PHASE EQUILIBRIA
OF THE SYSTEM CAPROLACTAM/WATER

A NOVEL APPARATUS FOR THE STUDY OF VAPOUR/LIQUID EQUILIBRIA

By

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I. Introduction

In the course of the manufacture of caprolactam, the raw product, the so-called "lactam oil" from the Beckmann rearrangement, is purified either directly by distillation or by extraction with a solvent and subsequent re-extraction with water. The aqueous caprolactam solution that results from re-extraction is evaporated, and this concentrated caprolactam is distilled under reduced pressure. In our experiments we endeavoured to find at various pressures the vapour liquid equilibria and boiling points needed for the design of the evaporators and distillation plant to be used in the processing of aqueous caprolactam solutions.

II. Experimental

a) *Materials used*

Commercially available caprolactam was distilled at a pressure of 5 mm Hg. By a second distillation no change of the boiling point, and the index of refraction was brought about.
Boiling point 5 mm Hg = 118.3 °C (116 °C given in the literature [1])

$$n_D^{75°} = 1.4788$$

Re-distilled water was used throughout.

b) *Apparatus used*

For the measurement of boiling point curves for the system caprolactam/water the *ebulliometer of* SWIETOSLAWSKI [2] was used.
For the determination of vapour/liquid equilibria the apparatus designed by OTSUKI and WILLIAMS [3] was used. In essence, this has been developed from the apparatus of GILLESPIE [4] and further modified by us to render it suitable also for the investigation of vapour/liquid equilibria of substances widely differing in their boiling points. The three devices are shown in *Figs*
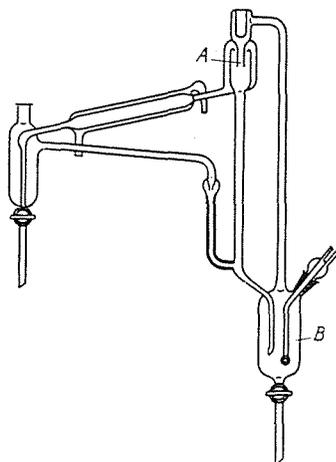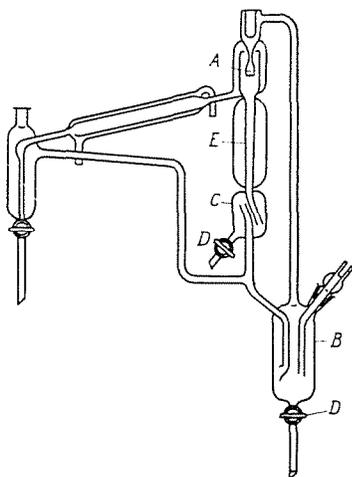
Fig. 1. Gillespie still

Fig. 2. Otsuki—Williams still

1, 2, and 3, respectively. A defect of the original Gillespie apparatus consists in that it does not measure the composition of the vapour, and the liquid pertaining to it, issuing from the A equilibrium chamber, but the composition of the vapour issuing from the A equilibrium chamber and that of the liquid in the B reboiler, this being not the equilibrium composition pertaining to the vapour. If the volume of the boiler is small, and the relative fugacity of the substance great, important deviations may result. This source of error OTSUKI and WILLIAMS tried to evade by leading the liquid from the A equilibrium chamber into a C sampling vessel and therefrom back into the B reboiler. In this case, in fact, the composition of the vapour separated in the A

equilibrium chamber and that of the equilibrium liquid pertaining to it can be measured. However, according to our experience there is a drawback in the use of the apparatus of OTSUKI and WILLIAMS, partly caused by sampling being through D stopcocks and the grease used for their lubrication interfering with analyses by refraction, partly by the fact that the comparatively long E tube above the liquid sampling orifice is filled with vapour which will partially condense in spite of the evacuated insulating jacket shown in the Figure,
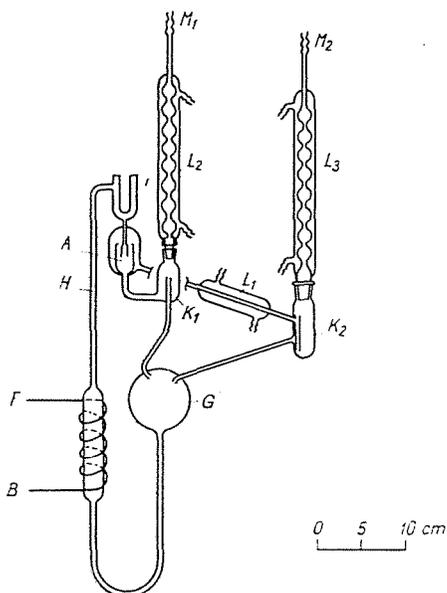

Fig. 3. Modified Gillespie still

especially if the boiling points of the respective liquids are wide apart, and thus will falsify the results. To avoid errors in analysis due to contamination with lubricating grease, and to prevent the partial condensation in the rather long drain tube, the apparatus was modified as shown in *Fig. 3.*

Description of the vapour/liquid equilibrium apparatus

Heating is provided for by an F thermosyphon similar to that in an ebulliometer, and to ensure uniform steady boiling some powdered glass is fused on to the inner wall of the B boiler tube. Into the G liquid container of the apparatus a liquid mixture of arbitrary composition is filled and heated by the F spiral of 30 ohm resistance. Voltage can be regulated by a toroid transformer. Through H Cotrell pump the vapour/liquid mixture which arrives

at J thermometer well is transferred into the equilibrium chamber where vapour and liquid separate. The liquid runs down to the K_1 liquid sampler and, by overflow, back into the G liquid container. Condensers L_2 and L_3 prevent the entrance of vapours into the pressure regulation system. Evacuation is effected through orificed M_1 and M_2. To minimize heat losses, boiler tube and equilibrium chamber are insulated by glass fibre cloth.

To ensure constant pressure a control system shown in *Fig. 4* is used.

The suction pipe of an A vacuum pump of 5 m³/hour capacity is connected to a B buffer tank of 80 litre volume where a nearly constant vacuum of 2...3 mm Hg is maintained. To this a smaller (3 litre) C buffer tank is

Fig. 4. Pressure regulating system

connected by a D electromagnetic valve. To the smaller buffer tank an E U-tube mercury manometer, the apparatus, and the F manostat are connected, the last is the sensor and the basic signal guard of the system. The lower mercury level in the U-tube manometer contacts a platinum wire, the upper level a tungsten wire. These contacts are connected by a relay to the electromagnetic valve.

The system operates as follows. Stopcock G is opened, and through the opened magnetic valve the system is evacuated to the required pressure level. The stopcock G is closed. If, due to leaks, air enters the apparatus and pressure increases, contact between mercury and tungsten wire is disrupted, the relay opens the magnetic valve and air is removed till the original pressure is reestablished, i.e. till mercury and tungsten wire come into contact again and the magnetic valve is closed.

If the system is nearly vacuum-tight, then some air is allowed to enter through the H side arm, since the magnetic valve cannot be made to close

perfectly. To absorb sudden variations of pressure, a *J* damper is inserted between the smaller buffer tank and the magnetic valve.

Readings of pressure values are made with a kathetometer.

c) *Testing of apparatus*

To *test* the correct operation *of the ebulliometer* and of the pressure control system, the tension data of water were measured and compared with those found in the literature *(Table I)*.

Table I

Ebulliometer-tests with water
Tension values of water, in mm Hg

at *t* (°C)	Found	Literature [5]
12.0	10.5	10.52
23.3	22.0	22.11
31.4	34.5	34.47
32.4	36.5	36.48
45.1	72.0	72.25
48.0	83.5	83.71
53.8	111.5	111.4
57.3	131.5	131.6
60.6	153.5	153.5
63.8	177.0	177.7
64.8	185.0	185.8
66.0	196.0	196.1
100.0	760.0	760.0

Testing of the equilibrium apparatus: To find out about entrainment at atmospheric pressure, a solution (10 per cent by weight) of potassium chloride was filled into the apparatus and heating was regulated so that a steady flow of 2...3 ml per minute of the liquid should result from the sampler on the vapour side. The solution sampled here showed no turbidity when mixed with a 0.1 N solution of silver nitrate; this indicated that no entrainment of droplets by the vapour separated from the liquid occurred. This experiment was repeated at 100 mm Hg and even so the apparatus performed well. Then the vapour/liquid equilibria of the system ethanol/water, and water/acetic acid, were measured and compared with data taken from the literature [6, 7]. Results of our measurements, and comparisons, are shown in *Tables II* and *III*, and in *Figs 5* and *6*, respectively. The diagrams show that our data and those in the literature agree very well, the deviations are within the limits of system-

atic errors. Observing the time needed for equilibrium to establish itself in the apparatus as modified by us, we found that after an operation for 15 minutes no change in composition occurred any more either in the sampler on the vapour side or in that on the liquid side. This fact we think worthy of being emphasized as a special advantage, since not only a quite rapid determination of equilibria, i.e. a saving in time, but also the guarding of heat sensitive substances against decomposition damage result. Apparatus described in the literature [13] need 2 to 3 hours for equilibrium to be established.
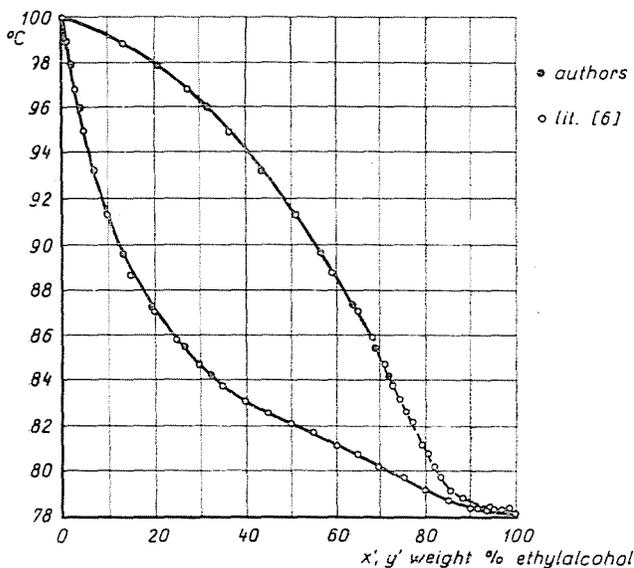
Fig. 5

Table II

Testing of equilibrium apparatus with a mixture of water and ethanol P = 760 mm Hg

t (°C)	x' ethanol % by weight	y'
97.9	2.0	20.6
96.0	3.8	31.4
93.3	7.3	43.8
89.7	13.1	56.4
87.3	19.4	64.1
85.5	26.1	69.0
84.2	32.5	72.0

Table III

Testing of equilibrium apparatus
with a mixture of water/acetic acid
P = 760 mmHg

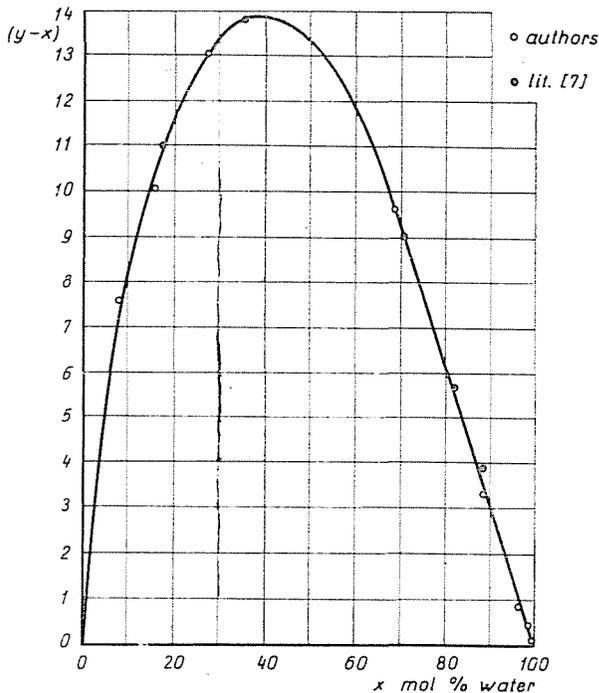| x	y	$(y - x)$
water mole per cent		
17.25	28.25	11.00
35.02	48.87	13.85
70.85	79.89	9.04
81.96	87.69	5.73
88.02	91.93	3.91

Fig. 6

d) *Analysis*

The most simple way to determine concentrations in the caprolactam/
water system is an analysis by refractometry. For the analysis of caprolactam
solutions of low concentration (0...15 per cent by weight) a thermostated
double-prism *Abbe*-type refractometer was used. The concentration values
assignable to readings on the scale at 25 °C are listed in *Table IV*.

Table IV

Readings on the refractometer scale and
concentrations of caprolactam assigned
thereto at 25 °C

Caprolactam per cent by weight	Readings on the scale
0.00	86.75
0.50	84.70
2.00	78.90
5.24	66.30
15.00	28.00

Solutions of intermediate concentrations (10...80 per cent by weight) were analysed with a *Zeiss—Abbe* refractometer at 25 °C. The refractive index *vs* concentration data are given in *Table V*.

Table V

Refractive indices, at 25 °C, and
concentrations of caprolactam

Caprolactam per cent by weight	n_D
9.49	1.3479
21.00	1.3672
29.90	1.3822
39.50	1.3993
49.45	1.4162
59.62	1.4338
65.48	1.4443
80.20	1.4673

Table VI

Refractive indices, at 75 °C, and
concentrations of caprolactam

Caprolactam per cent by weight	n_n^{75}
50.0	1.4012
60.0	1.4175
80.0	1.4480
90.0	1.4645
100.0	1.4788

High concentrations of caprolactam (more than 80 per cent by weight) cannot be analysed at 25 °C because the solidification point in such solutions is relatively high, therefore the refractive index at 75 °C was used for the analysis of concentrated solutions. Values measured are given in *Table VI*.

e) *Boiling point curves of the system caprolactam/water*

Tension values of aqueous solutions containing 0, 20, 40, 60, 80, 90 and 100 per cent by weight of caprolactam were measured in an ebulliometer according to SWIETOSLAWSKI. From measured data, and using the least square method, the constants A and B of the so-called "two-constants" *Antoine*-equation describing the tension of solutions of various concentrations,

$$\log p = A - \frac{B}{t+230}$$

were determined. These values are listed in *Table VII*.

Table VII

Antoine constants for caprolactam solutions

Caprolactam per cent by weight	A	B
0	7.9931	1687.6
20	7.9761	1686.0
40	8.0069	1699.2
60	8.0074	1707.3
80	7.7743	1675.5
90	7.6222	1701.8
100	7.8042	2474.8

For pure caprolactam only boiling points at several discrete pressures can be found in the literature [8—10], no formula valid for wider pressure intervals is given. MORAVEK [11] has published a formula $\log p = 6.78 - \frac{2344}{T}$ for the range 1 mm Hg to 10 mm Hg; and a diagram of *National Aniline* [1] is known for the range 3 mm Hg to 50 mm Hg.

Boiling points at 10 mm Hg are the following:

139   °C, measured value [8]
132.9 °C, calculated by the tension formula [11]
132.2 °C, read from the diagram [1]
133.7 °C, calculated by the Antoine equation as here proposed

The boiling point values deduced from the three tension curves are in good agreement.

Using the constants as given for the Antoine equation, the data of boiling point curves pertinent to various pressures were calculated and are given in *Table VIII.*

Table VIII

Boiling points (caprolactam per cent by weight)

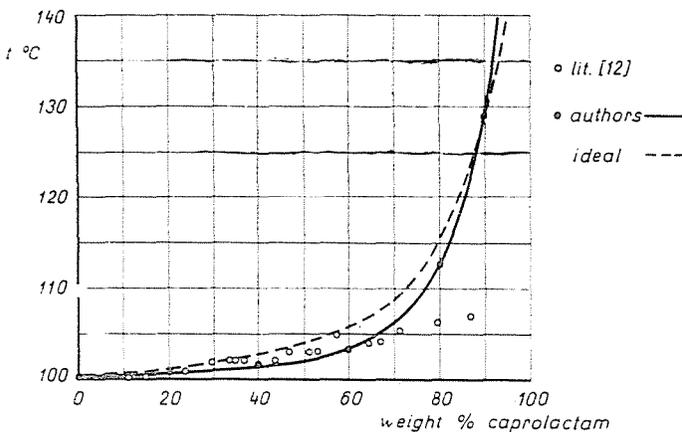| P mm Hg	0%	20%	40%	60%	80%	90%	100%
	temperatures, °C						
760	100.1	100.9	101.5	103.0	112.4	128.9	272.7
180	64.1	64.5	65.4	66.8	73.6	87.1	216.0
80	47.1	47.6	48.4	49.7	55.4	67.6	189.4
30	29.0	29.4	30.2	31.4	36.1	46.9	161.1

Fig. 7. Caprolactam/water boiling point diagram

Fig. 7 shows the boiling point curve for $P = 760$ mm Hg in a comparison with data taken from the literature [12]. Also shown are boiling points calculated from the tension data of the two pure substances on the assumption that they behave ideally. This Figure shows that the deviation from ideal behaviour is not great, not more than $+2 \ldots 3$ °C at $60 \ldots 70$ per cent by weight.

f) *Vapour/liquid equilibria of the system caprolactam/water*

In the literature [11, 12] equilibrium data pertinent to 760 mm Hg, and to 50 mm Hg pressures, are given for the system caprolactam/water. In the course of our experiments, and with the help of our apparatus, vapour/liquid equilibria for the system caprolactam/water were measured at 760, 180, 80
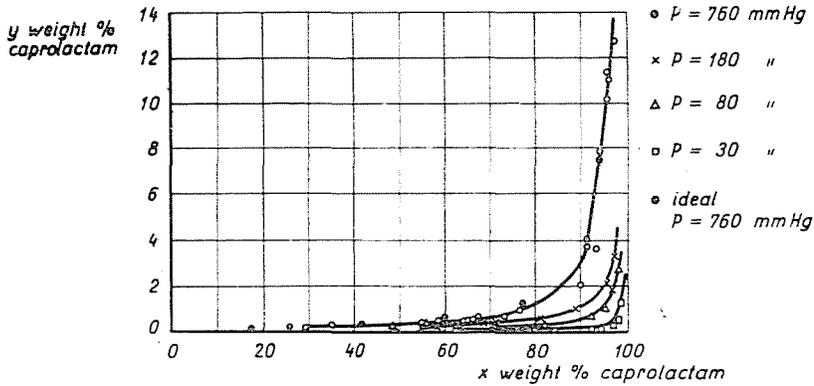
Fig. 8. Caprolactam/water equilibrium data measured by the authors

and 30 mm Hg. These data are listed in *Tables IX—XII*, and shown in *Fig.* 8. This Figure contains equilibrium data calculated on the assumption of ideal behaviour for $P = 760$ mm Hg. Here also the deviation is rather small.

Table IX	
$P = 760$ mm Hg	
caprolactam	
per cent by weight	
x	*y*
29.0	0.17
35.0	0.25
58.5	0.50
59.5	0.62
64.8	0.45
65.0	0.50
66.0	0.50
73.0	0.70
76.5	0.87
90.0	2.05
91.0	3.75
93.0	3.65
94.0	7.90
95.5	10.10
95.5	11.40
96.0	11.00
97.0	12.70

Table X	
$P = 180$ mm Hg	
caprolactam	
per cent by weight	
x	*y*
55.0	0.12
58.5	0.16
68.5	0.30
71.0	0.40
81.0	0.50
88.5	0.95
95.5	2.05
96.5	1.82
97.0	3.25

Table XI

P = 80 mm Hg
caprolactam
per cent by weight

x	y
48.5	0.15
55.5	0.12
71.0	0.15
82.0	0.20
92.0	0.60
95.0	0.95
98.0	2.62

Fig. 9 contains the data pertaining to normal, and 50 mm Hg pressures, communicated by TUMOVA et al. [12]. The Figures in our paper suggest that contrary to the data of TUMOVA et al. a decrease of pressure substantially enhances separation by distillation. The data given by TUMOVA et al. show that the OTHMER-type apparatus used by them for the determination of vapour/liquid equilibria is not suitable for substances of such high relative fugacities to be handled under reduced pressure, perhaps because unsteady boiling and entrainment of droplets occur.

Table XII

P = 30 mm Hg
caprolactam
per cent by weight

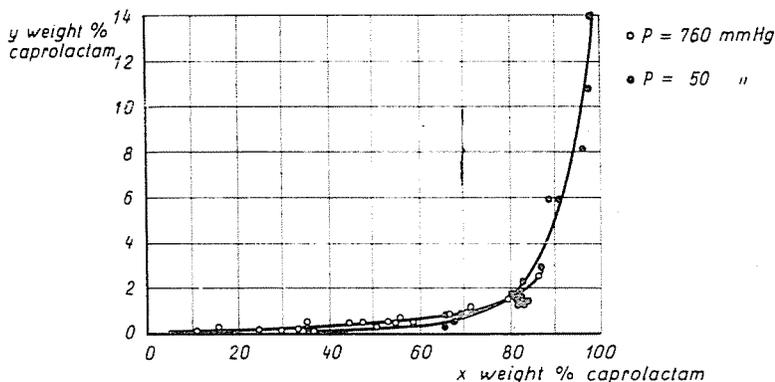| x	y
62.0	0.05
80.0	0.08
84.0	0.05
92.0	0.12
93.0	0.12
94.0	0.12
97.0	0.30
98.0	0.50
98.5	1.25

Fig. 9. Caprolactam/water equilibrium data (measured by Tumova et. al. [12])

Summary

An apparatus for measuring vapour/liquid equilibria has been constructed which is suitable for the determination of vapour/liquid equilibria. both at normal and reduced pressures, of substances with boiling points wide apart. Equilibria are established within 15 minutes. The boiling points, and vapour liquid equilibria of the system caprolactam/water at $P = 760$, 180, 80 and 30 mm Hg have been determined. On the basis of these data it can be stated, on the one hand. that the behaviour of this mixture deviates but slightly from the ideal, on the other hand, that contrary to data in the literature, a change of pressure affects the equilibrium conditions of this system in a high degree.

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