

LXXXI.—*The Miscibility of the Pyridine Bases with Water and the Influence of a Critical-solution Point on the Shape of the Melting-point Curve.*

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A PREVIOUS investigation (Flaschner, *Zeitsch. physikal. Chem.*, 1908, **62**, 493; Flaschner and McEwen, *Trans.*, 1908, **93**, 1000) on the mutual solubility of some bases of the pyridine and piperidine series and water has shown that the introduction of a methyl group decreases the solubility. This influence is strongest when the methyl group is attached to the nitrogen atom; thus 1-methylpiperidine has a lower critical-solution temperature of  $48.3^{\circ}$ , and the data point to the existence of an upper one of about  $290^{\circ}$ ; 2-methylpiperidine forms with water a complete solubility ring between  $79.3^{\circ}$  and  $227^{\circ}$ . In the present paper the attempt to determine the solubility of the  $\beta$ - and  $\gamma$ -substituted homologues is described.

The physical properties of these substances as determined by previous observers are not in good agreement.  $\gamma$ -Picoline is usually isolated from the mixture of pyridine bases as the fraction  $143\text{--}146^{\circ}$ , and is then converted into the mercury double salt, which is recrystallised. Ladenburg (*Annalen*, 1888, **247**, 11) heated pyridine methiodide to  $300^{\circ}$  and fractionated the products of the reaction.  $\beta$ -Picoline can be isolated in small quantities from bone oil or from the mixture obtained by heating glycerol with ammonium phosphate and phosphoric oxide (Ladenburg, *Ber.*, 1890, **23**, 2688; Stöhr, *J. pr. Chem.*, 1892, [ii], **45**, 23), or ammonium sulphate and sulphuric acid (Storch, *Ber.*, 1886, **19**, 2458). Marcuse and

Wolffenstein (*Ber.*, 1899, 32, 2526) removed the  $\alpha$ -picoline by converting it into its aldehyde condensation product. It is evident that there is no practicable method of synthesising one of the homologues, as these always occur mixed together, and cannot be completely separated. As will be pointed out later, the recrystallisation of the mercury double salt does not improve the purity of the product much, even if one employs the following strange method described by Constam and White (*Amer. Chem. J.*, 1903, 29, 1): "On account of the number of impurities present, all of which form difficultly soluble chlorides with mercury, differing very little in point of solubility from that of the  $\beta$ -salt, the crystallisation had to be controlled by means of the magnifying glass, and only when an absolutely uniform product was obtained were we satisfied as to its purity." I have now found that all these homologues are isomorphous, and therefore form mixed crystals, the composition of which even Constam and White could hardly detect by means of a lens. It seems far more advisable to adopt a process of purification by determining a physical constant.

The initial material employed in this research was 800 grams of so-called  $\beta$ -picoline (Schuchardt). This was fractionated with a Young's three-chamber "evaporator" fractionating column, fractions being collected between 126° and 160°, first at intervals of 1° and finally of 0.25° until further fractionation did not change the weights of the single fractions. This stage was reached after eight fractionations. The main part distilled at the following temperatures:

143.75—144.00° .....	22.5 grams.	144.75—145.00° .....	51.3 grams.
144.00—144.25 .....	29.3 "	145.00—145.25 .....	46.6 "
144.25—144.5 .....	46.8 "	145.25—145.5 .....	24.2 "
144.5—144.75 .....	59.5 "		

The fractions 144.25° to 145.25° were again united and a part was transformed into the mercury double salt. This was recrystallised four times from water and then decomposed with potassium hydroxide. The free base was now fractionated. The mother liquors were united, the base set free, and fractionated as well. The result was that neither in the recrystallised product nor in the mother liquor was a substance of constant boiling point accumulated. It is therefore impossible to obtain a reasonable purification by employing the mercury salt, which hitherto has always been used in such cases. In view of the greater differences between the melting points of the zinc double salts, the attempt was now made to use these as a means of purification of the basic mixture. An amount of zinc chloride greater by one half than that required for the combination was dissolved in water, the solution filtered, and poured into a cooled solution of the base in water (1:5). The zinc salt was precipitated and recrystallised twice from alcohol. Water cannot be used, because it dissolves the salt sparingly and

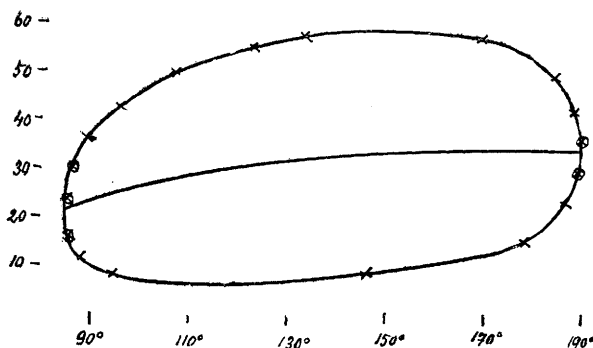
causes loss by hydrolysing the salt at higher temperatures to a great extent.

The recrystallised zinc salt was decomposed and the base fractionated. It boiled constantly at  $145.05^{\circ}$ . The base was again transformed into the zinc salt and recrystallised three times; it was then isolated and fractionated. It distilled completely at  $145.08^{\circ}$ , showing that the substance thus obtained was pure.

The boiling point of  $\gamma$ -picoline given by different observers varies between  $142.5^{\circ}$  and  $144.5^{\circ}$ . It was concluded from the solubility in water that the substance obtained was  $\gamma$ -picoline. The purity of the product is proved by (1) the constancy of its boiling point, and (2) the modified method of Crismer explained later on.

The mother liquors of the zinc salts contained apparently  $\beta$ -picoline

FIG. 1.



and 2:6-lutidine. By a combination of fractional crystallisation of the zinc salt and fractional distillation of the free bases, I was able to separate two products. The first boiled at  $143.2^{\circ}$  and was very probably 2:6-lutidine. The second, which boiled at  $143.9^{\circ}$ , was present in greater quantity and was regarded as  $\beta$ -picoline. Although the purity of both substances was far from being so satisfactory as that of  $\gamma$ -picoline, determinations of their solubilities were made in view of the fact that these are very nearly equal.

The  $\beta$ - and  $\gamma$ -picolines were reduced in alcoholic solution with sodium and the products were purified by fractionation.

The solubility of these bases in water was determined by Alexéeff's method. In the case of the reduced bases, the operation was carried out in Jena-glass tubes. The percentage compositions of the mixtures by weight are as follows.

*4-Methylpiperidine and Water (Fig. 1).*

Percentage of base.	Lower solution-point.	Upper solution-point.	Percentage of base.	Lower solution-point.	Upper solution-point.
57.5	133.0°	168.5°	30.0	85.9°†	188.8°†
55.0	122.7	—	23.7	84.9*	186.2
49.4	106.9	183.6	16.0	85.1†	178.0
42.4	95.5	187.5	11.6	87.6	157.8
36.2	88.8	189.5 *	8.9	94.2	146.0

\* Strong critical opalescence.

† Critical opalescence. The points where critical opalescence was visible are marked in the diagram by small rings.

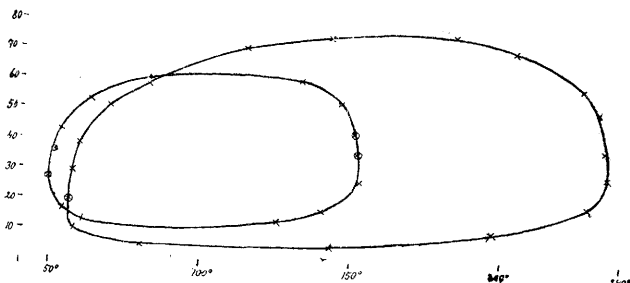
The purity of the substance was tested by Crismer's method, which consists in determining the critical-solution points of the first fraction :

29.9                      89.4°                      184.5°

and the last fraction :

29.7                      86.5°                      187.6°

FIG. 2.



Considering that with the small amount of 4-methylpiperidine (b. p. 126°) available a complete separation from picoline (b. p. 145.08°) is impossible, the result of the test is satisfactory. Using larger quantities, however, it might be worth while precipitating the picoline with mercuric chloride in order to separate it from the reduced base.

*β-Picoline and Water.*

Percentage of picoline.	Lower solution-point.	Upper solution-point.	Percentage of picoline.	Lower solution-point.	Upper solution-point.
59.7	83.5°	133.3°	26.4	49.4°*	152.5°
52.3	63.3	146.5	16.4	54.5	140.0
42.3	53.7	151.0*	12.7	61.0	125.7
35.5	51.4*	152.0	9.7	homogeneous.	

\* Critical opalescence.

These numbers are shown in Fig. 2 by the narrower ring.

x x 2

*3-Methylpiperidine and Water.*

Percentage of 3-methyl-piperidine.	Lower solution-point.	Upper solution-point.	Percentage of 3-methyl-piperidine.	Lower solution-point.	Upper solution-point.
74.8	142.2°	184.0°	29.2	57.5°	235.0°
70.1	115.0	204.0	19.2	56.9	228.5
58.2	82.0	226.5	9.9	58.1	197.0
50.5	69.8	232.0	4.8	80.0	143.0
38.1	59.9	234.0			

Represented by the wide ring in Fig. 2.

*2:6-Lutidine and Water*

Percentage of 2:6-lutidine.	Lower solution-point.	Upper solution-point.	Percentage of 2:6-lutidine.	Lower solution-point.	Upper solution-point.
79.1	homogeneous.		33.8	45.4*	164.9°
66.9	92.2°	130.5°	27.2	45.3	164.0
54.8	59.3	157.0	18.1	48.1	153.5
46.4	50.2	161.6*	12.1	57.7	132.7
40.6	47.7	163.4*	9.5	74.5	105.0

\* Critical opalescence.

First fraction :

30.2                      49.3°                      162.7°

Last fraction :

28.7                      47.4°                      162.4°

The lutidine boiled at 143.2°. As can be seen from the last figures, it was contaminated with substances of lower and higher boiling points respectively, both of which are more soluble than itself, namely,  $\alpha$ - and  $\beta$ -picoline. The miscibility of 2:6-lutidine with water is represented by a closed curve with a lower critical temperature of about 45° and an upper one of 163.5. As it does not differ in shape from the other ones, no diagram is given.

Discussing the question how the solubility is influenced by chemical constitution, one can only expect regularities if one does not depend on the accidental position of the temperature of experiment. This is avoided by determining the mutual solubility as far as the critical-solution point. The distance between the lower and upper critical-solution points, that is, the width of the solubility ring, gives a comparable measure of the miscibility of two liquids. Of course it will often occur that the lower critical-solution point cannot be reached on account of the appearance of a solid phase, whilst the upper critical-solution point may lay higher than the critical-evaporation point of one or other of the liquid layers (Büchner, *Zeitsch. physikal. Chem.*, 1906, 56, 267; Kuenen and Robson, *Zeitsch. physikal.*

*Chem.*, 1894, **28**, 345). Addition of a third substance affords a means of bringing the critical solution-temperature into a region, where it can be measured. By extrapolating, we can easily determine the critical-solution temperature of the pure substance, which is otherwise not accessible. On the other hand, it will often occur that the mutual solubility of two liquids at all temperatures is complete. What is the measure for the miscibility of such liquids?

Timmermans has recently published a paper (*Bull. Soc. chim. Belg.*, 1909, **23**, 129) in which he again draws attention to the influence of the external pressure on the critical-solution point, and concludes that two partially miscible liquids, when exposed to a certain pressure, will become completely miscible. Timmermans calls this point in the pressure-concentration-temperature diagram, according to Büchner's nomenclature, a terminal critical-solution point (kritischer Lösungs-*endpunkt*). If we consider the mutual solubility in the neighbourhood of such a terminal critical point, we see that increase of pressure will cause a rise of the lower and a fall of the upper critical-solution point, that is, shrinking of the solubility ring. The following cases have hitherto been observed: Kuenen (*Phil. Mag.*, 1903, [vi], **6**, 637) found that between 1 and 100 atmospheres an increase of pressure of 1 atmosphere depresses the upper critical-solution point of the system propane-methyl alcohol by  $0.044^{\circ}$  and raises the lower critical-solution temperature of the system triethylamine-water by  $0.021^{\circ}$ . By studying the influence of increasing pressure on a system with very small solubility ring, as, for example, 4-methylpiperidine and water, one could determine the alteration of both critical-solution temperatures on the same system. The solubility ring of such a system is only the section of the *p, c, t* diagram, for  $p_c = 1$  atm. If we increase the pressure, we reach a certain point—the terminal critical-solution point—where the upper and lower critical-solution temperatures become identical, that is, the solubility ring shrinks to a single point which is completely determined with regard to pressure, temperature, and concentration. At that point the system becomes completely miscible. By further increasing the pressure, we are not able to detect any difference in the miscibility, which has already become complete. A pair of completely miscible liquids, such as  $\gamma$ -picoline and water, shows at normal pressure the same behaviour as 4-methylpiperidine and water when exposed to a pressure slightly higher than the terminal pressure. If we now relieve this pressure, or if we exert a negative pressure, opalescence will be observed, owing to the formation of two liquid phases. This diminution of pressure, which may be called the "separation pressure" (*Entmischungsdruck*), is characteristic of the miscibility of a pair of liquids which are completely miscible under normal pressure. The separation-pressure of

the system pyridine-water is far greater than that of the system  $\gamma$ -picoline-water. In the majority of cases, however, it will prove impossible to reach a sufficiently high negative pressure to cause séparation. It is therefore necessary to introduce into our definition of the "separation pressure" a magnitude which can easily be determined experimentally. Such a one is the concentration of a third substance added to the system. Timmermans (*Zeitsch. physikal. Chem.*, 1907, 58, 129) has studied the influence of added substances on the critical-solution point, and has found that substances soluble to the same extent in both liquids increase the mutual solubility, that is, they have the same effect as increased pressure in the example given above. Substances soluble only in one of the two liquids decrease the mutual solubility, that is, they act like decreased pressure. Tammann has pointed out that liquids exposed to an external pressure show an analogous behaviour to solutions, that is, liquids the internal pressure of which is increased by dissolving in them a second substance. Tammann ("*Beziehungen zwischen den inneren Kräften, etc.*," p. 183) himself drew attention to the fact that a gas may be expelled from a liquid by dissolving a salt in it. Ritzel (*Zeitsch. physikal. Chem.*, 1907, 60, 319) has shown that the solubility of an indifferent gas in organic solvents is directly proportional to the compressibility of the liquid. But since the compressibility of solution of salts is smaller than that of the solvent, a less solubility of the gas is to be expected. Similar considerations follow if one employs, instead of a gas, a second liquid, which does not dissolve the salt added. A salt dissolved in a mixture of two liquids will therefore cause an increase of the internal pressure of the one liquid and so force the other out, that is, it will have the same effect as exerting an external pressure by means of a semipermeable pressure piston, or in the case discussed above, as a decrease of external pressure. A salt which is equally soluble in both liquids will increase the mutual attraction of the liquid molecules, that is, it will increase the mutual solubility or have the same effect as increase of the pressure in the above case.

There are systems known in which an increased pressure raises the upper critical-solution point (van der Lee, *Zeitsch. physikal. Chem.*, 1900, 33, 622; Kuenen, *loc. cit.*). They are very far from the terminal critical pressure—if they belong to the same class of systems at all—and are not included in the above considerations.

As there is such a close connexion between the influence of a dissolved third substance and that of external pressure, it may be sufficient to determine the numerical relation between small pressures and dissolved substances, and then to carry on the experiments with the latter until separation into two liquid layers takes place. The

concentration of a salt (or third substance) which just effects liquid separation in the critical region at normal pressure corresponds with the "separation pressure" and may be called "separation concentration."

For practical purposes of comparison it may be more convenient, instead of using the term separation concentration, to speak of the width of that solubility ring which, starting from the terminal critical point, is reached by the same concentration of salt as the terminal point itself. This ring may be called the "characteristic negative ring," because it lies as far behind the terminal critical point as the normal pressure lies in front of it. The characteristic negative ring is thus the ring which shrinks into a single point under the separation pressure. Such negative rings afford a comparable measure for the miscibility of completely miscible liquids.

For the experimental determination of the characteristic negative ring, it is in the first place necessary to salt out different mixtures of the two liquids and select that concentration as critical which is accompanied by the strongest critical opalescence. Then one determines for that special concentration the lower and upper critical-solution temperature, adding two or three different quantities of salt, and connects these points in a  $t, c$  diagram by a parabolic curve. The concentration which corresponds with the vertex of the curve is the separation concentration. The solubility ring which is obtained when the concentration is twice as great as the separation concentration is the characteristic negative solubility ring.

Values for the negative rings of some pairs of completely miscible liquids will now be given.

#### *Pyridine and Water.\**

The critical concentration was first determined and was found to be about 34.6 per cent. of the base. A solution of this strength shows a strong critical opalescence in the neighbourhood of the upper and lower critical-solution points if a salt like potassium chloride is added.

Percentage of potassium chloride.	Lower critical-solution point.	Upper critical-solution point.
8.9	93.0°	130.0°
10.2	59.4	180.4

If one therefore adds to an aqueous solution containing 34.6 per cent. of pyridine 8.7 per cent. of potassium chloride, one just reaches the limit where the two liquids become miscible in all proportions, and, on the other hand, a further trace of salt effects separation into two

\* I am indebted to Mr. Rankin for making this determination.



layers. The characteristic ring corresponding with 17.4 per cent. of potassium chloride in this case can only be extrapolated and is about 340°.

*Piperidine and Water.*

The critical concentration is about 33.3 per cent. of the base. The negative ring had previously (*Zeitsch. physikal. Chem.*, 1908, 62, 494) been determined on the assumption that the change of the critical-solution temperature is proportional to the amount of salt added. As this is not correct in the immediate neighbourhood of the terminal point, the ring had to be recalculated.

Percentage of potassium chloride.	Homogeneous solution.	
3.7	155.2°	200°
3.9	123.5	258
5.0		

The separation concentration is 3.75 per cent. of potassium chloride; the characteristic ring about 240° (90—330).

*α-Picoline and Water.*

The critical concentration is 29.6 per cent. of the base.

Percentage of potassium chloride.		
0.6	104.0°	112.7°
1.0	84.4	131.7
1.5	68.8	155.4

The separation concentration is 0.56 per cent. of potassium chloride; the characteristic ring corresponding with 1.12 per cent. of potassium chloride lies between 77.5° and 142°, and has thus a width of 64.5°. See Fig. 3.

*γ-Picoline and Water.*

The critical concentration is 31 per cent. of the base.

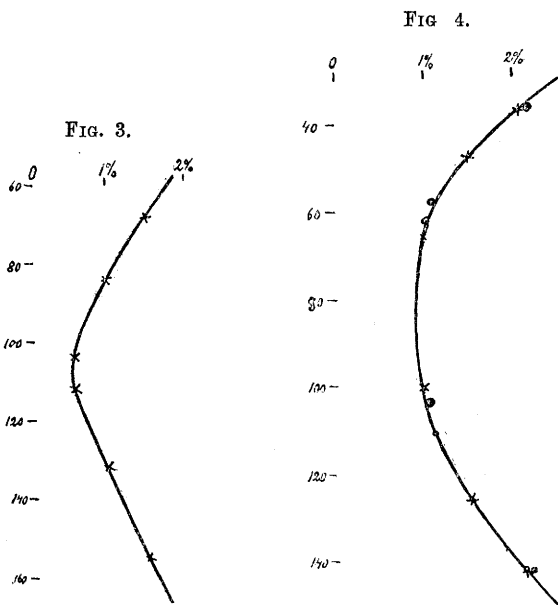
Percentage of potassium chloride.	Homogeneous solution.	
0.54	65.8°	100.6°
1.0	47.3	126.1
1.5	37.3	143.0
2.1		

These numbers are shown in Fig. 4.

The terminal critical point is 82.5°, corresponding with 0.86 per cent. of potassium chloride. The characteristic ring lies between 43° and 133.5°, and has thus a width of 90.5°.

*The Modified Method of Crismer.*

Crismer's method for testing the purity of a liquid consists in the determination of the critical-solution point of the single fractions. The general use of this method has hitherto been limited for lack of a second liquid, which gives with the liquid to be tested an easily accessible critical-solution point. The difficulty may be overcome by employing solutions instead of pure liquids. In the present case, the purity of  $\gamma$ -picoline was examined. The critical concentration of the



middle fraction was first determined by observing the strength of the critical opalescence, and was found to be 31 per cent. of the base. The shape of the critical zone was next determined in the manner described, and was marked in Fig. 4 by points. Then two points of the critical zone were determined, employing the first fraction as one liquid, and an aqueous solution of potassium chloride as the other.

Percentage of  
potassium chloride.

0.0

1.1

2.1

Homogeneous solution.

57.4°

37.8

111.1°

142.2

In the same way, two points with the last fraction were determined :

1.04	62.8°	103.9°
2.16	37.6	142.8

The points of the first fraction are marked in the figure as small rings, the points of the last fraction as ○. If the liquid is quite pure, all these points must lie on the same curve. It can be seen from the figure that the  $\gamma$ -picoline was of a high degree of purity.

The method is also available for a pair of liquids which are too little miscible at the ordinary temperature if one adds a third substance which is almost equally soluble in both liquids.

### *Nitrosopiperidine and Water.*

As nitrosopiperidine can easily be obtained, I determined its solubility with water.

Percentage of nitroso-piperidine.	Upper solution-point.	Lower solution-point.	Percentage of nitroso-piperidine.	Upper solution-point.	Lower solution-point.
94.6	31.5°	—	43.3	150.3°	—
85.9	103.5	—	38.5	150.3	—
75.6	133.4	—	30.1	148.0	—
67.0	143.5	—	22.7	141.5	—
58.9	147.7	—	15.2	124.0	—
51.9	149.3	—	8.1	73.5	14.5°

The upper critical-solution temperature is 150.3°; the critical concentration 43 per cent.; the centre of the solubility ring is about 15°. Introduction of a nitroso-group attached to the basic nitrogen atom greatly decreases the solubility.

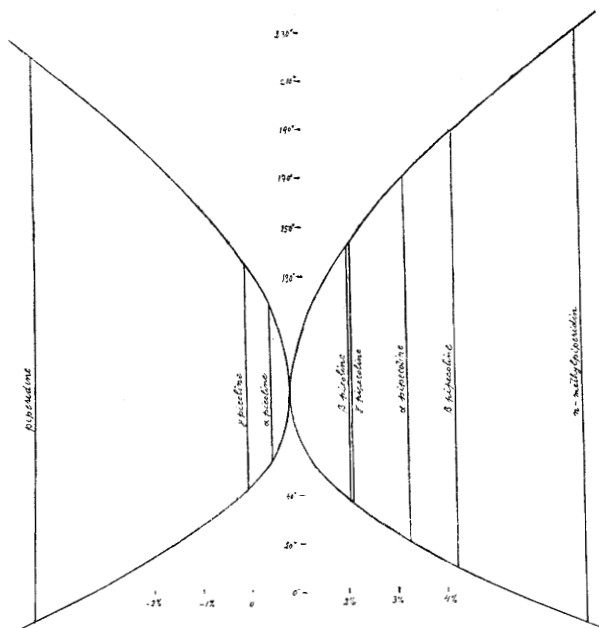
The results obtained are collected below :

			Per cent. KCl.
Pyridine + water	negative ring, 340.0°	Separation concentration	8.7
$\alpha$ -Picoline + water	" " 64.5	" " "	0.56
$\beta$ -Picoline + water	positive ring, 103.0	" " "	—
$\gamma$ -Picoline + water	negative ring, 90.5	Separation concentration	0.86
Piperidine + water	" " 240.0	" " "	3.75
1-Methylpiperidine + water.	positive ring, 242.0	" " "	—
2-Methylpiperidine + water.	" " 148.0	" " "	—
3-Methylpiperidine + water.	" " 178.1	" " "	—
4-Methylpiperidine + water.	" " 104.6	" " "	—

A convenient survey of the mutual solubilities of different members of a homologous series can be obtained if one determines first for one homologue, as, for example,  $\gamma$ -picoline and water, the critical zone by adding different amounts of a third salt. It is convenient to take a homologue which requires a very small separation concentration of salt. Now, in the vertex of the parabolic curve, the mirror of that curve is constructed as shown in Fig. 5. In the left part of the mirror the homologues with a negative solubility ring are drawn as ordinates

at such a distance from the vertex as the separating concentration indicates. In the right part of the mirror the width of the solubility rings are drawn at such a distance that they just fit the curve. The distances between these lines are differences in concentration of the third substance, and can easily be expressed in atmospheres of external pressure if the ratio is known. They are a direct measure of the mutual solubility of the members of the homologous series. The method is so far not quite correct, as the centres of the different rings are often shifted.

FIG. 5.



From Fig. 5 it is evident that the methyl group has the greatest influence when attached to the nitrogen, then follow the 2-, 3-, and 4-positions in the series of pyridines and their reduction products.

#### *The Melting-point Curve in the Neighbourhood of a Critical-solution Point.*

In the majority of cases the shape of the melting-point curve is well expressed by the equation (van't Hoff, *Kongl. Svenska Akad. Handl.*, 1886, **21**, 17; Le Chatelier, *Compt. rend.*, 1885, **100**, 441; T. Schröder, *Zeitsch. physikal Chem.*, 1893, **11**, 449):

$$\frac{d \ln \eta}{dT} = \frac{Q}{RT^2}$$

$\eta$  expressing the volume concentration and  $Q$  the heat of solution. This equation does not show an inflexion point. A more general equation is deduced by Rothmund (*Löslichkeit*, p. 50), following van der Waals :

$$\frac{d\ln c}{dT} = - \frac{Q}{RT^2(1-c)\left(\frac{d\ln p}{dc}\right)_{\tau}},$$

where  $c$  means the mass solubility and  $p$  the vapour pressure. By this equation we can discuss the results found in the present case. If  $\frac{d\ln p}{dc}$  is very small, then  $\frac{d\ln c}{dT}$  becomes very large, that is, the melting-point curve will ascend very steeply. If  $\frac{d\ln p}{dc} = 0$ , the melting-point curve at that point is vertical. If  $\frac{d\ln p}{dc}$  becomes positive, the concentration will decrease if the temperature rises. In reality the partial pressure cannot rise when the concentration of an added substance increases. Also, the vapour pressure of a gas cannot decrease when the volume decreases. But as in the latter case condensation takes place, so in the former, separation of a second liquid layer will be observed. Van Laar (*Zeitsch. physikal. Chem.*, 1908, **63**, 216), employing the idea of thermodynamical potential, has deduced a quite general formula which embraces a region of solid as well as liquid separation. In all the cases, however, where liquid separation into two layers is observed, the range of miscibility in the solid phases is exceedingly small and, as in our case, practically vanishes. Van Laar (*Zeitsch. physikal. Chem.*, 1908, **64**, 274) has now shown by his equation that if the melting-point curve shows a vertical inflexion point, this point must be identical with the critical-solution point. This case nearly occurs in the system  $\gamma$ -picoline zincchloride-octyl alcohol. If the critical-solution temperature rises, the melting-point curve is cut by the solubility curve, that is, the substance melts below the solution: above zinc salt + water, above zinc salt + hexadecyl alcohol. If the critical-solution point is low, its neighbourhood is shown by a more or less steep sloping of the melting-point curve: above zinc salt + methyl to amyl alcohol. The same change of the shape of the melting-point curve is observed in the neighbourhood of an upper critical-solution point: salicylic acid and water (Alexéeff, *Wied. Annalen*, 1886, **28**, 330), potassium salt of trinitrophenylnitramine and water (Roozeboom, *Rec. trav. chim.*, 1889, **8**, 2); in the neighbourhood of a lower critical-solution point: nitrobenzene and carbon dioxide, *o*-nitrophenol and carbon dioxide, and *m*-chloro-

phenol and carbon dioxide (Büchner, *Zeitsch. physikal. Chem.*, 1906, **54**, 665).

The same is to be expected with the melting-point curves of the homologues of the pyridine series. Fusion below the solution in the neighbourhood of an upper critical-solution point has hitherto been observed in the following cases: benzoic acid and water (Alexéeff, *Wied. Annalen*, 1886, **28**, 330), resorcinol and benzene (Rothmund, *Zeitsch. physikal. Chem.*, 1894, **26**, 433), succinonitrile and water (Schreinemakers, *Zeitsch. physikal. Chem.*, 1897, **23**, 418), phenol and water, *p*-toluidine and water (Walker, *Zeitsch. physikal. Chem.*, 1892, **5**, 190), thallium and aluminium (or copper) (Doerincel, *Zeitsch. anorg. Chem.*, 1906, **48**, 184), sodium and aluminium (magnesium) (Matthewson, *Zeitsch. anorg. Chem.*, 1902, **48**, 192), bismuth and aluminium (Gwyer, *Zeitsch. anorg. Chem.*, 1906, **49**, 311).

Fusion below the solution in the neighbourhood of a lower critical-solution point, which then lies in the metastable or unstable field, has been observed for: *o*-bromonitrobenzene and carbon dioxide, dichloronitrobenzene and carbon dioxide, urethane and carbon dioxide, *m*-chloronitrobenzene and carbon dioxide (Büchner, *loc. cit.*), and pyridinium methiodide and pyridine (Aten, *Zeitsch. physikal. Chem.*, 1905, **54**, 124).

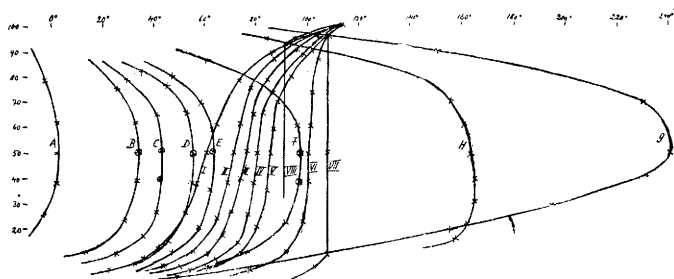
On recrystallising  $\gamma$ -picoline zincchloride from alcohol it was found that by quickly cooling the solution the zinc salt was separated out of solution as a second liquid layer. On the other hand, the somewhat cooled liquid was found to be supersaturated with regard to solid crystals. It appeared therefore evident that the same kind of system was present as was first observed in the case of salicylic acid and water. For reasons shown above, it seemed of interest to determine the shape of the melting-point curve as well as that of the solubility curve, which here lies, of course, in the metastable zone. These curves were therefore determined for the first members of the series of aliphatic alcohols, water and benzyl alcohol. The method was as follows: A certain mixture of solid zinc salt and alcohol contained in a small glass tube was heated in a sulphuric acid bath until the last crystal vanished. Thus a rough value of the melting point was obtained. Then the temperature was allowed to fall a little, but not so far as the critical-solution temperature. A tiny crystal was now thrown into the solution and the tube was constantly shaken, so that from the supercooled solution crystals of quite a minute size separated out. Then the temperature was very slowly raised, the tube being constantly shaken. The temperature at which the last crystal vanished was regarded as the melting point. I found that the results obtained by this method were sufficiently accurate. The bath was finally cooled down, and the temperature determined at which separation into two liquid layers took place.

*$\gamma$ -Picoline Zincichloride and Methyl Alcohol.*

Percentage of salt.	Melting point.	Solution point.	Percentage of salt.	Melting point.	Solution point.
89.0	86.4°	—	37.9	56.7°	+1.1°
78.5	73.5	-3.0°	25.2	52.0	-3.5
61.5	64.2	+1.5	12.7	41.5	—
49.7	60.5	+1.9	6.0	31.5	—

The critical point of the solubility curve lies at +1.9° for a concentration of 50 per cent. Although the distance of that point from the melting-point curve is about 60°, the liquid separation has already a considerable influence on the shape of the melting-point curve, which shows clearly a point of inflexion. In Fig. 6, the solubility curve is marked *A*, the melting-point curve, *I*.

Fig. 6.

 *$\gamma$ -Picoline Zincichloride and Ethyl Alcohol † (*B* and *II* in Fig. 6).*

Percentage of salt.	Melting point.	Solution point.	Percentage of salt.	Melting point.	Solution point.
86.9	88.7°	—	38.5	68.5°	32.9°*
75.5	78.8	25.5°	23.8	64.5	28.4
61.6	73.1	32.4	10.7	55.0	12.8
50.2	71.0	33.4*	5.0	43.5	—

\* Critical opalescence.

† The alcohol was absolute and prepared by Sydney Young's method.

 *$\gamma$ -Picoline Zincichloride and n-Propyl Alcohol (*C* and *III* in Fig. 6).*

Percentage of salt.	Melting point.	Solution point.	Percentage of salt.	Melting point.	Solution point.
90.3	96.0°	—	26.6	70.2°	40.7°
78.3	84.0	29.2°	17.0	67.1	35.4
65.1	78.6	40.7	10.0	60.5	25.0
50.9	76.3	52.5*	5.0	50.0	—
39.7	73.8	42.0*			

\* Critical opalescence.

*$\gamma$ -Picoline Zincichloride and isoButyl Alcohol* (b. p. 107.8°) (*D* and *IV*).

Percentage of salt.	Melting point.	Solution point.	Percentage of salt.	Melting point.	Solution point.
88.8	98.6°	—	37.9	78.4°	54.6*
82.1	—	35.0°	25.9	76.7	52.1
76.3	87.5	44.7	14.9	72.5	45.4
65.5	82.7	52.3	8.0	64.3	35.6
49.5	80.0	55.0*	4.0	54.7	22.7

\* Critical opalescence.

 *$\gamma$ -Picoline Zincichloride and isoAmyl Alcohol* (b. p. 131.5°) (*E* and *V*).

Percentage of salt.	Melting point.	Solution point.	Percentage of salt.	Melting point.	Solution point.
88.1	99.8°	—	35.0	83.9°	61.8°
80.0	93.7	46.5°	20.5	79.8	57.1
69.6	88.1	57.9	10.8	74.0	46.5
59.4	86.5	62.2	4.7	61.0	—
50.0	85.4	62.9*			

\* Critical opalescence.

 *$\gamma$ -Picoline Zincichloride and Methylhexylcarbinol* (b. p. 179.5°) (*F* and *VI*).

Percentage of salt.	Melting point.	Solution point.	Percentage of salt.	Melting point.	Solution point.
86.2	104.0°	60.5°	38.2	100.0°	96.5°
73.5	101.8	86.6	22.2	97.7	91.1
60.1	100.3	95.8	10.7	91.7	76.0
49.4	100.2	97.0	3.8	77.0	—

The solubility and melting-point curves nearly touch each other, therefore the latter rises nearly vertically in the critical region.

 *$\gamma$ -Picoline Zincichloride and Cetyl Alcohol* (*G* and *VII*).\*

Percentage of salt.	Melting point.	Solution point.	Percentage of salt.	Melting point.	Solution point.
95.8	108°	104°	20.0	—	155.0°
89.5	—	150	9.7	108.0°	120.6
69.7	—	230	4.9	102.5	92.0
50.0	108	241	1.0	54.0	48.0
30.0	—	195			

The alcohol used was purified as follows: It was dissolved in benzene, the solution was then cooled to 0°, and the crystals which formed were quickly collected, pressed between filter paper, and heated for some hours to 130°. On cooling, the pure alcohol crystallised out and melted at 48°. As seen in Fig. 6, the solubility curve cuts the melting-point curve. The zinc salt, therefore, below its alcoholic solution, melts constantly at 108°.

\* The determination of this pair was carried out by Mr. Rankin.



*$\gamma$ -Picoline Zincichloride and Water (H and VIII).*

Percentage of salt.	Melting point.	Solution point.	Percentage of salt.	Melting point.	Solution point.
95.0	95°	84.0°	40.4	—	164.6**
92.9	91	89.5	30.6	—	164.6
80.0	—	142.2	21.8	—	161.7
70.5	—	155.0	16.1	—	156.5
61.6	—	160.0	12.5	—	144.0
49.5	91	163.0*			

\* Critical opalescence.

At higher concentrations of water an exact determination of the solubility point is impossible on account of the hydrolysis of the zinc salt. In this case, also, fusion below the solution takes place. It is surprising that the behaviour of water towards the zinc salt is similar to that of an aliphatic alcohol with about twelve carbon atoms, whereas one might expect that the solubility curve would lie below that of methyl alcohol. This exceptional position of water proves that a comparison of physical properties ought always to be restricted to members of the same homologous series.

 *$\gamma$ -Picoline Zincichloride and Benzyl Alcohol.*

Percentage of salt ...	90.0	76.7	62.9	50.4	39.3	26.3
Melting point .....	101.7°	86.7°	70.1°	57.1°	46.3°	34.0°

A 50 per cent. solution remains clear even on cooling to  $-78^{\circ}$ ; also, from the shape of the melting-point curve, which differs but little from a straight line, it is evident that it must lie very far above the solubility curve. It would rather have been expected that the parts played by water and benzyl alcohol would be reversed.

As the melting-point curve illustrates the change of the osmotic pressure in a solution, it is possible to give an account of the  $\pi, c$  curves in the neighbourhood of the critical-solution point. In a  $t, c$  diagram is drawn the melting-point and solubility curves of the two liquids which show the highest critical-solution point ( $\gamma$ -picoline zincichloride and cetyl alcohol). As the lower alcohols show an additive behaviour towards the higher ones, the melting-point curves of the different alcohols are comparable. Therefore the melting curves of the other members of the same series are drawn at the given distances from this critical point, as only this distance influences inflexion. In the following table are given the slopes of the melting-point curves in the critical region and the distance from the critical-solution point.

	Distance.	$\frac{dc}{dt}$
Zinc salt and methyl alcohol.....	58°6'	3·1
„ ethyl alcohol .....	37·6	4·7
„ isobutyl alcohol .....	25·0	7·3
„ isoamyl alcohol .....	22·5	10·0
„ methylhexylcarbinol .....	3·2	56·0

This research was carried out in the summer of 1908 in the chemical laboratory of Trinity College, Dublin. I wish to express my sincerest thanks to Prof. Sydney Young for his keen interest and advice, and for the facilities he placed at my disposal.

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