17. *Solubility Influences. Part V. The Influence of Aliphatic Alcohols on the Solubility of Ethyl Acetate in Water.*

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The three-component systems consisting of water, ethyl acetate, and each of the following alcohols: methyl, ethyl, *n*- and *iso*-propyl, *n*-, *iso*-, *sec.*- and *tert.*-butyl, have been studied at 0° and 20°. In each case a number of the conjugate solutions, *i.e.*, aqueous and ester layers, were examined and their compositions determined; from the results the distribution ratio of ethyl acetate between the two layers was calculated. The addition of small amounts of alcohol to water appears to decrease the solubility of ethyl acetate, especially at low temperatures, but the effect is due to the decrease in activity (concentration) of the ethyl acetate in the ester layer because of the presence of appreciable amounts of alcohol. The distribution ratio is a corrected solubility which allows for the change in activity and shows no such decrease. By plotting the distribution ratio against the molecular ratio of alcohol to water in the aqueous layer, curves are obtained showing the influence on the corrected solubility of ethyl acetate of replacing water molecules by an equal number of molecules of alcohol. In this way the relative effects of the different alcohols can be compared and discussed. Four main factors are shown to affect the solubility of ethyl acetate in alcohol–water mixtures. At low concentrations of alcohol, complex formation between ester and water and its modification due to depolymerisation of the water by the alcohol is most important, but as the concentration is increased, first the relative areas of the non-polar and polar parts of the alcohol molecules and then their relative internal pressures become the dominant factors. Complex formation between alcohol and ester is shown by the results to have an unimportant influence on the solubility of ethyl acetate in aqueous-alcoholic solution.

AFTER an investigation of the factors influencing the solubility of esters had been commenced, Kendall (*Trans. Faraday Soc.*, 1937, **33**, 2) gave an account of the freezing points of solutions of ethyl acetate in aqueous ethyl alcohol. From the data the conclusion was drawn that, at low temperatures at least, ethyl alcohol diminishes the solubility of ethyl acetate in water, and a tentative explanation of the surprising result was proposed by one of us (Glasstone, *ibid.*, p. 8). In the course of experiments designed to confirm the observations and to test the hypothesis, it became evident that the decrease of solubility was apparent rather than real. When excess of ethyl acetate is added to water, the ester dissolves very little water and so the upper layer consists of almost pure ester, but if instead of water an aqueous alcohol is used, the upper layer may contain appreciable amounts of alcohol and water, with the result that the mol.-fraction of ester is reduced considerably below unity. This is particularly the case with the higher alcohols which have a limited solubility in water yet are completely miscible with ethyl acetate. The decrease in solubility of the ester in the aqueous layer found under these conditions is not remarkable, since the ethyl acetate with which it is in equilibrium is at a much lower activity than in the pure state. It was clear, therefore, that reliable information on the influence of alcohols on the solubility of ethyl acetate in water could only be obtained by a complete investigation, involving the analysis of both liquid layers, for a series of alcohols over a range of concentrations.

For this reason the liquid-phase equilibria in the three-component systems, consisting of water, ethyl acetate, and an alcohol were studied at 0° and 20°, and the results plotted on triangular diagrams. In each case a number of tie-lines, joining the points giving the compositions of the conjugate layers, were determined. The results obtained with methyl, ethyl, *n*- and *iso*-propyl, and *n*-, *iso*-, *sec*.-, and *tert*.-butyl alcohols are now described and discussed.

EXPERIMENTAL.

Materials.—*Ethyl acetate.* In the preliminary experiments three different products were employed: (i) A quantity of the ester was prepared from glacial acetic acid and absolute alcohol by Roberts's method (*J. Soc. Chem. Ind.*, 1924, **43**, 295T); it was dried over anhydrous potassium carbonate, refluxed several times with fresh portions of phosphoric oxide, and then fractionated over a small quantity of the latter substance. The fraction of b. p. 77·0—77·2°/760 mm. was collected. (ii) A good commercial specimen was kept over calcium chloride and distilled, the portion coming over between 74° and 78° being collected. This was treated with phosphoric oxide and fractionated as described above. (iii) A similar specimen was washed three times with an equal volume of half-saturated sodium chloride solution and twice with water; it was then stood over calcium chloride and fractionally distilled. A number of solubility determinations in water were made with the three products described, and in every case the results were the same within the limits of experimental error; expressed in g. of ethyl acetate per 100 g. of water, the solubilities were:

At 0°, 10·70 ± 0·05; at 20°, 8·40 ± 0·04; at 40°, 6·97 ± 0·04.

The value for 20° is in good agreement with that (8·42 g.) obtained by Schlesinger and Kubasowa (*Z. physikal. Chem.*, 1929, **142**, *A*, 27), although most of the results in the literature show a considerable variation. Since the specimens described above had almost identical solubilities, most of the measurements recorded in this paper were made with the third product.

Alcohols. Good commercial specimens were fractionated, and the portions distilling within a narrow range of the recorded b. p.'s were collected and used. The densities agreed very closely with the best values found in the literature (*e.g.*, Butler *et al.*, J., **1933**, **674**; **1935**, 280). *tert.*-Butyl alcohol was not distilled, but was cooled until partly frozen; the supernatant liquid was poured off, and the remaining solid retained.

Method of Experiment.—The data for the solubility curves were generally obtained by the synthetic method: known amounts of ethyl acetate and water were mixed and sufficient of the appropriate alcohol was run in to make the system homogeneous. The addition of the alcohol was carried out very slowly and the temperature was kept constant, although the effect of a slight raising or lowering of temperature frequently proved useful as a test for saturation. Many of the results were confirmed by analysis of the saturated solutions, the ester being determined in the usual manner by hydrolysis with alkali. To obtain the tie-lines, the general practice was to make up a mixture with known weights of the three components and to determine the amount of ethyl acetate in the upper layer by analysis. These data, together with the solubility curve, enable the position of the tie-line to be fixed. On account of the shape of the curves, this method was found to be more reliable than determining the ester concentration of both liquid layers. Measurements were made at 0° and 20°

Results.—The results obtained were plotted on triangular diagrams, portions of which are shown in Figs. 1 and 2: all compositions are in terms of weight percentages. The data for the conjugate ternary liquids, as obtained from the extremities of the tie-lines, are given in Table I.

FIG. 1.

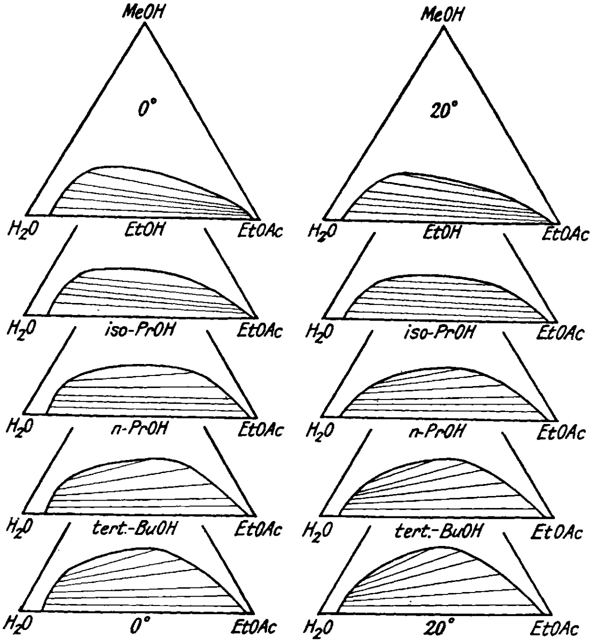
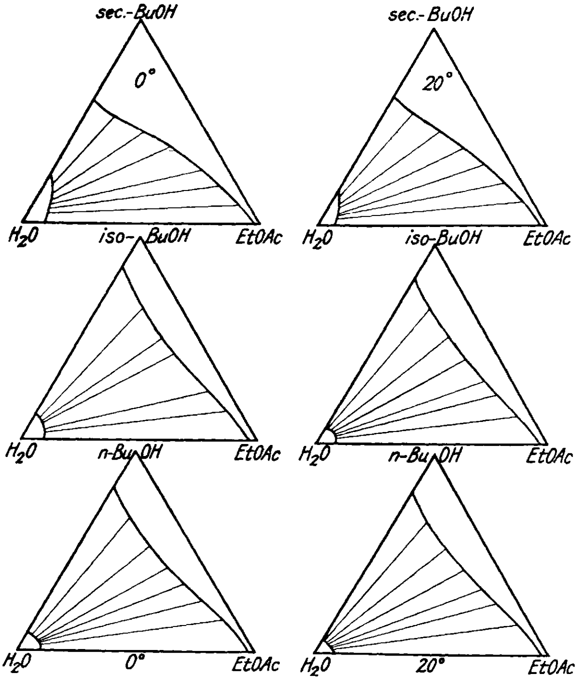


FIG. 2.



In order to see more clearly the significance of the results in Table I, the distribution ratios of ethyl acetate between the aqueous and the ester layer, with concentrations expressed in

TABLE I.

Compositions of conjugate solutions expressed as weight %.

Temp. 0°.						Temp. 20°.					
H_2O.	EtOAc.	ROH.	H_2O.	EtOAc.	ROH.	H_2O.	EtOAc.	ROH.	H_2O.	EtOAc.	ROH.
90·4	9·6	0·0	2·3	97·7	0·0	92·2	7·8	0·0	2·8	97·2	0·0
Methyl alcohol.											
85·4	9·5	5·1	2·6	97·1	0·3	87·8	8·0	4·2	3·4	95·6	1·0
80·8	9·5	9·7	3·2	95·5	1·3	83·0	8·4	8·6	4·3	92·6	3·1
75·5	10·2	14·3	3·7	94·1	2·2	79·0	9·3	11·7	5·8	88·9	5·3
72·0	11·2	16·8	4·8	91·1	3·9	74·6	10·5	15·0	6·3	87·4	6·3
60·4	16·3	23·3	7·9	84·4	7·7	65·2	14·5	20·3	10·2	79·8	10·0
						55·1	21·4	23·5	15·0	71·3	13·7
Ethyl alcohol.											
86·9	9·3	3·8	2·4	97·5	0·1	88·1	7·9	4·0	3·6	94·4	2·0
84·2	9·1	6·7	2·9	95·6	1·5	84·0	8·4	7·6	5·3	89·2	5·5
80·2	9·0	10·8	3·6	93·1	3·3	80·4	9·2	10·4	7·0	85·2	7·8
76·9	9·2	13·9	4·6	89·6	5·8	75·6	10·7	13·7	8·6	81·2	10·2
73·8	9·7	16·5	6·7	84·1	9·2	70·5	13·0	16·5	13·4	72·1	14·5
68·9	11·3	19·8	10·7	75·9	13·4	62·6	17·9	19·5	21·3	60·4	18·3
*iso*Propyl alcohol.											
87·0	9·0	4·0	3·0	96·2	0·8	88·7	7·9	3·4	4·2	91·7	4·1
83·6	8·8	7·6	4·4	89·9	5·7	84·8	8·5	6·7	5·8	86·6	7·6
81·4	8·7	9·9	5·8	85·4	8·8	82·0	9·2	8·8	8·4	79·8	11·8
77·5	8·7	13·8	9·3	76·2	14·5	78·2	10·0	11·8	12·3	71·3	16·4
73·9	9·3	16·8	16·0	63·3	20·7	74·0	11·4	14·6	18·8	59·4	21·8
						69·5	13·7	16·8	26·6	48·3	25·1
n-Propyl alcohol.											
87·7	9·2	3·1	4·0	91·6	4·4	88·7	7·8	3·5	4·2	90·4	5·4
84·7	9·1	6·2	5·2	87·3	7·5	85·9	8·0	6·1	7·6	80·4	12·0
82·6	8·9	8·5	9·6	75·7	14·7	84·0	8·3	7·7	11·3	71·5	17·2
78·9	9·2	11·9	16·0	61·3	22·7	81·3	9·0	9·7	17·9	58·4	23·7
74·1	10·2	15·7	29·0	43·6	27·4	79·0	9·7	11·3	23·7	49·6	26·7
						72·6	12·2	15·2	34·7	36·5	28·8
tert.-Butyl alcohol.											
87·5	8·8	3·7	3·2	94·1	2·7	88·9	7·6	3·5	5·0	88·9	6·1
84·6	8·4	7·0	5·3	85·1	9·6	86·8	7·5	5·7	7·7	79·4	12·9
82·3	8·0	9·7	6·9	79·5	13·6	84·3	7·4	8·3	11·4	68·0	20·6
80·5	7·8	11·7	12·0	66·1	21·9	81·5	7·7	10·8	17·4	54·2	28·4
78·0	7·7	14·3	17·4	55·9	26·7	79·8	7·8	12·4	22·6	45·5	31·9
76·2	7·8	16·0	25·0	43·7	57·3	75·5	8·8	15·7	35·7	30·5	33·8
sec.-Butyl alcohol.											
87·1	8·7	4·2	5·2	85·9	8·9	89·8	7·2	3·0	5·2	82·7	12·1
85·3	8·2	6·5	8·8	72·5	18·7	88·9	6·8	4·3	9·0	69·2	21·8
83·9	7·5	8·6	12·4	61·5	26·1	88·5	6·5	5·0	13·1	56·0	30·9
82·1	6·7	11·2	19·3	43·5	37·2	86·5	5·3	8·2	17·7	43·3	39·0
80·3	5·6	14·1	26·5	28·9	44·6	85·4	4·2	10·4	23·6	28·8	47·6
77·6	3·7	18·7	35·2	12·8	52·0	83·7	2·6	13·7	30·5	13·1	56·4
*iso*Butyl alcohol.											
88·8	8·5	2·7	5·6	80·6	13·8	90·8	7·3	1·9	6·5	79·4	14·1
88·1	7·7	4·2	8·9	67·5	23·6	90·6	6·9	2·5	9·5	65·6	24·9
87·1	5·7	7·2	14·4	43·4	42·2	89·9	6·3	3·8	11·4	57·0	31·6
87·1	4·9	8·0	15·7	34·6	49·7	90·0	4·8	5·2	14·2	42·7	43·1
86·9	3·0	10·1	16·6	18·5	64·9	90·3	3·6	6·1	16·2	30·1	53·7
						91·1	2·0	6·9	17·7	15·0	67·3
n-Butyl alcohol.											
89·7	8·0	2·3	6·4	78·3	15·3	92·0	6·3	1·7	7·0	78·6	14·4
89·3	7·3	3·4	10·0	65·2	24·8	92·0	5·8	2·2	10·7	63·4	25·9
89·2	6·8	4·0	13·5	53·0	33·5	92·1	5·3	2·6	13·3	54·0	32·7
89·1	6·3	4·6	16·0	42·5	41·5	92·2	4·2	3·6	16·2	41·5	42·3
89·0	4·8	6·2	18·3	29·3	52·4	92·4	3·4	4·2	18·3	28·6	53·1
89·7	3·7	7·6	19·6	14·3	66·1	93·0	1·8	5·2	19·6	14·3	66·1

mol.-fractions, have been plotted in Figs. 3 and 4 against the molecular ratio of alcohol to water in the aqueous layer for various concentrations of alcohol. The distribution ratio may be regarded as a corrected solubility which allows for the decrease in activity of the ethyl acetate in the ester layer; as an approximation this activity is assumed equal to the mol.-fraction. The curves obtained permit of a direct comparison of the relative effects of different alcohols; they show the influence on the corrected solubility of ethyl acetate of replacing varying proportions of the total number of water molecules by an equal number of molecules of alcohol.

FIG. 3.

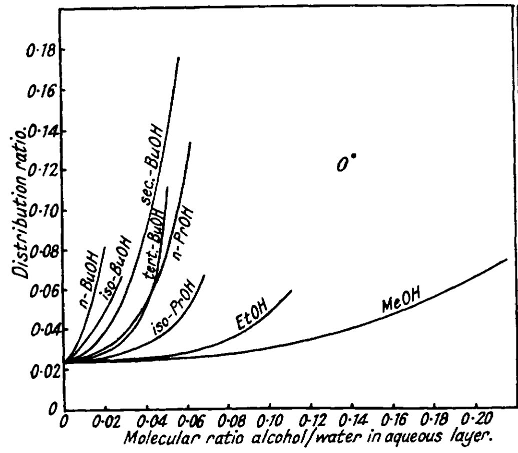
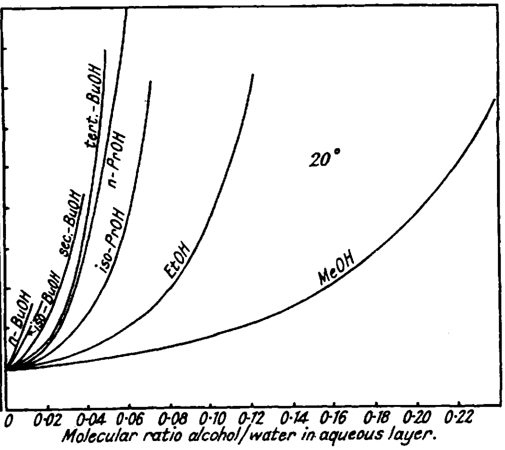


FIG. 4.



DISCUSSION.

It will be seen from the curves in Figs. 3 and 4 that there is no evidence of a fundamental decrease in the solubility of ethyl acetate as a result of the addition of an alcohol, although at low concentrations methyl and ethyl alcohols, especially, appear to be little more effective than water as solvents in spite of the fact that they are miscible with ethyl acetate in all proportions. At higher concentrations, however, all the alcohols bring about a large increase in the solubility of the ester, particularly at the higher temperature.

There are at least four factors, dependent on the nature of the alcohol and on temperature, which will affect the solubility of ethyl acetate in a water–alcohol system: these will be considered in turn.

(*a*) The unexpectedly large solubility of ethyl acetate in water, the negative temperature coefficient, and the fact that the system is pseudo-ideal (Kendall and King, J., 1925, **127**, 1778) indicate that ester–water complexes, presumably involving a hydrogen bond, are formed and these are the main cause of the relatively high solubility. Since liquid water is now generally regarded as virtually a large associated molecular structure (Bernal and Fowler, *J. Chem. Physics*, 1933, **1**, 515; Sidgwick, *Ann. Reports*, 1934, **31**, 42), it is probable that only free single molecules will be able to take part in the complex formation with the ester. When an alcohol is added to water, there result, first, mutual depolymerisation [Jones and Murray, *Amer. Chem. J.*, 1903, **30**, 193; Jones and Veazey, *ibid.*, 1907, **37**, 405; see also Butler, Thomson, and Maclennan, J., 1933, 674 (685)], and secondly, the formation of alcohol–water complexes, involving the simple molecules to a great extent. The former of these two effects, by producing more single water molecules, will tend to bring about an increase in the solubility of ethyl acetate, but the latter, which would be operative even if there were no depolymerisation, will decrease the solubility because the alcohol will compete with the ester for the free water molecules. The net influence on the solubility of ethyl acetate will depend on the relative magnitudes of the two effects, of which some indication may be obtained from the measurements of Young and Fortey (J., 1902, **81**, 717) on the thermal and volume changes resulting when water and various alcohols are mixed. Since depolymerisation will be accompanied by the absorption of heat, and probably an increase of volume, whereas complex formation will have the opposite effects, it appears that the influence of complex formation, which tends to lower the solubility of the ester, should be greatest with methyl alcohol but should become less as the hydrocarbon chain is lengthened. Although chain branching also favours compound formation, as shown by the existence of a stable solid hydrate of *tert.*-butyl alcohol, the thermal effect on mixing this alcohol with water suggests that there is considerable depolymerisation, and so the influence on solubility may not be marked. It may be noted that the conclusions drawn from thermal and volume changes are in agreement with those reached from general considerations, based on the probable influence of the electron-repelling tendencies of the alkyl groups and the size of the alcohol molecule on complex formation and depolymerisation.

Increase of temperature would be expected to decrease the concentration of alcohol–water complexes and possibly to increase the depolymerisation : hence the general effect of the operation of these factors would be in the direction of causing a relative increase in the solubility of ethyl acetate at 20° as compared with 0°.

(*b*) Since water and ethyl acetate are able to form a complex, it is reasonable to suppose that the ester will unite in an analogous manner with an alcohol, although to a smaller extent; evidence for this view has been obtained from infra-red absorption measurements on mixtures of methyl alcohol and esters (Williams and Gordy, *J. Amer. Chem. Soc.*, 1937, **59**, 817). The stability of the complexes is, however, probably not very great (cf. Merriman, J., 1913, **103**, 1774). The formation of such complexes probably involves a hydrogen bond between the alcohol and the ester, thus $R{\cdot}O{\cdot}H \cdots O\!<$, consequently the presence of electron-repelling alkyl groups in the radical R of the alcohol should result in a decrease of stability. The effect of combination between ethyl acetate and the alcohol would be to increase the solubility of the ester, and this factor will evidently become less as the length and branching of the hydrocarbon chain of the alcohol are increased. Increase of temperature will decrease the extent of complex formation and any consequent influence on solubility will be diminished.

(*c*) The more the internal pressures of two liquids approximate to one another the greater will be their mutual solubility (Hildebrand, *J. Amer. Chem. Soc.*, 1916, **38**, 1452; " Solubility," 1936). Water and ethyl acetate have internal pressures which are markedly different, but the values for the alcohols, especially the butyl alcohols, are much closer to those of the ester. Although the internal pressure of a mixture of water and an alcohol is not exactly the mean of the values for the two constituents, nevertheless it will be much nearer to that of the ester than is the internal pressure of pure water (see Westwater, Frantz, and Hildebrand, *Physical Rev.*, 1928, **31**, 135) : consequently, the ester should be more soluble in the alcohol–water mixture. The relative extents of the increase to be expected for the different alcohols may be assessed from their relative internal pressures : the values given below have been calculated by means of the formula $(5280 + 24{\cdot}5t)/v$, where t is the boiling point of the liquid on the Centigrade scale and v is the molar volume (see Hildebrand, *op. cit.*, p. 103). These may be compared with a figure of 73 for ethyl acetate.

Relative internal pressures.

H_2O.	MeOH.	EtOH.	*n*-PrOH.	*iso*-PrOH.	*n*-BuOH.	*iso*-BuOH.	*sec.*-BuOH.	*tert.*-BuOH.
429	161	116	94	88·5	80	78	76·5	71

It is evident, therefore, that as far as internal pressure is concerned all the alcohols should enhance the solubility of ethyl acetate, the effect increasing approximately in the order given. Raising the temperature, however, might be expected to bring about a relatively greater increase of solubility for the lower alcohols, because the influence of internal pressure differences is diminished as the temperature is raised.

(*d*) The relative areas of the polar and non-polar portions of a molecule have some effect on its solubility (cf. Harkins, Brown, and Davies, *J. Amer. Chem. Soc.*, 1917, **39**, 354; Langmuir, *Coll. Sym. Monographs*, 1925, **3**, 48; Butler, Thomson, and Maclennan, *loc. cit.*, p. 681), and this factor may have some influence on the extent to which ethyl acetate dissolves in the aqueous alcohol. Although ethyl acetate contains polar groupings, it behaves virtually as a non-polar substance from the standpoint of solubility, as seen for example by its complete miscibility with hexane; increasing the relative non-polar area of an alcohol should thus result in an increase of solubility. Increasing chain length should, therefore, have this effect, whereas branching of the chains would probably operate in the opposite direction.

An examination of the curves in Figs. 3 and 4 in the light of the above considerations shows that at small concentrations of alcohol, especially for the lower members of the series, complex formation between alcohol and water must be a very important factor, since in no other way is it possible to account for the increase in solubility of ethyl acetate being so small in the presence of these lower alcohols. That the same factor is effective with the higher alcohols, although generally masked by other influences which act in the opposite direction, is shown by the fact that the distribution ratio increases at first slowly with increasing alcohol concentration, and especially by the crossing of the curves for *n*-propyl and *tert.*-butyl alcohols at 0°. The greater tendency of the latter to form a complex with water molecules may account for this result; at 20°, where the extent of complex formation is diminished, the curves do not cross. Depolymerisation is, however, a factor of importance, especially with the higher alcohols; otherwise *tert.*-butyl alcohol would be expected to cause a much lower solubility than is actually observed, because of the stability of the alcohol–water complex which is probably much greater than that for ethyl alcohol. In fact, for the higher alcohols, depolymerisation is probably the dominating influence in determining the solubility of the ester in alcohol–water mixtures. Even for the lower alcohols, where the contributions of the internal pressure and relative polarity factors are probably small at low concentrations, the effect of alcohol–water complex formation cannot predominate, for otherwise the distribution ratio of ethyl acetate would fall below the value for water alone.

As the concentration of alcohol is increased it is evident that the other factors already discussed, all of which tend to increase the solubility of the ester, become more effective; of these, the formation of alcohol–ester complexes may be ruled out as being relatively unimportant, since its effect would decrease with increasing chain length. It is to be expected that the influence of the internal pressure and relative polarity factors should become more marked at higher alcohol concentrations, and these are probably responsible for the rapid rise in the distribution ratio. The former of these would lead to the solubilities of the ester in the alcohol–water mixtures containing the butyl alcohols increasing in the order *n* < *iso* < *sec.* < *tert.*, whereas the reverse is actually the case; this implies that the relative polarity, which would operate in the observed order, is the more effective. The direction of the curves for *tert.*- and *sec.*-butyl alcohols suggests that they would cross at very high concentrations, which are actually beyond the solubility limits, both at 0° and 20°; hence, under these conditions the internal pressure factor seems to become the more important.

The authors' thanks are due to the Department of Scientific and Industrial Research for a maintenance grant to one of them (D. G. B.) for part of the time during which this work was in progress.

THE UNIVERSITY, SHEFFIELD 10. [*Received, December 8th,* 1937.]