

CIX.—*The Temperature of Critical Solution of a Ternary Mixture as a Criterion of Purity of n-Butyl Alcohol. The Preparation of Pure n-Butyl Alcohol.*

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SINCE the introduction of the fermentation process, *n*-butyl alcohol prepared from starch has become a common industrial product which will certainly find a use in chemical industry and not improbably as a solvent.

We have examined some of its solubility relations with the object of finding in the temperature of critical solution ("c.s.t.") with other media a rapid and certain method of following the course of a fractionation by which butyl alcohol is being purified, or of detecting the presence of impurity in a specimen of butyl alcohol. It was pointed out in a previous paper (this vol., p. 1055), on a similar use of this method for toluene, that different impurities both present together in the liquid under investigation may have an opposite effect on the c.s.t. as on other physical properties. Usually, however, the c.s.t. of a number of fractions

into which the liquid has been divided by distillation will reveal the true condition of the liquid.

The solubility relations with water of the three isomerides of *n*-butyl alcohol have been studied by Alexéev (*Ann. Phys. Chem.*, 1886, [iii], **28**, 305) and Timmermans (*Zeitsch. physikal. Chem.*, 1907, **58**, 129).

tert.-Butyl alcohol is miscible with water at the ordinary temperature, whilst the solubility curve of *isobutyl* alcohol has a c.s.t. at 130° (Alexéev), and *sec.*-butyl alcohol one at 113.7° (Alexéev, Timmermans). Both curves show a maximum of mutual insolubility in the neighbourhood of 50° . The solubility curve of *n*-butyl alcohol has not been followed up to the c.s.t., which will be well above 150° , but it shows a similar maximum of insolubility at about 50° .

As a criterion of purity, the binary c.s.t. with water would not only be at an inconvenient temperature and pressure, but useless for detecting the commonest impurity, namely, water. No other binary mixture seems available, for although ethyl alcohol forms a binary with petroleum, which has found a similar application in Crismer's hands, and methyl alcohol with carbon disulphide, the higher alcohols are completely miscible with these liquids. A ternary mixture was therefore sought.

A 14 per cent. (13.994 grams per 100 grams of solution) solution of hydrochloric acid was chosen, as both very convenient for our purpose and sufficiently sensitive; it gives an upper c.s.t. at 43.55° and a lower at 9.6° with *n*-butyl alcohol.

n-Butyl alcohol is completely miscible with concentrated hydrochloric acid (20 per cent.) at the ordinary temperature (Lieben and Rossi, *Annalen*, 1871, **158**, 137). The presence of hydrochloric acid causes a contraction of the solubility ring of the system butyl alcohol-water, in the same way as does ethyl alcohol that of the system methyl ethyl ketone-water (Bruni, *Atti R. Accad. Lincei*, 1899, [v], **8**, 141).

Fig. 1 represents the change in the system *n*-butyl alcohol-water when hydrogen chloride is introduced. The solubility ring, *KK'*, of water and butyl alcohol has, as yet, been followed over only a small section of the lateral portions; the intervention of the solid-liquid curve, *sl*, prevents the realisation of the lower c.s.t. *K'*. When hydrogen chloride is present, the ring contracts; *L'*, the lower c.s.t., appears above the ice line, and *L*, the upper, is now at a lower temperature. As the concentration of the hydrogen chloride increases, the ring further contracts until, finally, miscibility is complete.

Aqueous sulphuric and nitric acids give upper ternary c.s.t.'s, but no lower c.s.t.'s were observed:

Sulphuric acid (24 per cent.) gave a c.s.t. at 8° , nitric acid (35 per cent.) at 5° .

Sulphuric acid (20 per cent.) gave a c.s.t. at 80° , nitric acid (31 per cent.) at 37° .

The method of determining the c.s.t., and the apparatus employed, have been fully described in an earlier paper (*loc. cit.*).

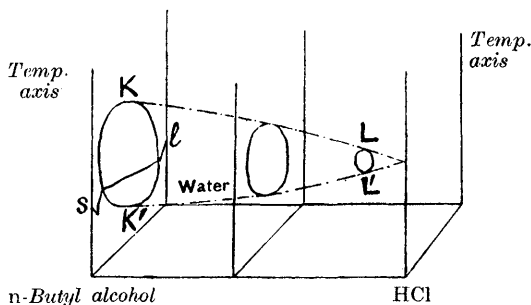
The quantities of the acid solution and butyl alcohol which gave very vividly the critical phenomena are:

Acid solution, 1 c.c.; butyl alcohol, 0.4958 c.c.

Pipettes of the type used for toluene were constructed and carefully calibrated to deliver these quantities with that exactness which we have shown (*loc. cit.*) to be so necessary.

The n-Butyl Alcohol.—In order to prepare a pure *n*-butyl

FIG. 1.



alcohol, several specimens from various sources have been examined. The untreated alcohols gave c.s.t.'s with the standard aqueous hydrochloric acid varying between such wide limits as an upper c.s.t. of 84° and complete miscibility, whereas pure butyl alcohol gives the value 43.55° .

Most of these crude alcohols, after treatment with ordinary chemical reagents—dilute acids to remove bases, sodium hydrogen sulphite to remove aldehydes and ketones, and boiling sodium hydroxide to decompose esters—and subsequent distillation, were found capable of giving a large percentage of material, the various fractions of which, on redistillation, gave the same c.s.t. about 43° . Some of the material, however, which was homogeneous so far as could be tested by distillation, gave c.s.t.'s varying widely from this value; as one example, the c.s.t. was about 50° , and as another about 60° .

As examples of the behaviour of these crude butyl alcohols on distillation, the following may be cited:

(1) A crude specimen (1000 c.c.) had an initial c.s.t. of 44.8° . After drying with potassium carbonate, the c.s.t. was reduced to 37.8° . On distillation through an eight-bulb still-head, the main fraction of 550 c.c., boiling at 116.5° , gave a c.s.t. of 46.8° .

After chemical treatment and redistillation, a considerable quantity of homogeneous material could be obtained from this main fraction (as well as from other specimens which had been similarly treated), the c.s.t. of which was $43-44^{\circ}$.

An alcohol (1000 c.c.) from another source, which was remarkable as being initially completely miscible with the standard hydrochloric acid, on mere distillation through an eight-column Young and Thomas dephlegmator furnished 750 c.c. of a homogeneous material giving a c.s.t. of 43° .

Two other examples may be mentioned of specimens which give after a similar treatment quite different values of the c.s.t.

Table I shows a record of fractionation of a specimen giving an initial c.s.t. of 66.7° .

TABLE I.

Temperature.	Volume of distillate.	Critical point.	Temperature.	Volume of distillate.	Critical point.
116.0°	10 c.c.	63.1°	116.3°	10 c.c.	61.5°
116.2	10 "	61.7	116.4	10 "	61.7
116.3	10 "	59.8	116.4	10 "	62.4
			116.5	10 "	64.6
			Residue.	7 "	above 90

Treatment with chemical reagents left the value of the c.s.t. unaltered.

The fractionation of another specimen, which gave after fractionation a homogeneous material with a c.s.t. of about 50° , is cited below (table II).

One was thus unable, in the absence of a pure synthetic alcohol, to decide definitely whether the homogeneous material, giving a c.s.t. of 43° , contained an impurity impossible to remove by distillation, which lowered the c.s.t., or whether the homogeneous material, giving a much higher c.s.t., contained impurities such as paraffins of similar boiling point, impossible to remove by distillation or chemical treatment, which raised the c.s.t.

It has been no simple matter to find a derivative of *n*-butyl alcohol which would provide a means of obtaining the pure substance. The derivative should preferably be a crystalline solid, into which the alcohol could be readily converted, and from which

as readily recovered without chemical change of the alcohol. The sodium salt of butyl salicylate meets these conditions.

A large quantity of the alcohol, the fractionation of which is shown in the table (table II), was converted into the salicylate;

TABLE II.

Fraction.	Volume.	Critical solution point.
1	40 c.c.	57.0°
2	252 "	50.0
3	415 "	49.3
4	295 "	49.0
5	28 "	50.05

the sodium salt is prepared by dropping the ester into a slight excess of 10 per cent. sodium hydroxide which is being vigorously stirred. The sodium salt crystallises out immediately; it is collected and freed from adherent liquor by pressure. The salt is reconverted into the ester by slowly adding both 10 per cent. hydrochloric acid and the solid salt to a large volume of cooled water which is being stirred. This process is repeated with the recovered ester. The ester is then hydrolysed by aqueous sodium hydroxide, and the butyl alcohol, saturated with water, is dried with potassium carbonate and distilled. Overheating, which would in itself lead to contamination, was avoided by using an oil-bath in this and other distillations. The table shows the values of the c.s.t.'s of the fractions in the final distillation.

TABLE III.

Fraction.	Weight of fraction. Grams.	Critical solution point.
1	10	43.7°
2	27	43.55
3	27	43.55
4	30	43.5
5	20	43.5
Residue	about 5	—

It is seen that the material is now remarkably homogeneous. This *n*-butyl alcohol, which gives an upper c.s.t. at 43.55° and a lower c.s.t. at 9.6° with 13.994 per cent. hydrochloric acid, has D_{15}^{44} 0.81617.

Relation between the Concentration of Hydrochloric Acid and the Ternary Critical Solution Temperatures observed with n-Butyl Alcohol.

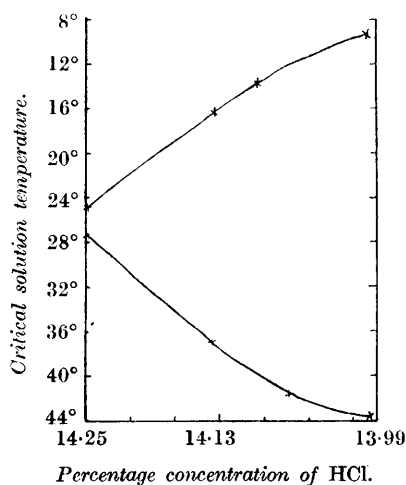
The c.s.t. is extremely sensitive to change in the concentration of the hydrogen chloride. Hydrochloric acid solutions of various

strengths were made up, and a definite volume (1 c.c.) was added to a definite volume of *n*-butyl alcohol (0.4958 c.c.) in the experimental tube. The table shows the experimental values, and Fig. 2 the curves constructed from them.

TABLE IV.

Concentration of acid. (Grams in 100 grams of solution.)	Critical solution points.	
	Upper.	Lower.
13.994	43.55°	9.6°
14.068	41.8	12.1
14.133	36.8	16.3
14.248	27.4	25.0

FIG. 2.



So small a change in the concentration of the hydrochloric acid as 0.254 per cent. alters the upper c.s.t. by 16.15°, and the lower by 15.4°. This great sensitiveness would afford a means of ascertaining whether two solutions of hydrochloric acid within a small range were of accurately identical concentration.

The measurement of the concentration of the hydrochloric acid solution has required exceptional care. As the most accurate process, a determination was chosen based on the measurements of the iodine (by *N*/20-thiosulphate, and starch indicator), set free from a mixture of potassium iodide and iodate, in which the amount of iodate is very accurately known. (Fuller details of the procedure will appear, it is hoped, in another place.) This method has been fully tested, and the accuracy with which

the solution of hydrochloric acid has been measured is represented by the number 14.248 ± 0.001 per cent. This mean error corresponds with a difference of 0.05° in the c.s.t. of the system *n*-butyl alcohol–water–hydrochloric acid. This particular solution of hydrochloric acid was used throughout the experiments on the purification of *n*-butyl alcohol.

Obviously, in preparing an aqueous hydrochloric acid for the purpose of following the purification of *n*-butyl alcohol, the concentration of the hydrochloric acid used need not be known with such accuracy. With the ordinary volumetric solutions, accurately standardised, and by using standard burettes, the concentration of the hydrochloric acid can be ascertained as 14.0 ± 0.02 per cent., and by a gravimetric analysis as 14.0 ± 0.005 per cent. The divergence in the c.s.t. corresponding with this mean error will amount to 1° in the one and to 0.25° in the other.

The Sensitiveness of the Critical Solution Temperature to Impurities.

Water.—Water is one of the components of the system, and its effect as an impurity in the *n*-butyl alcohol is seen from table V to be comparatively slight; 1 per cent. of water raises the upper c.s.t. by 1° . Here, as in all these experiments on the effects of impurities, the concentration of the hydrogen chloride remains constant, the composition of the system only altering in the relative proportions of *n*-butyl alcohol and water. The immensely different effect produced when the concentration of the *n*-butyl alcohol remains constant, while the ratio $\frac{\text{concentration of HCl}}{\text{concentration of H}_2\text{O}}$ is varied, is seen from the results on the relation between the concentration of the hydrochloric acid and the c.s.t., when a change of 0.25 per cent. leads to a fall or rise in the c.s.t. of 16° .

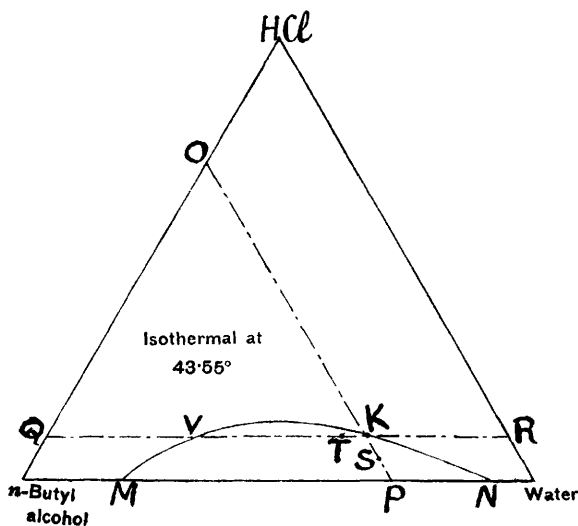
An explanation of this divergence is forthcoming from a consideration of the isothermal diagram at 43.55° .

In Fig. 3, *M* (80 per cent. of butyl alcohol) and *N* (8 per cent. of butyl alcohol) represent, roughly, the composition of a saturated solution of water in *n*-butyl alcohol and of alcohol in water at this temperature. *K* represents the composition of the system at the ternary c.s.t. at 43.55° . (HCl=10.15; *n*-butyl alcohol=27.45; water=62.4 per cent.)

From these results, it appears that the binodal curve has the general form shown—a curve with a very flat top. The line *OKP* represents the composition of the system with constant concentration of *n*-butyl alcohol, and the line *QKR* the composition of

the system with constant concentration of hydrochloric acid. From *K*, movement along *KSP*, that is, decrease in the concentration of the hydrochloric acid, with a corresponding increase in the concentration of water, the concentration of the alcohol being constant, brings the system into the heterogeneous region; by movement along *KTQ*, that is, decrease in the concentration of water, with a corresponding increase in the concentration of the alcohol, the concentration of the hydrochloric acid being constant, the system is brought again into the heterogeneous region, but at

FIG. 3.



no point is it far removed from the binodal curve, which it again cuts at *V*.

Let *KT* represent a 1 per cent. change in the ratio $\frac{n\text{-butyl alcohol}}{\text{water}}$, the concentration of the hydrochloric acid being constant, then *KS*, which equals *KT*, represents a 1 per cent. change in the ratio $\frac{\text{hydrochloric acid}}{\text{water}}$, the concentration of the alcohol being constant. *S* is obviously very much further removed from the binodal surface than *T*. Hence, as a result of the form of the binodal curves, a far larger change of temperature would be required to bring the system at *S* on to a binodal curve than the system at *T* on to a curve.

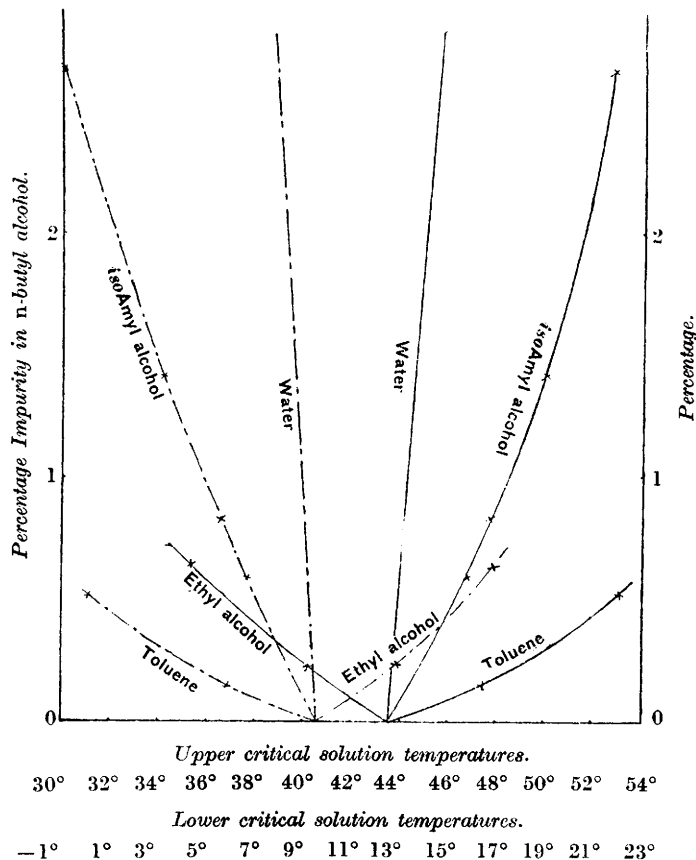
The results obtained with the other substances, namely, toluene,

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ethyl alcohol, and amyl alcohol, which have been tested, appear in table V and Fig. 4.

The c.s.t. is extremely sensitive to the presence of such a substance as toluene, the solubility of which in water so greatly differs from that of *n*-butyl alcohol. One per cent. of toluene in the butyl alcohol raises the upper and depresses the lower c.s.t. by 19°. Paraffin, which is less soluble, has a still greater effect.

FIG. 4.



Discontinuous curves represent the effect of impurity on the lower c.s.t.

Continuous curves represent the effects on the upper c.s.t.

The c.s.t. is thoroughly sensitive to the presence of homologues. One per cent. of ethyl alcohol lowers the upper c.s.t. by 11°, and 1 per cent. of amyl alcohol raises the upper c.s.t. by 5°, correspond-

ing alterations being observed in the lower c.s.t. Rough experiments with *n*-propyl, *isobutyl*, and *sec.*-butyl alcohols show a less, but still an appreciable, effect. One per cent. of *n*-propyl alcohol lowers the c.s.t. by 6.1° , 1 per cent. of *isobutyl* alcohol by 0.7° , and 1 per cent. of *sec.*-butyl alcohol by 1.9° . The relations of the c.s.t.'s of isomerides are being more fully examined.

The values of the c.s.t. in table V were obtained when the quantities of the two constituents delivered respectively by the two pipettes were used, that is, 1 c.c. of the standard hydrochloric acid and 0.4958 c.c. of impure *n*-butyl alcohol. The "percentage" of admixture is by weight in the *n*-butyl alcohol.

TABLE V.

Water present, per cent.	0	2.677	2.796	10.75	4.034
Upper c.s.t.	43.55°	45.7°	46.2°	52.35°	47.95°
Lower c.s.t.	9.6	8.2	7.9	3.0	6.5
Toluene present, per cent.	0	0.1422	0.3157	0.5077	
Upper c.s.t.	43.55°	47.4°	50.1°	53.2°	
Lower c.s.t.	9.6	5.8	3.15	-1.15	
Amyl alcohol present, per cent.	0	0.5910	0.8366	2.666	1.415
Upper c.s.t.	43.55°	46.95°	47.6°	53.8°	50.1°
Lower c.s.t.	9.6	6.75	5.8	-0.9	3.25
Ethyl alcohol present, per cent.	0	0.6288	0.2381		
Upper c.s.t.	43.55°	35.3°	40.1°		
Lower c.s.t.	9.6	16.8	12.8		

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