

ATTACHMENT XVIII

NITROGEN DIVISION OPPAU

Experiments by Dr. Fr. Winkler
Hydrocarbon Experiments. Op. 198/339
(Dr. Hauber)

Absorption of Olefins by Cuprous Salt Solutions

Second Report *

Spot Translation:

(Report No. 90)

Oppau, July 27, 1942

The work reported under Op 198/339 (Hydrocarbon Experiments, Dr. Fr. Winkler - Dr. Hauber) relates to absorption by means of a cuprous salt solution of olefins (chiefly ethylene) produced in the thermal cracking of gaseous paraffin hydrocarbons. The copper solution employed until 1939 was the same as the one used for separating CO in the purification of hydrogen and consisted of an ammoniacal solution of cuprous carbonate. Olefin contents of more than 95% were obtained.

Owing to the quantities of CO₂ and NH₃ which had to be continuously recycled to the process and because of the comparatively low absorptive power of this copper solution, attempts were made to develop a solution of considerably higher absorptive power, not giving off any volatile constituents.

From the beginning it became evident that the absorption could only be raised by increasing the copper content. Concentrated copper solutions, however, have many disadvantages, as indicated by their inability to absorb carbon monoxide satisfactorily, which include instability, high solidification or crystallization points, high

*) First report: (No. 67) Dr. Hauber-Dr. Hagen of March 25, 1941:
"Solubility of Lower Monoolefins in a Solution of Ethanolamine and Cuprous Nitrate".

viscosity and low absorption speed. The ideal solution, therefore, must not have these undesirable properties.

A large number of cuprous salt solutions were tried: solubility curves are given for ethylene and propylene in such cuprous solutions of different composition. The ammoniacal cuprous carbonate solution formerly used was found unsatisfactory because of the reasons mentioned above. The copper content cannot be increased simply by adding more cuprous oxide because in that case the solution practically becomes saturated. A simultaneous increase of the ammonia and CO_2 content is necessary (in accordance with the findings of Dr. Steinheil). A solution made up to contain 2.5 times the original Cu(I) content only absorbs 1.5 times as much ethylene as before. This poor absorption was found to be a result of the high concentration, because on dilution of the solution to the same Cu(I) content as that of the original solution, its absorptive power was restored. Diagram 2 shows how the α -value (absorption factor) in a carbonate solution varies with the Cu(I) content. The α -value slope falls off with increasing copper concentration and, finally, for a concentration $c = 25$ g/100 cc the curve is practically flat. An increase in the copper content of the carbonate solution beyond 25 g/100 cc is therefore useless for operation at normal pressure and temperature.

Attempts were made to use other cuprous salts for which the α -value would be more satisfactory. A number of salts were prepared by dissolving cuprous oxide and the respective ammonia salt in aqueous ammonia. The properties of such solutions are shown in Tables 3 and 4.

Table 3 shows that the majority of these solutions has a much higher absorption power than a saturated cuprous carbonate solution. (No. 11).

These absorption values are often three times as high and cannot be caused by a higher copper content but are evidently due to specific effects of the anion, as illustrated in Table 4.

Table 3

| No. | Cuprous salt | α 20 | No. | Cuprous salt | α 20 |
|-----|------------------------|-------------|-----|-------------------|-------------|
| 1 | Rhoda n ide | 1.28 | 16 | Nitrobenzoate | 5.88 |
| 2 | Sulfite | 1.60 | 17 | Oxalate | 6.90 |
| 3 | Sulfate | 2.00 | 18 | Glycocollate | 7.46 |
| 4 | Perchlorate | 2.44 | 19 | Acetate | 8.32 |
| 5 | Ferrocyanide | 2.60 | 20 | Formate | 8.60 |
| 6 | Glycolate | 2.80 | 21 | p-Oxybenzoate | 9.16 |
| 7 | Bromide | 3.28 | 22 | Phenylacetate | 10.00 |
| 8 | Fluoride | 3.28 | 23 | Sulfanilate | 10.28 |
| 9 | Metavanadate | 4.00 | 24 | Benzene sulfonate | 11.04 |
| 10 | Phthalate | 4.45 | 25 | Anthranilate | 11.80 |
| 11 | Carbonate | 4.55 | 26 | Benzoate | 11.80 |
| 12 | Chloride | 4.87 | 27 | Nitrate | 12.44 |
| 13 | Citrate | 5.04 | 28 | Sulfosalicylate | 14.20 |
| 14 | Acrylate | 5.50 | 29 | Salicylate | 14.80 |
| 15 | Phenolate | 5.55 | | | |

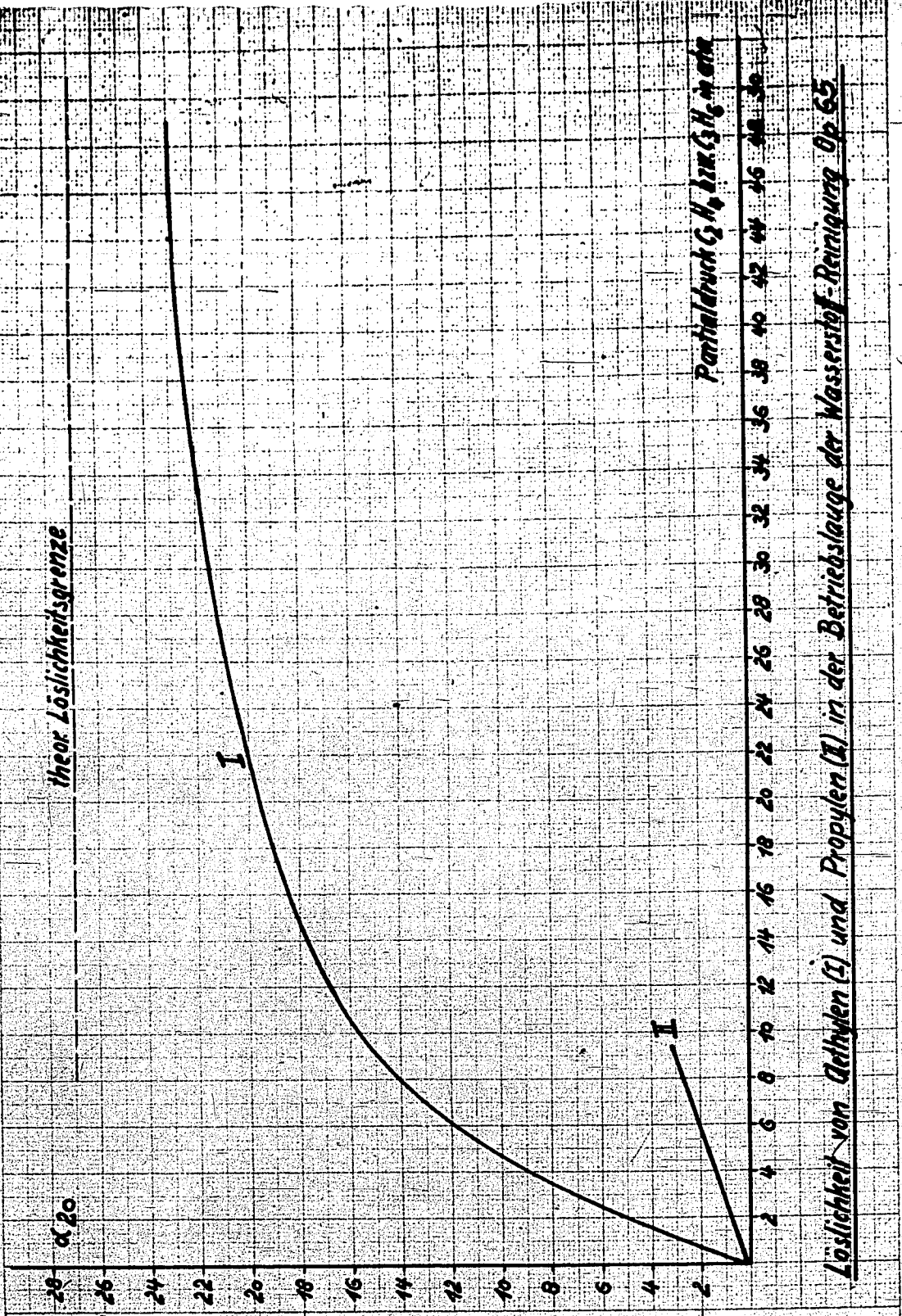
Table 4

| No. | Cuprous salt | Total-Cu g/100 cc | Cu(I) g/100 cc | α 20 |
|-----|-------------------|----------------------|-------------------|-------------|
| 1 | Fluoride | 30.4 | 26.4 | 3.56 |
| 2 | Carbonate | 24.3 | 19.3 | 4.55 |
| 3 | Chloride | 17.8 | 15.4 | 4.87 |
| 4 | Citrate | 26.9 | 23.7 | 5.04 |
| 5 | Formate | 31.1 | 28.1 | 8.60 |
| 6 | Benzene sulfonate | 21.4 | 18.1 | 11.04 |
| 7 | Benzoate | 20.2 | 18.1 | 11.80 |
| 8 | Nitrate | 24.5 | 23.6 | 12.44 |
| 9 | Sulfosalicylate | 23.8 | 21.1 | 14.20 |
| 10 | Salicylate | 23.1 | 20.2 | 14.80 |

Continuous research in this field disclosed that cuprous nitrate was the most satisfactory cuprous salt to use and that the absorptive power, when using cuprous nitrate or certain organic cuprous salts, increased very rapidly with increasing copper content. The disadvantages of such solutions (high ammonia vapor pressure and high crystallization point) were eliminated by replacing the ammonia with monoethanolamine. Of all cuprous salt solutions having a high copper concentration and made up with monoethanolamine, those containing cuprous nitrate have the highest and the most rapid absorption. The optimum composition, physical properties and absorptive power of ethanolamine-cuprous nitrate solution are given in tables and charts, showing absorption, density, viscosity and absorption rate of ethanolamine solutions of various composition.

Ethanolamine-cuprous nitrate solutions may also find application for other purposes than in the concentration of ethylene, ethylene-propylene or other similar mixtures. It may also be used for absorbing CO and for removing traces of oxygen from gases. The solution is not suitable for concentrating butylene.

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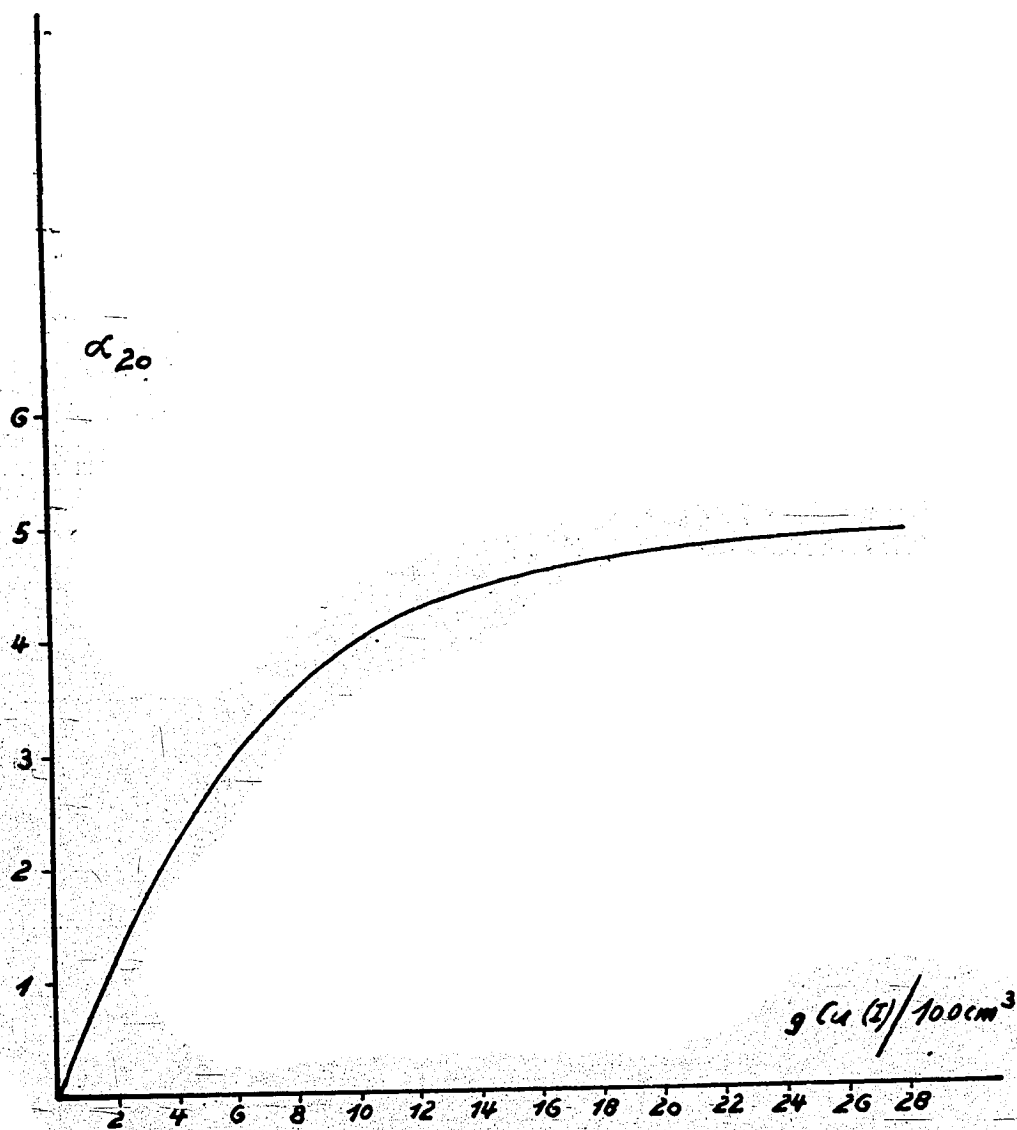


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SKIZZE 1

Löslichkeit von Äthylen (I) und Propylen (II) in der Betriebslösung der Wasserstoff-Reinigung Op 65

3. 11. 42. K. K.

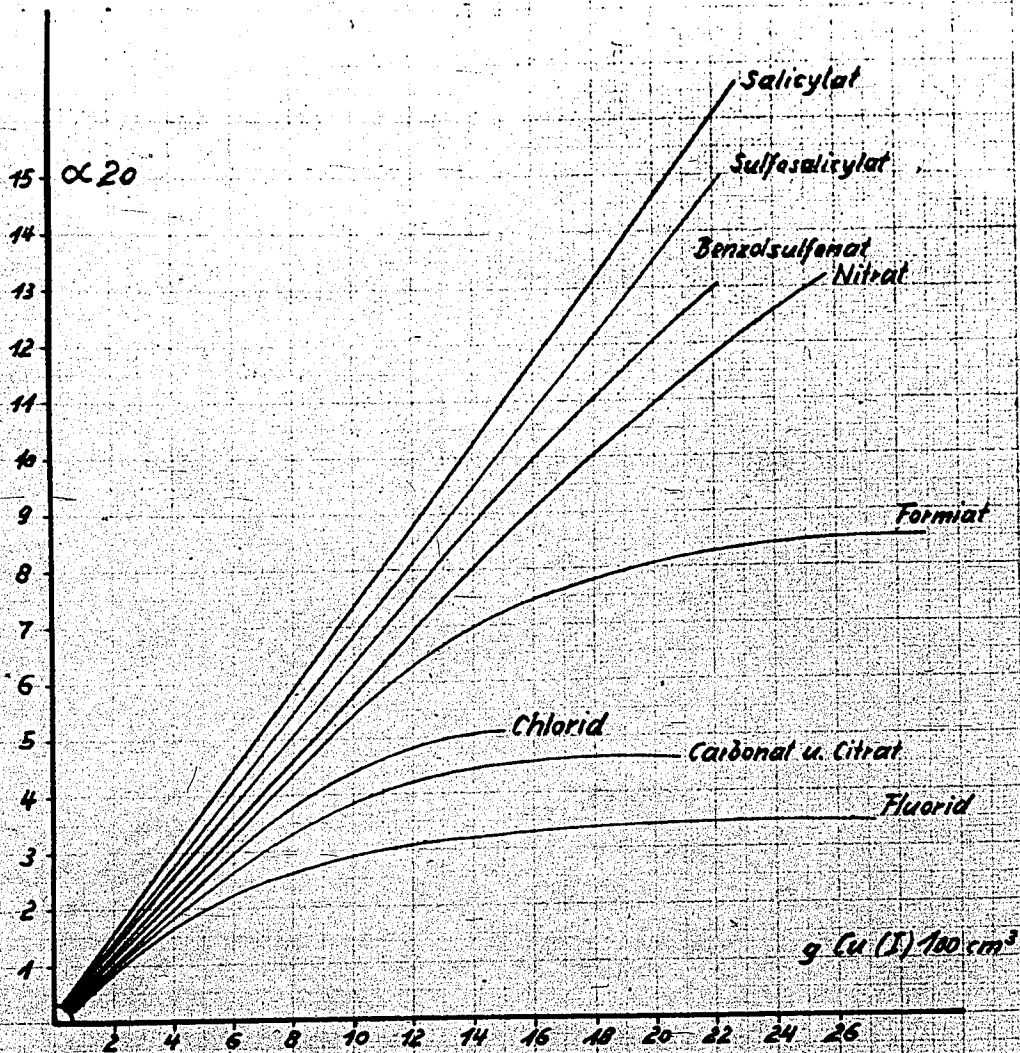


Löslichkeit von Äthylen in ammoniakalischer Cupro-carbonatlösung in Abhängigkeit von der Cu (I)-Konzentration.

Skizze 2

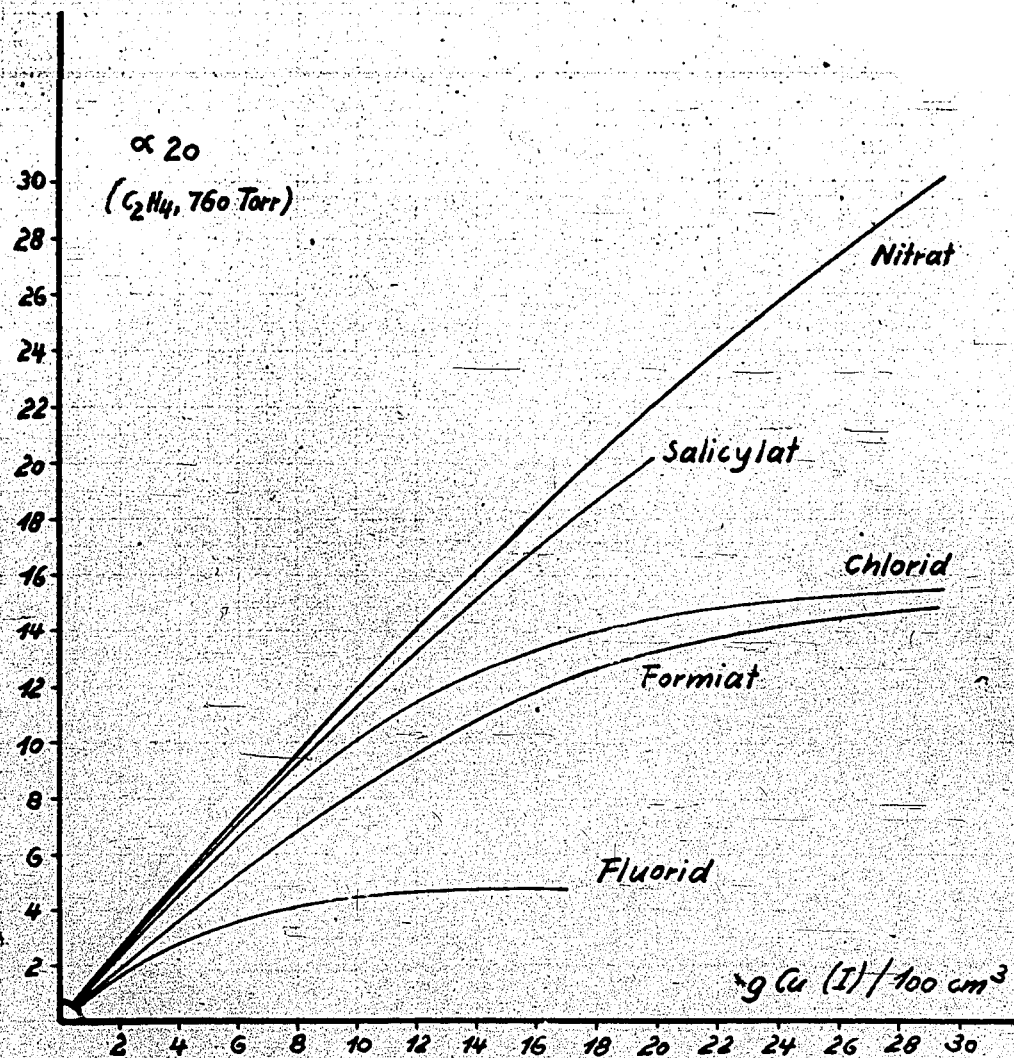
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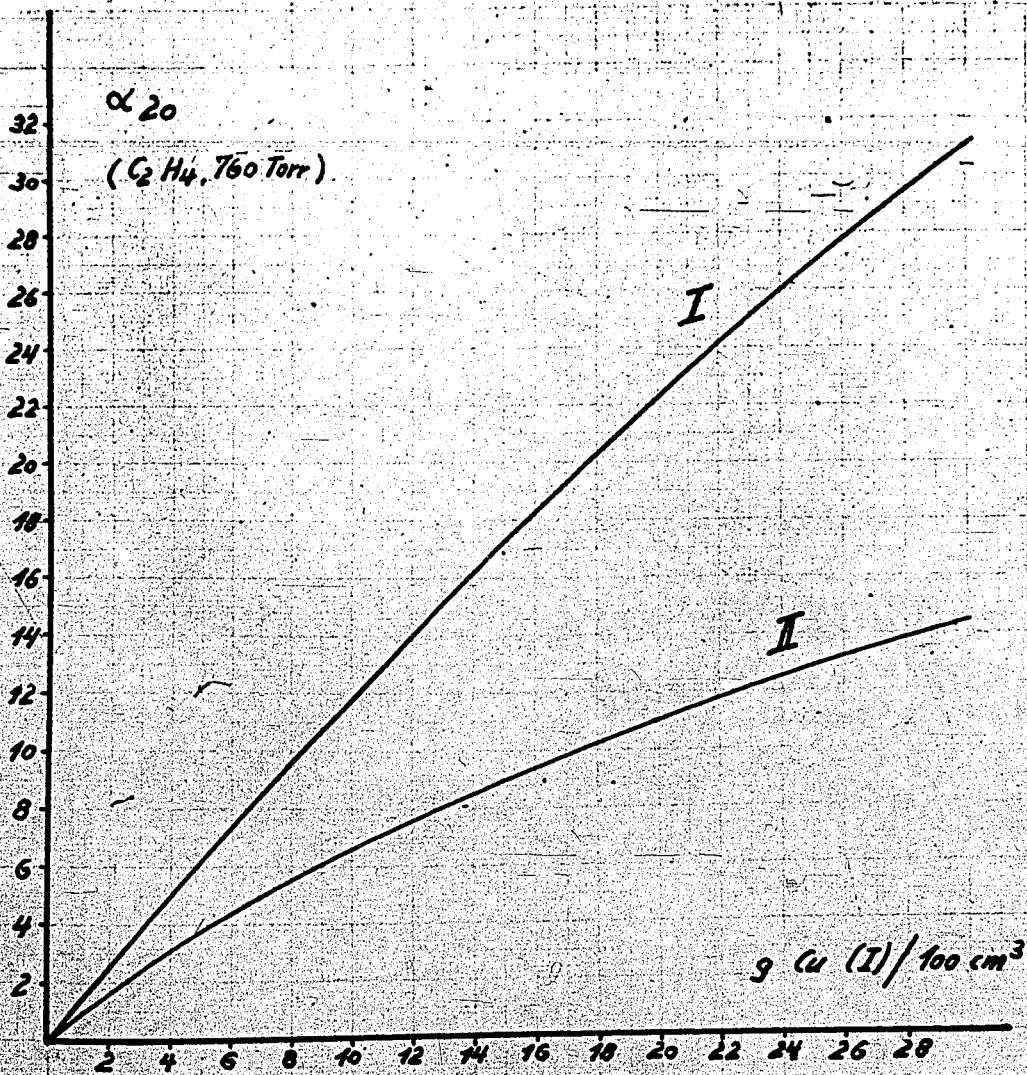


Absorptionsfähigkeit für Aethylen bei N-druck und 20°
von ammoniakalischen Lösungen verschiedener Cupro-
salze.

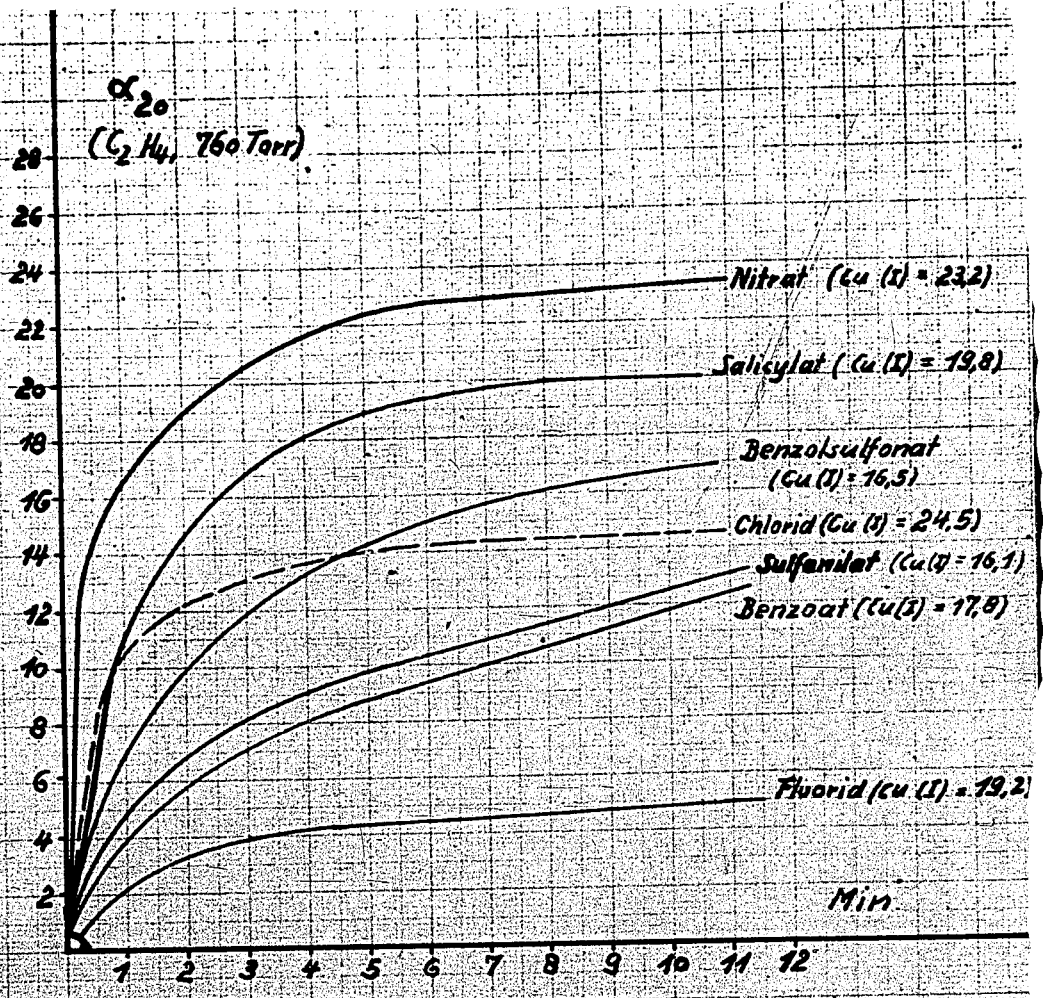
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Aufnahmefähigkeit einiger Aethanolaminlaugen
für Aethylen bei Normaldruck und 20°.

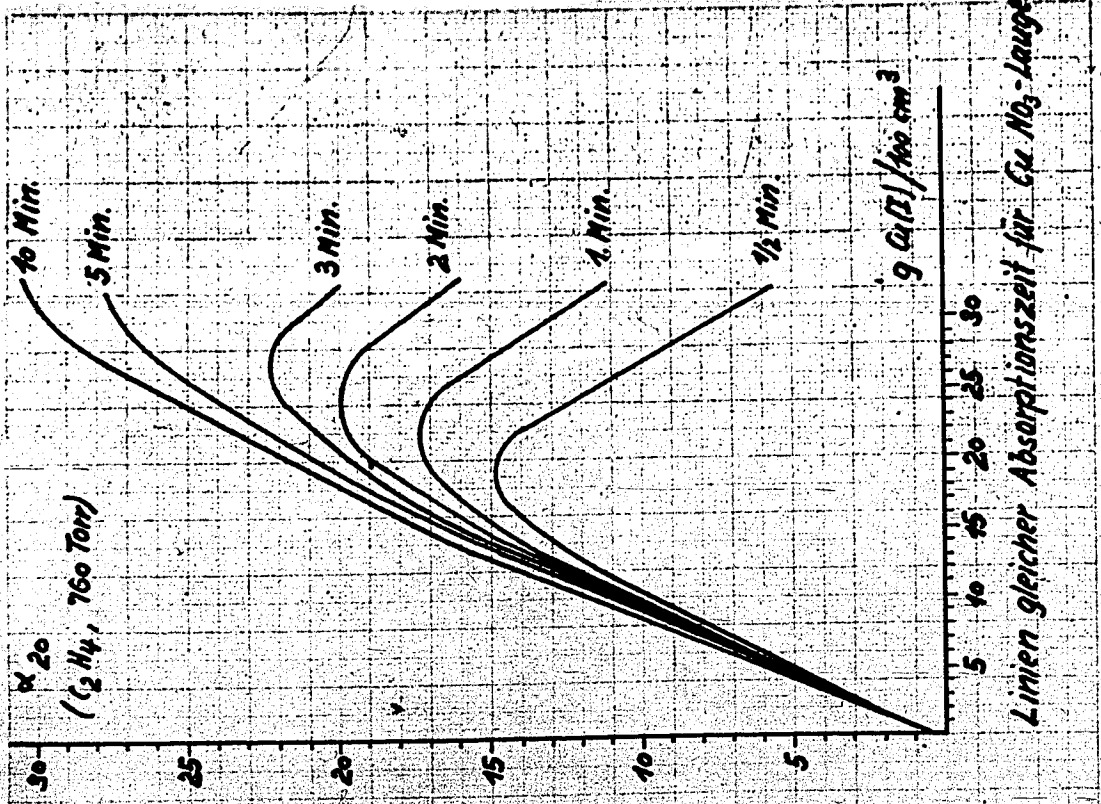


Absorptionsfähigkeit von Cupronitratlösungen, die
Aethylamin (I) bzw. Ammoniak (II) als Base
enthalten.

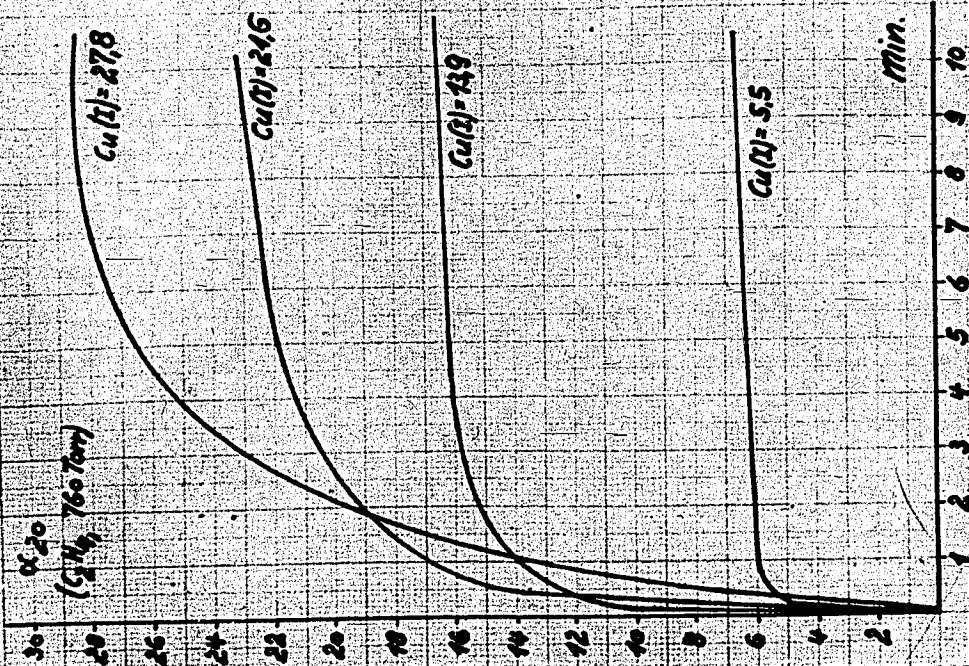


Absorptionsgeschwindigkeiten verschiedener
Aethanolaminlaugen.

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Linien gleicher Absorptionszeit für $\text{Cu}(\text{NO}_3)_2$ -Lösung



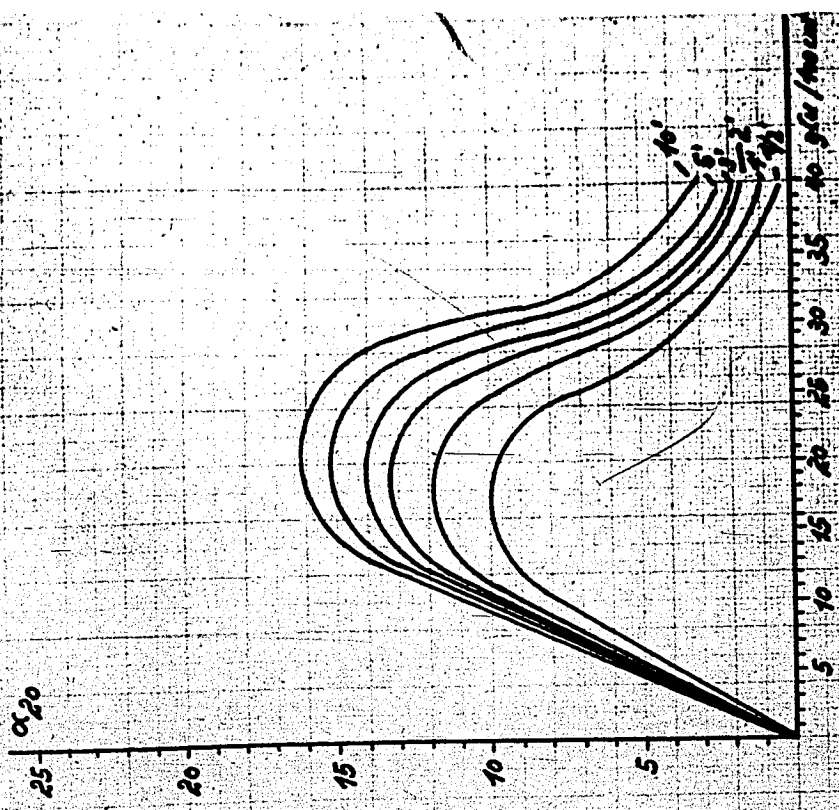
Absorptionsgeschwindigkeitskurven von $\text{Cu}(\text{NO}_3)_2$ -Lösungen mit verschiedenem $\text{Cu}(\text{NO}_3)_2$ -Gehalt.

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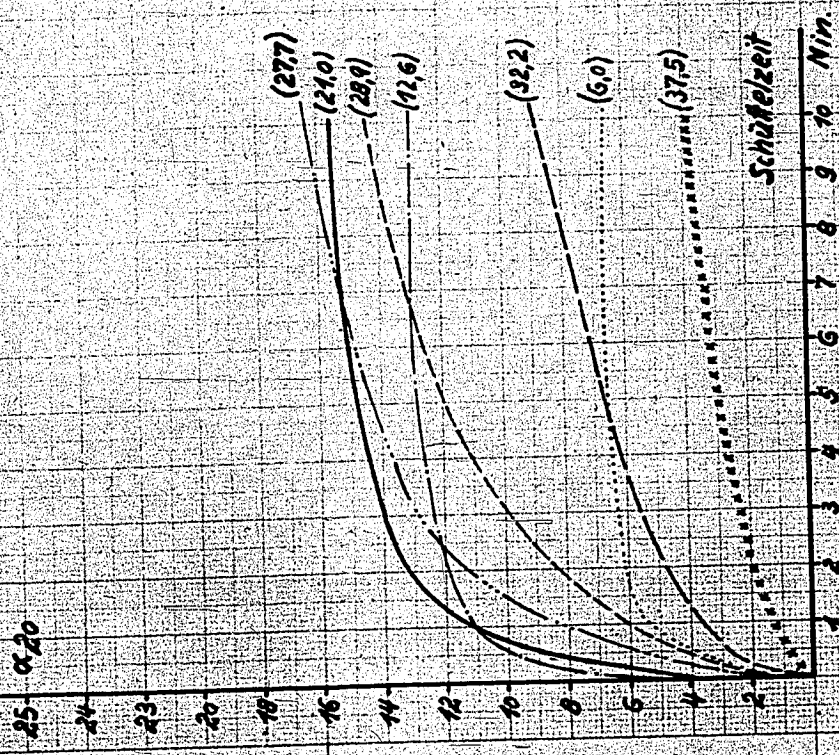
Skizze 7

7. VII. 42 Keller

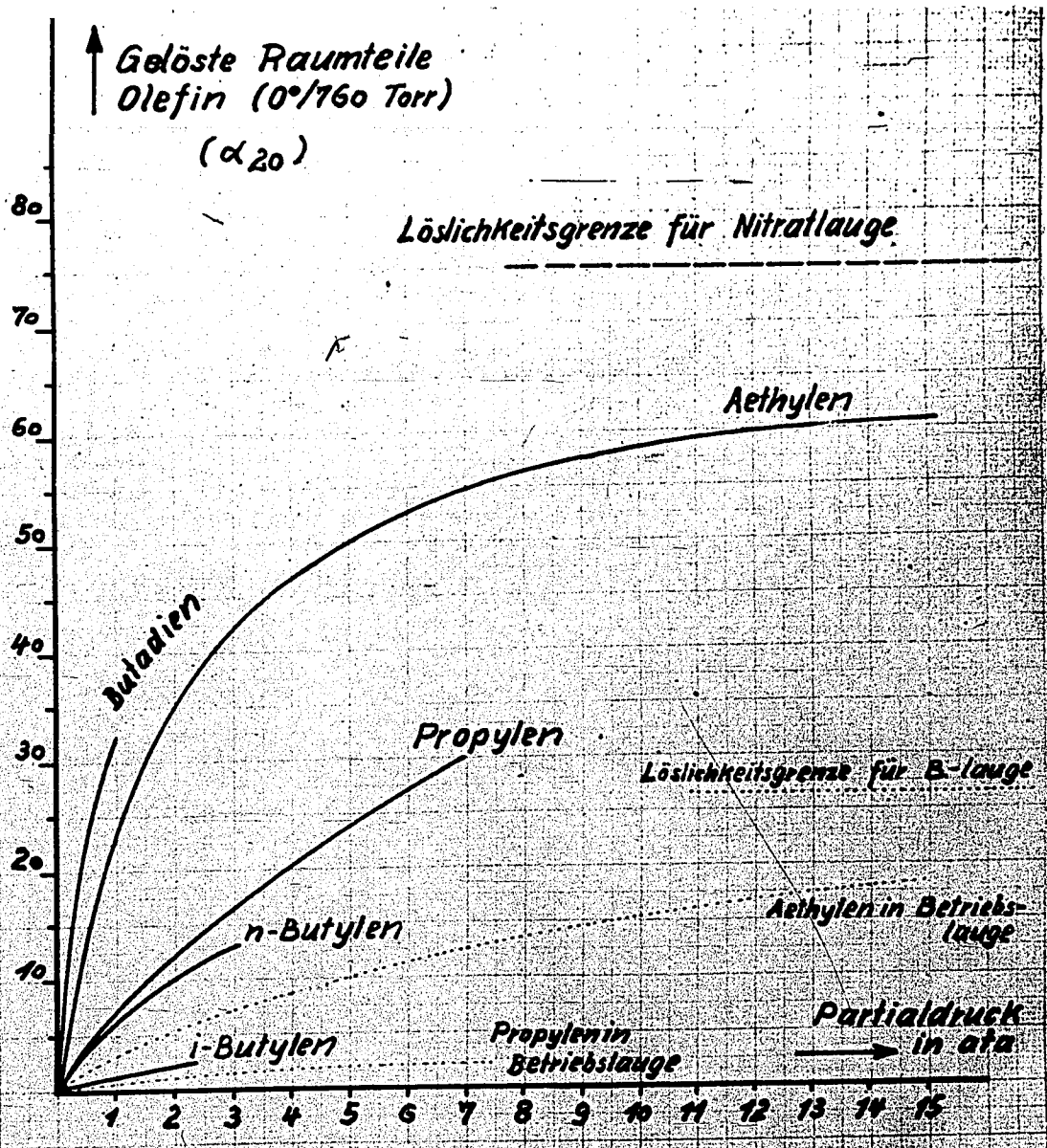
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Linien gleicher Absorptionszeit für
CuCl₂-Lauge.



Absorptionsgeschwindigkeitskurven für CuCl₂-Lö-
sungen mit verschiedenem Cu(II)-Gehalt



Löslichkeit gasf. Olefine in Nitrat- und Betriebslauge bei 20° in Abhängigkeit vom Druck