EQUILIBRIA OF THE TERNARY SYSTEM CAPROLACTAM /WATER/ ORGANIC SOLVENT, IN THE LIQUID STATE

By

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Solvent extraction in the manufacture of caprolactam is generally used for the purification of the raw product. This operation is necessary to attain higher yields, but it is indispensable when the high grade of purity is to be reached, which alone can satisfy the rather stringent requirements of artificial fibre manufacture. The beginning in Hungary of the commercial production of caprolactam, particularly the design of a caprolactam extraction plant, made it imperative that the distribution factors of caprolactam, in various liquid media, be investigated. This investigation had also to be undertaken, because in similar plants built in neighbouring countries, the caprolactam extraction process had not yet been completely mastered at the time of these experiments.

For a first approximation the distribution of caprolactam between water and some of the obvious organic solvents has been investigated. In the course of these experiments the miscibility curves of caprolactam/water/organic solvents systems have been determined, and the distribution of caprolactam between water and organic solvents, *viz.* benzene, nitrobenzene, chloroform, carbon tetrachloride, trichloroethylene, has been measured.

Experimental

1. First the equilibrium data have been determined by plotting the equilibrium curves. Turbidimetric titrations were used for this end. Into well-stoppered flasks the organic solvent was weighed to an accuracy of 0.01 g. Its temperature was adjusted to, and kept constant at, 20 ± 0.1°C in an ultrathermostat, then titrated with water from a micro-buret till the appearance of turbidity. Thus the solubility of water in the organic solvent in question (point *a* in Fig. 1) has been established. As the next step, to the *a* mixture a certain quantity of a nearly-saturated solution of caprolactam, in the same solvent, was added from a micro-buret. This mixture, now containing a known quantity of caprolactam, was put into the thermostat, and then titrated as before. Repeating this procedure with gradually-increased quantities of capro-

lactam, points between a and b_1 on the solvent branch of the equilibrium curve have been established also involving part of the "aqueous" branch beyond plait point K. As soon as the curvature of the plot made it feasible (from point a_1 on), the saturated solution of caprolactam prepared with the solvent was supplanted by an 80% aqueous solution of caprolactam. Thus, greater quantities of caprolactam could be dissolved in the same volumes. The "aqueous" branch of the equilibrium curve up to point b_1 has been established by a similar procedure. In this case water was measured into the flask and this was titrated, alternately, with the solvent and the 80% aqueous solution of caprolactam, up to point b_1. The meeting of the two branches of the curve at point b_1 show that the measurements were sufficiently correct. The principle which underlies this procedure, and the separate titration steps, are shown in Fig. 1.

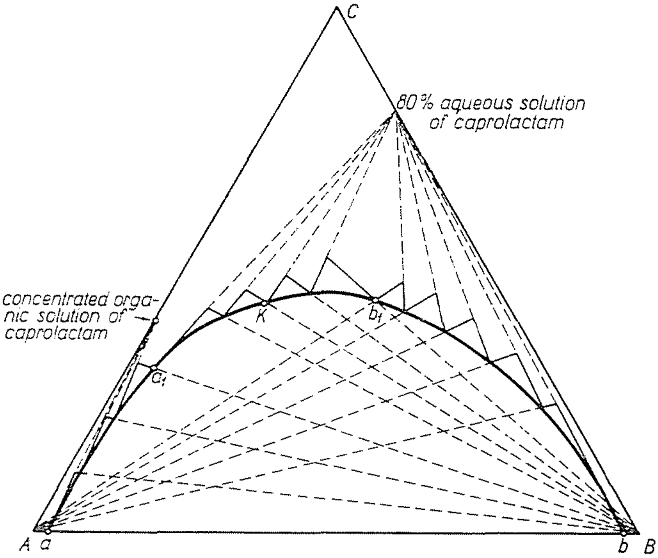

Fig. 1. Principle of the turbidimetric titrations
A) solvent
B) water
C) caprolactam
K) plait point
a) solvent saturated with water
b) water saturated with solvent

2. In a next series of measurements the distribution coefficients, and the tie-lines, have been established. On a microanalytical balance solid caprolactam was weighed into ground glass stoppered test tubes, and, from a microburet, water and organic solvent were added. The test tubes were immersed in the thermostat, and after one hour equilibrium was attained by vigorous shaking. This shaking had to be of short duration to prevent changes in the

temperature of the sample, it was best to repeat shaking and thermostating alternately. It could be noted that whereas keeping the temperature constant during equilibrium measurements was imperative, the values of the distribution coefficient were less sensitive to changes in temperature.

The caprolactam contents of the separate phases was measured next.

The plait-point K was graphically determined from plots traced on the basis of the values measured.

For trichloroethylene the numerical values shown by saturation curves and tie-lines (distribution coefficients) are those actually measured, for other solvents the graphically-smoothed values are presented.

Kudrjavceva and Krutikova [1] carried out similar measurements with dichloroethane, chloroform, and dichloromethane as solvents. The values pertaining to chloroform are in good agreement with the results of our measurements.

3. For the assay of caprolactam three methods were used, *viz.* refractometry, dielectrometry, and potentiometric titration.

a) *Refractometric assay.* In general, a refractometer of the Zeiss-Abbé type was used, and four decimal digits noted; for very dilute solutions a Zeiss immersion refractometer was used, allowing the precision to be carried one digit further. By refractometry the concentration of caprolactam could be measured with sufficient accuracy only in aqueous solutions, the difference between the indices of organic solvents and caprolactam being too small to allow the use of this method in other than aqueous media. Another obstacle is the disturbing effect of the substantially-different refractive index of the water dissolved, though in small quantities, in the organic phase. Therefore, whenever the analysis of the solvent phase could not furnish trustworthy data (small concentration of caprolactam in organic solvent), the concentration of caprolactam was established by a material balance based on the analysis of the aqueous phase. In these instances the solvent:water ratio was made large, in order to minimize the influence of analytical errors. The curves, refractive indices *vs.* concentrations, were plotted from the data of several parallel measurements. These measurements were carried out both on aqueous solutions free of, and saturated with, the organic solvent. (Table 7.)

b) *Dielectrometric assay.* The concentration of caprolactam can also be found by registering the dielectric constant of the sample solution.* In the absence of salts and in an aqueous solution this presents no difficulties. From solutions in organic solvents water has to be eliminated, *e. g.* with sodium sulphate, because the high value of the dielectric constant of water interferes. The water content of the sample is first determined by the Karl Fisher method. The evaluation of the dielectric data is based on calibration curves (Table 8).

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* The assay of caprolactam by dielectrometry had been treated by S. B. Nagy, of the Research Institute of Industrial Organic Chemistry and Plastics, Budapest.

The correlation between dielectric constants and concentrations of caprolactam proved to be linear. The measurements were carried out with an RFT-129 istrument, at 20°C, and 1 MHz frequency.

c) *Potentiometric titration.* The use of this method is based on the observation* that caprolactam, when boiled for some hours in a surplus of hydrochloric acid, hydrolyses and forms the hydrochloride of 5-aminocaproic acid. If such a hydrolisate is titrated with standard sodium hydroxide, first the neutralization point of the free hydrochloric acid is registered, a second potential step indicates the neutralization of the hydrochloric acid split off the aminohydrochloride (Fig. 2). The milliliters of standard sodium hydroxide used up between the two potential steps give the equivalent to the aminocaproic acid present, thus indicate the quantity of the caprolactam, in the sample solution.

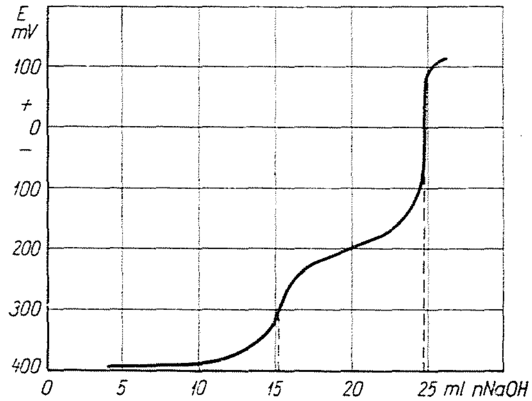

Fig. 2. Potential curve of the titration of a hydrochloric solution of 5-aminocaproic acid hydrochloride

4. *Results of measurements*

a) The system benzene/water/caprolactam (Table 1, Fig. 3). Equilibrium concentrations up to 30% in the aqueous phase were determined by refraction, higher concentrations were measured chemically. The caprolactam content of the benzene phase was determined by measuring the dielectric constants of the samples.

b) The system nitrobenzene/water/caprolactam (Table 2, Fig. 4). Equilibrium concentrations up to 30% in the aqueous phase were determined by refraction, higher concentrations were measured chemically. The caprolactam content of the nitrobenzene phase was determined by measuring the dielectric constants of the samples.

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* L. MARKUS and A. KAYSER: Magyar Kémikusok Lapja, **15**, 86 (1960).

Table 1

Equilibrium data at 20°C of the system benzene/water/caprolactam

a) Graphically-smoothed data of the saturation curve

% water	%caprolactam	%benzene
99,92	0,00	0,08
88,8	11,1	0,09
79,2	20,7	0,11
67,8	31,9	0,32
58,0	40,3	1,75
51,4	45,4	3,22
43,3	50,5	6,17
39,0	52,8	8,22
35,9	54,0	10,1
31,7	55,5	12,7
30,2	55,8	14,0
26,0	55,8	18,2
23,6	54,1	22,3
21,7	53,0	25,3
16,1	48,4	31,5
8,50	38,3	53,2
4,20	30,1	65,8
2,02	20,3	77,7
0,48	10,2	89,3
0,05	0,0	99,95

b) Equilibrium concentrations of the immiscible phases

% caprolactam in the	
aqueous phase	benzene phase
11,5	2,2
28,0	6,0
40,2	10,5
53,5	20,0
55,0	29,7

Table 2

Equilibrium data at 20°C of the system nitrobenzene/water/caprolactam

a) Graphically-smoothed data of the saturation curve

%water	%caprolactam	%nitrobenzene
99,81	0,0	0,19
89,5	10,2	0,32
78,5	21,0	0,45
69,5	29,9	0,57
62,4	36,5	1,14
56,7	42,7	2,65
43,9	48,9	7,22
38,4	51,0	10,6
31,8	52,1	16,1
29,0	50,4	20,6
26,4	49,1	24,5
24,8	48,2	27,0
17,9	42,3	36,8
13,3	37,9	48,8
8,64	31,4	61,0
6,42	27,7	65,9
2,15	19,8	78,0
0,44	9,9	89,7
0,22	0,0	99,78

b) Equilibrium concentrations of the immiscible phases.

%caprolactam in the	
aqueous phase	nitrobenzene phase
1,5	11,3
3,2	21,1
5,5	33,4
9,0	43,7
12,0	49,0
16,5	52,2

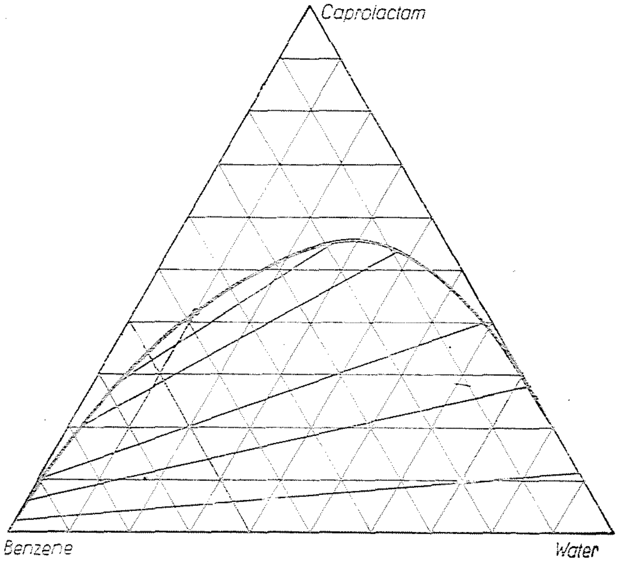

Fig. 3. Triangular plot of the system benzene/water/caprolactam

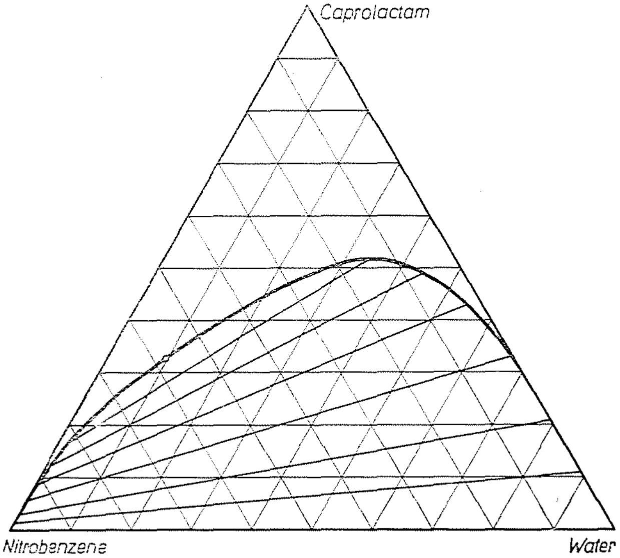

Fig. 4. Triangular plot of the system nitrobenzene/water/caprolactam

c) The system cyclohexanol/water/caprolactam (Table 3, Fig. 5). For this system only the staturation curve was plotted.

Table 3

Graphically-smoothed values of the saturation curve of the cyclohexanol /water/ caprolactam system

%water	%caprolactam	%cyclohexanol
94,4	0,0	5,61
84,4	7,9	7,72
73,0	14,4	12,6
60,6	18,2	21,2
52.6	19,4	28,0
47,8	19,8	32,4
43,4	19,8	36,8
31,4	18,4	50,2
23,1	16,1	60,8
17,7	11,8	70,5
13,6	8,4	78,0
9,21	4,2	86,6
6,30	0,0	94,7

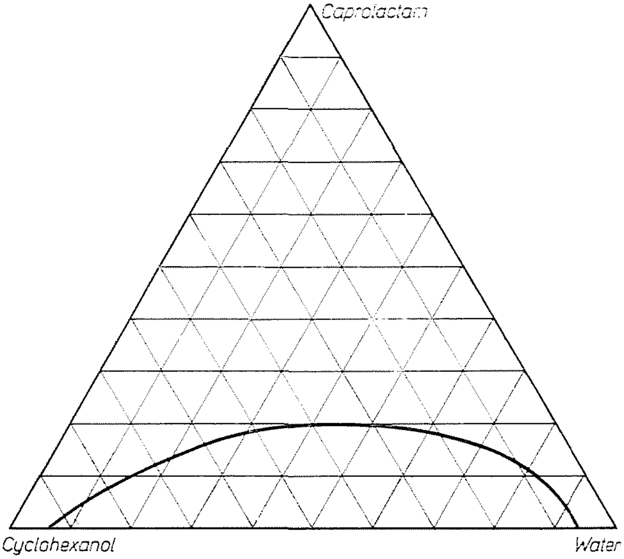

Fig. 5. Triangular plot of the system cyclohexanol/water/caprolactam

d) The system chloroform/water/caprolactam (Table 4, Fig. 6). Equilibrium concentrations in the aqueous phase were determined by refraction, in the chloroform phase, by chemical means.

Table 4

Graphically-smoothed equilibrium values at 20° C for the system chloroform /water/ caprolactam

a) Values of the saturation curve

%water	%caprolactam	%chloroform
99,18	0,0	0,82
88,6	10,1	1,25
78,6	19,8	1,61
67,8	30,1	2,05
57,8	36,4	5,80
38,5	44,3	17,2
30,9	45,9	23,2
23,4	45,9	30,7
19,0	45,8	33,2
16,0	45,0	39,0
11,3	43,9	44,8
8,15	41,7	50,2
6,75	40,2	53,0
1,52	32,9	65,6
0,55	20,1	79,3
0,27	10,7	89,0
0,07	0,0	99,9

b) Equilibrium concentrations of the immiscible phases

%caprolactam in the	
aqueous phase	chloroform phase
4,4	9,2
10,0	21,4
15,2	30,0
20,8	37,8
27,4	44,0
33,5	46,0

Table 4/c

Equilibrium values at 20° C for the system chloroform/water/ caprolactam*

Values of the saturation curve		
%water	%caprolactam	%chloroform
99,16	0,0	0,84
88,93	9,88	1,19
78,92	19,73	1,35
56,50	37,67	5,83
31,37	47,06	21,57
11,51	44,36	44,24
11,08	44,25	44,56
5,27	37,89	56,84
0,75	19,85	79,40
0,45	9,95	89,60
0,99	0,0	99,01

Equilibrium concentrations of the immiscible phases

%caprolactam in the	
aqueous phase	chloroform phase
4,49	10,76
8,30	19,70
12,51	26,46
16,19	32,20
20,00	38,20

e) The system carbon tetrachloride/water/caprolactam (Table 5, Fig. 7). Equilibrium concentrations up to 30% in the aqueous phase were determined by measurements of refraction, higher concentrations were analyzed by the chemical method. The concentration of caprolactam in the organic phase was determined by the chemical method.

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* Values found by Kudrjavceva, G. I. and Krutikova, A. D.: Zh. prikl. Khim. **26** 1190. (1953)

Table 5

Graphically-smoothed equilibrium values at 20° C for the system carbon tetrachloride/water/ caprolactam

a) Values of the saturation curve

%water	%caprolactam	%carbon tetrachloride
99,9	0,0	0,07
89,6	10,3	0,14
80,6	19,2	0,19
68,4	31,4	0,24
58,4	40.7	0,51
50,9	47,9	1,20
42,9	54,0	3,15
37,3	57.5	5,20
27,4	58.8	13,8
24,2	57,8	18,0
20,1	56.1	23,8
15,9	51,9	32,2
11,3	64,3	42,4
9,00	42,0	49,0
6,85	37,3	55,8
4,65	31,6	63,8
2,85	25,3	71,9
1,65	19,0	79,4
0,21	10.2	89.6
0,01	0,0	99,9

b) Equilibrium concentrations of the immiscible phases

%caprolactam in the	
aqueous phase	carbon tetrachloride phase
20.2	1.0
36.0	1.9
52,4	4.0
54,1	9,6

Table 6

Equilibrium values at 20° C of the system trichloroethylene/water/caprolactam

a) Values of the saturation curve

%water	%caprolactam	%trichloroethylene
99,9	0,0	0,10
81,7	17,8	0,51
73,3	25,8	0.88
63,0	35,6	1,43
57,2	40,9	1,85
53,2	44,0	2,77
47,2	48,2	4,63
39,4	52,0	8,62
32,0	53,7	14,3
27,9	52,8	19,3
24,2	51,3	24,5
19,8	49,0	31,2
14,1	43,5	42,4
9,03	38,1	52,9
6,28	34,1	59,6
5,04	31,6	63,4
3,82	28,9	67,3
2,47	25,2	72,4
1,53	20,6	77,9
0,18	14,2	85,6
0,08	0,0	99,9

b) Equilibria between solid caprolactam and its solutions

%water	%caprolactam	%trichloroethylene	%water	%caprolactam	%trichloroethylene
0,0	36,5	63,5	5,1	66,3	28,6
1,3	49,4	49,3	8,6	73,2	16,2
3,2	58.1	38,7	12,4	79,0	8,2
			20,7	79,3	0,0

c) Equilibrium concentrations of the immiscible phases (actually-measured values):

%caprolactam in the					
aqueous phase	trichloroethylene phase	aqueous phase	trichloroethylene phase	aqueous phase	trichloroethylene phase
0,3	0,021	3,8	0,48	10,2	2,20
0,3	0,025	4,3	0,73	11,2	2,80
0,5	0,055	4,5	0,75	11,5	2,58
0,6	0,06	5,8	1,05	12,3	3,05
0,8	0,12	6,8	1,38	14,0	3,46
1,0	0,11	7,4	1,45	14,5	3,63
1,4	0.17	7,4	1,50	14,8	3,96
1,5	0,20	8.1	1,77	16,0	4,10
1,6	0,25	9,9	2,27	16,6	4,08
2,3	0,33	10,0	2,17	16,9	4,46
				17,6	4,72
				17,8	4,24

%caprolactam	
aqueous phase	trichloroethylene phase
19.0	5,20
21,1	5,5
21.7	5,77
22,0	6,2
24,4	7,11
24,6	7,07
26,1	8,1
26,8	8,3
27,0	8,1
29,4	8,9
29,6	9,4
31,3	10,1
31,6	10,0
36,2	12,5
38,9	13,6
45,1	18,0

Table 7

Refractive indices of aqueous caprolactam solutions

Caprolactam % weight (X)	n_D^{20}, refractive		n_D^{20}, computed
	index of free of solvent	aqueous solutions saturated with solvent	$X = \frac{n_{40} - n_0}{40}$
0	1,3330	1,330	1,3330
5	1,3413	1,3414	1,3415
10	1,3495	1,3497	1,0500
15	1,3577	1,3579	1,3584
20	1,3660	1,3662	1,3669
25	1,3749	1,3756	1,3754
30	1,3834	1,3840	1,3838
35	1,3921		1,3924
40	1,4009		1,4009

Table 8

Dielectric constants of aqueous caprolactam solutions

Caprolactam % weight	Dielectric constant
0	80,4
5	78,9
10	77,4
15	75,8
20	74,1
25	72,2

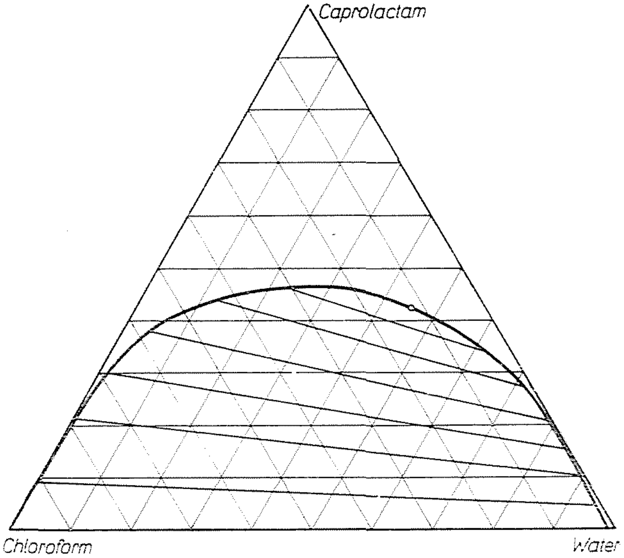

Fig. 6. Triangular plot of the system chloroform/water/caprolactam

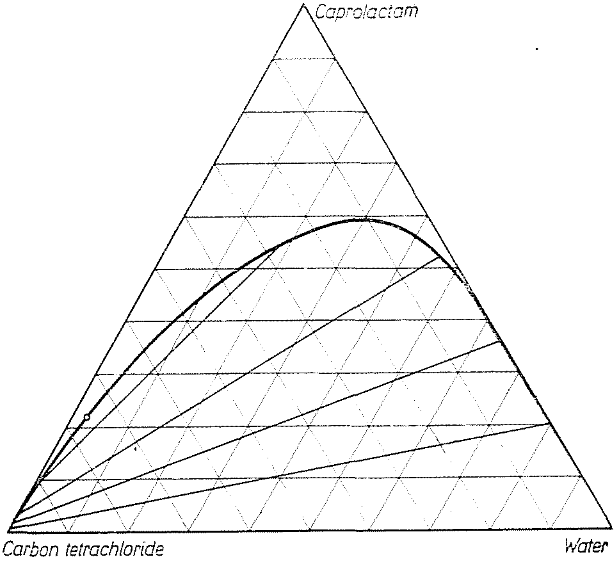

Fig. 7. Triangular plot of the system carbon tetrachloride/water/caprolactam

f) The system trichloroethylene/water/caprolactam (Table 6, Fig. 8). From a practical point of view, this system is the most important one, therefore, many measurements were made on it, especially at lower concentrations. The concentration of the aqueous phase was determined using an Abbé refractometer capable of showing five decimal digits. The caprolactam content of the

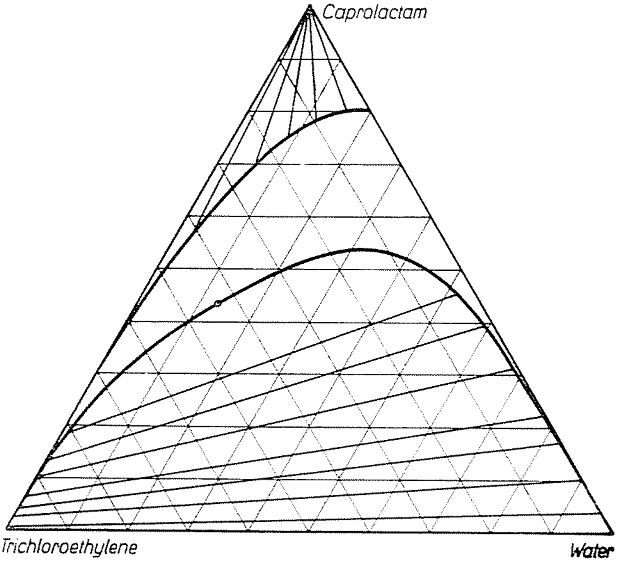

Fig. 8. Triangular plot of the system trichloroethylene/water/caprolactam

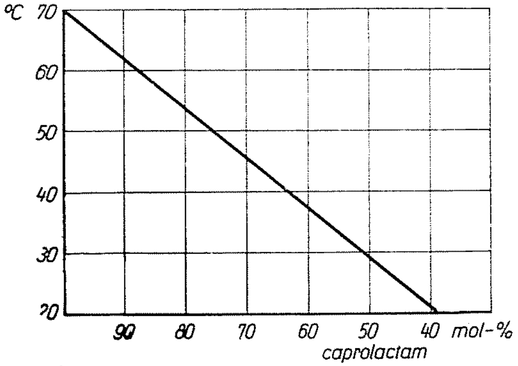

Fig. 9. Freezing points of aqueous caprolactam solutions

organic phase with low concentration was established by computation, as in this range neither dielectric measurements nor chemical means were adequate. At higher concentrations, because of their pronounced mutual solubility, the contents of caprolactam was determined by the chemical method in both phases. It is noteworthy that at low concentrations the distribution of caprolactam tends to favour the aqueous phase.

In this system, equilibria of solid caprolactam with its saturated solutions were also measured for in industrial practice the thickening of caprolactam solutions is part of the manufacturing process. The solubility at 20°C of caprolactam in mixtures with different ratios trichloroethylene : water has

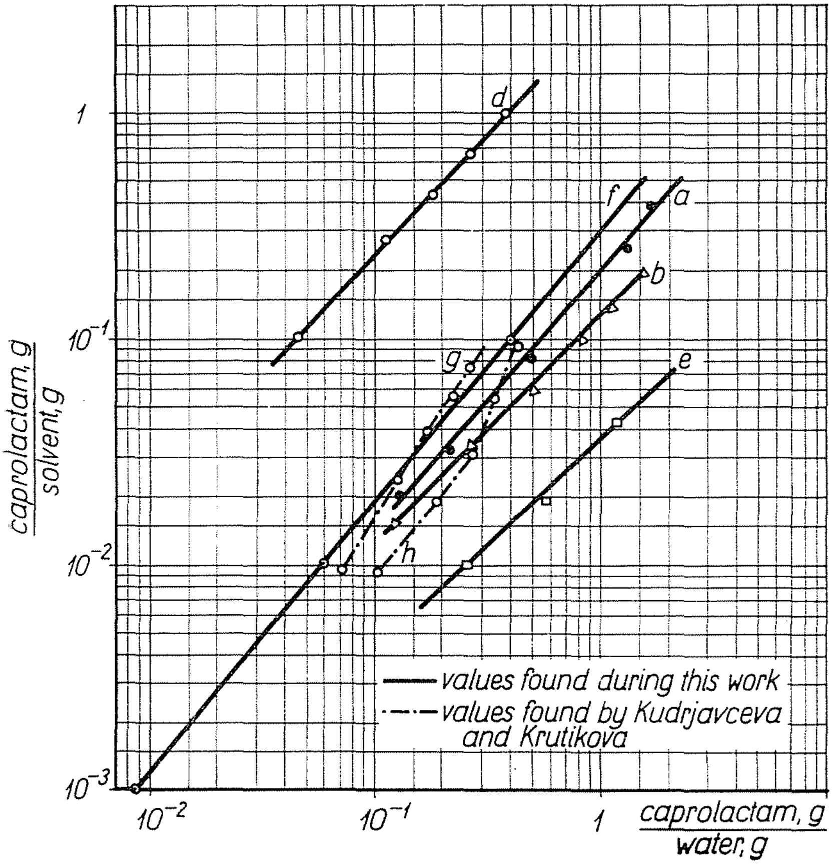

Fig. 10. HAND-diagrams for the systems: organic solvents/water/caprolactam

a) benzene
b) nitrobenzene
d) chloroform
e) carbon tetrachloride
f) trichloroethylene
g) methylene chloride
h) dichloroethane

been determined by extrapolating to 20°C the freezing-point curves plotted for corresponding molar concentrations (Fig. 9 refers to water). Fig. 10 presents the logarithms of the equilibrium concentrations (g caprolactam/g solvent) referred to the pure solvent (*Hand* co-ordinates). When normal distribution circumstances obtain, these co-ordinates form straight lines. For every solvent under investigation in this work, such straight lines could be plotted.

Whilst this paper was being printed, an article of MORACHEVSKIJ and SABININ [2] dealing with a similar subject has been published. There, results of measurements with three pairs of solvents, viz.: — benzene, — carbon tetrachloride, and — dichloroethane, are given. From among these there is a good agreement with data resulting from our measurements on benzene, and carbon tetrachloride.

Summary

The distribution of caprolactam between organic solvents and water has been measured, and the boundary-curve of the two-phase zone plotted, for the following systems: caprolactam-/water/benzene, —/nitrobenzene, —/cyclohexanol/, —/chloroform, —/carbon tetrachloride, and —/trichloroethylene.

Considering prices, availability, health hazards, inflammability, and distribution characteristics, trichloroethylene proved to be the most suitable for the industrial extraction of caprolactam.

The data as established by these investigations have been used in the design of an xtraction plant.

Literature

[1] KUDRJAVCEVA, G. I. and KRUTIKOVA, A. D.: Zh. prikl. Khim. **26**, 1190 (1953).
[2] MORACHEVSKIJ, A. G. and SABININ, B. E.: Zh. prikl. Khim. **33**, 1775 (1960).

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