CXI.—*The Systems* n-*Butyl Alcohol–Water and* n-*Butyl Alcohol–Acetone–Water.*

By David Charles Jones.

Orton and Jones (J., 1919, **115**, 1194) found that a 13·994% hydrochloric acid solution gave with pure *n*-butyl alcohol an upper and a lower ternary critical solution temperature (*C.S.T.*) of 43·55° and 9·6°, respectively, for the concentrations given in that paper. The complete solubility ring so produced contracts on an increase, and expands on a decrease, in the concentration of the hydrochloric acid solution. The ternary *C.S.T.*'s with hydrochloric acid solution were extremely sensitive to typical impurities in the *n*-butyl alcohol, and the data were utilised in following the purification of *n*-butyl alcohol, obtained from various sources; the method thus devised proved to be far more sensitive to most impurities (except water) than those based on any other physical property, and in order to obtain a specimen of the alcohol which was so pure that all its fractions behaved uniformly according to this criterion, it was necessary to prepare a crystalline derivative and subsequently regenerate the alcohol.

The solubilities of isomeric alcohols, such as the butyl alcohols, are of considerable theoretical interest, and it was therefore decided to determine the binary solubility curve with water of *n*-butyl alcohol thus purified, the purity having been confirmed by the use of this sensitive criterion. The ternary system *n*-butyl alcohol–acetone–water was also investigated from −15° to the temperature of the binary *C.S.T.*, *viz.*, 124·74°, and in all cases the ternary *C.S.T.*'s were far more sensitive to impurities than the binary.

The System n-*Butyl Alcohol–Water.*

The *n*-butyl alcohol was prepared as before (Orton and Jones, *loc. cit.*), and dried with calcium oxide before the final fractional distillation through a twelve-bulb pear still-head. The several fractions gave identical *C.S.T.*'s with a hydrochloric acid solution. The values for the density and refractive index of the pure material were $D_{14\cdot4^\circ}^{14\cdot4^\circ}$ 0·81417 and $n_C^{20\cdot0^\circ}$ 1·39711. The water was freshly boiled conductivity water obtained from a Bousfield still. The synthetic method of determining the solubility points was used, and the experimental details were essentially as described by Jones and Betts (J., 1928, 1179). It was found that ordinary soda glass, even if well steamed, could not be used for accurate determinations, for redeterminations just above 120° gave readings as much as 1° higher. This did not occur with well-steamed Pyrex glass, even if readings were repeated during a period of several months, and tubes of this glass were used, since the readings obtained were identical with those in control experiments with quartz-glass tubes in the neighbourhood of the *C.S.T.* The thermometer was tested, during the period when the work was done, at the National Physical Laboratory. The results are given in Table I (where *u* and *l* refer to upper and lower miscibility temperatures obtained with the same concentration of solution) and shown graphically in Fig. 1, Curve 1.

TABLE I.

n-$C_4H_{10}O$, %	6·03[1]	6·47[2]	9·79[3]	12·72[4]	15·15[5]	17·51[4]
Temp.	65·0° *u* 40·0° *l*	81·0° *u* 19·3° *l*	107·72° *u* −3·11° *l*	117·40° *u* −18·01° *l*	120·30°	122·45°
n-$C_4H_{10}O$, %	27·88	28·16[6]	30·39[7]	32·49[8]	32·85[9]	33·79[5]
Temp.	124·74°	124·74°	124·73°	124·74°	124·75°	124·72°
n-$C_4H_{10}O$, %	38·05[6]	41·30[10]	44·03	48·01	57·80	63·44
Temp.	124·66°	124·05°	123·75°	122·60°	115·00°	106·05°
n-$C_4H_{10}O$, %	76·27	79·51[11]	80·46	80·82[11]		
Temp.	58·50°	29·82°	13·0°	−5·0°		

[1] Accuracy ±2°; slightly cloudy between these temperatures.

[2] Accuracy ±2°.

[3] Rising temperature, 107·72°; falling, 107·60°.

[4] Observation accurate to 0·02°; rising and falling temperatures identical within these limits of accuracy. This applies to all the following determinations until the system containing 79·51% of *n*-butyl alcohol is reached.

[5] Repeated after three months.

[6] Slight critical opalescence; striations almost absent.

[7] Lower layer very large.

[8] Equal volumes; clearest critical phenomena.

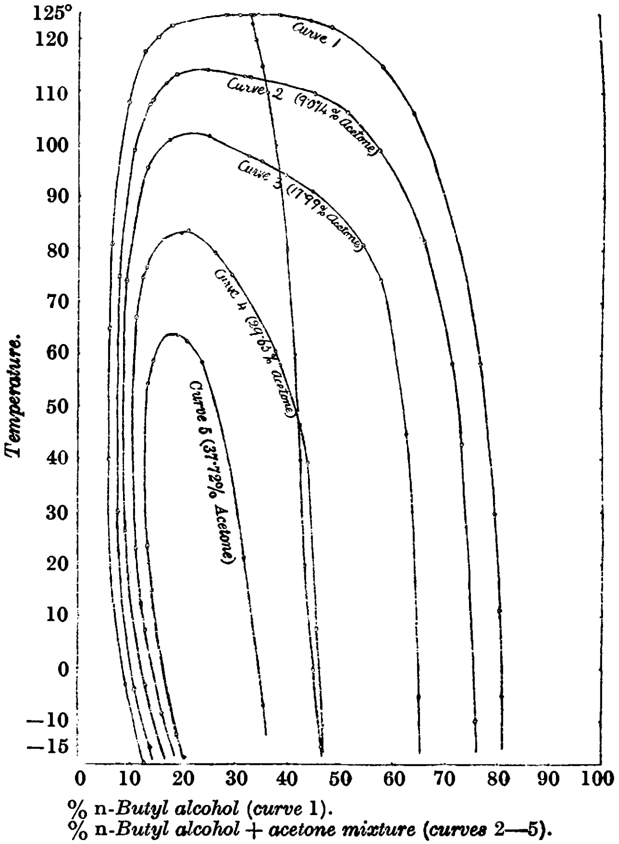
[9] Upper layer greater than lower; quartz experimental tube.

[10] Determinations made at intervals up to eight days; no change observed even after heating to a temperature of 130°.

[11] Accuracy of determination 0·1°; difference of 1° between rising and falling temperatures.

The upper portion of the curve is flat, no change of miscibility temperature exceeding 0·02° being detectable within the concentration limits 28—34% of *n*-butyl alcohol. From the extrapolation of the mean concentration line, the critical solution concentration is 32·4% *n*-butyl alcohol. Several points were determined in the immediate neighbourhood of the *C.S.T.* in cylindrical Pyrex-glass tubes, and an endeavour was made to determine the critical concentration by the direct readings of the volumes of the phases. The 32·49% mixture gave layers of almost equal volume, the 32·85% mixture a greater upper layer, and the 30·39% a much greater lower layer. The 32·4% n-butyl alcohol corresponds to a molar fraction of 0·1044, or 10·44 mols.%.

FIG. 1.



The *C.S.T.* is at 124·75°, which is lower than that given by Hill and Malisoff (*J. Amer. Chem. Soc.*, 1926, **48**, 924), *viz.*, 125·15°. Such a difference would be easily possible if these authors used ordinary glass. Alternatively, although their specimen boiled constantly within 0·1°, it may have contained a trace of impurity, for certain impurities, if they happen to be present in the original sample, can scarcely be removed by even prolonged distillation methods (Orton and Jones, *loc. cit.*); on the other hand, this binary *C.S.T.* is very insensitive to typical impurities. Other sensible deviations from the determinations of Hill and Malisoff occur mainly in the portion of the curve representing the water-rich phase; thus, at 20° the value obtained was 6·5% of n-butyl alcohol, whereas Hill and Malisoff give 7·81%, a value apparently corroborated by the determination of Reilly and Ralph, *viz.*, 7·90% (*Sci. Proc. Roy. Dubl. Soc.*, 1919, **15**, 597). The last two values, however, were both obtained by a volume method, and it is possible that at least a part of the discrepancy may be due to the difficulty of separating the phases accurately—frequently thin emulsions persist for a very long time. That Reilly and Ralph's value is really confirmatory, however, is to be doubted, since they state that the saturated solution of the alcohol in water, as prepared, was slightly cloudy, but on raising the temperature this cloudiness disappeared—owing to the minimum on the solubility curve, the solution should have become *more* cloudy under these conditions.

The solubility curve was followed as far below the freezing-point curve as possible, in order to determine whether a metastable lower *C.S.T.* could be observed, or whether the system was similar to that of methyl ethyl ketone–water (with maxima of mutual insolubility on both arms) or to that of *sec.*-butyl alcohol–water, where some workers have found a waist in the curve (Timmermans, *Z. physikal. Chem.*, 1907, **58**, 129; Dolgolenko, *ibid.*, 1908, **62**, 499). It was possible to follow the solubility curve to approximately — 20°, *i.e.*, 17° below the invariant freezing point of the two-layer system. As is evident from the curve, the solubility in water of the n-butyl alcohol increases very rapidly as the temperature falls, but no maximum of mutual insolubility, such as occurs at approximately 52° with the water-rich phase, occurs on the other arm of the curve, even down to — 20°.

The mean-concentration curve, which from 50° up to the *C.S.T.* is slightly curved, bending as is usual towards the axis representing the more volatile component, shows at about 50° a point of inflexion, and from this point to lower temperatures it moves at an increasing rate towards a greater concentration of n-butyl alcohol. It will be seen that at —15° the mean concentration has already reached a value of 46·5% of alcohol. This is the behaviour that would be expected if the lower terminus of the line were at a hypothetical lower *C.S.T.*

Table II contains the solubility results (read from an enlargement of Fig. 1) from which the points on the mean-concentration line were calculated; S_w and S_a represent respectively the percentages of the alcohol in the water-rich and alcohol-rich phases, and the fourth column gives the mean.

TABLE II.

Temp.	S_w.	S_a.	Mean.	Temp.	S_w.	S_a.	Mean.
124·75°	32·4	32·4	32·4	80°	6·4	72·7	39·6
123	19·0	46·8	32·9	60	6·0	76·2	41·1
120	14·7	52·5	33·6	40	6·0	78·6	42·3
115	11·7	57·8	34·75	20	6·4	80·2	43·3
110	10·2	61·5	35·85	0	9·1	80·6	44·85
100	8·2	66·4	37·3	−15	12·0	81·0	46·5

Discussion.—The butyl alcohols are in the following order with regard to their *C.S.T.*'s with water : *iso*>*n*>*sec.*>*tert.* The same order obtains for the *iso*- and *n*-butyric acids, but it is reversed in the corresponding aldehydes. Below 60°, *iso*butyl alcohol is more soluble than the *n*-alcohol in water, the curves crossing at about this temperature.

The extent of the mutual solubility of two liquids is determined by two factors : (1) the relative intermolecular attractions between the molecules of the same kind, and that between the molecules of different kinds, and (2) any chemical combination between the molecules of different kinds.

It is very probable that the mutual solubility of alcohols and water is due to both these factors; (1) is endothermic, and becomes predominant as the temperature is raised, whilst (2) is exothermic, and predominates at lower temperatures. As a result, there is a maximum of mutual insolubility, such as is observed at 52° in the case of *n*-butyl alcohol and water. The mutual solubility of alcohols in saturated hydrocarbons must be ascribed to (1) alone; in no case of this kind does the solubility increase with fall of temperature.

It is possible that the mutual solubilities of the ethers and water provide an illustration of effect (2) alone. Thus, it is a remarkable fact that, if the first few members of both series be neglected, the ethers have very similar boiling points to the saturated hydrocarbons of approximately the same molecular weight, *e.g.*,

	M.	B. p.		*M.*	B. p.
$CH_3{\cdot}O{\cdot}C_4H_9$ ...	88	70·3°	C_6H_{14}	86	68·9°
$CH_3{\cdot}O{\cdot}C_7H_{15}$ ...	130	149·8	C_9H_{20}	128	149·5
$CH_3{\cdot}O{\cdot}C_8H_{17}$ ...	144	173·0	$C_{10}H_{22}$	142	173·0

(Kauffmann, " Beziehungen zwischen physikalischen Eigenschaften und Chemischer Konstitution," 1920, p. 151.)

The same similarity occurs between the boiling points of the isomeric hexanes and the corresponding methyl butyl ethers (Bennett and Philip, J., 1928, 1930) :

n-Hexane	68·9°	Methyl *n*-butyl ether	70·0°
β-Methylpentane	62·0	Methyl *iso*butyl ether	58·0
γ-Methylpentane	64·0	Methyl *sec.*-butyl ether	59·0
ββ-Dimethylbutane	49·6	Methyl *tert.*-butyl ether	54·0

Thus the introduction of ethereal oxygen into a hydrocarbon apparently does not increase the mutual attraction of the molecules. It is possible, therefore, that apart from factor (2) the ethers would be as insoluble in water as the hydrocarbons. In that case the mutual solubility of the ethers is dependent on the formation of hydrates, their distribution between the ethereal and aqueous phases, and their consequent mutual solvent effects. The ether hydrates should be distributed far more in the aqueous phase, and this would account for the much larger solubilities of the ethers in water than of water in the ethers. Moreover, this hypothesis explains the form of the solubility curves. The reversible heat of solution is positive in all cases in the aqueous phase, and it is quite possible that the variable slope, sometimes positive, sometimes negative, of the ether-rich phase is due to the superposition of the two effects, (i) positive heat of solution due to hydrate formation, and (ii) the negative heat of solution due to mutual solvent action. Bennett and Philip (*loc. cit.*) have made some interesting speculations regarding the solubilities of methyl butyl ethers in water, explaining the extent of this as due to the Harkins–Langmuir effect of the length of the hydrocarbon chain, and to the electron-repelling effects of the positive alkyl groups attached to the oxygen.

Harkins (see, *e.g.*, Harkins and King, *J. Amer. Chem. Soc.*, 1919, **41**, 970) has shown, from surface-energy considerations, that the attraction of hydrocarbon for hydrocarbon is less than that of hydrocarbon for hydroxyl. By similar reasoning, the solubility of *n*-butyl alcohol in water, neglecting hydration, would be mainly determined by (*a*) the very large attraction of the hydroxyl groups of water for those of the alcohols, (*b*) the smaller, but still considerable attraction of the alkyl groups of the alcohol for water, and (*c*) the very large attraction of the water molecules for one another. The length of the hydrocarbon chain attached to the hydroxyl of the alcohol has a large effect on the solubility, owing, mainly, to (*c*), because any solution of alcohol in water means the substitution of a hydrocarbon–water interface for a water–water interface.

As regards factor (2), *i.e.*, the extent of hydrate formation, any definite conclusion is a matter of great difficulty. Bennett and Philip (*loc. cit.*) have put forward the view that, in the case of the methyl butyl ethers, increased electron-repelling effects of the secondary and tertiary radicals (see Allan, Oxford, Robinson, and Smith, J., 1926, 401) increase the tendency of the oxygen of the ethers to donate a lone pair of electrons to the hydrogen of the water, and thus increase the hydration and the solubilities of these ethers in water (see Sidgwick, "The Electronic Theory of Valency," p. 137).

Applying these views to the isomeric butyl alcohols, we can say that, neglecting factor (2), there is sufficient decrease in the hydrocarbon–water interface between *n*- or *iso*-butyl alcohol and *tert.*-butyl alcohol to account for the difference in the solubility in water, *e.g.*, the hydrocarbon–water interface in *tert.*-butyl alcohol is not much greater than that of *n*-propyl alcohol, which is completely miscible with water.

It is very probable that the solubility curves of *iso*- and *sec.*-butyl alcohol have not been obtained with the pure substances (see Timmermans, *loc. cit.*, and Dolgolenko, *loc. cit.*). However, the experimental values available indicate that *iso*butyl alcohol is slightly more soluble in water than *n*-butyl alcohol at ordinary temperatures, but it has a higher *C.S.T.* (*viz.*, 133°), and this can be ascribed quite clearly to the very large difference in solubility of *water* in the alcohols (at 20° its solubility in *n*-butyl alcohol is 20%, and in *iso*butyl alcohol 16%).

The *C.S.T.* of *sec.*-butyl alcohol is 115°, *i.e.*, 9·7° below that of *n*-butyl alcohol, but there are very marked maxima of mutual insolubility on both arms of its curve, so that at ordinary temperatures the *sec.*- has a very much larger solubility than the *n*-compound (at 20° the solubility of the *sec.*-alcohol is 37%). If the results at the lower temperatures are not due to an impurity acting as a mutual solvent, there would appear to be distinct evidence here of a large hydrate formation, which may be evidence of the electron-repelling effect of a secondary alkyl group of a similar character to that to which the high dissociation constant of the secondary amines has been ascribed. The solubility results at the higher temperatures are qualitatively what would be expected from the decreased hydrocarbon–water interface.

It is of interest to examine the available physicochemical evidence for the electron-repelling effect of alkyl groupings similar to those present in the butyl alcohols. The dissociation constants of the isomeric aliphatic acids should afford information; thus, the four C_5 acids have the same alkyl groups as are present in the butyl alcohols, and the dissociation constants (Kauffmann, *loc. cit.*) are *n*-valeric acid 0·00161; methylethylacetic acid 0·00168; *iso*valeric acid 0·00173; trimethylacetic acid 0·000978.

The tertiary radical is acting in an electron-repelling character, but this is not evident in the case of the *iso*- or *sec.*-butyl radical. Butyric and *iso*butyric acids have almost the same values, and in the C_6 acids the same marked fall in the constant occurs when a tertiary alkyl radical is present, *i.e.*, in dimethylethylacetic acid; but in diethylacetic acid, where a secondary radical is present, the dissociation constant (0·00203) is greater than that of *n*-hexoic acid (0·00146). In the case of the amines, on the other hand, the secondary amine is stronger than either the primary or the tertiary (Moore and Winmill, J., 1907, **91**, 1373; 1912, **101**, 1635).

The evidence in other directions is unfortunately ambiguous; for example, since the mechanisms of association and of hydration are similar, both effects involving donation from oxygen to the hydrogen of another alcohol molecule in the one case and to the hydrogen of water in the other, it might be thought that there would be a connexion between the two, in the sense that the more associated alcohol would be hydrated to a greater extent. Biltz (*Z. physikal. Chem.*, 1899, **29**, 249) determined cryoscopically the relative association of these alcohols in dilute benzene solution, and concluded that the relative association is in the order *n*>*sec.*>*tert.* This could not be due to the greater positivity of the vapour-pressure curves of, *e.g.*, the tertiary alcohol, because this alcohol would be much less soluble in non-polar solvents such as benzene.

The boiling points of these isomeric alcohols lead to the same conclusion about the extent of association as the cryoscopic results recorded above. Branching of the carbon chains in the hydrocarbon produces a lowering of the boiling point, but the difference in the boiling points of the butyl alcohols is much greater than would be expected from the branching of the chain alone. [The boiling points are *n*-, 117°; *iso*-, 107·5°; *sec.*-, 99°; *tert.*-, 82·9°. Compare with these the values given for the corresponding hexanes and methyl butyl ethers (p. 804).] The high boiling points of alcohols as compared with hydrocarbons or ethers are probably due to a physical attraction between the hydroxyl groups, and to the association as well. It is difficult to ascribe the high value of the critical pressure and of the van der Waals constant *a* to association alone (Berthoud, *J. Chim. physique*, 1918, **16**, 245). Branching of the hydrocarbon chain in the alcohols tends, therefore, not only to reduce the mutual attraction of the hydrocarbon portions of the molecule for one another, as in the hexanes, but also to produce a greater normalising tendency. However, one cannot be sure that this latter effect is due to a decrease in the donative powers of the oxygen, for the increased negativity of the oxygen might affect adversely the acceptor properties of the hydrogen in another alcohol molecule. This effect would not occur in hydration. Moreover, steric effects may be important in the association.

The dielectric constants of these alcohols are in the order $n(\varepsilon = 19{\cdot}2) > iso > sec. > tert.$ $(\varepsilon = 11{\cdot}4)$. Thus they afford an illustration of a very unusual effect, since, especially with isomerides, the higher solubilities in water usually accompany the larger values of ε. Smyth (*J. Amer. Chem. Soc.*, 1924, **46**, 215) has calculated the dipole moments of these alcohols, and they are in the order *n*, *iso*>*sec.*>*tert.*, but the differences between the values are small. An increased electron-repelling effect due to the secondary or tertiary alkyl groups would tend of itself to *increase* the electric moment, the centre of gravity of the negative charge being displaced nearer to the nucleus of the oxygen atom; but this effect may be outbalanced by an increase in the angle of attachment of the two positive groups, hydrogen and alkyl, with a consequent decrease in the distance between the centres of gravity of the positive and negative charges. It would appear, therefore, that at present any attempt to place the butyl alcohols in their relative order of extent of hydration would be of little value.

Two interesting results which follow from the study of the mutual solubilities of two liquids, of which one is water, may be mentioned here. (1) If the concentration of the components in the coexisting phases are expressed as g.-mols.%, the water has in all cases a much greater solubility in the phase rich in the second component than has the second component in the water-rich phase. (2) If one compares the solubility of water in oxygen-containing compounds which have about the same solubility in the water-rich phase, it is evident that they are clearly divisible into two groups: water is much more soluble in those compounds that contain a hydroxyl group, *e.g.*, alcohols, phenols, and carboxylic acids. Table III summarises some of the results; S_a is the solubility of the second component in water, and S_b that of water in the second component, both as g. per 100 g. of solution; A_2 and B_1 are the corresponding mol. fractions.

TABLE III.

Second component.	Temp.	S_a.	S_b.	A_2.	B_1.	A_2/B_1.	ϕ_A/ϕ_B.
Methyl ethyl ketone	20°	24·00	10·00	0·074	0·306	0·241	0·48
sec.-Butyl alcohol ...	20	20·00	37·00	0·057	0·708	0·081	
*iso*Butyric acid	20	22·8	44·6	0·057	0·798	0·071	1·04
Acetylacetone	30	15·5	5·0	0·031	0·225	0·142	0·70
Ethyl acetate	20	8·53	3·07	0·016	0·152	0·106	0·68
Ethyl ether	20	6·95	1·20	0·022	0·048	0·469	0·41
n-Butyl alcohol	20	6·50	20·00	0·015	0·507	0·030	
Phenol	20	8·3	28·0	0·017	0·670	0·025	
Furfuraldehyde	40	8·2	6·3	0·016	0·265	0·062	
Benzoic acid	70	6·0	17·0	0·009	0·582	0·016	1·21
Salicylic acid	70	8·0	36·0	0·011	0·809	0·014	

The first four materials mentioned in the table have a large solubility in water, but the values given show how much more soluble water is in the compound-rich phase when the compound contains a hydroxyl group. The results for acetylacetone are interesting; the low solubility of water in this compound is clear additional evidence for the absence of the hydroxyl groups owing to the chelate ring structure. The other materials in the table are typical oxygen-containing compounds, having a solubility in water of 6—8%. It is obvious that, in the case of the alcohols, phenols, and acids, water has a very great solubility in the compound-rich phase. The values for salicylic acid and ether ($A_2/B_1 = 0{\cdot}014$ and 0·469, respectively) are especially striking. In all cases, as the fractional value of A_2/B_1 shows, the mol. fraction of the water in the compound-rich phase is greater than that of the compound in the water-rich phase.

In any comparison of the solubilities of a series of liquids with another liquid, such as water, the extent of the solubility will depend considerably on the composition of the phase which is in equilibrium with the water-rich phase. The solubility of one pure liquid in another cannot be determined directly, as can the solubility of a solid in a liquid. Langmuir (*Colloid Symposium Monograph*, 1925, **3**, 62) has applied his theory of " independent surface action " to the case of mutual liquid solubility, and, making use of Boltzmann's equation, has derived the formulæ

$$(1)\ \frac{A_1}{A_2} = e^{\frac{S_A\phi_A}{kT}(\beta_2^2 - \beta_1^2)}; \qquad (2)\ \frac{B_1}{B_2} = e^{\frac{S_B\phi_B}{kT}(\alpha_2^2 - \alpha_1^2)}.$$

The subscripts 1 and 2 refer to the two liquid phases concerned. A and B are the mol. fractions, and α and β the surface fractions of the two liquid components; S_A and S_B are their molecular surfaces; k is Boltzmann's constant, and T the absolute temperature. The symbol ϕ is a function of the partial interfacial surface tensions exerted between the various groups in the molecules of the liquids, and should give the same value in both equations, *i.e.*, if calculated from the distribution of either component in phases 1 and 2. The distribution of A between the two phases will be markedly affected by the relative distribution of B; this is covered by the term $(\beta_2^2 - \beta_1^2)$. The low values of A_2/B_1 are accounted for by the relatively small surface area of the water molecule. In Table III the ratio ϕ_A/ϕ_B is given for a few typical cases. This ratio should be equal to unity, and any deviation may be ascribed to effects such as hydration and association, which are not taken into account in the derivation of the formulæ. It will be noticed that substances which give a high value for A_2/B_1 give a very low value for this ratio, *e.g.*, methyl ethyl ketone and ethyl ether, whereas benzoic acid and *n*-butyl alcohol, and to a less extent *iso*butyric acid, give a value greater than unity. Values less than unity would mean that water has a smaller solubility in the second component-rich phase than it theoretically should, and values greater than unity denote a too great concentration of water in this phase. Possibly these deviations may be due to hydrate formation, and subsequent distribution between the two layers. In the case of ethyl ether this hydrate may be distributed largely in the aqueous phase, whereas in the compound containing a hydroxyl group there would be a much more even distribution between the two phases. The calculations show that even in the case of *n*-butyl alcohol the very great disparity in the solubility of the two components in one another (S_a and S_b) is largely accounted for on this theory by the difference in the molecular surface extents.

The System n-*Butyl Alcohol–Acetone–Water.*

Since the binary solubility curve has only one maximum of mutual insolubility, it was of interest to determine the effect of a third component that would act as a mutual solvent. For this purpose acetone was chosen, and the ternary system was studied in sufficient detail to construct the complete binodal surface, from the binary *C.S.T.* at 124·74° down to −15°.

The acetone used for these determinations was A.R. material (B.D.H.). It was purified as described by Reilly and Ralph (*loc. cit.*), and redistilled several times through a six-foot fractionating column of the type described by Clarke and Rahrs (*J. Ind. Eng. Chem.*, 1923, **15**, 349). It had b. p. 56·3°/760 mm. The method adopted was as follows: Mixtures of *n*-butyl alcohol with various proportions of acetone were made up by weight, and the solubility curve of each of these mixtures with water was determined by the synthetic method; the curves thus obtained are shown in Fig. 1 (curves 2 to 5), the abscissæ representing the percentage by weight of the acetone–*n*-butyl alcohol mixture. The actual values obtained are given in Table IV. From these curves the binodal curves for the system can be constructed as on the triangular diagram in Fig. 2. This is done in the following way: Table V shows the miscibility concentrations read from the curves 2 to 5 in Fig. 1, at the various temperatures indicated. Thus when the mixture contained 9·07% of acetone, from curve 2 are read the miscibility concentrations at 25°, *i.e.*, 7·9% and 75% of the mixture. The water present is therefore 92·1% and 25% respectively. In the ternary diagram (Fig. 2), all systems composed of the 9·07% mixture and varying proportions of water will lie on the line joining the water apex to the point X representing the composition 9·07% acetone, 90·93% *n*-butyl alcohol. At 25° the two miscibility points will lie on the intersection of this line and the lines LM and NO parallel to the base and representing 92·1% and 25% of water respectively; α and β therefore represent two points on the binodal curve for 25°. Each mixture will give two such other points and thus the isotherm can be plotted. Fig. 2 shows the isotherms for five chosen temperatures. KK′ is the critical curve. This method provides a very simple and accurate method for plotting the binodal curves at any desired temperature. The binodal curve at 20° is in good agreement with the determination of Reilly and Ralph (*loc. cit.*)

FIG. 2.

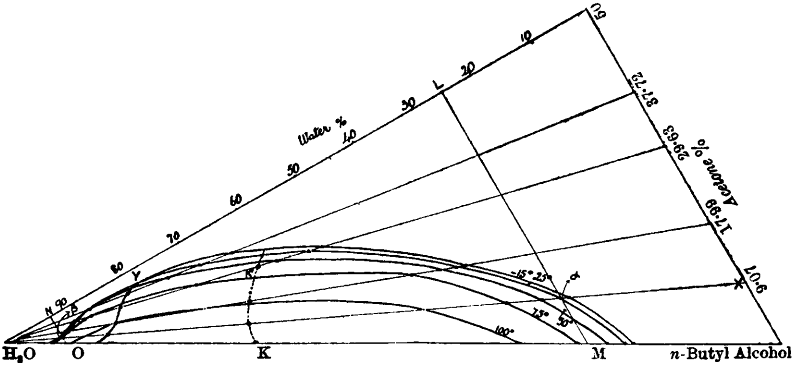


TABLE IV.

9·07% Acetone in *n*-butyl alcohol. % Mixture.	Temp.	17·99% Acetone in *n*-butyl alcohol. % Mixture.	Temp.	29·63% Acetone in *n*-butyl alcohol. % Mixture.	Temp.	37·72% Acetone in *n*-butyl alcohol. % Mixture.	Temp.
7·82	74·8° *u*	9·15	73·8° *u*	11·13	67·10° *u*	13·54	54·5° *u*
	app. 30·0 *l*		26·1 *l*		23·01 *l*		23·5 *l*
10·73	98·7 *u*	13·16	95·5 *u*	12·32	74·85 *u*	14·34	58·7 *u*
	−4·0 *l*		−3·2 *l*		12·5 *l*		15·0 *l*
13·56	107·5 *u*	17·25	100·8 *u*	13·19	76·6 *u*	18·83	63·7 *u*
	−14·0 *l*		−12·0 *l*		7·4 *l*		−13·0 *l*
14·09	108·3 *u*	24·80	101·6	16·17	81·8 *u*	20·52	62·5 *u*
	−15·0 *l*				−8·6 *l*		−17·0 *l*
16·71	111·6 *u*	32·57	97·65 [3]	19·68	82·9 *u*	23·55	58·5
	below −20·0 *l*				below −19 *l*		
18·57	113·1	34·69	96·75 [1] [2]	21·01	83·85	31·71	21·2
24·46	114·15	39·22	94·3 [1]	25·84	79·35	35·52	−7·0 [3]
31·59	112·9 [1] [3]	44·43	91·1	28·99	75·1		
32·47	112·9 [1] [2]	54·02	80·85	37·52	60·75		
44·98	109·7	57·55	74·2	38·31	58·15 [1] [2]		
51·19	106·1	62·30	45·1	42·16	46·45		
57·25	98·9	65·0	−5·2	43·54	39·40		
65·66	81·7			45·47	7·65		
71·20	58·4			46·60	−11·00		
73·15	43·0						
75·70	−10·0						

[1] Critical phenomena very distinct.

[2] Very close to equal volumes.

[3] Lower layer greater.

with the exception of the portion representing the high concentrations of water. The actual composition of the ternary mixtures at each point represented on Fig. 2 is given in Table V.

TABLE V.

% Acetone in mixture used.		$T = -15°$.		$T = 25°$.		$T = 50°$.		$T = 75°$.		$T = 100°$	
		%	%	%	%	%	%	%	%	%	%
0	Water	19·1	87·9	20·16	93·8	22·53	94·0	26·30	93·78	33·60	91·33
	Acetone	0	0	0	0	0	0	0	0	0	0
	n-$C_4H_{10}O$	80·9	12·1	79·84	6·2	77·47	6·0	73·70	6·22	66·4	8·67
9·07	Water	24·0	86·0	25·0	92·1	27·6	92·4	32·4	92·18	43·5	89·05
	Acetone	6·89	1·27	6·8	0·72	6·57	0·69	6·13	0·71	5·12	0·99
	n-$C_4H_{10}O$	69·10	12·73	68·2	7·18	65·83	6·91	61·47	7·10	51·38	9·96
17·99	Water	34·9	83·9	36·2	90·85	38·45	91·4	42·75	90·8	71·57	84·64
	Acetone	11·71	2·90	11·48	1·65	11·08	1·55	10·30	1·66	5·12	2·76
	n-$C_4H_{10}O$	53·39	13·20	52·32	7·50	50·47	7·05	46·95	7·54	23·31	12·60
29·63	Water	54·0	82·2	55·45	88·87	58·8	89·24	71·01	86·81		
	Acetone	13·63	5·27	13·20	3·30	12·21	3·19	8·59	3·91		
	n-$C_4H_{10}O$	32·37	12·53	31·35	7·83	28·99	7·57	20·40	9·28		
37·72	Water	64·1	80·5	69·00	86·52	74·02	86·68				
	Acetone	13·54	7·35	11·69	5·08	9·80	5·02				
	n-$C_4H_{10}O$	22·36	12·15	19·31	8·40	16·18	8·30				

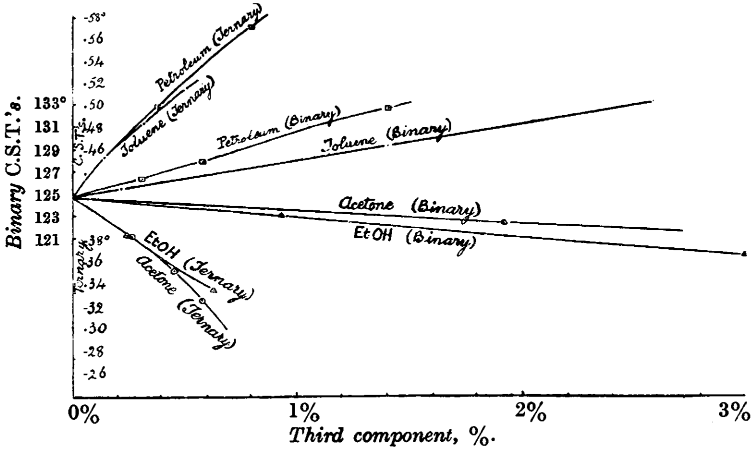
From the projections of the various binodal curves in Fig. 2, the effect of acetone at the various temperatures can be visualised. The isotherms cross one another only in the small region at the left-hand side of the diagram, representing the systems containing a high percentage of water. Only systems having a composition within this region would show a lower miscibility point above −15°, and points in this area are far removed from the critical region. The −15° and 25° isotherms cut at the point Y, representing a system having the composition 78% water, 9% acetone, and 13% *n*-butyl alcohol.

The acetone behaves as would be expected of a third component that acts purely as a mutual solvent for the other two. It becomes increasingly more effective as its concentration in the system increases, so that the critical line falls quite slowly from the binary *C.S.T.*, and then curves and falls increasingly steeply down to −15°. Except in the small region mentioned above, a fall of temperature is always accompanied by a decrease of solubility. This is shown also by the various vertical sections of the binodal surface that are represented by the curves 2 to 5 in Fig. 1, *i.e.*, no addition of acetone produces a maximum on that portion of the solubility curve representing saturated solutions rich in *n*-butyl alcohol. Thus, as shown on Fig. 1, curve 5, even when the upper *C.S.T.* has fallen below −15° there is no maximum on the right-hand arm of the curve. No solubility ring is produced which possesses critical points.

It must be concluded either that the binary solubility curve has no lower metastable *C.S.T.* and the complete solubility ring cannot be assumed present in the system, or that such a lower *C.S.T.* is at an extremely low temperature.

Other mutual solvents, such as ethyl alcohol and acetic acid, were examined qualitatively, and gave the same results as did acetone. No complete solubility ring was formed, and only one maximum of mutual insolubility was present on the arm of the curve representing the phase rich in water, even with the highest concentrations of the third component. It has been shown, however (Orton and Jones, *loc. cit.*), that hydrochloric acid as a third component would produce a complete ring containing an upper and a lower *C.S.T.* It seems very probable that this is an effect due, not to the mutual solvent action of the third component, but rather to its chemical combination with the other two components of the system. Hydrobromic and hydriodic acids act similarly, although higher concentrations are required to produce the same *C.S.T.*'s.

FIG. 3.



Comparison of Effects of Typical Impurities on the Binary C.S.T. *and the Ternary* C.S.T. *with Hydrochloric Acid.*

Table VI collates the results, which are also shown graphically in Fig. 3.

It will be seen that the ternary *C.S.T.* is extremely sensitive to typical impurities in the alcohol, *e.g.*, 1% of acetone produces a decrease of approximately 20° in the upper ternary *C.S.T.*, and of only 1·14° in the binary *C.S.T.*; the results for 1% petroleum show an increase of approximately 19° and 5°, respectively. The figures given show plainly that a binary *C.S.T.* cannot be regarded as a trustworthy criterion of the purity of a liquid. Only for certain

TABLE VI.

Comparison of the effect of impurities on the ternary and binary C.S.T.'*s*.

	Ternary *C.S.T.*				Binary *C.S.T.*					
% Acetone	0	0·262	0·437	0·575	0	1·92	9·07	18·02	29·53	37·73
C.S.T. *u*	41·90°	38·40°	35·35°	32·66°	124·75°	122·72°	112·90°	96·75°	58·13°	< −15°
l	11·84	15·25	18·25	21·00						
% Petroleum	0	0·377	0·799		0	0·310	0·581	1·405		
C.S.T. *u*	41·90°	49·96°	57·10°		124·75°	126·55°	128·10°	132·92°		
l	11·84	4·45	0·35							
% EtOH	0	0·238	0·629		0	0·927	3·78	23·8	35·22	47·65
C.S.T. *u*	41·90°	38·45°	33·65°		124·75°	123·30°	118·40°	74·70°	38·46°	3·70°
l	11·84	15·10	19·10							
% Toluene	0	0·142	0·316	0·508	0	1·406	2·586			
C.S.T. *u*	41·90°	45·75°	48·45°	51·55°	124·75°	129·63°	133·55°			
l	11·84	8·10	5·45	—						

The petroleum had b. p. 171—175°; purification of this specimen is described by Jones and Betts (*loc. cit.*, p. 1179).
u = Upper *C.S.T.* *l* = Lower *C.S.T.*

impurities in certain particular liquid pairs do we find this property valuable in this connexion, and then it is frequently of great sensitiveness. Ternary *C.S.T.*'s are of much more general use for this purpose.

The results show that the specimen of *n*-butyl alcohol used in this work was of a high degree of purity. In fact the criterion of purity used was much more sensitive than was necessary for the determination of the binary *C.S.T.* constants of the *n*-butyl alcohol.

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