LXIII.—*The System m-Xylene-Ethyl Alcohol-Water.*

By ALFRED HOLT and NORMAN MURRAY BELL.

THE present communication had its origin in some observations made by one of us while attempting to separate a substance dissolved in wet alcohol by means of *m*-xylene. It appears that in the presence of a large volume of *m*-xylene a very small quantity of water enables extraction to be carried out satisfactorily, and some rough experiments seemed to warrant the idea that the system *m*-xylene-ethyl alcohol-water was worthy of a further and more detailed examination.

The system resembles that of benzene-acetic acid-water studied by Waddell (*J. Physical Chem.*, 1898, **2**, 233) and benzene-alcohol-water. The latter system has been examined by Taylor (*ibid.*, 1897, **1**, 461), but the present investigation covers a somewhat more extended field of the physical properties.

Absolute ethyl alcohol and nearly pure *m*-xylene were employed, these substances, like ethyl alcohol and water, being miscible in all proportions. The question whether *m*-xylene and water are miscible to any appreciable extent has been tested by the determination of the freezing point of distilled water both before and after shaking with xylene, and also by treating xylene previously shaken with water with anhydrous copper sulphate. In both cases negative results were obtained, and very recently Campbell (*Phil. Mag.*, 1913, [vi], **26**, 1044) has shown that moisture does not affect the electrical resistance of *m*-xylene. For all practical purposes, these two liquids may, therefore, be regarded as non-miscible. The first series of experiments were directed to a determination of the amount of water which could be added to mixtures of xylene and alcohol of varying composition and at different temperatures without causing separation into two layers. The method of procedure was as follows: a known volume of xylene was taken, and successive equal small portions of alcohol were added. After each addition of alcohol, water was run in until a distinct milkiness was produced through separation of one phase in minute drops. The mixture was kept at constant temperature and was shaken repeatedly. Experiments at 98° were not easy, and had to be carried out in closed vessels, and it was also difficult to determine the end point on account of the boiling of the liquid.

Table I contains a summary of the results thus obtained, the values representing composition being expressed in mols. per cent.; whilst in Fig. 1 these values are represented graphically, mols. of

FIG. 1.

FIG. 2.

Mols. of alcohol in 100 mols. of alcohol-xylene mixture.

Mols. of water added to 100 mols. of alcohol-xylene mixture.

water being plotted against mols. of alcohol in 100 mols. of alcohol and xylene. The curved lines represent the isotherms.

Since, however, mols. per cent. is an inconvenient way of representing the system graphically, the results plotted in synthetic volumes (that is, vols. of water added to 100 vols. of a xylene-alcohol mixture) are given in Fig. 2, thus forming a direct comparison with Taylor's figures for the system benzene-alcohol-water.

TABLE I.

0°.			19°.			41°.		
Xylene.	Alcohol.	Water.	Xylene.	Alcohol.	Water.	Xylene.	Alcohol.	Water.
49.18	41.12	9.70	48.36	40.43	11.21	46.08	38.53	15.39
31.89	53.35	14.76	30.31	50.69	19.00	28.22	47.19	24.59
23.23	58.27	18.50	21.31	53.44	25.25	19.79	49.63	30.58
17.83	59.61	22.56	16.36	54.71	28.93	15.17	50.75	34.08
14.46	59.07	26.47	13.18	56.37	30.45	12.14	50.75	37.11
11.96	60.02	28.02	10.87	54.52	34.61	9.98	50.07	39.95
8.73	58.43	32.84	9.22	53.98	36.80	5.57	46.61	47.82
6.00	55.22	38.78	6.91	52.00	41.09	4.42	44.37	51.21
4.50	52.71	42.79	4.04	47.31	48.65	3.36	41.22	55.42
3.62	51.43	44.95	2.23	42.89	54.88	2.68	40.35	56.97

63°.			100°.		
Xylene.	Alcohol.	Water.	Xylene.	Alcohol.	Water.
44.35	37.08	18.57	18.81	39.56	41.63
33.22	41.67	25.11	7.59	38.24	54.17
28.14	47.06	24.80	3.75	40.97	55.28
21.63	45.22	33.15			
18.36	46.06	35.58			
15.87	46.44	37.69			
12.48	45.64	41.88			
9.93	45.66	44.41			
7.66	44.95	47.39			
4.19	40.35	55.46			

The isotherms for mols. per cent. mixtures containing up to about 70 per cent. of alcohol can be fairly represented by the expression:

$$\frac{\text{Percentage of alcohol}}{\sqrt[1.8]{\text{Percentage of water}}} = \text{constant } (K),$$

and for mixtures with a greater alcohol content by the expression:

Percentage of alcohol $\times \sqrt[1.4]{\text{percentage of xylene}} = \text{constant } (K')$,
the isotherms consisting of two curves of the same general shape. The accuracy of the values is shown in Fig. 3, where plotting the logarithms yields nearly straight lines.

Further, these lines are about equidistant, and as the temperature intervals were almost the same, it follows that the constant varies directly with the temperature. This relation is given by the expressions:

$$Kt_x = Kt - 0.085t_x$$

and

$$K't_x = K't_0 + 4.40t_x$$

as will be seen from the following table:

Temperature.	<i>K</i> .		<i>K'</i> .	
	Obs.	Calc.	Obs.	Calc.
0°	14.28	14.28	314	314
19	12.41	12.67	390	398
41	10.66	10.80	480	494
63	9.20	8.93	605	591
98	—	—	765	745

FIG. 3.

The synthetic volume isotherms for mixtures with an alcohol content from 0 to 75 per cent. can also be closely represented by the same expression :

$$\frac{\text{Percentage of alcohol}}{\sqrt{\text{Percentage of water}}} = \text{constant},$$

the temperature relation being in this case :

$$W_{t_x} = K - 0.125t_x.$$

where, as in the expressions above, K_{t_x} is the constant at a temperature t_x , and K_{t_0} the value at 0° .

In view of the fact that, under favourable conditions, it is not possible to determine the end-point of the phase of complete miscibility of the three liquids nearer than 0.1 to 0.2 c.c. water in a total mass of liquid of about 60 c.c., it is seen that if the xylene content is large, the error in the volume of water added may be very considerable, whilst, as has already been pointed out, with little xylene the conditions are unfavourable for a sharp end-point. The above values are, therefore, in quite fair agreement under the conditions of the experiments. Four tie-lines were determined, and are represented by the lines TT' , T_2T_2' , T_3T_3' , and T_4T_4' in Fig. 2. The composition of the conjugate solutions was arrived at by different methods of analysis, and since the tie-lines have practically a common vanishing point V , it follows that they must possess considerable accuracy. In the first method the xylene was separated from the mixture by the addition of a large excess of water. Its volume was measured, and thence the percentage volume in the phase under investigation, the amounts of alcohol and water being calculated by the formula already given.

This procedure assumes that by the addition of a large volume of water all the xylene is separated, a point to which reference will be made later, but for mixtures rich in xylene it probably gives fairly true values. When, however, little of the hydrocarbon is present, the great volume of water necessary for its separation tends to prevent accurate estimation through breaking the xylene phase into small globules which cannot readily be brought together. In a variation of this method the density of the phase was first determined, and then the xylene was separated and its percentage volume measured. From the data thus obtained, the density and composition of the mixture of alcohol and water, after removal of the xylene, could be calculated. Thus it was possible to arrive at a direct measure of the volumes of each constituent liquid. On account of the contraction resulting from the admixture of water and alcohol, all calculations had to be carried out in terms of weight per cent., and finally transformed into volumes.

This method is probably most suitable for mixtures poor in xylene, for the amount of hydrocarbon left in the solution after addition of water would be relatively very small compared with the alcohol content, and hence analysis of the alcohol-water mixture by density should give good results. The tie-line $T'T'$ was determined in a totally different manner. It was observed that when water was gradually added to mixtures of xylene and alcohol varying from 75 to 25 per cent. by volume of xylene, the phase rich in the hydrocarbon separated initially as the lower layer, but on increasing the amount of water, a critical point could be obtained when the conjugate solutions had the same specific gravity. Further additions of water placed the xylene layer on top. Determinations with these different mixtures of xylene and alcohol showed that this critical density composition lay in each case in the same straight line, hence there is only one phase rich in xylene, and one rich in alcohol, which have identical specific gravities; consequently the line passing through the points is a tie-line. In Fig. 2 it is seen that it vanishes in the same point as the others.

The letters K , K_1 , K_2 , K_3 , and K_4 in the figure represent the points when the tie-lines become non-existent, and the dotted line shows that, at any rate, over a temperature ranging from 0° to 98° they lie on an almost straight line. From an inspection of the form of the isotherms it is, however, clear that at temperatures above 100° , the line joining them will have an upward trend.

The following table gives the analyses of the conjugate solutions for each tie-line, and is expressed both in mols. per cent. and synthetic volumes.

TABLE III.

Tempera- ture.	Xylene phase.		Alcohol phase.	
	Mols. per cent. of xylene.	Vol. per cent. of xylene.	Mols. per cent. of xylene.	Vol. per cent. of xylene.
0°	80.18	91.22	0.93	3.40
0	69.95	85.10	2.29	7.20
19	82.12	91.29	1.05	3.80
19	58.40	78.30	5.27	15.26

The connexion between the volume of xylene phase separated and the amount of water added is given in the following table:

TABLE IV.

Composition of 100 c.c. of xylene-alcohol mixture taken, 75.11 c.c. of xylene 24.89 c.c. of alcohol.		Composition of 100 c.c. of xylene-alcohol mixture taken, 50.15 c.c. of xylene 49.85 c.c. of alcohol.		Composition of 100 c.c. of xylene-alcohol mixture taken, 25.01 c.c. of xylene 74.99 c.c. of alcohol.	
Vol. of water added to 100 c.c. of above mixture.	Vol. of phase rich in xylene which separates.	Vol. of water added to 100 c.c. of above mixture.	Vol. of phase rich in xylene which separates.	Vol. of water added to 100 c.c. of above mixture.	Vol. of phase rich in xylene which separates.
2.11 c.c.	—	6.30 c.c.	—	15.92 c.c.	—
2.65 "	85.00 c.c.	6.80 "	27.00 c.c.	18.45 "	6.25 c.c.
3.15 "	82.55 "	7.80 "	34.75 "	19.70 "	8.50 "
3.79 "	80.75 "	8.80 "	38.50 "	22.20 "	12.25 "
6.40 "	78.75 "	9.80 "	42.00 "	27.70 "	16.25 "
8.79 "	78.25 "	11.30 "	44.50 "	Xylene phase changes from bottom to top with 17.2 c.c. of water.	
13.90 "	77.50 "	14.05 "	46.25 "		
Xylene phase changes from bottom to top with 4.39 c.c. water.		22.80 "	49.00 "		
		Xylene phase changes from bottom to top with 10.8 c.c. water.			

Reference to Fig. 2 shows that proceeding along the isotherm for 19° the phase rich in xylene separates out as the top layer between the points *A* and *T*, and as the bottom layer between *T* and *K*, and that above about 64° two phases with the same specific gravity cease to exist.

MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,
THE UNIVERSITY, LIVERPOOL.