# CL.—*Some Miscibility Relations of Acetic Anhydride.*

By David Charles Jones and Harold Frederick Betts.

Orton and Jones (J., 1912, **101**, 1722) determined the solubility of water in acetic anhydride at 15°, and Lumière and Barbier (*Bull. Soc. chim.*, 1905, **33**, 783) state that acetic anhydride is soluble in water to the extent of 12% at the ordinary temperature. No other data regarding the mutual solubility of acetic anhydride and any other liquid are given in the literature.

The solubility of pure acetic anhydride in carbon disulphide, *cyclo*hexane, and a petroleum fraction has now been determined, and found to be much less in each solvent than that of acetic acid itself (see Jones, J., 1923, **123**, 1374). The effect of acetic acid, present as an impurity in the anhydride, on the critical solution temperatures (C.S.T.) has also been investigated.

At first sight it seemed very remarkable that the stable compound formed by chemical union between two acetic acid molecules with the elimination of *water* should prove to be less soluble in these solvents than the associated acid. The much greater solubility of acetic acid than of its anhydride in water is roughly what would be expected from $C_2$ and $C_4$ compounds and their respective water-soluble groups. With petroleum as solvent, since we are dealing with the associated acid, in both cases we have $C_4$ compounds, and a greater similarity in the solubility would be expected, *i.e.*, the solubility of the anhydride would be relatively increased. The *greater* solubility of the associated acid in petroleum must then be ascribed to its smaller polarity. In the process of association, the highly polar carboxyl groups, which are active in promoting solubility in water, are conjugated in such a way that the resulting compound is less polar than its anhydride. All the known facts concerning the physical properties of the (pure, associated) acid are in agreement with this conclusion; *e.g.*, acetic acid, $\varepsilon_{19^\circ} = 6{\cdot}29$, $\gamma_{20^\circ} = 27{\cdot}90$; acetic anhydride, $\varepsilon_{20^\circ} = 20{\cdot}5$, $\gamma_{20^\circ} = 32{\cdot}69$ ($\varepsilon$ = dielectric constant; $\gamma$ = surface tension). It follows that, if its true solubility could be determined, pure, associated acetic acid should be much less soluble in water than the anhydride.

Acetic anhydride, although it has a fairly high dielectric constant, is a typical non-associated liquid if examined by all the usual criteria. Its mutual solubility with solvents of the petroleum type affords a rare example of partial miscibility of liquids neither of which is associated. A calculation of the internal pressure of the anhydride by some of the usual methods leads to values which place it somewhere near benzene in the internal-pressure series; and therefore, according to the theories of solubility put forward by Hildebrand and his collaborators, acetic anhydride should prove completely miscible in these solvents.

## EXPERIMENTAL.

*Purification of Materials.—Acetic anhydride.* For the purification of this material the method used by Orton and Jones (*loc. cit.*) was found very effective. Kahlbaum's "homologue-free" acetic anhydride was distilled several times through a six-section Young and Thomas evaporator-column stillhead. The apparatus was so arranged that the distillate could be collected in fractions and drawn off into bottles when required, and was carefully designed to prevent the entrance of moisture. Three fractions were finally obtained and the boiling points were immediately determined in an all-glass apparatus similar to that described by Edwards (*J. Soc. Chem. Ind.*, 1918, **37**, 38T) but having ground glass joints and a ground-in stopper, from which the thermometer was suspended by means of a platinum wire and a glass hook. The following results were obtained : Fraction 1, 100 c.c., b. p. 138·80°/760 mm.; fraction 2, 75 c.c., b. p. 139·36°/760 mm.; fraction 3, 50 c.c., b. p. 139·47°/760 mm.

A determination of the C.S.T.'s of fractions 2 and 3 with *cyclo*hexane gave results agreeing to within 0·03°. These two fractions were mixed and refractionated, the distillate having b. p. 139·41—139·47°/760 mm. and $d_{4^\circ}^{18^\circ}$ 1·0853 (compare Orton and Jones, *loc. cit.*, who gave b. p. 139·55°/760 mm., $d_{4^\circ}^{15^\circ}$ 1·0876, $d_{4^\circ}^{20^\circ}$ 1·0820). The material was kept in a well-stoppered bottle in a vacuum desiccator, and was used throughout the work.

cyclo*Hexane.* A sample of *cyclo*hexane (Poulenc Frères' "pur," m. p. 5·8°) was purified by repeated fractional freezing, and a final fraction obtained with m. p. 6·4°.

*Carbon disulphide.* A. R. material (B.D.H.) was subjected to a long shaking with mercury and distilled. It was then kept over phosphoric oxide for some time, and redistilled through the stillhead described above. The final fraction obtained, b. p. 43·23°/760 mm., was immediately used for the experiments, and was almost free from the usual odour, having in fact a distinctly pleasant ethereal smell.

*Petroleum.* A high-boiling petroleum fraction was purified as described in a former paper (Jones, *loc. cit.*), a final fraction, b. p. 170—180°, being used. This was the material with which curve C, Fig. 2, was obtained. It was further purified by refluxing several times with the nitrating mixture, and distilled through an 8-bulb pear stillhead under reduced pressure. The fraction, b. p. 171—175°, so obtained gave results from which curve D, Fig. 2, was drawn. (*n*-Decane has b. p. 173°/760 mm.)

*Acetic acid.* The acetic acid used was Kahlbaum's "homologue-free" material. It was purified by fractional freezing, a final fraction, m. p. 16·60°, being used. A certain amount was treated in the manner described by Orton and Bradfield (J., 1924, **125**, 960); the fraction obtained after several distillations, m. p. 16·5°, was fractionally crystallised and finally had m. p. 16·60°.

All the above liquids were kept in well-stoppered glass bottles in desiccators over phosphoric oxide.

*Determination of the Solubility Curves.*—The synthetic method was used for the solubility determinations. Weighed quantities of the two liquids were sealed up in thin-walled glass bulbs, of about 2 c.c. capacity, and the miscibility temperature taken. Owing to the hygroscopic nature of acetic anhydride, great precautions were necessary in filling the tubes. This was done in a manner similar to that used by Ewins for formic acid (J., 1914, **105**, 350). The tube was first weighed empty, the *cyclo*hexane run in, the tube reweighed, the anhydride run in, and the tube sealed off in the blowpipe. The two portions were allowed to cool, and the whole was reweighed. By careful withdrawal of the delivery tubes, wetting of the walls could be avoided.

The temperature of mixing was determined as described in a former paper (Jones, *loc. cit.*). The best method for the determination of the clearing point was found to be the observation of the filament of an electric lamp placed behind the bath. Even then some difficulty was experienced, especially in the carbon disulphide system, but the temperature error involved was small. In the critical region the mean of the temperature of the disappearance of the striations, which show up very clearly on shaking just below the miscibility temperatures, and the temperature of clouding was taken as the true miscibility temperature. If the tubes were vigorously shaken when near the mixing point there was found to be very little "lag," the greatest difference between the upper and lower readings being 0·1°. The thermometers used throughout this work were either standardised at the N.P.L. or compared with others so standardised, the correction for exposed stem being made.

The low-temperature miscibility points on the curve were determined in a bath of ether contained in an unsilvered Dewar flask of large capacity, and cooled below the necessary temperature by the addition of solid carbon dioxide.

The critical phenomena exhibited in the three cases differed markedly in degree. In the anhydride–petroleum system there was an almost complete absence of any critical phenomena; in the anhydride–*cyclo*hexane system the phenomena were more marked, but still comparatively slight; in the anhydride–carbon disulphide system the phenomena were most pronounced—in the neighbourhood of the C.S.T. very persistent emulsions formed on shaking, and there was a very intense and beautiful opalescence, which was strongest immediately above the C.S.T., and persisted for several degrees. This was presumably due to the similar

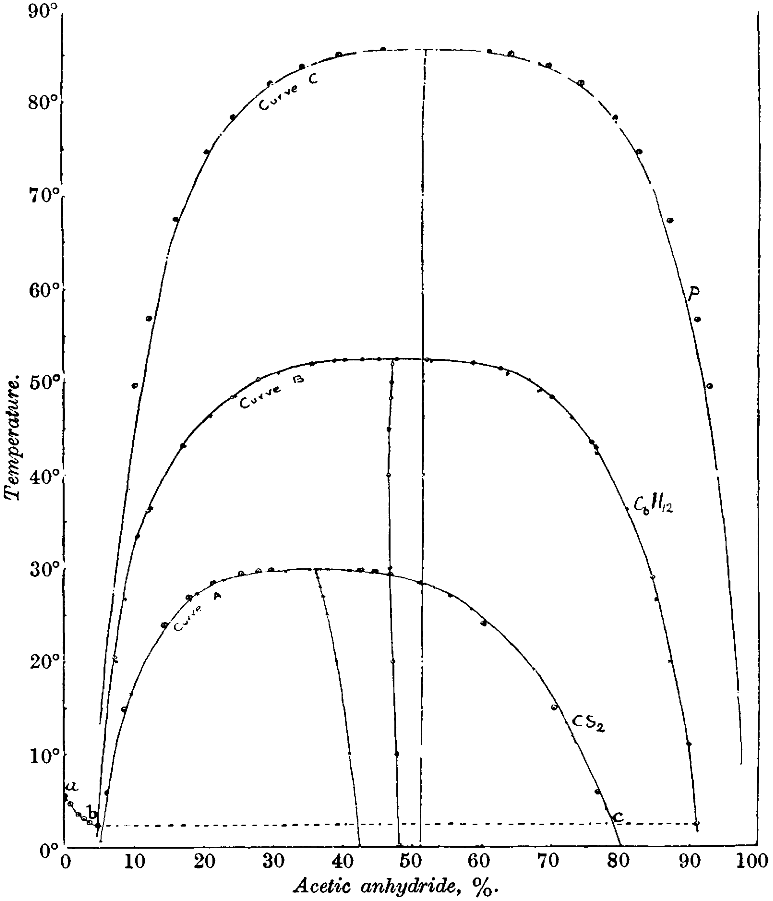
TABLE I.

Showing the miscibility temperature, *T*, corresponding to various proportions (% by weight) of acetic anhydride.

| % $C_4H_6O_3$. | *T*. | % $C_4H_6O_3$. | *T*. | % $C_4H_6O_3$. | *T*. | % $C_4H_6O_3$. | *T*. |
|---|---|---|---|---|---|---|---|
| Acetic anhydride–carbon disulphide. | | | | | | | |
| 5·27 | 0·7° | *35·36* | *29·83*° | 42·85 | 29·65° | 58·57 | 25·7° |
| 9·66 | 16·5 | 36·39 | 29·85 | 44·20 | 29·5 | 67·60 | 19·1 |
| 18·27 | 26·7 | *36·93* | *29·80* | 52·04 | 28·3 | 72·18 | 13·45 |
| 19·18 | 27·2 | 38·01 | 29·80 | 53·22 | 27·9 | 77·98 | 4·00 |
| 32·10 | 29·7 | 41·10 | 29·65 | | | | |
| Acetic anhydride–*cyclo*hexane. | | | | | | | |
| 7·20 | 20·4° | 27·97 | 50·3° | 52·25 | 52·37° | 76·03 | 43·50° |
| 10·40 | 33·5 | 39·03 | 52·25 | 58·83 | 52·00 | 84·71 | 29·00 |
| 12·09 | 36·2 | 43·01 | 52·40 | 62·77 | 51·40 | 89·83 | 11·00 |
| 16·90 | 43·1 | *45·35* | *52·42* | 70·16 | 48·30 | | |
| 24·32 | 48·3 | *47·84* | *52·45* | | | | |
| Acetic anhydride–petroleum. | | | | | | | |
| 7·14 | 27·6° | 30·83 | 82·0° | 60·67 | 85·25° | 79·85 | 77·35° |
| 9·46 | 38·5 | 35·00 | 83·5 | 67·87 | 84·00 | 84·91 | 71·00 |
| 14·95 | 63·5 | 42·67 | 85·1 | 72·08 | 82·55 | 94·10 | 40·00 |
| 22·59 | 76·1 | *50·33* | *85·47* | 76·73 | 80·27 | 96·8 | 16·5 |
| 22·83 | 76·5 | *53·50* | *85·52* | 79·2 | 78·15 | 98·97 | 45·5 |
| 26·90 | 80·0 | | | | | | |

densities and different refractive indices of the phases in this system. In all cases there were the usual flattening of the meniscus and appearance of flickering striations throughout the liquid just before

Fig. 1.



*A. Mutual solubility of acetic anhydride and carbon disulphide.*
*B.* ,, ,, ,, ,, ,, cyclo*hexane.*
*C.* ,, ,, ,, ,, ,, *petroleum.*

*The calculated solubility values are indicated by circles on curves A and C and by crosses on curve B; and the other points on each curve are experimentally determined.*

the critical point was reached. Very similar results were obtained with acetic acid (Jones, *loc. cit.*).

*Discussion of Solubility Curves.*—The solubility results are shown in Table I and graphically in Fig. 1. Curves C, B, and A represent the mutual solubility of the systems acetic anhydride–petroleum, acetic anhydride–*cyclo*hexane, and acetic anhydride–carbon disulphide, respectively. The mean-concentration curves for the three systems and, in the case of the system acetic anhydride–*cyclo*hexane, the freezing-point curve *abc* are also shown. The invariant point where solid *cyclo*hexane is in equilibrium with two liquid phases is at 2·269°. All the curves have the usual flattened-top form, and in two of the systems (*cyclo*hexane and petroleum) the mean-concentration curves are almost parallel to the temperature axis, the effect of temperature on the solubility of acetic anhydride in both phases being almost the same. In those two systems in which the freezing-point curve is very low (petroleum and carbon disulphide), an attempt was made to see whether either of these systems showed any inclination to become closed curves, with a complete miscibility area, at lower temperatures, but at the lowest temperature used (solid carbon dioxide and ether) there was no indication of such a trend.

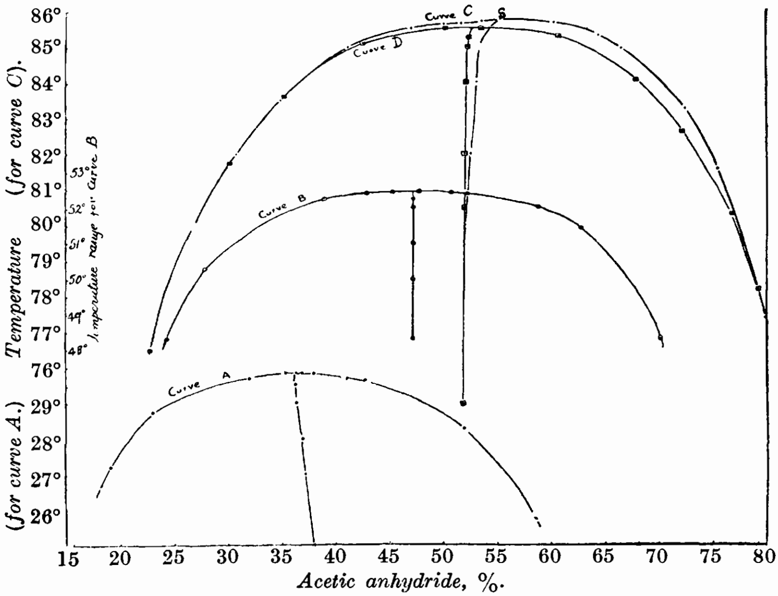
Table II contains the critical solution data, *i.e.*, the critical solution temperatures and the critical solution concentrations expressed in several ways.

TABLE II.

| | C.S.T. | Critical concentration of acetic anhydride, %. By wt. | By vol. | By mols. |
|---|---|---|---|---|
| Acetic anhydride–carbon disulphide | 29·83° | 36·17 | 39·86 | 29·69 |
| Acetic anhydride–*cyclo*hexane ...... | 52·45 | 47·33 | 39·31 | 40·63 |
| Acetic anhydride–petroleum ......... | 85·50 | 52·11 | 42·76 | 62·47 |

*The Mean-concentration Curve.*—It is well known that if the mean value of the concentrations (as g. per 100 g. of solution) of the two coexisting phases is plotted against the corresponding temperature, in a large number of cases a curve is obtained which differs very slightly, if at all, from a straight line. Certain important qualifications must be made to this statement. Frequently, quite marked irregular deviations from the mean-concentration curve have been observed in the neighbourhood of the C.S.T. It is precisely in this region that the accuracy of the experimental observations of the miscibility temperature is greatest : in all the systems investigated here it was possible to read the miscibility temperature to about 0·02° in this region. On the other hand, at this point the curve is very flat, and considerable changes in the concentration produce very slight miscibility-temperature changes. In other cases, the mean-concentration line is definitely curved only in the immediate neighbourhood of the C.S.T. It will be shown here that this can frequently be ascribed to the presence of an impurity, a third component, in the system. Most marked deviation is observed throughout the mean-concentration curve when the system exhibits a lower C.S.T. It is quite possible that this may be due (at least partly) to impurities produced in the system, *e.g.*, the formation of a hydrate in a system of which water is one component. The curvature of the mean-concentration line in the direction of the more volatile component with increasing temperature may, in some instances, be due to neglect of the correction to the concentration necessitated by the unequal volatility of the components. In many cases quoted in the literature, the temperatures have not been estimated in the critical region to less than 0·1°. It is of interest, therefore, that, if the curves are accurately determined, no irregular deviations can be detected in the immediate neighbourhood of the C.S.T. (see large-scale curves, Fig. 2).

FIG. 2.



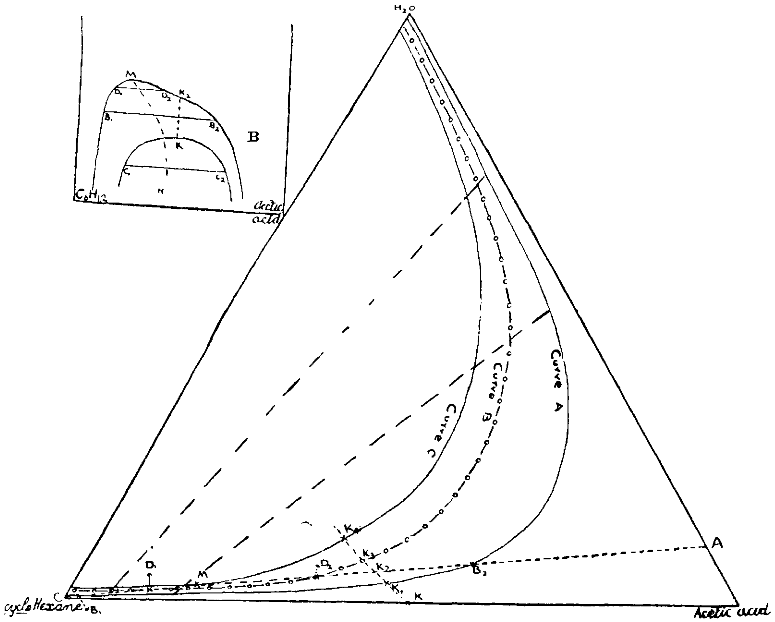
*Curves A, B, and C are enlargements of A, B, and C (Fig. 1). Curve D is based on results obtained after further purification of the petroleum which originally gave curve C.*

Furthermore, by the use of calibrated cylindrical tubes of 2—3 c.c. volume it was found possible to determine the critical concentrations to within about 1% by direct observation of the relative volumes of the phases at about 0·05° below the miscibility temperatures : at the critical solution concentration the volumes of the coexisting phases should be equal. (It is evident, from work now proceeding, that the critical solution concentrations could be determined by this method, using larger liquid volumes, with very considerable accuracy.) We were thus able to compare the values of the critical concentration, as given by the point of intersection of the solubility curve and the mean-concentration curve, with the values obtained by direct volumetric observation. In Table I, the two concentrations in each system which are italicised are those in which a determination of phase volume had shown that the critical solution point was intermediate in concentration between them ; *e.g.*, in the carbon disulphide–acetic acid system the 36·93% mixture gave a lower layer greater than the upper ; in the 35·36% mixture the reverse was the case.

It is clear from these results that in the carbon disulphide–acetic anhydride system, although the curvature of the mean-concentration line was considerable, it intersected the solubility curve in the critical solution concentration point. This affords evidence that the curvature is not due to impurities in the system, as might have been suspected on the grounds that water in the acetic anhydride would undoubtedly have had the effect of curving the mean-concentration line in this same direction. A curvature of this line may then be due to impurities in the system, or it may be inherent in the system. A determination of the critical concentration by alternative methods distinguishes these two cases. If the critical phenomena are distinct and impurity is present in fairly large quantity, the diminution of this alone may serve to indicate whether the maximum point on the curve which is always one terminus of the mean-concentration curve is the C.S.T.

These results may be compared with the methyl alcohol–hexane curve determined by Rothmund (*Z. physikal. Chem.*, 1898, **26**, 433). Neglecting the points in the immediate neighbourhood of the C.S.T., and drawing a straight line through the mean concentrations at lower temperatures, he obtained values for the critical solution concentrations and the C.S.T. From his results it is clear that if the values in the neighbourhood of the C.S.T. are used and the mean concentrations plotted, the line shows quite definite curvature leading to a maximum temperature on the solubility curve at quite a different concentration from that of the critical solution point. This is undoubtedly due to a trace of water in the methyl alcohol used. His results may be compared with those obtained by one of us in the system acetic acid–*cyclo*-hexane (Jones, *loc. cit.*, p. 1387, Fig. 2) : with only 0·28% of water in the acetic acid, the maximum temperature on the curve is no longer that of the C.S.T., the concentration corresponding to the maximum temperature is approximately 75% *cyclo*hexane, and the critical solution concentration is approximately 50% (curve B, *loc. cit.*). The effect is much more marked when the proportion of water in the acetic acid is 1·2% (curve C, *loc. cit.*). That this is the result to be expected can be seen most clearly from a ternary diagram of the system. On Fig. 3A the curves A, B, and C represent typical isothermal curves that would be obtained in the system acetic acid–water–*cyclo*hexane at three increasing temperatures.

Fig. 3B. Fig. 3A.



Owing to the fact that the acetic acid distributes itself mainly in the aqueous phase, the tie-lines would run somewhat as marked in broken lines for the curve A, and the ternary critical temperature line would be represented by $KK_4$. AC represents the composition of all mixtures of *cyclo*hexane and an aqueous acetic acid, and the points where this line cuts the projection of the binodal curves will be miscibility points of the system. $B_1$ and $B_2$ at one temperature, and $D_1$ and $D_2$ for a higher temperature, represent four of these points, which in Fig. 3B are plotted in a two co-ordinate system. At the temperature of the isothermal curve C, AC becomes tangential at the point M, and this point would be the maximum point as plotted on Fig. 3B. $K_2$ is represented in the same figure as the C.S.T. for the aqueous acetic acid represented by A on Fig. 3A, and this corresponds to the point where the line AC cuts the critical line.

In Fig. 3B, the line MN represents the mean-concentration curve for Curve B, Fig. 3B (*cyclo*hexane–aqueous acetic acid). Only one case can occur in which, in the presence of a third component, the maximum point of the curve plotted in a two co-ordinate system would coincide with the critical point, and that is when the ternary critical solution concentrations are such that the line AC, Fig. 3A, is tangential to the binodal curve at the ternary critical solution point. The difference in concentration of the maximum point M and the critical solution point $K_2$ is dependent largely on the distribution ratio of the third component between the two phases. The volumes of the phases would be equal at a temperature just below $K_2$ for a system of this composition, and quite different at a temperature just below M for a system whose composition is represented by this point. This is clearly seen from Fig. 3A.

In the *cyclo*hexane–acetic anhydride system, the mean concentration curve (in this case, almost a straight line) cuts the solubility curve in a point which is in agreement with the critical solution point obtained by direct volumetric observation.

In the petroleum–acetic anhydride system the curve (mean concentration curve, corresponding to Curve C, Fig. 2) again showed marked deviation from linearity, but in the opposite direction to that in the case of carbon disulphide–acetic anhydride. When the phase volumes at the concentration represented by the point of intersection of the solubility curve (point S, Fig. 2) were compared, a large excess of anhydride was found, *i.e.*, the volume of the lower layer was much greater than that of the upper layer, at a temperature very close to the miscibility temperature. Observations of volume indicated that the critical concentration was on the linear extension of the lower points of the mean-concentration line. From the direction of deviation of the line it seemed probable that the impurity present would be a higher fraction. The petroleum was treated again with the nitrating mixture and carefully refractionated, as described above, and the solubility determinations were repeated. The solubility curve obtained is represented as Curve D, Fig. 2. As is seen, the curvature in the mean-concentration line was reduced considerably, thus affording evidence that an impurity of this type was present in the original fraction.

In view of these results, it can be concluded that, in the systems examined here, in two cases the mean-concentration line is straight, within the limits of experimental error, right up to within 0·02° of the C.S.T., and in the other case the line has a definite curvature which is not due to impurities. It would seem that the arguments used in this section would apply if the impurities were produced in the system by, for instance, chemical combination between the components, or by polymerisation of one or other of the components; and in this way it could be determined whether the marked curvature of the mean-concentration line in the case of, *e.g.*, nicotine and water near its lower C.S.T. was due to the presence of the hydrate as impurity.

Table III contains the figures from which the mean-concentration curves were plotted.

TABLE III.

| Temp. | $C_1$. | $C_2$. | Mean. |
|---|---|---|---|
| Carbon disulphide–acetic anhydride. | | | |
| 0° | 5·00 | 80·00 | 42·50 |
| 10 | 7·20 | 74·67 | 40·94 |
| 20 | 11·87 | 66·43 | 39·15 |
| 25 | 16·20 | 59·60 | 37·90 |
| 27 | 18·70 | 55·70 | 37·20 |
| 28 | 20·87 | 53·00 | 36·94 |
| 29 | 24·33 | 48·37 | 36·35 |
| 29·5 | 28·40 | 44·20 | 36·30 |
| 29·84 | 36·17 | 36·17 | 36·17† |
| *cyclo*Hexane–acetic anhydride. | | | |
| 0° | 5·00 | 91·0 | 48·00* |
| 10 | 6·00 | 90·0 | 48·00 |
| 20 | 7·23 | 87·67 | 47·45 |
| 30 | 9·37 | 84·27 | 46·82 |
| 40 | 14·40 | 78·87 | 46·69 |
| 45 | 18·67 | 74·57 | 46·67 |
| 48·3 | 24·32 | 70·16 | 47·24 |
| 50 | 27·17 | 67·08 | 47·13 |
| 51 | 30·58 | 64·17 | 47·37 |
| 52 | 35·90 | 58·83 | 47·36 |
| 52·25 | 39·03 | 55·66 | 47·34 |
| 52·45 | 47·33 | 47·33 | 47·33† |

| Temp. | $C_1$. | $C_2$. | Mean. |
|---|---|---|---|
| Petroleum–acetic anhydride. (Curve D, Fig. 2.) | | | |
| 0° | 5·00 | 97·26 | 51·13 |
| 10 | 5·60 | 96·9 | 51·25 |
| 20 | 6·43 | 96·60 | 51·51 |
| 30 | 7·69 | 95·37 | 51·53 |
| 40 | 9·17 | 94·10 | 51·63 |
| 50 | 11·00 | 92·32 | 51·66 |
| 60 | 13·50 | 89·90 | 51·70 |
| 70 | 18·00 | 85·60 | 51·80 |
| 75 | 22·00 | 82·00 | 52·00 |
| 80 | 26·90 | 77·17 | 52·03 |
| 82 | 30·85 | 73·34 | 52·09 |
| 84 | 36·70 | 67·83 | 52·26 |
| 85 | 41·75 | 63·08 | 52·41 |
| 85·25 | 44·30 | 60·70 | 52·50 |
| 85·50 | 52·11 | 52·11 | 52·11† |
| Petroleum–acetic anhydride. (Curve C, Fig. 2.) | | | |
| 80° | 26·90 | 77·33 | 52·12 |
| 82 | 30·66 | 74·66 | 52·66 |
| 84 | 36·50 | 70·01 | 53·25 |
| 85 | 41·20 | 65·80 | 53·50 |
| 85·5 | 46·66 | 61·66 | 54·16 |
| 85·75 | 56·00 | 56·00 | 56·00‡ |

* Extrapolated.

† Extrapolated values read from intersection of solubility curve and mean-concentration curve.

‡ Maximum temperature: concentrations are not critical.

## *The Law of Corresponding States.*

In view of the facts that we are dealing with the solubility curves of acetic anhydride in a series of closely related non-polar solvents, and that acetic anhydride is, as far as can be seen, a non-associated substance (see next section), it seemed desirable to investigate whether at corresponding C.S.T.'s the saturation concentrations were also corresponding. Rothmund (*loc. cit.*) investigated this question for a series of 12 different liquid mixtures, all of which contained an associated compound, and concluded that the law of corresponding states was not valid.

In Table IV are the results of the calculation of the reduced concentrations at various reduced temperatures extending over the whole solubility curve up to within 0·1° of the C.S.T.

TABLE IV.

| 1. Reduced temp. | 2. System. | 3. Temp. | 4. $C_1$. | 5. $C_1/C_k$. | 6. $C_1$ (calc.). | 7. $C'_1/C'_k$. | 8. $C_1$ (calc.). | 9. $C_2$. | 10. $C_2/C_k$. | 11. $C_2$ (calc.). | 12. $C'_2/C'_k$. | 13. $C_2$ (calc.). |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0·9995 | I | 29·68° | 31·58 | 0·8732 | 31·19 | 0·8149 | 29·93 | 42·00 | 1·161 | 41·88 | 1·278 | 43·96 |
| | II | 52·28 | 39·75 | 0·8399 | 40·80 | 0·7341 | 41·80 | 55·17 | 1·166 | 54·80 | 1·369 | 53·89 |
| | III | 85·32 | 45·50 | 0·8732 | 44·92 | 0·7672 | 45·79 | 59·84 | 1·148 | 60·34 | 1·368 | 58·47 |
| 0·999 | I | 29·53 | 28·67 | 0·7929 | 29·14 | 0·7098 | 28·03 | 44·00 | 1·217 | 43·71 | 1·387 | 46·68 |
| | II | 52·13 | 37·83 | 0·7993 | 38·13 | 0·6772 | 38·74 | 57·75 | 1·220 | 57·20 | 1·522 | 55·84 |
| | III | 85·14 | 43·00 | 0·8252 | 41·99 | 0·6933 | 43·01 | 62·08 | 1·191 | 62·98 | 1·505 | 60·69 |
| 0·998 | I | 29·22 | 26·00 | 0·7190 | 26·91 | 0·6201 | 25·72 | 46·75 | 1·293 | 45·79 | 1·550 | 49·09 |
| | II | 51·80 | 35·00 | 0·7396 | 35·22 | 0·5994 | 35·82 | 60·30 | 1·275 | 59·93 | 1·690 | 58·04 |
| | III | 84·78 | 40·30 | 0·7734 | 38·77 | 0·6203 | 39·85 | 64·09 | 1·230 | 65·98 | 1·641 | 63·58 |
| 0·995 | I | 28·32 | 21·72 | 0·6006 | 23·07 | 0·4898 | 21·74 | 51·83 | 1·433 | 49·69 | 1·900 | 54·40 |
| | II | 50·82 | 29·75 | 0·6287 | 30·18 | 0·4714 | 30·94 | 64·75 | 1·368 | 65·03 | 2·045 | 63·13 |
| | III | 83·7 | 35·67 | 0·6844 | 33·24 | 0·5096 | 34·32 | 68·87 | 1·322 | 71·60 | 2·033 | 67·53 |
| 0·99 | I | 26·80 | 18·40 | 0·5087 | 19·75 | 0·3979 | 18·30 | 56·20 | 1·553 | 57·12 | 2·264 | 60·25 |
| | II | 49·19 | 25·67 | 0·5424 | 25·82 | 0·3843 | 26·43 | 68·70 | 1·452 | 69·71 | 2·443 | 68·14 |
| | III | 81·91 | 30·58 | 0·5868 | 28·43 | 0·4048 | 29·90 | 73·60 | 1·413 | 76·75 | 2·563 | 69·62 |
| 0·98 | I | 23·77 | 14·90 | 0·4120 | 15·94 | 0·3090 | 14·46 | 61·5 | 1·700 | 56·94 | 2·820 | 68·28 |
| | II | 45·94 | 20·57 | 0·4347 | 20·85 | 0·2882 | 21·40 | 73·67 | 1·557 | 75·30 | 3·114 | 74·05 |
| | III | 78·33 | 24·77 | 0·4753 | 22·96 | 0·3025 | 24·55 | 79·00 | 1·517 | 82·91 | 3·457 | 71·52 |
| 0·97 | I | 20·75 | 12·33 | 0·3409 | 13·24 | 0·2482 | 11·82 | 65·40 | 1·808 | 60·37 | 3·336 | 73·47 |
| | II | 42·69 | 16·57 | 0·3501 | 17·32 | 0·2184 | 18·06 | 76·73 | 1·621 | 79·00 | 3·670 | 78·34 |
| | III | 74·75 | 21·20 | 0·4068 | 19·07 | 0·2473 | 20·41 | 82·15 | 1·577 | 86·98 | 4·236 | 72·70 |
| 0·95 | I | 14·69 | 8·90 | 0·2461 | 9·88 | 0·1725 | 8·74 | 71·40 | 1·974 | 64·60 | 4·405 | 82·81 |
| | II | 36·18 | 12·00 | 0·2536 | 12·93 | 0·1518 | 13·39 | 81·27 | 1·718 | 84·33 | 4·831 | 85·98 |
| | III | 67·58 | 16·67 | 0·3199 | 14·24 | 0·1838 | 15·36 | 86·90 | 1·667 | 92·87 | 6·095 | 72·85 |
| 0·92 | I | 5·60 | 6·17 | 0·1706 | 7·09 | 0·1161 | 6·29 | 77·17 | 2·134 | 68·59 | 5·967 | 94·02 |
| | II | 26·41 | 8·33 | 0·1760 | 9·28 | 0·1011 | 9·60 | 85·67 | 1·810 | 89·74 | 6·655 | 93·56 |
| | III | 56·82 | 12·60 | 0·2418 | 10·22 | 0·1325 | 11·09 | 90·93 | 1·745 | 98·80 | 9·181 | 71·96 |
| 0·90 | I | −0·45 | 5·04 | 0·1393 | 6·03 | 0·0937 | 5·24 | 80·17 | 2·217 | 70·52 | 7·134 | 99·21 |
| | II | 19·90 | 7·17 | 0·1515 | 7·89 | 0·0860 | 8·12 | 87·73 | 1·854 | 92·24 | 7·957 | 97·30 |
| | III | 49·65 | 10·92 | 0·2095 | 8·69 | 0·1127 | 9·45 | 92·53 | 1·775 | 101·60 | 11·39 | 71·75 |

System I: Acetic anhydride–carbon disulphide.
„ II: „ „ –*cyclo*hexane.
„ III: „ „ –petroleum.

From the experimental results, by the synthetic method, the values of the saturation concentrations, $C_1$ and $C_2$, are obtained in g. per 100 g. of solution. $C_k$ represents the critical solution concentration expressed in the same way. Cols. 5 and 10 give the values of the reduced concentrations $C_1/C_k$ and $C_2/C_k$ thus expressed. Cols. 6 and 11 contain the values of $C_1$ and $C_2$ calculated by multiplying the average reduced concentration for each reduced temperature by $C_k$. For the $C_1$ values there is an average deviation of 1·12%. For the $C_2$ values, the deviation, although small at the higher reduced temperatures, becomes very large at the lower temperatures.

It is possible that concentrations would be more correctly expressed as g. per 100 c.c. of solution. It can be shown (Rothmund, *loc. cit.*) that if they were so expressed, and if the law of corresponding states held, then the expression $C_1(100 - C_k)/C_k(100 - C_1)$

should be constant. It is obvious from the form of this expression that this is really the reduced concentration if the actual concentration is expressed as g. of one component per 100 g. of the second component, usually considered as solvent. The reduced concentrations calculated in this way are given in cols. 7 and 12 under the headings $C'_1/C'_k$ and $C'_2/C'_k$ (acetic anhydride being considered as solute). Cols. 8 and 13 give the values of $C_1$ and $C_2$ calculated from the average reduced concentrations expressed in this way. The deviations for $C_1$ are smaller than before, and those for $C_2$ again show very large variations at lower reduced temperatures.

The fair constancy of the $C'_1/C'_k$ values, and the possibility of the calculation of the $C_1$ value, seemed worthy of fuller consideration. For reduced temperatures of 0·998 to 0·9995, in the neighbourhood of the C.S.T.'s, the deviations are within the experimental error of the method used. For 0·98—0·998, the deviations are less, but it is in this region of the curves that the accuracy should be greatest, and the deviation cannot be ascribed to experimental error. For 0·90—0·98, the deviation tends to increase; this covers a region of the curves in which there is difficulty in observing the exact miscibility temperature, but the deviations are much greater than could be accounted for on these grounds.

The calculated values of $C_1$ are shown in Fig. 1, and are in general agreement with experimental values. The results indicate that the law of corresponding states holds with a fair degree of accuracy up to certain concentrations of acetic anhydride, *viz.*, 46·75%, 60·30%, and 64·09% in carbon disulphide, *cyclo*hexane, and petroleum, respectively. This agreement is rendered more striking when it is considered that the C.S.T.'s concerned varied from 29·83° to 85·50°, and the critical solution concentrations from 36·17% to 52·11% of acetic anhydride.

In spite of the deviations between found and calculated values of $C_2$, it is clear that, in general, the mean-concentration curve can be regarded as approximately linear, for even in the case of carbon disulphide–acetic anhydride the maximum error involved is only about 1%. If, therefore, in addition to the critical solution data, the solubility at one other temperature is determined, so as to give one other point on the mean-concentration line, the rest of the solubility curve can be calculated. This has been done, and the calculated values of $C_2$ are in Table V (col. 4), and represented in Fig. 1. The deviations (col. 5) are of the same order of magnitude as those found in the calculation of $C_1$, the average for the three systems being 0·89%.

In this way the whole solubility curves can be calculated with

TABLE V.

| Temp. | $C_1 + C_2$ (calc.). | $C_1$ (calc.). | $C_2$ (calc.). | Deviation. |
|---|---|---|---|---|
| | | Carbon disulphide–acetic anhydride. | | |
| −0·45° | 85·21% | 5·24% | 79·97% | +0·20% |
| 5·60 | 82·64 | 6·29 | 76·35 | −0·82 |
| 14·69 | 78·77 | 8·74 | 70·03 | −1·37 |
| 20·75 | 76·20 | 11·82 | 64·38 | −1·02 |
| 23·77 | 74·92 | 14·46 | 60·46 | −1·04 |
| 26·80 | 73·63 | 18·30 | 55·33 | −0·87 |
| 28·32 | 72·98 | 21·74 | 51·24 | −0·59 |
| 29·22 | 72·60 | 25·72 | 46·88 | +0·13 |
| 29·53 | 72·46 | 28·03 | 44·43 | +0·43 |
| 29·68 | 72·41 | 29·93 | 42·48 | +0·48 |
| | | *cyclo*Hexane–acetic anhydride. | | |
| 19·90 | 94·90 | 8·12 | 86·78 | −0·95 |
| 26·41 | 94·85 | 9·60 | 85·25 | −0·42 |
| 36·18 | 94·78 | 13·39 | 81·39 | +0·12 |
| 42·69 | 94·73 | 18·06 | 76·67 | −0·06 |
| 45·94 | 94·70 | 21·40 | 73·30 | −0·37 |
| 49·19 | 94·68 | 26·43 | 68·25 | −0·45 |
| 50·82 | 94·67 | 30·94 | 63·73 | −1·02 |
| 51·80 | 94·66 | 35·82 | 58·84 | −1·46 |
| 52·13 | 94·66 | 38·74 | 55·92 | −1·83 |
| 52·28 | 94·66 | 41·80 | 52·86 | −2·31 |
| | | Petroleum–acetic anhydride. | | |
| 49·65 | 103·46 | 9·45 | 94·01 | +1·48 |
| 56·82 | 103·63 | 11·09 | 92·53 | +1·60 |
| 67·58 | 103·84 | 15·36 | 88·48 | +1·58 |
| 74·75 | 104·00 | 20·41 | 83·59 | +1·42 |
| 78·33 | 104·06 | 24·55 | 79·51 | +0·51 |
| 81·91 | 104·14 | 29·90 | 74·24 | +0·64 |
| 83·70 | 104·18 | 34·32 | 69·86 | +0·99 |
| 84·78 | 104·20 | 39·85 | 64·35 | +0·24 |
| 85·14 | 104·22 | 43·01 | 61·21 | −0·87 |
| 85·32 | 104·22 | 45·79 | 58·43 | −1·41 |

Col. 3 contains the values of $C_1$ calculated from the reduced concentrations $C'_1/C'_k$ (Col. 8, Table IV). Col. 2 contains the calculated values of $C_1 + C_2$ assuming a linear mean-concentration line. Col. 4 contains the $C_2$ values calculated as the difference between the foregoing.

very fair precision, as seen from the coincidence of the calculated and observed solubility curves in Fig. 1.

This research is being extended to the determination of the mutual solubility of acetic anhydride with a larger range of non-polar liquids (*e.g.*, a series of the saturated hydrocarbons), and to that of other non-associated polar liquids, such as aniline and nitrobenzene, in these non-polar solvents.

### *The Influence of Acetic Acid on the* C.S.T.

This part of the work was undertaken in the hope that the C.S.T. might be utilised as a means of estimating acetic acid present as an impurity in the anhydride. The procedure was to introduce into the pure anhydride a known amount of acetic acid, and to determine the effect on the C.S.T. After the introduction of the liquids by means of pipettes, graduated to deliver critical proportions, the experimental tubes were sealed off as before and the miscibility temperatures taken.

From the curves obtained it was found that proportions of acetic acid (up to 0·5%), such as might occur in the anhydride as impurity, have very little effect on the C.S.T., and in no case was the lowering greater than 1° for 5% of acid. There was distinct flattening of the upper end of all three curves, making the lowering due to the first 1—2% of acid scarcely detectable, and rendering the method of little value. On the other hand, 1% of anhydride in acetic acid raises its C.S.T. with petroleum by 2°, *i.e.*, 0·1% of anhydride in acetic acid could be detected.

### Table VI.

The effect of acetic acid on the systems acetic anhydride and (1) *cyclo*hexane, (2) carbon disulphide, (3) petroleum.

| (1) | | (2) | | (3) | |
|---|---|---|---|---|---|
| Acid, %. | C.S.T. | Acid, %. | C.S.T. | Acid, %. | C.S.T. |
| — | *52·45° | — | 29·83° | — | 85·50° |
| 2·94 | 51·80 | 5·28 | 28·93 | 24·90 | 81·70 |
| 4·05 | 51·70 | 23·14 | 25·03 | 48·65 | 72·80 |
| 22·37 | 45·70 | 40·66 | 20·53 | 72·87 | 60·45 |
| 50·6 | †33·75 | 59·97 | 14·68 | 100 | 39·2 |
| 50·98 | 34·15 | 73·91 | 10·98 | | |
| 74·6 | 19·95 | 100 | 4·20 | | |
| 87·1 | 12·30 | | | | |
| 100 | 4·30 | | | | |

* This C.S.T. was redetermined after a period of 4½ months, and the variation was found to be less than 0·02°. This proves the absence of any moisture in the original anhydride and its exclusion during filling.

† The acid in this case was that specially purified by Orton's method (see above). The corresponding curve is very slightly lower than that given by the other acid, the temperature difference at this concentration being, however, less than 0·1°.

### *Internal Pressure and Solubility.*

It has been shown, *e.g.*, by Hildebrand ("Solubility," p. 110), that the internal pressure, $K$, may as a first approximation be put proportional to $\gamma/V^{\frac{1}{3}}$. The calculated value of this function for acetic anhydride at 20° is 7·175, which places it a little higher than benzene (6·48) in the internal-pressure series calculated in this manner. Carbon disulphide has the much higher value 8·7 and hexane and *cyclo*hexane the values 3·80 and 5·56, respectively. Acetic acid gives 5·75 for the dimeric and 7·24 for the monomeric molecule. From Vespignani's value (*Gazzetta*, 1903, **33**, i, 77) for the critical constants of acetic anhydride, *viz.*, $t_c = 296°$, $p_c = 46·2$

atms., the value of *a* in van der Waals's equation is calculated to be $3967 \times 10^{-5}$, and $a/V^2$ becomes $441{\cdot}8 \times 10^{-8}$, where $V$ is the molecular volume at 20°. This places the substance just below benzene ($472 \times 10^{-8}$) in the internal-pressure series thus calculated; the values of $a/V^2 \times 10^8$ for hexane and carbon disulphide are 290 and 610, respectively. Both methods of calculation lead to a similar relative position for acetic anhydride in the series.

Although there is a considerable difference in internal pressure between the anhydride and hexane, yet its proximity to benzene does not agree with the solubility of the anhydride in the solvents used in this research; it is very close to *cyclo*hexane in the series, and moreover, carbon disulphide has a considerably greater internal pressure. It should be noted, however, that the internal pressure of acetic anhydride so calculated is not at all what one would expect from the value of its dielectric constant.

## *Summary.*

(1) The mutual liquid-solubility curves for the binary systems composed of acetic anhydride with carbon disulphide, *cyclo*hexane, or a saturated petroleum fraction (decane) have been determined.

(2) The degree of concordance of the solubility values with the theory of corresponding states has been discussed. The systems investigated show good agreement with the theory in the phase rich in the less polar constituent.

(3) The mean-concentration curves for these systems are linear in two cases and slightly curved in one case (carbon disulphide). The possible causes for deviation from linearity are discussed, and the conclusions tested by a direct determination of the critical solution concentration in these systems.

(4) The position of acetic anhydride in the internal-pressure series is considered in relation to the solubility results.

(5) The effect of acetic acid on the critical solution temperatures is evaluated.

One of the authors (H. F. B.) wishes to thank the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of this investigation.

EAST LONDON COLLEGE,
UNIVERSITY OF LONDON.

[*Received, January 23rd*, 1928.]