8. *The Solubility of Water in Benzene Solutions of Ethanolamine Oleate.*

By Richard C. Pink.

Solutions of ethanolamine oleate in benzene and other organic solvents dissolve relatively large amounts of water. The absorption of the water is accompanied by a rise in the viscosity of the system. Small quantities of various phenols increase the amounts of water taken up to a remarkable extent.

In a recent paper on water-in-oil emulsions (this vol., p. 1252), in which the effect of adding water to solutions of magnesium oleate in benzene was described, the author showed that small quantities of water were first dissolved by the solution and that further addition of water caused practically complete precipitation of the soap in a form containing water. It was found that the amounts of water taken up before precipitation of the hydrated soap commenced were proportional to the concentration of the magnesium oleate.

This power of taking up water possessed by solutions of soap in organic solvents has already been observed by Weichherz (*Kolloid-Z.*, 1929, **49**, 158), and the phenomenon is undoubtedly related to the property which aqueous soap solutions possess of dissolving various organic substances (Pickering, J., 1907, **91**, 2001; 1917, **111**, 86; Lester Smith, *J. Physical Chem.*, 1932, **36**, 1401, 1672, 2455; Lawrence, *Trans. Faraday Soc.*, 1937, **33**, 325; *Proc. Roy. Soc.*, 1935, *A*, **148**, 59). Weichherz examined, in great detail, the effect of adding water to solutions of phenol and sodium oleate in xylene, and showed that small quantities were dissolved by such systems; *e.g.*, the ternary system consisting of xylene 79·94%, phenol 12·91%, and sodium oleate 7·15%, remained homogeneous after the addition of 4·66% of water. This absorption of water could not be explained on the basis of the mutual solubility of the constituents of the mixture, and must have been caused by adsorption at the interface soap–xylene, or possibly by internal solution in the soap micelle. In a previous paper (*Kolloid-Z.*, 1929, **47**, 133) Weichherz had shown that the xylene–sodium oleate solution alone did not possess the power of dissolving water. Addition of water caused, instead, the formation of an oil-continuous emulsion, and further additions caused the inversion of this system to one in which water was the continuous phase.

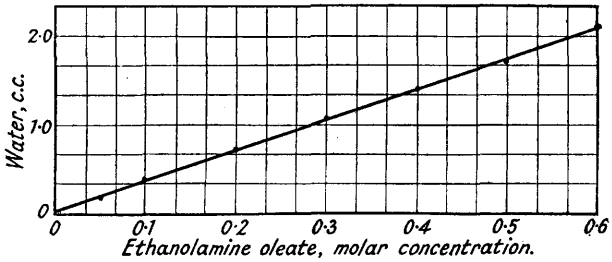
It is now shown that when water is added to a solution of ethanolamine oleate in benzene (or certain other solvents) and the mixture is vigorously shaken, the water is rapidly taken up, and a clear solution is obtained. Further addition of water causes the precipitation of the soap in a white curdy form, and the addition of much water brings about an inversion of the system. Water becomes the external phase and a very stable oil-in-water emulsion is formed. Ethanolamine oleate normally gives rise to this type of emulsion when dissolved in water (Cheesman and King, *Trans. Faraday Soc.*, 1938, **34**, 594). This inversion from the oil-continuous to the water-continuous type of system can be shown readily by means of drop tests (Briggs, *J. Physical Chem.*, 1914, **18**, 34) or, better, by the electrical conductivity method (Clayton, *Brit. Assoc. Colloid Reports*, 1918, **2**, 114). Cheesman and King (*loc. cit.*) have noted that ethanolamine soaps can stabilise both types of system, and the oil-continuous system was described by them as a water-in-oil emulsion. Microscopic examination indicated that the heterogeneous oil-continuous systems examined in the course of this investigation, in which the oil was benzene, toluene, or xylene, resembled more closely the " quasi-emulsions " described by Briggs and Schmidt (*J. Physical Chem.*, 1915, **19**, 478).

EXPERIMENTAL.

Absorption of Water by Solutions of Ethanolamine Oleate in Benzene, Toluene, and Xylene.—A M-solution of ethanolamine oleate in the organic solvent was prepared and diluted to the required concentrations (*C*, in mols./l. of solution). The solvents were previously rendered anhydrous by standing over sodium and redistillation immediately before use. The oleic acid was obtained from Kahlbaum and the ethanolamine was a specially purified sample.

The experiments were carried out in 4-oz. glass-stoppered bottles. 50 C.c. of the soap solution were introduced into the bottle, water was added from a microburette, and the mixture was vigorously shaken by hand after each addition until the water had been taken up and a clear solution was obtained. The point was recorded at which the last small addition of water caused the appearance of a faint cloudiness. Each experiment was carried out a number of times and the probable error in the readings was not greater than 0·02 c.c. The results are summarised below, and those for benzene are also shown graphically in Fig. 1.

FIG. 1.

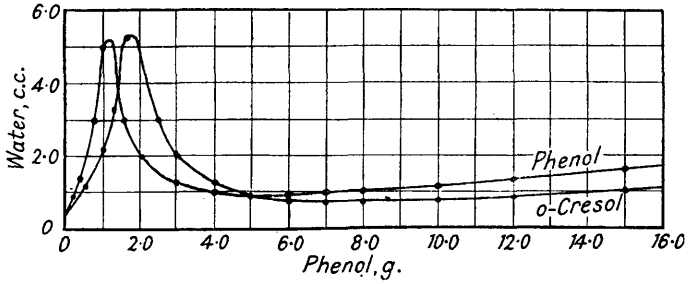


	C.c. of H_2O dissolved per 50 c.c. of solution.				C.c. of H_2O dissolved per 50 c.c. of solution.		
c.	C_6H_6.	C_6H_5Me.	$C_6H_4Me_2$.	*c.*	C_6H_6.	C_6H_5Me.	$C_6H_4Me_2$.
0·05	0·18	0·17	0·18	0·40	1·40	1·32	1·36
0·10	0·38	0·34	0·36	0·50	1·70	1·68	1·68
0·20	0·70	0·68	0·69	0·60	2·08	2·03	2·07
0·30	1·06	1·05	1·08	0·70	2·35	2·34	2·36

No readings could be obtained for 0·8M or greater concentration, for in these cases, after the addition of a small amount of water, the solutions became so viscous as to make accurate measurements impossible. It will be seen from the figure that the quantities of water dissolved by the soap solutions are proportional to the concentration of the soap. The viscous systems were examined with the aid of the polarising microscope and found to be isotropic optically. Although the dry solutions of the soap showed little tendency to foam, the solutions to which water had been added formed an exceedingly stable foam when shaken, especially when just insufficient water had been added to cause the precipitation of the soap.

The marked effect of phenol on the system xylene–sodium oleate has already been noted. A similar effect has been observed when phenols are added to the benzene–ethanolamine oleate system. The addition of small quantities of phenol or one of its homologues increases the quantity of water dissolved to a remarkable extent. Thus, if to one of the bottles to which sufficient water had been added to bring about precipitation of the soap, a small amount of phenol was added and the bottle was vigorously shaken, a clear solution was obtained with a much smaller tendency to form a stable foam. Addition of further quantities of phenol caused the solution to become cloudy again. This effect was examined more closely as follows. Weighed amounts of phenol were added to solutions of ethanolamine oleate in benzene, and water was added as before, until the solutions became cloudy. Each solution contained 39·04 g. of benzene and 3·43 g. of ethanolamine oleate. At the concentration of phenol at which the maximum amount of water was taken up, a strong greenish opalescence developed when a certain amount of water had been added, and after some time the solution became cloudy. Experiments were carried out with *o*-, *m*-, and *p*-cresols, and in each case a very similar effect was observed. The results for phenol and *o*-cresol are shown in the following table and also graphically in Fig. 2.

FIG. 2.



The amount of water taken up by the soap solution increases rapidly on the addition of small amounts of the phenol, and then decreases to about the original amount when more phenol is added.

Ph·OH, g.	H_2O, c.c.	Ph·OH, g.	H_2O, c.c.	Ph·OH, g.	H_2O, c.c.
0·00	0·45	2·50	1·55	7·00	0·90
0·30	1·30	3·00	1·25	8·00	1·05
0·75	3·00	4·00	0·95	10·00	1·13
1·00	4·90	5·00	0·80	12·00	1·40
1·50	3·00	6·00	0·85	15·00	1·68
2·00	1·90				

o-Cresol, g.	H_2O, c.c.	*o*-Cresol, g.	H_2O, c.c.	*o*-Cresol, g.	H_2O, c.c.
0·00	0·45	2·50	3·00	7·00	0·65
0·50	1·13	3·00	1·90	8·00	0·75
1·00	2·15	4·00	1·30	10·00	0·75
1·25	3·30	5·00	0·80	12·00	0·80
1·50	5·30	6·00	0·70	15·00	1·00
2·00	4·80				

A complete explanation of these phenomena must be deferred until more information is obtained on the nature of soap solutions in organic solvents. Work along these lines is being carried out in these laboratories. The results, however, indicate that the general rule, stated by Weichherz (*loc. cit.*), that a wholly or partly hydrated soap is insoluble in hydrocarbon solvents, is invalid.

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