

CLXIX.—*The Critical Solution Temperature of the System Methyl Alcohol-cycloHexane as a Means of detecting and estimating Water in Methyl Alcohol.*

By DAVID CHARLES JONES and SIMON AMSTELL.

THE sensitiveness to impurities of a critical solution temperature (*C.S.T.*), either binary or ternary, varies considerably with the impurity: in some cases the effects produced are very small, but in others they are so large as to constitute one of the most sensitive of the known criteria of liquid purity (J., 1923, 123, 1374, 1384).

It is now shown that the *C.S.T.* in the system methyl alcohol-cyclohexane is very sensitive indeed to the presence of water in the alcohol. This is of interest because, in many investigations, it is this impurity in the alcohol which it is necessary to detect and estimate from time to time. Moreover, the other common impurities are removable by chemical means and do not reappear in the alcohol. *cycloHexane* was chosen as the second component because it is readily obtained, can be purified easily, and has, in its melting point, a very sensitive criterion of its own purity.

EXPERIMENTAL.

*Preparation of Materials.*—*Methyl alcohol.* This was from two sources, commercial "absolute" and A.R. methyl alcohol (B.D.H.). Large quantities (2000 c.c. approx.) were fractionated through a ten-foot column of the type suggested by Clarke and Rahrs (*J. Ind. Eng. Chem.*, 1923, 15, 349), and the intermediate fractions (1500 c.c. approx.) subjected to the treatment of Bates, Mullaby, and Hartley (J., 1923, 123, 401) to remove acetone, and again fractionated through the column. The result is shown in Table I. Throughout the process of purification the dryness of the alcohol was tested by a miscibility temperature (*M.T.*) with pure *cyclohexane*, 69.15% of the latter being present. For the dry alcohol the value is 45.52°, very close to the *C.S.T.*; 0.01% of water in the alcohol produces a rise of 0.15°. The details of the determination of the miscibility temperature are described later.

TABLE I.

Fraction.	Vol., c.c.	<i>M.T.</i>	Water content, % calc. ( $\pm 0.01\%$ ).	Alcohol content, %.
Original	2400	—	42 (app.)	58 (app.)
First	750	47.42°	0.12	99.88
Second	300	49.90	0.29	99.71
Third	200	52.28	0.48	99.52

These results show very clearly the efficiency of the ten-foot column. A 90% yield of the alcohol, containing less than 0.5% of

water, is obtained after one distillation from a solution originally containing 58% of alcohol. The acetone in the fractions was estimated as 0.002% by the method suggested by Bates, Mullaby, and Hartley (*loc. cit.*). The mercuric cyanide test for acetone (Hartley and Raikes, J., 1925, **127**, 524) and Mayer's test for pyridine gave negative results.

In order to dry the alcohol, Fractions 2 and 3 (above) were mixed and treated with aluminium amalgam, following the procedure of Hartley and Raikes (*loc. cit.*). The alcohol was distilled off in an apparatus where every care was taken to exclude moisture, and the two middle fractions were collected. The miscibility temperatures of these were determined and the results are in Table II. Fraction 1, Table I, was fractionally distilled through the ten-foot column, with the results shown in Table III. It would appear that distillation through an efficient column gives a drier alcohol than the use of aluminium amalgam.

TABLE II.

Fraction.	Vol., c.c.	M.T.
Original	500	50.8°
First	200	48.22
Second	200	52.96

TABLE III.

Fraction.	Vol., c.c.	M.T.
Original	750	47.42 <sup>2</sup>
First	40	46.55
Second	500	45.51
Third	100	45.52
Fourth	100	46.65

Fractions 1 and 2, Table II, were mixed, distilled through the column, and examined, with the results shown in Table IV. Again the distillation method is effective.

TABLE IV.

Fraction.	Vol., c.c.	M.T.
Original	400	50.0°
First	30	46.2
Second	100	45.72
Third	250	45.64

TABLE V.

Fraction.	Vol., c.c.	M.T.
Original	620	47.02°
First	20	46.85
Second	200	45.52
Third	50	45.56
Fourth	200	45.60

It has been shown by several workers (*e.g.*, Noyes, *J. Amer. Chem. Soc.*, 1923, **43**, 857) that freshly burnt lime removes water very effectively from alcohol, although it is a wasteful process. A fairly dry specimen of our alcohol, that had been freed from other impurities, was treated with lime. The alcohol was siphoned off from the lime and distilled through the column. The miscibility temperature results are in Table V. It will be noticed that 73% of the total distillate gives a miscibility temperature of approximately 45.5°. This was the value given by the one distillation alone through the column (see Table III, Fractions 2 and 3) and for 80% of the original material. Certainly, therefore, distillation alone produces quite as

dry a product as the lime treatment followed by distillation, and the large loss of alcohol is avoided. In view of the known efficacy of the lime treatment, the result indicated that acetone-free, dry methyl alcohol gave a miscibility temperature with *cyclohexane*, when the concentration of the latter was 69.15% by weight, of 45.52°.

A number of fractions of almost dry alcohol were mixed and twice redistilled through the column, every possible precaution being used to avoid the incursion of moisture. Table VI shows the miscibility temperature corresponding to the fractions collected in the second distillation. The results show that the alcohol is almost entirely water-free. The main fractions were siphoned over into a storage flask and used in the subsequent miscibility work. From time to time, redeterminations of the miscibility temperature were made to ensure that no moisture had entered the alcohol. The b. p. was 64.70°/760 mm., as determined in the apparatus described by Jones and Betts (J., 1928, 1177).

TABLE VI.

Fraction	Original	1	2	3	4	5	6
Vol., c.c.	2000	80	400	500	500	400	80
M.T.	45.62°	45.56°	45.53°	45.52°	45.53°	45.54°	45.66°

*cycloHexane*. This was from three sources: (a) *cyclohexane* "pur," Poulenc Frères, (b) *cyclohexane* "pure," Hopkin and Williams, and (c) synthetic material obtained by the catalytic method. The first two specimens had m. p. 2.6° and 1.0° respectively. Sabatier and Senderens give m. p. 6.5° for the pure material, whilst we have observed 6.48° both from the two purified commercial samples, and from the synthetic material obtained by us. Fractional freezing did not raise this m. p.

The *cyclohexane* melting at 2.6° was subjected to the usual process of purification by fuming sulphuric acid, but after two repetitions of the process the m. p. of the product still remained low, 4.2°. Moreover, there was considerable loss of material. The *cyclohexane* failed to decolorise potassium permanganate, and the impurity could not be removed by nitration. Fortunately, although distillation through a 12-bulb pear still-head produced no improvement, distillation through the ten-foot column, previously mentioned, gave good results, as the following record shows, 50% of the material being obtained pure in one distillation:

Fraction.	Vol., c.c.	M. p.	Fraction.	Vol., c.c.	M. p.
Original	430	2.6°	Fifth	40	5.8°
First	20	— 5.0	Sixth	50	6.1
Second	20	3.2	Seventh	30	6.3
Third	20	4.4	Eighth	200	6.48
Fourth	30	5.0	Residue	10	— 6.0

A similar difficulty was experienced with the second commercial sample (m. p.  $1^{\circ}$ ). Very slight purification resulted on continued sulphonation, but on distillation through the column, 50% of the original quantity was obtained with m. p. above  $6.0^{\circ}$ , and there was no difficulty in getting a pure specimen from this.

*Acetone.* A.R. Acetone (B.D.H.) was purified as described by Reilly and Ralph (*Sci. Proc. Roy. Dublin Soc.*, 1919, **15**, 597), and distilled twice through a twelve-pear column. It had b. p.  $56.35^{\circ}/760$  mm.

*Benzene.* Kahlbaum's benzene (for analysis) was fractionally crystallised several times, and a fraction of m. p.  $5.45^{\circ}$  was used throughout the work.

*Determination of the Solubility Curves.*—The synthetic method of determining the solubility curves has been described by Jones and Betts (*J.*, 1928, 1177). Owing to the hygroscopic nature of the alcohol, simple but quite effective precautions were taken to avoid contact with atmospheric moisture. The containers of the alcohol and *cyclohexane* were fixed in desiccators containing phosphoric oxide. The lid of each desiccator had a ground-in vacuum stopper to which was firmly attached the stopper of the container, so that the two vessels were opened simultaneously. Small pipettes, themselves carefully protected against moisture, could be inserted into the liquid which yet remained in contact with the dry atmosphere. The lower stopper was of cork covered with tinfoil. The liquid was transferred to the experimental tubes, which were made of Pyrex glass and had been thoroughly dried by heating in the blowpipe and then kept in a desiccator. The filling of the tubes was effected inside a small box, 12" long,  $5\frac{1}{2}$ " wide, and  $5\frac{1}{2}$ " deep, with a glass front and back, and containing a vessel filled with calcium chloride. In the top of the box was a small hole which allowed a pipette to be inserted, and directly below this was a larger hole fitted with a cork, in which the weighed experimental tubes could be placed. Air, dried by calcium chloride and phosphoric oxide, was blown through the box during the filling. The *cyclohexane* was first run into the tube, the tube reweighed, reinserted in the cork, and the alcohol run in, forming the bottom layer. The tube was quickly taken out, sealed off, allowed to cool, and reweighed. That this simple procedure was sufficient to prevent any incursion of moisture was proved by the constancy of the miscibility temperature of dry methyl alcohol throughout several months. In the case of the systems methyl alcohol-acetone-*cyclohexane* and methyl alcohol-benzene-*cyclohexane*, solutions were made up in double stoppered bottles, the fillings being carried out as described above.

The thermometers used had been standardised recently at the N.P.L.

*Solubility Curve: Methyl Alcohol-cycloHexane.*—The miscibility temperatures,  $t^\circ$ , corresponding to various proportions (% by weight) are given in Table VII, and shown graphically in Fig. 1, Curve F. The critical phenomena are exceedingly clear, persistent emulsions are formed on shaking, and the intense blue colour

FIG. 1.

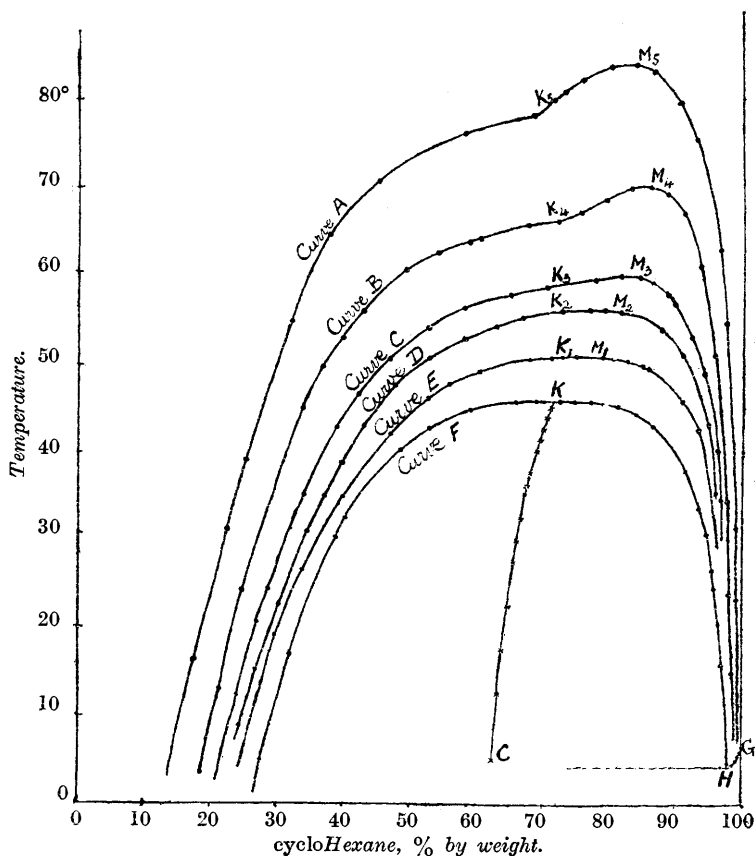


TABLE VII.

$C_6H_{12}$ , %.	$t$ .	$C_6H_{12}$ , %.	$t$ .	$C_6H_{12}$ , %.	$t$ .	$C_6H_{12}$ , %.	$t$ .
32.23	17.1°	66.18	45.45°	72.81	†45.58°	86.93	42.80°
39.40	30.4	69.15	45.52	77.60	45.53	91.47	37.5
48.96	40.05	69.86	45.56	79.26	45.45	93.40	32.3
53.60	42.68	70.80	*45.58	80.64	45.32	95.50	30.6
59.49	44.62	72.00	†45.60	81.25	45.10	97.30	6.1

\* Lower layer greater.

† Critical solution point; volumes of layers equal.

‡ Upper layer greater.

observable when the solution is examined in reflected light persists for several degrees above the *C.S.T.*

*The Effect of Water on the Solubility Curve.*—Solutions of methyl alcohol-water were made up in the dry box, and the determinations were carried out as usual. The results are in Table VIII and are shown graphically in Fig. 1, Curves E, D, C, B, A. The critical phenomena were slightly diminished in the presence of a trace of water, but with larger amounts they were more intense in the region of the ternary critical point; this was not the maximum point on these curves. Significant points are annotated as follows:

- |                          |                         |
|--------------------------|-------------------------|
| 1 = Lower layer greater. | 3 = Upper layer greater |
| 2 = Volumes equal.       | 4 = Maximum point.      |

TABLE VIII.

C <sub>6</sub> H <sub>12</sub> , %.	<i>t.</i>	C <sub>6</sub> H <sub>12</sub> , %.	<i>t.</i>	C <sub>6</sub> H <sub>12</sub> , %.	<i>t.</i>	C <sub>6</sub> H <sub>12</sub> , %.	<i>t.</i>
0.331% Water in the alcohol.							
29.00	17.50°	47.16	42.08°	71.11	50.31°	84.90	49.51°
30.05	19.30	51.98	45.30	73.11	50.52	85.49	49.20
31.57	21.80	52.83	46.10	75.09	50.53(4)	90.80	45.35
34.10	26.75	55.84	47.78	78.90	50.40	93.50	42.09
39.60	34.35	65.70	50.10	80.10	50.35	95.60	36.20
40.10	35.06	66.73	50.26(1)	82.50	49.80		
0.800% Water in the alcohol.							
22.28	3.5°	56.15	51.57°	77.98	55.58°	92.07	49.55°
30.45	22.95	62.84	54.11(1)	85.90	54.64	95.49	42.8
43.82	43.20	71.25	55.64(3)	90.58	50.96	96.00	35.0
44.95	44.45	72.97	55.81(4)	91.79	50.10	97.57	25.5
53.09	50.61						
1.114% Water in the alcohol.							
24.30	12.5°	58.90	56.16°	81.84		59.43° (4)	
27.29	20.8	65.16	57.35 (1)	86.68		58.75	
29.17	24.35	70.76	58.23 (2)	89.82		56.47	
39.50	42.72	74.92	58.75	97.19		36.20	
47.17	50.20	78.04	59.04				
2.031% Water in the alcohol.							
21.83	13.05°	67.66	65.35° (1)	91.41		66.72°	
29.77	34.72	72.30	65.61 (3)	92.09		63.95	
37.78	49.62	79.84	68.24	95.66		50.83	
49.80	60.50	83.55	69.16	97.70		34.0	
59.10	63.38	86.32	69.42 (4)				
3.900% Water in the alcohol.							
17.78	16.5°	45.55	70.50°	72.79	80.30°	93.45	75.03°
22.41	31.30	52.95	73.67	75.80	81.75	93.68	74.39
24.40	36.42	58.35	75.76	80.20	83.15	94.83	73.10
25.52	39.20	65.84	77.65 (1)	83.40	83.16 (4)	94.43	59.25
32.50	54.98	69.18	77.75 (2)	86.25	82.75	99.22	16.6
38.00	64.87	71.14	79.25	89.45	80.60		

The ternary critical solution points,  $K_1$  to  $K_5$ , Fig. 1, and the corresponding maximal points,  $M_1$  to  $M_5$ , show increasing divergence as the concentration of water is increased. It is clear from the

figure that, by choosing a concentration of *cyclohexane* greater than the critical concentration, a greater rise in miscibility temperature would be obtained for a given percentage of water present in the alcohol. But it is necessary to preserve the accuracy of the reading itself, therefore 75% by weight of *cyclohexane* has been chosen as the optimum concentration, and pipettes were calibrated to give these proportions by weight in the system *cyclohexane*–anhydrous methyl alcohol. Our pipettes, which were constructed as described by Orton and Jones (J., 1919, **115**, 1065), had the following volumes at 15°: for *cyclohexane*, 0.7570 c.c.; for anhydrous and aqueous methyl alcohol, 0.2485 c.c. We have confirmed in this work the great accuracy which can be obtained with this kind of pipette. A further improvement was made by grinding the tip, and bending the capillary at right angles about 4 mm. from the end. Table IX gives the miscibility temperatures which are obtained by using the relative volumes of liquids given above. The results when plotted indicate that the method becomes more sensitive as the percentage of water in the alcohol decreases. It is possible to estimate water within  $\pm 0.002\%$  if the miscibility temperature is read to 0.02°, a degree of accuracy which is readily obtainable with a little practice. An estimation within  $\pm 0.01\%$  could be made with ease.

TABLE IX.

Water content of alcohol, % ...	0.0	0.331	0.800	1.114	2.031	3.900
M.T. ....	45.55°	50.52°	55.74°	58.75°	66.50°	81.56°

The pipette volumes could be varied to give a percentage of *cyclohexane* within the limits 73—75% without appreciably affecting either the sensitiveness of the experimental reading or the quantitative figures given in Table IX, so long as the percentage of water in the alcohol was not greater than 1%.

A similar method may be developed in the case of ethyl alcohol, since this forms a *C.S.T.* with *cyclohexane* at (very roughly) — 15°, and preliminary experiments show that traces of water affect the binary *C.S.T.* to a large extent.

*Effect of Benzene and Acetone on the System Methyl Alcohol–cycloHexane.*—Solutions of benzene in *cyclohexane* and of acetone in methyl alcohol were prepared, and used for the determination of the miscibility temperatures.

*Benzene in cyclohexane.* The miscibility results obtained when 10.19% of benzene is present in the *cyclohexane* are in Table X. It was found that the *C.S.T.* was lowered by approximately 12.3°, i.e., 1% of benzene lowers the *C.S.T.* by 1.21°. A noteworthy point was that the critical phenomena which were so marked in the system methyl alcohol–*cyclohexane* were almost entirely absent at

the ternary critical point, but nevertheless the saturation points were very sharp and easily read to 0.02°. At the ternary critical point the percentage by weight of methyl alcohol was less than at the maximum saturation point.

TABLE X.

$C_6H_{12} + C_6H_6$ mixture, % (by wt.)	33.81	38.50	45.99	47.99	58.27	58.84	61.60	64.36
<i>M.T.</i> .....	11.6°	18.05°	26.55°	27.92°	32.96°	33.02°	33.32°	*33.50°

$C_6H_{12} + C_6H_6$ mixture, % (by wt.)	69.25	71.47	76.51	80.37	83.10	86.34	90.45	95.00
<i>M.T.</i> .....	33.35°	†32.85°	32.43°	31.42°	30.87°	29.50°	26.70°	18.1°

\* Critical point—volumes equal.

† Maximum saturation point.

*Acetone in methyl alcohol.* In Table XI are given similar results obtained when 9.18% of acetone is present in the methyl alcohol. The *C.S.T.* was lowered by 6.15°, *i.e.*, 1% of acetone lowers the *C.S.T.* by 0.67°. The mixture at the maximum saturation point contained a greater percentage of *cyclohexane* than that at the ternary critical point. The critical phenomena were more pronounced than in the binary system.

TABLE XI.

$C_6H_{12}$ , % .....	27.50	33.86	42.60	46.74	54.61	62.51	69.62
<i>M.T.</i> .....	7.5°	17.4°	28.75°	33.10°	36.35°	38.45°	*39.45°
$C_6H_{12}$ , % .....	75.79	79.38	82.83	84.15	89.80	94.33	98.60
<i>M.T.</i> .....	†40.15°	40.12°	39.85°	39.42°	37.25°	34.60°	25.0°

\* Critical point—volumes equal.

† Maximum saturation point.

The sensitiveness of the miscibility temperature to such impurities as acetone in the alcohol or benzene in the *cyclohexane* is of advantage when the purpose is to estimate the percentage of water present. Moreover, their effects on the miscibility temperature are but slightly altered by the presence of up to 0.5% of water in the alcohol.

EAST LONDON COLLEGE,  
UNIVERSITY OF LONDON.

[Received, April 23rd, 1930.]