# *Miscibility Phenomena in Ternary Systems containing Diphenyl Ether, Water, and an Aliphatic Alcohol or Acid.*

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Binodal curves and tie-lines of eight systems have been determined in order to ascertain the influence of alcohols and fatty acids on the miscibility of diphenyl ether and water. For a series of homologous third components there is no simple relation between the composition of the critical mixture and the position of the component in the series, but for systems containing the straight-chain alcohols the concentrations corresponding to the summits of the binodal curves are linearly related to the number of carbon atoms in the molecule. The observed equilibria do not conform to Bancroft's equation over the entire range of composition. The system containing *n*-propanol exhibits solutropism (see p. 544) involving reversal of slope of the tie-lines.

The hypothesis that tie-lines for non-solutropic systems meet at a point focus is not substantiated by the results of the present work. A study of the methods of tie-line correlation reveals that they are not generally applicable and that the method proposed by Othmer and Tobias is the most satisfactory.

APART from the studies of Washburn, Graham, Arnold, and Transue (*J. Amer. Chem. Soc.*, 1940, **62**, 1454), there have been no systematic investigations of the relation between the molecular structure of a liquid and its solvent power for a pair of immiscible or partially miscible liquids. The behaviour of water and diphenyl ether in the presence of an aliphatic alcohol or acid has now been studied primarily in order (*a*) to ascertain whether there is any relation between homology and the composition of the critical mixture or that corresponding to the summit of the binodal curve, (*b*) to examine the applicability of Bancroft's distribution equation, (*c*) to test the hypothesis that tie-lines of non-solutropic systems meet at a point focus, and (*d*) to assess the accuracy of the various methods of tie-line correlation.

## EXPERIMENTAL

Weights were standardised by Richards's method, and thermometers were tested against Anschutz thermometers calibrated at the N.P.L. Unless otherwise stated, b. p.s refer to 760 mm. pressure. Densities were corrected for buoyancy, and refractive indices were determined by means of an Abbé refractometer with its prisms kept at constant temperature by a stream of water from a thermostat.

*Purification of Materials.—Diphenyl ether.* Repeated fractional distillation of the commercial ether gave a product with b. p. 258·4°, f. p. 26·9°, $n_D^{27}$ 1·5780.

*Alcohols.* The alcohols were dried by partial conversion into the magnesium alkoxide (Lund and Bjerrum, *Ber.*, 1931, **64**, 210), and were then fractionated through a Dufton all-glass column in a distillation apparatus provided with a guard-tube ($CaCl_2$) : methanol, b. p. 64·6°, $D_4^{25}$ 0·78665, $n_D^{25}$ 1·3272; ethanol, b. p. 78·4°, $d_4^{25}$ 0·78504, $n_D^{25}$ 1·3596; *n*-propanol, b. p. 97·2°, $d_4^{25}$ 0·79988, $n_D^{25}$ 1·3840; *iso*propanol, b. p. 82·1°, $d_4^{25}$ 0·78088, $n_D^{25}$ 1·3764; butanol, b. p. 117·7°, $d_4^{25}$ 0·80574, $n_D^{25}$ 1·3970.

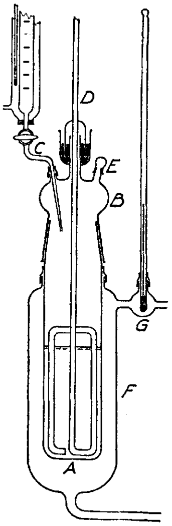
*Acids.* Fractional freezing of acetic acid followed by distillation gave a product with f. p. 16·6°, b. p. 118·1°, $d_4^{25}$ 1·04367, $n_D^{25}$ 1·3698.

The other acids were purified by distillation : propionic acid, b. p. 141·3°, $d_4^{25}$ 0·98842, $n_D^{25}$ 1·3848; butyric acid, b. p. 164·0°, $d_4^{25}$ 0·95091, $n_D^{25}$ 1·3958.

*Miscibility Apparatus.*—The miscibility vessel (Fig. 1) consisted of the flat-bottomed Pyrex tube *A* (20 cm. long and 4 cm. in diameter) with a ground joint at its upper end for fitting into the cap *B*, which was provided with three collars to take the delivery tube of the burette *C*, the mercury-sealed stirrer *D*, and the ground-glass cap *E*, respectively. The burette (10 ml.) was furnished with a glass jacket through which water at 25·0° was circulated, and the upper end of the burette was fitted with a guard-tube ($CaCl_2$) to maintain a dry atmosphere above the organic liquid during its introduction into the miscibility vessel. The stirrer *D* was driven by an electric motor at a rate of about 300 r.p.m., so that thorough agitation of the liquid was effected without splashing. The ground-glass joints of the apparatus were lubricated with Apiezon L grease to prevent intrusion of atmospheric moisture.

Owing to the peculiar optical effects accompanying the phase changes in the systems under study, it proved extremely difficult to observe the clearing and turbidity points when the miscibility vessel was immersed in the water of an ordinary thermostat. This difficulty was largely overcome by surrounding the miscibility vessel with the glass jacket *F* (25 cm. long and 6·5 cm. in diameter) through which water from a thermostat was circulated at high speed by means of a rotary pump driven by an electric motor. The exit tube of the jacket was provided with the small reservoir *G* to accommodate the bulb of a thermometer. The thermostat was kept at 25° ± 0·05° by means of a bimetallic element operating a vacuum switch relay in circuit with an immersion heater. The speed at which the water was circulated through the jacket was such that the temperature of the issuing stream did not differ by more than 0·05° from that of the thermostat.

Fig. 1.



*Determination of Binodal Curves.*—The binodal curve of a system was generally determined in three stages. In the first diphenyl ether (about 6 g.) and water (about 0·05 ml.) were introduced into the miscibility vessel, and the mixture was stirred until thermal equilibrium was attained (20—30 min.). The third component was then added dropwise from the burette until the mixture formed a homogeneous solution. The addition was made very slowly in the neighbourhood of the miscibility point, and the stirring was momentarily interrupted when it was necessary to observe the state of the system. Normally, determination of a miscibility point occupied 30—45 min. The weights of water and third component in the system were calculated from the known values of the densities.

Small samples of the solution were withdrawn for refractometric analysis by the use of a long capillary tube with a small bulb (0·5 ml.) at one end. The bulb was warmed, the cap *E* removed, and the capillary tube inserted into the miscibility vessel so that its open end was immersed in the solution. After a sufficient amount of the liquid had been drawn into the capillary, the sampler was removed and allowed to cool further so that the liquid was drawn into the bulb. The sampler was then sealed by directing a small flame at a point about 2 cm. from the open end. After cooling to room temperature, it was weighed, and from a knowledge of the composition of the mixture, allowance was made for the amount of each component withdrawn from the miscibility vessel. Further quantities of water were added to the mixture, and the miscibility points were determined for the range 70—15% of diphenyl ether.

In the second stage about 1 g. of diphenyl ether was employed to cover the range 50—5%, and in the third stage the amount was reduced to 0·1 g. to enable measurements to be made in the range 5—0%. Measurements on systems containing more than 70% of diphenyl ether presented difficulty owing to the small amounts of water in the equilibrium mixtures. Moreover, systems containing more than 80% of water formed a suspension of fine droplets, and the change from clarity to turbidity was not sufficiently sharp to permit accurate determination of the miscibility points.

In systems of moderately high diphenyl ether content approach to the miscibility point was characterised by the appearance of a marked turbidity which could be cleared by the addition of one drop of the third component. Intense opalescence was invariably observed in the neighbourhood of the plait point, and the measurements in this region were the most accurate of the series. The sharpness of the end-points deteriorated with increasing concentration of water in the systems.

An indication of the accuracy attainable by the use of the present apparatus is furnished by the data for the system containing butanol. The binodal curve for this system is found to cut the water–butanol axis at a point corresponding to 20·25% of water, which is very close to the value (20·27%) recorded by Hill and Malisoff (*J. Amer. Chem. Soc.*, 1926, **48**, 918) for the solubility of water in this alcohol at 25°.

The miscibility data and the refractive indices of the solutions are recorded in Table 1.

The binodal curve can be formulated mathematically by referring the miscibility data to rectangular co-ordinates, one comprising the base of the triangle and the other drawn at right angles at the end of the base. Separate cubic equations can then be developed to represent the two curves on either side of the summit of the binodal curve. The limits of the equation are expressed in terms of $x$, the concentration of water in moles % on the two co-ordinate diagram.

Values of the co-ordinate $y$ are obtained in terms of multiples of 10% intervals along the $x$-axis. By plotting the curve in this way, it is only necessary to draw the equilateral triangle upon the base $x = 0$—100% in order to obtain the actual compositions in terms of the three components. The equations representing the binodal curves of the various systems are of the type

$$(1) \quad y = \alpha x + \beta x^2 + \gamma x^3$$

$$(2) \quad y = \alpha_1(100 - x) + \beta_1(100 - x)^2 + \gamma_1(100 - x)^3$$

where equation (1) represents the diphenyl ether-rich side and equation (2) the water-rich side of the binodal curve. The limiting values of $x$, and the values of the coefficients in the above equations are given in Table 2. The applicability of the equations is shown by the examples in Table 3.

*Determination of Tie-lines.*—Mixtures corresponding to points inside the heterogeneous region of the phase diagram were prepared by weighing the components into constricted test-tubes which were then hermetically sealed. The tubes were vigorously shaken in the thermostat

TABLE 1. *Miscibility data.*

| $Ph_2O$, % | $H_2O$, % | MeOH, % | $n_D^{25}$ |
|---|---|---|---|
| 49·26 | 1·24 | 49·50 | — |
| 42·70 | 1·50 | 55·80 | — |
| 31·27 | 2·53 | 66·20 | — |
| 26·59 | 3·40 | 70·01 | — |
| 22·74 | 4·76 | 72·50 | — |
| 18·71 | 6·06 | 75·23 | — |
| 16·55 | 7·40 | 76·05 | — |
| 13·20 | 9·60 | 77·20 | — |
| 9·04 | 13·75 | 77·21 | — |
| 6·55 | 17·05 | 76·40 | — |
| 4·11 | 20·24 | 75·65 | — |
| 4·50 | 21·70 | 73·80 | — |
| 2·88 | 25·12 | 72·00 | — |
| 2·37 | 27·41 | 70·22 | — |
| 1·45 | 30·59 | 67·96 | — |
| 1·12 | 34·08 | 64·80 | — |
| 0·88 | 35·76 | 63·36 | — |
| 0·31 | 38·92 | 60·77 | — |

| $Ph_2O$, % | $H_2O$, % | EtOH, % | $n_D^{25}$ |
|---|---|---|---|
| 71·35 | 1·65 | 27·02 | 1·5030 |
| 67·93 | 1·95 | 30·12 | 1·4953 |
| 56·60 | 3·23 | 40·17 | 1·4685 |
| 56·09 | 3·22 | 40·69 | 1·4682 |
| 49·43 | 3·88 | 46·69 | 1·4541 |
| 44·97 | 4·51 | 50·52 | 1·4451 |
| 43·75 | 4·94 | 51·29 | 1·4420 |
| 36·82 | 6·50 | 56·68 | 1·4325 |
| 32·60 | 7·70 | 59·70 | 1·4195 |
| 27·30 | 9·10 | 63·60 | 1·4136 |
| 22·30 | 10·80 | 66·90 | 1·4041 |
| 19·53 | 11·76 | 68·71 | 1·3968 |
| 15·83 | 14·72 | 69·45 | 1·3902 |
| 15·34 | 15·41 | 69·25 | 1·3888 |
| 13·10 | 17·10 | 69·80 | 1·3860 |
| 11·98 | 18·04 | 69·98 | 1·3832 |
| 10·97 | 19·57 | 69·46 | 1·3820 |
| 10·00 | 20·70 | 69·30 | 1·3804 |
| 8·97 | 22·60 | 68·43 | 1·3788 |
| 8·82 | 21·78 | 69·40 | 1·3784 |
| 6·55 | 26·30 | 67·15 | 1·3746 |
| 6·04 | 27·70 | 66·26 | 1·3738 |
| 3·56 | 33·00 | 63·44 | 1·3689 |
| 2·00 | 39·20 | 58·80 | 1·3652 |
| 2·23 | 40·80 | 56·97 | 1·3641 |
| 1·18 | 44·30 | 54·52 | 1·3626 |
| 0·71 | 52·40 | 46·89 | 1·3571 |

| $Ph_2O$, % | $H_2O$, % | $Pr^nOH$, % | $n_D^{25}$ |
|---|---|---|---|
| 94·34 | 0·45 | 5·18 | 1·5653 |
| 84·81 | 1·33 | 13·86 | 1·5422 |
| 76·89 | 2·37 | 20·84 | 1·5249 |
| 66·90 | 4·17 | 28·96 | 1·5018 |
| 64·11 | 4·60 | 31·29 | 1·4959 |
| 58·40 | 5·71 | 35·89 | 1·4839 |
| 56·65 | 6·18 | 37·15 | 1·4803 |
| 47·07 | 7·93 | 45·00 | 1·4616 |
| 41·46 | 9·56 | 48·98 | 1·4505 |
| 39·48 | 10·30 | 50·22 | 1·4480 |
| 36·36 | 11·22 | 52·42 | 1·4411 |
| 29·52 | 13·73 | 56·82 | 1·4289 |
| 23·95 | 16·85 | 59·20 | 1·4184 |
| 22·75 | 18·38 | 59·87 | 1·4160 |
| 19·44 | 20·86 | 59·74 | 1·4098 |
| 18·65 | 21·91 | 59·44 | 1·4084 |
| 16·37 | 23·92 | 59·71 | 1·4035 |
| 14·25 | 26·60 | 59·15 | 1·3995 |
| 12·35 | 28·75 | 58·94 | 1·3950 |
| 11·05 | 31·83 | 57·12 | 1·3922 |
| 9·66 | 34·41 | 55·92 | 1·3884 |
| 6·39 | 41·72 | 51·89 | 1·3805 |
| 5·34 | 44·20 | 50·46 | 1·3781 |
| 3·33 | 52·66 | 44·01 | 1·3702 |
| 1·85 | 60·64 | 37·53 | 1·3632 |
| 0·98 | 67·20 | 32·01 | 1·3578 |
| 0·47 | 74·50 | 25·03 | 1·3528 |

| $Ph_2O$, % | $H_2O$, % | $Pr^iOH$, % | $n_D^{25}$ |
|---|---|---|---|
| 68·03 | 3·66 | 28·31 | 1·5032 |
| 53·46 | 4·84 | 41·70 | 1·4716 |
| 49·39 | 5·36 | 45·25 | 1·4625 |
| 40·99 | 6·35 | 52·66 | 1·4460 |
| 34·31 | 8·25 | 57·44 | 1·4345 |
| 28·06 | 10·97 | 60·97 | 1·4223 |
| 22·97 | 13·98 | 63·05 | 1·4120 |
| 18·37 | 17·17 | 64·46 | 1·4029 |
| 14·89 | 20·37 | 64·74 | 1·3966 |
| 12·64 | 23·38 | 63·98 | 1·3922 |
| 8·72 | 28·47 | 62·81 | 1·3858 |
| 6·11 | 33·99 | 59·90 | 1·3798 |
| 5·13 | 38·37 | 56·50 | 1·3769 |
| 3·64 | 42·46 | 53·90 | 1·3742 |
| 2·09 | 49·91 | 48·00 | 1·3689 |
| 0·67 | 59·10 | 40·23 | 1·3632 |
| 0·42 | 63·86 | 35·72 | 1·3601 |
| 0·29 | 66·70 | 33·01 | 1·3583 |
| 0·25 | 68·00 | 31·75 | 1·3575 |

| $Ph_2O$, % | $H_2O$, % | $Bu^nOH$, % | $n_D^{25}$ |
|---|---|---|---|
| 94·30 | 0·37 | 5·33 | 1·5649 |
| 84·80 | 0·67 | 14·53 | 1·5430 |
| 78·39 | 1·32 | 20·39 | 1·5298 |
| 75·11 | 1·49 | 23·40 | 1·5228 |
| 67·72 | 2·21 | 30·07 | 1·5084 |
| 63·56 | 2·75 | 33·69 | 1·4991 |
| 62·60 | 2·76 | 34·64 | 1·4979 |
| 52·10 | 4·11 | 43·79 | 1·4775 |
| 49·77 | 4·51 | 45·72 | 1·4730 |
| 45·41 | 5·10 | 49·49 | 1·4651 |
| 39·03 | 6·37 | 54·60 | 1·4534 |
| 36·47 | 7·36 | 56·17 | 1·4510 |
| 28·68 | 8·89 | 62·43 | 1·4357 |
| 23·90 | 9·65 | 66·45 | 1·4285 |
| 20·20 | 11·21 | 68·59 | 1·4223 |
| 15·83 | 12·96 | 71·21 | 1·4141 |
| 14·50 | 12·80 | 72·70 | 1·4129 |
| 12·55 | 14·31 | 73·16 | 1·4096 |
| 9·83 | 15·06 | 75·11 | 1·4049 |
| 7·31 | 16·00 | 76·69 | 1·4013 |
| 6·35 | 16·60 | 77·05 | 1·3996 |
| 6·00 | 16·90 | 77·10 | 1·3990 |
| 3·84 | 17·54 | 78·62 | 1·3954 |
| 3·79 | 17·91 | 78·30 | 1·3955 |
| 2·15 | 18·70 | 79·15 | 1·3928 |
| 1·97 | 18·64 | 79·39 | 1·3917 |
| 0·98 | 19·34 | 79·68 | 1·3902 |
| 0·67 | 19·68 | 79·65 | 1·3900 |
| 0·24 | 20·10 | 79·66 | 1·3891 |

TABLE 1. (*Continued.*)

| $Ph_2O$, % | $H_2O$, % | $Me{\cdot}CO_2H$, % | $n_D^{25}$ |
|---|---|---|---|
| 77·20 | 1·00 | 21·80 | 1·5282 |
| 64·76 | 1·55 | 33·69 | 1·5034 |
| 53·76 | 2·47 | 44·77 | 1·4812 |
| 52·38 | 2·65 | 44·97 | 1·4792 |
| 48·95 | 3·05 | 48·00 | 1·4721 |
| 42·61 | 3·65 | 53·74 | 1·4590 |
| 36·54 | 4·60 | 58·86 | 1·4465 |
| 34·30 | 5·34 | 60·36 | 1·4420 |

| $Ph_2O$, % | $H_2O$, % | $Me{\cdot}CO_2H$, % | $n_D^{25}$ |
|---|---|---|---|
| 25·96 | 6·96 | 67·08 | 1·4240 |
| 23·79 | 7·41 | 68·80 | 1·4201 |
| 18·75 | 9·19 | 72·06 | 1·4100 |
| 16·13 | 10·02 | 73·85 | 1·4046 |
| 13·40 | 10·96 | 75·64 | 1·3995 |
| 10·50 | 12·90 | 76·60 | 1·3934 |
| 9·04 | 14·10 | 76·86 | 1·3904 |

| $Ph_2O$, % | $H_2O$, % | $Me{\cdot}CO_2H$, % | $n_D^{25}$ |
|---|---|---|---|
| 7·79 | 15·17 | 77·04 | 1·3878 |
| 5·59 | 17·40 | 77·01 | 1·3846 |
| 4·65 | 18·93 | 76·42 | 1·3828 |
| 4·30 | 20·07 | 75·63 | 1·3817 |
| 1·55 | 26·15 | 72·30 | 1·3777 |
| 0·68 | 35·47 | 63·85 | 1·3752 |
| 0·55 | 31·45 | 68·00 | 1·3741 |

| $Ph_2O$, % | $H_2O$, % | $Et{\cdot}CO_2H$, % | $n_D^{25}$ |
|---|---|---|---|
| 78·61 | 1·08 | 20·31 | 1·5318 |
| 68·63 | 1·84 | 29·53 | 1·5120 |
| 61·09 | 2·86 | 36·05 | 1·4975 |
| 49·93 | 5·16 | 44·91 | 1·4759 |
| 44·16 | 6·88 | 48·96 | 1·4650 |
| 38·36 | 8·70 | 52·94 | 1·4551 |
| 33·45 | 10·75 | 55·80 | 1·4451 |
| 28·60 | 13·11 | 58·90 | 1·4362 |

| $Ph_2O$, % | $H_2O$, % | $Et{\cdot}CO_2H$, % | $n_D^{25}$ |
|---|---|---|---|
| 23·29 | 15·74 | 61·66 | 1·4263 |
| 19·07 | 18·40 | 63·55 | 1·4180 |
| 14·67 | 21·28 | 64·05 | 1·4086 |
| 12·29 | 23·90 | 63·90 | 1·4032 |
| 11·35 | 24·71 | 63·94 | 1·4012 |
| 8·25 | 28·62 | 63·13 | 1·3947 |
| 6·07 | 32·32 | 61·61 | 1·3889 |
| 4·15 | 37·35 | 58·52 | 1·3837 |

| $Ph_2O$, % | $H_2O$, % | $Et{\cdot}CO_2H$, % | $n_D^{25}$ |
|---|---|---|---|
| 2·97 | 40·21 | 56·82 | 1·3810 |
| 2·20 | 44·45 | 53·35 | 1·3769 |
| 1·57 | 57·31 | 51·12 | 1·3741 |
| 1·03 | 52·35 | 46·62 | 1·3700 |
| 0·55 | 57·01 | 42·44 | 1·3662 |
| 0·28 | 62·51 | 37·21 | 1·3620 |
| 0·09 | 72·86 | 27·05 | 1·3528 |

| $Ph_2O$, % | $H_2O$, % | $Pr{\cdot}CO_2H$, % | $n_D^{25}$ |
|---|---|---|---|
| 74·71 | 0·81 | 24·48 | 1·5286 |
| 62·11 | 1·75 | 36·14 | 1·5051 |
| 54·78 | 2·57 | 42·65 | 1·4920 |
| 46·54 | 3·91 | 49·55 | 1·4759 |
| 40·12 | 5·54 | 54·34 | 1·4634 |
| 34·80 | 7·90 | 57·30 | 1·4541 |

| $Ph_2O$, % | $H_2O$, % | $Pr{\cdot}CO_2H$, % | $n_D^{25}$ |
|---|---|---|---|
| 29·66 | 9·90 | 59·44 | 1·4435 |
| 23·73 | 12·99 | 63·28 | 1·4330 |
| 20·24 | 16·49 | 63·27 | 1·4255 |
| 15·43 | 21·08 | 63·49 | 1·4153 |
| 10·59 | 27·25 | 62·16 | 1·4042 |
| 6·00 | 36·40 | 57·60 | 1·3930 |

| $Ph_2O$, % | $H_2O$, % | $Pr{\cdot}CO_2H$, % | $n_D^{25}$ |
|---|---|---|---|
| 3·70 | 43·68 | 52·62 | 1·3835 |
| 1·87 | 57·72 | 40·41 | 1·3700 |
| 1·07 | 66·63 | 32·30 | 1·3626 |
| 0·58 | 73·15 | 26·27 | 1·3565 |
| 0·31 | 77·98 | 21·71 | 1·3525 |

TABLE 2.

| Third component | $x$ limit | $\alpha$ | $\alpha_1$ | $10^4\beta$ | $10^4\beta_1$ | $10^6\gamma$ | $10^6\gamma_1$ |
|---|---|---|---|---|---|---|---|
| Methanol ............... | 50 | 0·078 | 0·081 | 1·78 | 6·45 | −5·10 | −15·60 |
| Ethanol ............... | 52 | 0·064 | 0·090 | 2·74 | 0·19 | −8·70 | −11·51 |
| Propanol ............... | 60 | 0·062 | 0·101 | −3·95 | −10·50 | −0·32 | − 2·86 |
| *iso*Propanol ......... | 55 | 0·050 | 0·093 | 0·89 | − 6·65 | −2·42 | − 2·00 |
| Acetic acid ............ | 59 | 0·045 | 0·089 | 1·70 | 8·00 | −7·65 | −25·00 |
| Propionic acid ...... | 52 | 0·066 | 0·086 | 0·81 | − 3·45 | −0·10 | − 0·11 |
| Butyric acid ......... | 50 | 0·084 | 0·092 | −6·70 | −11·81 | −1·71 | 5·00 |

TABLE 3.

| Third component: propanol | | | | | | Third component: propionic acid | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $x$ | $y$, calc. | $y$, obs. | $x$ | $y$, calc. | $y$, obs. | $x$ | $y$, calc. | $y$, obs. | $x$ | $y$, calc. | $y$, obs. |
| 10 | 0·58 | 0·58 | 60 | 2·24 | 2·19 | 10 | 0·62 | 0·62 | 60 | 2·16 | 2·15 |
| 20 | 1·08 | 1·08 | 70 | 2·02 | 2·02 | 20 | 1·26 | 1·26 | 70 | 1·99 | 1·98 |
| 30 | 1·50 | 1·49 | 80 | 1·58 | 1·52 | 30 | 1·76 | 1·76 | 80 | 1·49 | 1·49 |
| 40 | 1·80 | 1·82 | 90 | 0·89 | 0·88 | 40 | 2·10 | 2·09 | 90 | 0·82 | 0·85 |
| 50 | 2·08 | 2·10 | | | | 50 | 2·18 | 2·18 | | | |

to establish equilibrium in the system, and were then kept in the bath for several hours to allow separation of the mixture into two liquid layers. The tubes were opened, and a small quantity of each layer was withdrawn by means of pre-heated sampling tubes so that the refractive index could be determined as described previously. The composition of the equilibrium mixture, expressed in terms of the concentration of both diphenyl ether and water, was plotted against the refractive index of the solution, and from the resulting curves the points on the isotherm representing the compositions of the conjugate solutions were ascertained. If, as occasionally happened, the straight line connecting these two points did not pass through the point in the binodal region representing the mixture under examination, the experiment was repeated.

The method gave reproducible results for all the systems except that containing methanol, and the liquid layers of this system were analysed by Karl Fischer's method (*Angew. Chem.*, 1935, **48**, 394). A titration cell being used with platinum electrodes connected with a potentiometer and a sensitive galvanometer, the Karl Fischer reagent was standardised by titration of methanol solutions containing known amounts of water, the operation being conducted in an

TABLE 4. *Tie-line data.*

| Wt. (%) in $H_2O$ layer | | | Wt. (%) in $Ph_2O$ layer | | | Wt. (%) in $H_2O$ layer | | | Wt. (%) in $Ph_2O$ layer | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $Ph_2O$ | $H_2O$ | MeOH | $Ph_2O$ | $H_2O$ | MeOH | $Ph_2O$ | $H_2O$ | EtOH | $Ph_2O$ | $H_2O$ | EtOH |
| 28·5 | 3·2 | 68·3 | 85·0 | 0·5 | 16·5 | 18·4 | 12·2 | 69·4 | 92·5 | 0·4 | 7·1 |
| 17·5 | 6·9 | 75·6 | 92·5 | — | 7·5 | 8·6 | 22·1 | 69·3 | 95·4 | 0·2 | 4·4 |
| 8·9 | 13·1 | 78·0 | 95·5 | — | 4·5 | 6·5 | 25·7 | 67·8 | 96·4 | 0·1 | 3·4 |
| 5·0 | 19·8 | 75·2 | 97·6 | — | 2·4 | 1·6 | 34·9 | 63·5 | 96·8 | 0·1 | 3·1 |
| 1·7 | 29·0 | 69·3 | 98·5 | — | 1·5 | 1·3 | 40·0 | 58·6 | 97·6 | — | 2·3 |
| 0·3 | 38·9 | 60·8 | 98·9 | — | 1·1 | 0·8 | 55·0 | 44·2 | 98·5 | — | 1·4 |
| — | 57·1 | 42·9 | 99·3 | — | 0·7 | 0·5 | 67·6 | 31·9 | 99·0 | — | 1·0 |
| — | 71·5 | 28·5 | 99·8 | — | 0·2 | 0·1 | 80·1 | 19·8 | 99·6 | — | 0·4 |
| $Ph_2O$ | $H_2O$ | Pr$^n$OH | $Ph_2O$ | $H_2O$ | Pr$^n$OH | $Ph_2O$ | $H_2O$ | Pr$^i$OH | $Ph_2O$ | $H_2O$ | Pr$^i$OH |
| 26·4 | 15·7 | 57·9 | 81·4 | 2·0 | 16·6 | 33·1 | 8·7 | 58·2 | 79·3 | 2·2 | 18·5 |
| 22·8 | 18·4 | 58·8 | 83·7 | 1·6 | 14·6 | 21·5 | 14·5 | 64·0 | 86·2 | 1·5 | 12·3 |
| 15·3 | 25·7 | 59·1 | 85·4 | 1·2 | 13·4 | 16·5 | 18·5 | 65·0 | 89·3 | 1·1 | 9·6 |
| 8·3 | 37·3 | 54·4 | 86·5 | 1·2 | 12·3 | 11·4 | 25·0 | 63·6 | 91·0 | 0·9 | 8·1 |
| 4·8 | 46·2 | 49·0 | 87·7 | 1·0 | 11·3 | 5·3 | 36·8 | 57·9 | 93·4 | 0·6 | 6·0 |
| 2·2 | 57·0 | 40·8 | 87·8 | 1·0 | 11·2 | 2·8 | 47·6 | 49·6 | 95·1 | 0·5 | 4·3 |
| 0·7 | 68·0 | 31·3 | 88·4 | 0·9 | 10·7 | 0·6 | 60·4 | 38·9 | 96·1 | 0·4 | 3·4 |
| 0·4 | 76·0 | 23·6 | 90·6 | 0·7 | 8·7 | 0·3 | 76·0 | 23·7 | 97·6 | 0·4 | 2·0 |
| 0·3 | 81·0 | 18·7 | 92·8 | 0·5 | 6·7 | 0·1 | 86·6 | 13·3 | 98·5 | 0·1 | 1·4 |
| 0·1 | 90·6 | 9·3 | 98·2 | 0·2 | 1·6 | | | | | | |
| $Ph_2O$ | $H_2O$ | Bu$^n$OH | $Ph_2O$ | $H_2O$ | Bu$^n$OH | $Ph_2O$ | $H_2O$ | Me·CO$_2$H | $Ph_2O$ | $H_2O$ | Me·CO$_2$H |
| — | 97·1 | 2·9 | 13·8 | 13·4 | 72·8 | 9·0 | 14·0 | 77·0 | 80·0 | 0·7 | 19·2 |
| — | 97·1 | 2·9 | 22·5 | 10·0 | 67·5 | 3·9 | 21·2 | 74·8 | 87·2 | 0·6 | 12·2 |
| — | 97·1 | 2·9 | 33·5 | 7·4 | 59·1 | 2·6 | 26·0 | 71·4 | 89·7 | 0·5 | 9·8 |
| — | 97·1 | 2·9 | 42·5 | 5·5 | 52·0 | 0·9 | 33·7 | 65·4 | 93·1 | 0·4 | 6·5 |
| — | 97·1 | 2·9 | 55·5 | 4·1 | 40·4 | 0·5 | 40·0 | 59·5 | 94·4 | 0·3 | 5·3 |
| — | 97·1 | 2·9 | 70·9 | 2·1 | 27·0 | 0·3 | 46·4 | 53·2 | 96·6 | 0·2 | 3·2 |
| — | 97·1 | 2·9 | 86·7 | 0·7 | 12·6 | 0·1 | 53·0 | 46·9 | 97·1 | 0·1 | 2·7 |
| | | | | | | 0·1 | 60·0 | 39·9 | 98·0 | 0·1 | 1·9 |
| | | | | | | — | 75·5 | 24·5 | 99·4 | — | 0·6 |
| $Ph_2O$ | $H_2O$ | Et·CO$_2$H | $Ph_2O$ | $H_2O$ | Et·CO$_2$H | $Ph_2O$ | $H_2O$ | Pr·CO$_2$H | $Ph_2O$ | $H_2O$ | Pr·CO$_2$H |
| 16·5 | 19·9 | 65·6 | 52·0 | 4·8 | 43·2 | 0·4 | 78·6 | 21·0 | 4·4 | 40·2 | 55·4 |
| 10·3 | 25·5 | 64·2 | 61·0 | 3·0 | 36·0 | 0·3 | 83·4 | 16·3 | 12·4 | 25·1 | 62·5 |
| 6·5 | 31·9 | 61·6 | 68·6 | 2·0 | 29·4 | 0·3 | 83·6 | 16·1 | 13·8 | 23·8 | 62·4 |
| 4·8 | 35·3 | 59·9 | 71·6 | 1·6 | 27·8 | 0·2 | 84·4 | 15·3 | 22·1 | 14·8 | 63·1 |
| 2·4 | 42·7 | 54·9 | 77·0 | 1·2 | 21·8 | 0·2 | 86·1 | 13·7 | 39·5 | 5·7 | 54·8 |
| 1·1 | 51·0 | 48·0 | 81·6 | 1·0 | 18·4 | 0·1 | 87·7 | 12·2 | 52·1 | 3·0 | 44·9 |
| 0·5 | 56·3 | 43·1 | 84·9 | 0·6 | 14·5 | 0·1 | 88·1 | 11·8 | 58·8 | 1·9 | 29·2 |
| 0·4 | 63·1 | 36·5 | 88·1 | 0·5 | 11·4 | 0·1 | 89·4 | 10·5 | 69·4 | 1·4 | 29·2 |
| 0·2 | 70·0 | 29·7 | 91·0 | 0·4 | 9·6 | — | 90·6 | 9·3 | 72·6 | 1·0 | 26·4 |
| | | | | | | — | 93·0 | 7·0 | 85·9 | 0·4 | 13·7 |
| | | | | | | — | 94·8 | 5·2 | 92·6 | 0·2 | 7·2 |

atmosphere of dry nitrogen. The reagent was used in a similar manner to determine the water content of the conjugate solutions. The method was also applied to determination of the water content of the water-rich layers in the system containing butanol. The tie-line data for the systems are tabulated in Table 4.

## DISCUSSION

The binodal curves and tie-lines for systems of diphenyl ether, water, and various third components are shown in Figs. 2—9, where the compositions are expressed in moles %. For the range of alcohols studied the slope of the tie-lines becomes less as the homologous series is ascended, and this feature, revealing as it does the increasing preference of the alcohol for the diphenyl ether layer, is most marked for butanol, which is only partially miscible with water. The same phenomenon is evident in the acid systems, and acetic acid strongly favours the aqueous phase while butyric acid favours the diphenyl ether phase to roughly the same extent. Although no simple relation is apparent between the position of the plait point in the phase diagram and the chain length of the alcohol, yet it is found that the summit concentration is given by 100—16·7*n*, where *n* is the number of carbon atoms in the alcohol molecule. A similar influence of homology is found in hydrocarbon–water–alcohol systems, where there is a decrement of about 21 moles % in the summit concentration for each additional carbon atom in the molecule of the third component. No such relation applies, however, when the third component is a fatty acid.

FIG. 2.

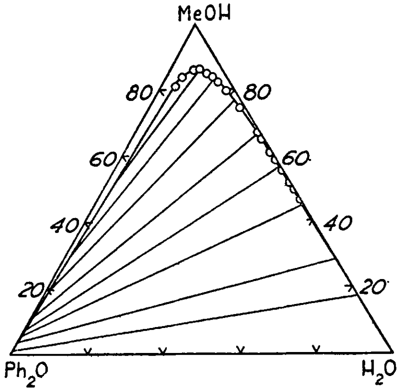


FIG. 3.

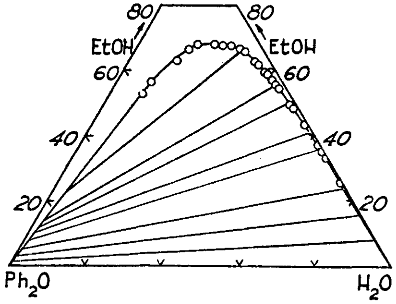


FIG. 4.

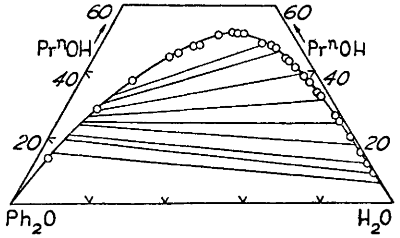


FIG. 5.

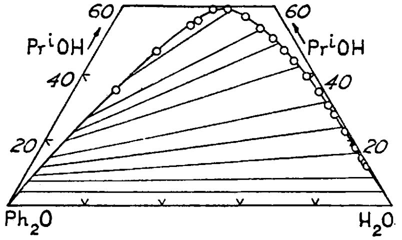


FIG. 6.

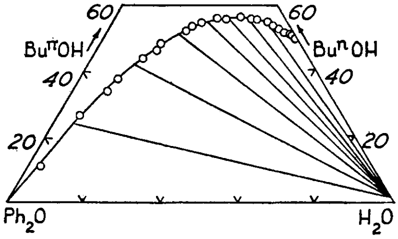


FIG. 7.

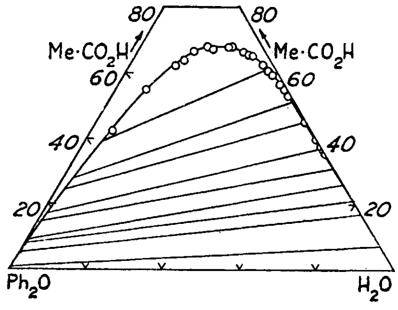


FIG. 8.

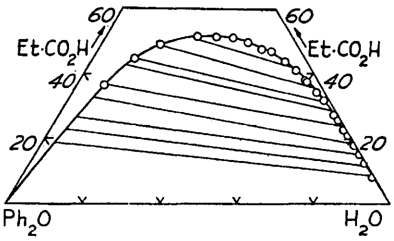
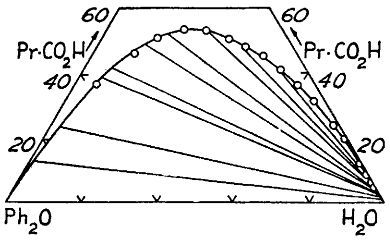


FIG. 9.



Solutropism involves the reversal of slope of the tie-lines, and the phenomenon has been shown to occur in some 30 systems when composition is in weight %, and in 35 systems when the composition is expressed in moles % (Smith, Stibolt, and Day, *Ind. Eng. Chem.*, 1951, **43**, 190). None of the systems examined in the present work is found to be solutropic on the former basis, but, as shown in Fig. 4, the system containing propanol exhibits the phenomenon when the composition is expressed in moles %.

According to Tarasenkov and Paulsen (*J. Phys. Chem., U.S.S.R.*, 1940, **14**, 1940), accurately determined tie-lines meet at a point focus when produced outside the binodal curve. In this connexion, Brancker, Hunter, and Nash (*Ind. Eng. Chem. Anal.*, 1940, **12**, 35) state that " insufficient information is available to determine whether the point focus is a general case and whether any deviations therefrom may be due, as is not completely improbable, to inaccurate tie-line data, to the presence of an unsuspected fourth component or to compound formation." The validity of the hypothesis can be tested on the systems under study inasmuch as the internal evidence shows that the tie-line data are of high precision. The test, which is made by plotting the data in terms of weight %, reveals that the systems containing methanol, ethanol, acetic acid, and propionic acid have tie-lines meeting at a point focus, whereas the tie-lines for each of the other systems meet to produce a caustic curve. In view of the close similarity between the chemical structures of the homologous components in these two types of system, it is highly improbable that compound formation is responsible for the different character of the tie-lines. We conclude accordingly that the point-focus hypothesis has no general validity and that tie-line correlation is not feasible on this basis.

The data obtained in the present work may also be used to assess the accuracy of the various methods of tie-line correlation. The reliability of the experimental measurements is shown by the fact that a smooth conjugation curve is obtained when the data are plotted in accordance with Coolidge's method (I.C.T., 1926, III, 398). The composition of each system at the plait point (corresponding to the intersection of conjugation and binodal curves) is given in section (*a*) of Table 5.

TABLE 5. *Composition in moles % at plait point.*

| Third component of system | (*a*) | | | (*b*) | | |
|---|---|---|---|---|---|---|
| | $Ph_2O$ | $H_2O$ | Third component | $Ph_2O$ | $H_2O$ | Third component |
| Methanol | 22·20 | 4·60 | 73·20 | 22·40 | 2·80 | 74·80 |
| Ethanol | 58·15 | 6·47 | 35·38 | 55·80 | 6·90 | 37·30 |
| *n*-Propanol | 29·70 | 24·30 | 46·00 | 39·10 | 19·50 | 41·40 |
| *iso*Propanol | 27·20 | 19·90 | 52·90 | 25·00 | 20·40 | 54·60 |
| Acetic acid | 39·10 | 7·80 | 53·10 | 25·30 | 12·00 | 62·70 |
| Propionic acid | 13·10 | 38·10 | 48·80 | 13·40 | 36·80 | 49·20 |
| *n*-Butyric acid | 0·05 | 92·10 | 7·85 | 0·05 | 92·70 | 7·25 |

According to Bancroft (*Phys. Review*, 1896, **3**, 21) and Lincoln (*J. Phys. Chem.*, 1900, **4**, 160), the equilibrium at constant temperature may be expected to conform to a mass-law equation of the type $(w_2/w_3)^m/(w_1/w_3) = K$, where $w_1$ and $w_2$ are the respective weights of immiscible liquids in a fixed weight $w_3$ of consolute liquid, and $m$ and $K$ are constants. The plot of log $(w_2/w_3)$ against log $(w_1/w_3)$ for each of the systems under study gives a sigmoidal curve, and the departures from the linear relation are much larger than can be accounted for by experimental error. The equilibrium in several systems was found by Hand (*ibid.*, 1930, **34**, 1961) to conform to the equation $X_{31}/X_{11} = k(X_{32}/X_{22})^m$, where $k$ and $m$ are constants, $X$ is weight fraction, and the subscripts refer to the three components, respectively. For the present systems, however, the logarithmic plot of $X_{31}/X_{11}$ against $X_{32}/X_{22}$ generally yields three straight lines of different slope as is found for other systems (Campbell, *Ind. Eng. Chem.*, 1944, **36**, 1158; Frere, *ibid.*, 1949, **41**, 2365). Although the equation is not applicable over the whole composition range, it may be used to determine the composition of the system at the plait point. The compositions evaluated in this way are recorded in section (*b*) of Table 5, and are more accurate than those listed in section (*a*) inasmuch as the plot based on Hand's relation is linear in the region of the plait point and extrapolation can be made with precision.

Bachman's method (*Ind. Eng. Chem. Anal.*, 1940, **12**, 38) has been extended by Othmer and Tobias (*Ind. Eng. Chem.*, 1942, **34**, 693), who find that a linear correlation is obtained by plotting log $[(1 - a_1)/a_1]$ against log $[(1 - b_2)/b_2]$, where $a_1$ is the fraction of the non-consolute liquid *a* in the layer mainly composed of *a*, and $b_2$ is the fraction of the other layer which is the non-consolute liquid *b*. Although for the majority of the systems examined in the present work the plot yields three intersecting lines, the superiority of the method is evident, and is further revealed by the fact that one straight line is obtained for the systems containing acetic acid and propionic acid, severally.

An interesting attempt to devise a variable ordinate scale based upon the tie-line relation of a " standard " system (water, toluene, acetic acid) has been made by Brancker, Hunter, and Nash (*loc. cit.*), who state that the plot of the relation between the weight percentages of the non-consolute liquids present in conjugate phases yields straight lines for a large number of systems, and that anomalies may be attributed to the presence of a fourth component or to inaccurate tie-line determinations. In this connexion, Dr. Brancker (personal communication) has pointed out that anomalies would also arise if there are factors retarding the attainment of equilibrium. When plotted on the above basis, the present data are found to conform to a linear relation over the entire composition range for the system containing ethanol, but the linear relation holds only over a limited range in the case of the other systems. Since there is no experimental evidence of compound formation in these systems, and independent tests reveal that the tie-line data are accurate and refer to completely equilibrated phases, it appears that the use of a variable ordinate scale in this way is not of general applicability.

We are indebted to Dr. A. V. Brancker for helpful discussion of the applicability of correlation methods.

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