \quad \log \frac{x}{100 - x}$$

may be used in computations.

Table 2

Tie-lines of the system ammonium sulphate/water/trichloro ethylene/caprolactam, at 20 °C

I. Ratio ammonium sulphate : water = 0.0527 (a = 0.5, n = 1.23)

% weight of caprolactam				
in the aqueous phase x	in the trichloro ethylene phase y	$\frac{x}{100-x}$	$\frac{y}{100-y}$	$\frac{y}{100-y-a_b}$
0.80	0.086	0.008	0.00086	
1.25	0.194	0.013	0.00195	
2.30	0.44	0.024	0.0044	
3.85	0.92	0.040	0.0093	
5.65	2.01	0.060	0.0205	
7.80	2.51	0.085	0.0257	
9.40	3.22	0.104	0.033	
11.55	4.04	0.130	0.042	
17.8	7.76	0.216	0.084	
21.5	8.93	0.275	0.098	
25.2	10.9	0.34	0.122	
30.6	14.3	0.44	0.167	

II. Ratio ammonium sulphate : water = 0.111 (a = 1.2, n = 1.33)

% weight of caprolactam				
in the aqueous phase x	in the trichloro ethylene phase y	$\frac{x}{100-x}$	$\frac{y}{100-y}$	$\frac{y}{100-y-a_b}$
0.55	0.125	0.0055	0.00125	
1.00	0.294	0.010	0.0030	
1.55	0.493	0.016	0.0050	
2.00	0.738	0.0205	0.0074	
3.80	1.72	0.040	0.0175	
5.85	3.00	0.062	0.031	
7.65	4.16	0.083	0.0435	
9.20	5.40	0.101	0.057	
13.6	8.8	0.157	0.0965	
17.8	16.1	0.216	0.19	

III. Ratio ammonium sulphate : water = 0.250 (a = 7, n = 1.4)

% weight of caprolactam				
in the aqueous phase x	in the trichloro ethylene phase y	$\frac{x}{100-x}$	$\frac{y}{100-y}$	$\frac{y}{100-y-a_b}$
0.60	0.56	0.006	0.0056	
1.05	1.36	0.0106	0.0138	
1.85	3.10	0.019	0.032	
3.50	7.05	0.036	0.076	
7.00	15.7	0.075	0.186	
8.70	22.0	0.095	0.28	0.29
11.10	25.8	0.125	0.35	0.36

IV. Ratio ammonium sulphate : water = 0.429 (a = 190, n = 1.77)

% weight of caprolactam				
in the aqueous phase x	in the trichloro ethylene phase y	$\frac{x}{100-x}$	$\frac{y}{100-y}$	$\frac{y}{100-y-a_b}$
0.90	4.60	0.0091	0.048	
1.30	7.64	0.013	0.083	
1.65	11.7	0.017	0.133	
2.00	15.0	0.0204	0.177	
2.40	19.5	0.0246	0.242	0.246
2.80	24.3	0.029	0.32	0.33
2.95	29.0	0.030	0.41	0.43
3.30	34.0	0.034	0.515	0.57

In case of pure water: a = 0.3, n = 1.2 (1).

With trichloro ethylene phase of higher caprolactam contents we have tried to take also its water contents into account. The value a_b for the water contents of the trichloro ethylene phase were taken from previous measurements [1]. Thus $b = 100 - y - a_b$. Since the values arrived at in this way were hardly different from those computed without taking into account the water contents, no trouble was taken to determine the water contents of that trichloro ethylene phase which is in equilibrium with the aqueous ammonium sulphate phase. The change in the values of the distribution coefficients does not conform with the known logarithmic correlation [4] $k = k_0 e^{-\text{const.}\, s}$, where k_0 is the distribution coefficient for the salt-free system, and s is the concentration of the salt.

The mathematical formula, and the physico-chemical interpretation of the observed correlations is still to be made. The study of the effect of salts upon the values of the distribution coefficients will be continued.

Table 3

Refractive indexes of the system ammonium sulphate/water, at 20 °C (6)

n_D^{20}	Aqueous caprolactam solution % caprolactam	Aqueous ammonium sulphate solution % ammonium sulphate
1.34	4.4	4.0
1.35	10.3	10.2
1.36	16.5	16.65
1.37	22.4	23.2
1.38	28.0	30.0
1.39	33.6	37.0
1.40	39.4	(44.3) extrapolated
1.41	45	(51.5) ,,

Experimental

1. *The system caprolactam/ammonium sulphate/water*

The saturation isotherms were plotted on the ground of data furnished by turbidity titrations, as described in a previous communication [1]. The tie-lines, *i. e.* the compositions of the phases in equilibrium with each other, were determined by measurements of refractive indices (see below). Results are shown in Table 1 and Fig. 1.

2. *The system ammonium sulphate/water/trichloro ethylene/caprolactam*

In this system the quantity in each phase, of ammonium sulphate, water, and tricholoro ethylene, and the total quantity of caprolactam being

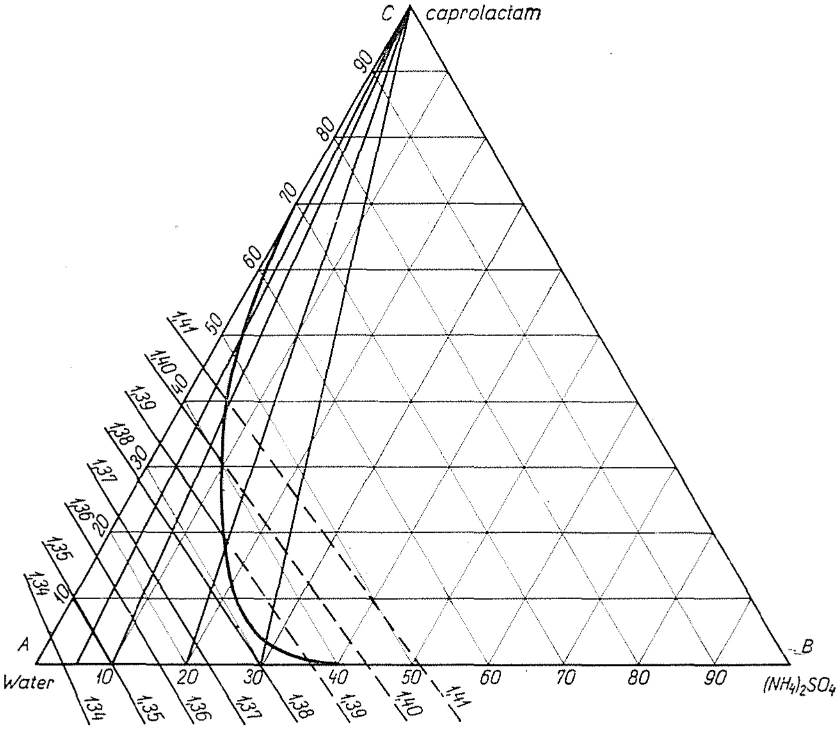

Fig. 2

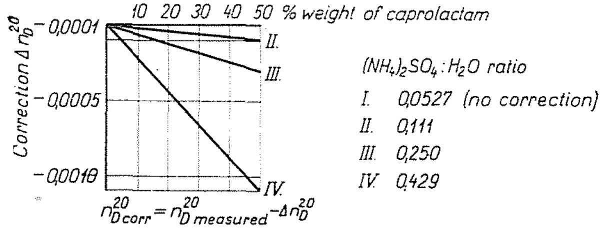

Fig. 3

known, only the quantity of caprolactam present in the phases in equilibrium with each other had to be determined. For these determinations, measuring the refractive indexes of dilute and not too concentrated solutions proved to be the most favourable. Higher concentrations of caprolactam are best determined by chemical analysis [5]. Owing to insufficient differences between the refractive indices of the caprolactam and the solvent, the trichloro ethyleen

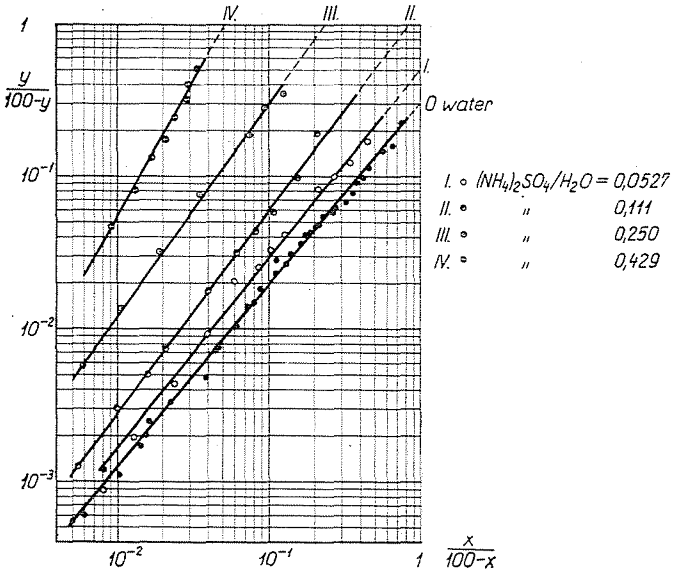

Fig. 4. Diagram after Hand, of the system water/ammonium sulphate/caprolactam/ trichloro ethylene

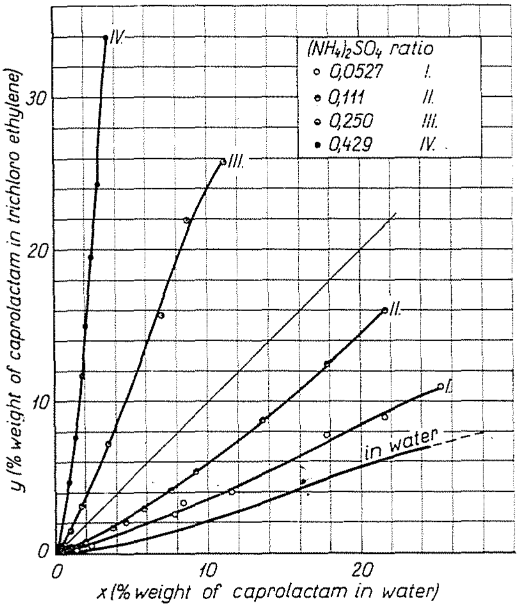

Fig. 5. Equilibrium diagram (x *vs* y) of the system caprolactam/water/ammonium sulphate/ trichloro ethylene

phase could not be analysed by refraction measurements. The concentration of this phase was computed on base of material balances, from the caprolactam contents of the aqueous phase. To minimize the errors, the solvent : water ratio was made fairly large (from fivefold to eightfold).

With the aid of a triangular plot, the caprolactam content has been determined from the refractive index of the ternary system ammonium sulphate/water/caprolactam (Fig. 2). The points of equal refractive indices of the system caprolactam/water [1] and of the system ammonium sulphate/ /water [6] were connected with straight lines. This method supposes a rigorous additivity of refractive indices.

The deviation from additivity, and especially the corrections with the more concentrated ammonium sulphate solutions were measured at several characteristic points, and these corrections were taken into account (Fig. 3). On Fig. 3 the correction found there as appertaining to an estimated caprolactam value must be subtracted from the measured refraction value and this *corrected refraction value* is to be used on the triangular plot (Fig. 2.). This correction is for deviations from the additivity rule.

On the triangular plot (Fig. 2) the intersection of the corrected refractive index and the known ratio of ammonium sulphate to water locates the composition of the sample.

Results of measurements are shown in Fig. 4 and Fig. 5, respectively in Table 2.

Summary

Investigations were made concerning the effectiveness of the extractive purification of raw caprolactam, with the possibility in mind that this process might be improved. The salting-out effect of ammonium sulphate has been measured in the system caprolactam/ /water/trichloro ethylene.

Correlations were found, and quantitatively formulated, for the salting-out effect of the ammonium sulphate.

Incidentally, an industrial application for the "sulphate brine" was found in the process itself.

Literature

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