Physics. — *The Three-Phase-Lines of the Systems: Water-Orthocresol, Water-Metacresol, and Water-Paracresol.* By A. MICHELS and E. C. F. TEN HAAF. 16th Communication of the VAN DER WAALS fund. (Communicated by Prof. J. D. VAN DER WAALS JR.)

(Communicated at the meeting of October 30, 1926).

The purpose of the following investigations was to examine in how far the mutual position of the CH_3 and OH groups has influence on the phenomenon of unmixing of cresol-water mixtures.

For the present we have confined ourselves to examining the three-phase curves by studying the unmixing in sealed glass tubes [1]).

For the preparation of the said cresols the homonymous toluidines were started from, which were supplied to us as being pure. These toluidines were first distilled, then converted into the oxalic acid salt, and this salt was purified by repeated out-crystallisation in alcohol. The final product, which was assumed by us to be pure, amounted to $^1/_4$ of the quantity started with.

Then the toluidine was regained from those salts, and the cresol was prepared from the toluidine by diazotation.

The cresols prepared in this way were purified again by distillation in a nitrogen atmosphere. This distillation was repeated so often till the last fraction and the last but one gave no difference in their crystallisation points.

For para- and ortho-cresol a crystallisation point was found corresponding to that generally recorded in the literature; it appeared, however, possible to us to raise the melting-point of metacresol, by purification, considerably above that reached till now.

While usually the melting-point of meta-cresol is stated to be $\pm 4°$, we obtained $\pm 10°.6$.

It is perhaps worth mentioning that all three cresols appeared to be colourless liquids as clear as water, which, however, in course of time gradually assumed a yellow to brown colour, even when they were kept in the dark under nitrogen.

With the cresols obtained in this way the investigations on the three-phase curves were carried out. The results are recorded in the subjoined table, the accompanying diagram giving a graphical representation of the "Consolute temperature" as it varies with the concentration.

---

[1]) Compare inter alia also: A. MICHELS. Stelsel isobutyl-alcohol en water, Archives Néerlandaises. Sér. IIIA T. VI (1923), p. 127.

N⁰.	Ortho-cresol		Meta-cresol		Para-cresol	
	Conc.	Temp.	Conc.	Temp.	Conc.	Temp.
1	1.3	< 0	2.7	50.8	2.21	29 à 30°
2	2.9	46.2	3.6	78.7	3.74	82.1
3	4.0	86.7	4.5	92.2	5.4	105.0
4	4.5	104.5	10.8	121.7	6.9	118.5
5	6.9	121.0	14.0	140.4	9.2	127.9
6	7.0	123	23.2	147.5	16.4	138.0
7	8.7	134.0	29.7	148.7	32.1	142.6
8	16.4	157.9	42.9	148.7	32.3	142.5
9	17.5	159.6	48.9	147.6	43.7	140.7
10	36.4	167.3	58.0	141.2	50.2	139.5
11	42.6	168.9	59.3	141.9	56.9	136.6
12	45.9	168.3	62.2	137.7	66.6	124.4
13	50.4	167.9	65.9	133.2	71.3	110.8
14	56.5	163.7	70.6	124.4	79.5	71.0
15	64.7	160.1	73.1	120.0	81.3	59.5
16	74.8	139.2	76.7	103	83.7	37.1
17	75.9	135.4	79.7	90.2	85.9	below 21.8
18	82.9	92.8	80.0	85.2		
19	84.1	87.3	80.7	82.6		
20	86.2	50.5	82.6	67.9		
21	88.5	in ice hom.	85.9	36.2		

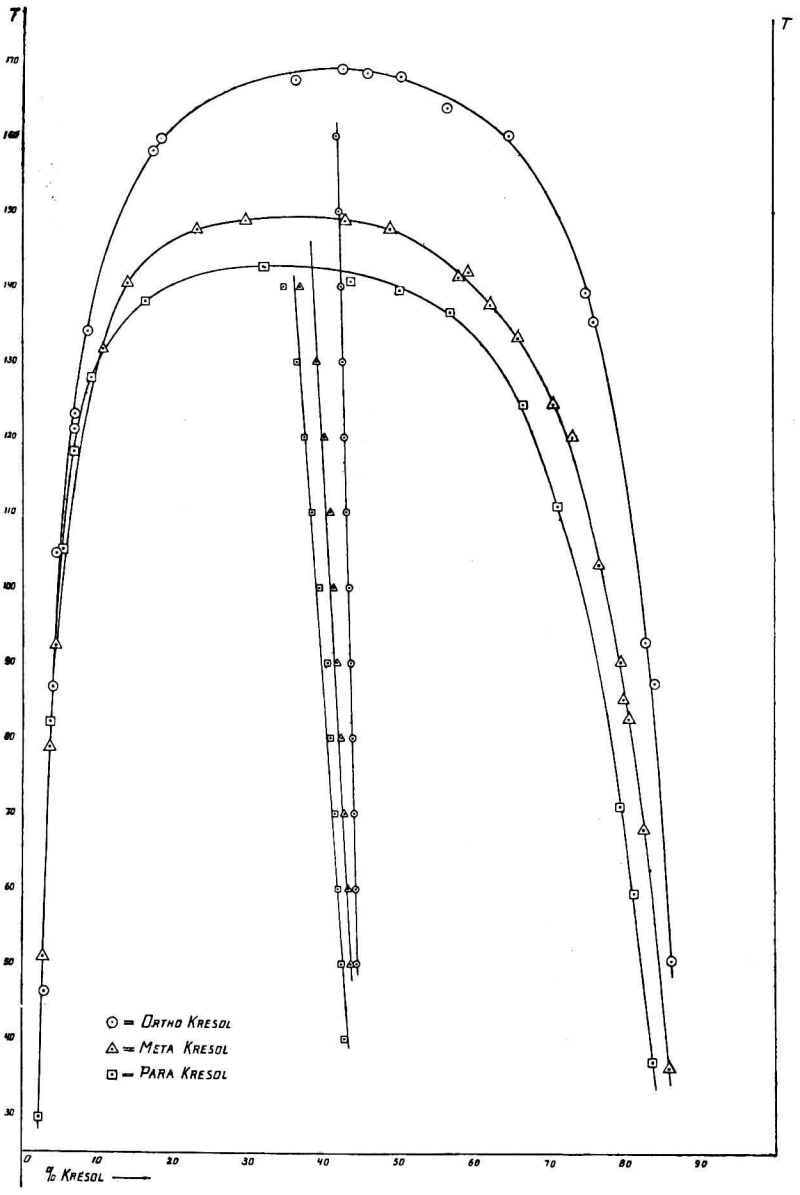
The upper critical endpoints appeared to be:
for ortho-cresol 168°.9 with a concentration of about 41 %.
for meta-cresol 148°.8 with a concentration of about 38 %.
for para-cresol 142°.6 with a concentration of about 36 %.
The values of these concentrations are graphically approximated by the aid of the known law of the rectilinear diameter.

In the diagram the points of the diameter are indicated, and the most probable straight line has been drawn through them. The deviation visible in the diagram is a very slight one, except at the top, where the accuracy of the measurement is much smaller.

It is also noteworthy that the phenomenon of barotropy occurred with all three cresols: while at low temperatures the phase rich in cresol was the heavier, the phase rich in water interchanged places with the other at a given higher temperature.

The exact transition temperature cannot be given with great precision,

because the viscosity was too great for the two phases to move easily through each other. Approximately the barotropic temperature for ortho-cresol lies at 145°, for meta-cresol at 148°, and for para-cresol at 138°.



Finally it may be stated that as soon as the cresols decompose sufficiently to change colour, this manifests itself at once in the position of the unmixing-points.