445. *The Occurrence of Two Liquid Phases and of a Minimum Density in the System Carbon Disulphide–Ethylene Dichloride.*

By Dalziel Ll. Hammick and John Howard.

It was shown by Whatmough (*Z. physikal. Chem.*, 1902, **39**, 129) that the composition–surface tension curve for mixtures of carbon disulphide and ethylene dichloride at 20° passes through a well-defined minimum. The surface tensions of the pure components being very nearly the same, this fact must be taken to mean that the van der Waals forces between the two types of molecule are less than the forces between the molecules of the pure substances themselves. It thus seemed probable that mixtures of the two liquids would separate into two liquid layers, and an investigation of solid–liquid equilibria in the system was therefore undertaken. Not only was this anticipation fulfilled, but, in addition, a minimum was found in the composition–density curve in the region of the equimolecular mixture.

Purification of Materials.—Carbon disulphide. A good commercial specimen was shaken for 3 hr. with 3 portions of $KMnO_4$ aq. (5 g./l.), then twice for 6 hr. with Hg, and finally with $HgSO_4$ aq. (2·5 g./l.). After drying over $CaCl_2$, it was fractionated to 0·2°; b. p. 46·3°, $D_{4^\circ}^{24\cdot7^\circ}$ 1·2563.

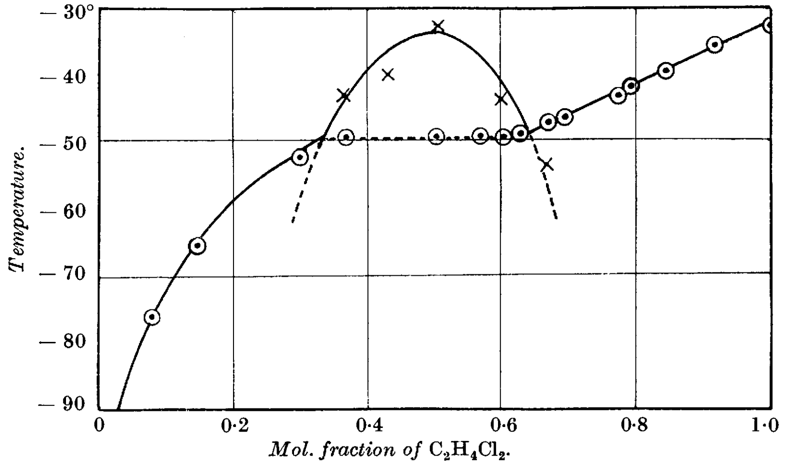
Ethylene dichloride. A Kahlbaum specimen was repeatedly fractionated with a 10-bulb Young column and a fraction obtained of b. p. 83·4—83·6°; the first and the last portion of this fraction had $D_{4^\circ}^{24\cdot7^\circ}$ 1·2444.

Temperatures of Solid–Liquid Equilibrium.—Mixtures of the two components were placed in a test-tube which was surrounded by a double air jacket, P_2O_5 being placed in the annular air spaces to prevent condensation of moisture. The jacketed tube was placed in a bath of liquid air, the solution in the innermost tube being stirred mechanically. Temps. were read on a C_5H_{12} thermometer previously standardised by determinations of the f. p.'s of pure CCl_4 (−23·0°), $CHCl_3$ (−63·2°), and CS_2 (−110°). Well-marked arrests were obtained, reproducible to ±1·0°. These results are given in Table I and are plotted in the fig. (The m.p. of $C_2H_4Cl_2$ was found to be −32·5°.)

TABLE I.

$C_2H_4Cl_2$, mols. % ...	0·0	8·0	14·8	30·4	36·7	50·2	56·8
Temp.	−110°	−77°	−66°	−53°	−49·5°	−49·0°	−49·0°
$C_2H_4Cl_2$, mols. % ...	60·4	62·7	67·0	69·7	77·4	84·7	91·8
Temp.	−49·5°	−48·5°	−47·3°	−46·5°	−43·0°	−39·5°	−35·5°

The flat portion of the curve at about −50° indicated that separation into two liquid layers had probably occurred. Direct observation being impossible under the conditions of the above solubility expts., mixtures were sealed into glass bulbs of about 2 c.c. capacity and immersed in a bath of ligroin which had been cooled in liquid air to the desired temp. Mixtures having compositions corresponding to the flat part of the solubility curve became turbid at various temps. below about −30°. Owing to the small difference between the densities of the components, distinct liquid layers were not observed and the temps. of complete miscibility could be determined only approx. (± 3°). The results are given below and are shown as crosses on the fig. :



$C_2H_4Cl_2$, mols. %	36·7	43·6	50·2	60·4	67·0
Temp.	−46°	−40°	−33°	−44°	−53°

The departure of the two liquids from the condition of ideal miscibility even at 50° above the crit. solution temp. is shown in Table II, where the densities of a series of mixtures are given : they were determined in a 12 c.c. pyknometer at 24·7° and are probably correct to 1 part in 10,000. The min. is at about 50%.

TABLE II.

$C_2H_4Cl_2$, mols. % ...	5·00	7·99	14·75	17·50	22·50	30·37
$D_{4°}^{24·7°}$	1·2563	1·2491	1·2445	1·2432	1·2417	1·2378
$C_2H_4Cl_2$, mols. % ...	43·58	56·76	69·66	84·73	91·96	100·0
$D_{4°}^{24·7°}$	1·2355	1·2353	1·2368	1·2400	1·2419	1·2444

THE DYSON PERRINS LABORATORY,
OXFORD.

[*Received, November 26th, 1932.*]