CLXXI.—*A Method for Determining the Solubility of Sparingly Soluble Substances.*

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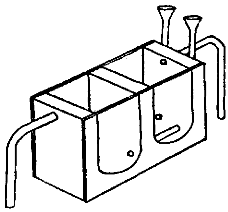
THE methods available for determining the solubility of sparingly soluble substances are of limited application. Electrical measurements are restricted to electrolytes, and chemical analysis is useful for only a few substances. The optical method now described can, however, be employed more generally.

For this work, an interferometer of the type described by Jamin (*Ann. Chim. Phys.*, 1858, **52**, 171) was constructed. Mercury green light ($\lambda = 5461$) was used throughout as the source of illumination. A special form of double cell was required in which liquids could be circulated through each compartment (Fig. 1). It was cut from a rectangular block of brass (2·5 cm. broad), and was fitted with inlet and outlet tubes of the same metal. The sides were made of the best quality optical glass cemented in position. Both compartments of the cell were first filled with water, and the compensator was adjusted so that the cross wires of the observing telescope coincided with one of the interference bands. When a dilute aqueous solution was gradually allowed to displace the water in one half of the cell, there was a movement of the bands. By means of a fine adjustment on the compensator the same band could be kept on the telescope cross wires.

FIG. 1.



Over the range considered, the compensator readings increased in proportion to the number of bands displaced, and therefore to the difference in refractive index between the contents of the two compartments of the cell (Table I).

TABLE I.

Bands.	0.	2.	4.	6.	8.	10.	12.	14.	16.	18.	20.
Compensator readings ...	10	13·6	17·0	20·5	24·0	27·7	31·5	35·0	39·0	43·0	46·5

As a preliminary it was necessary to investigate the nature of the curves correlating compensator readings and concentration. To do this, a number of saturated solutions of substances slightly soluble in water were prepared at room temperature. A series of dilutions of each was made, and these together with a quantity of water were allowed to stand until all were at the same temperature. Both divisions of the cell were then filled with water, and the zero-reading was taken. Water was allowed to circulate through one compartment, and the most dilute solution through the other. When no further movement of the bands took place, the reading was noted. The next solution was then allowed to displace the more dilute, and so on till the saturated solution was reached. A number of results are shown in Table II and Fig. 2. All substances so far investigated give straight lines with the exception of benzene. In view of this exception, it will always be necessary to plot a graph of % *saturation* against *compensator readings* as a preliminary to a solubility determination by this method. When the graph is a straight line, only one weighing is necessary to calibrate the concentration scale, and if the reading for the saturated solution is

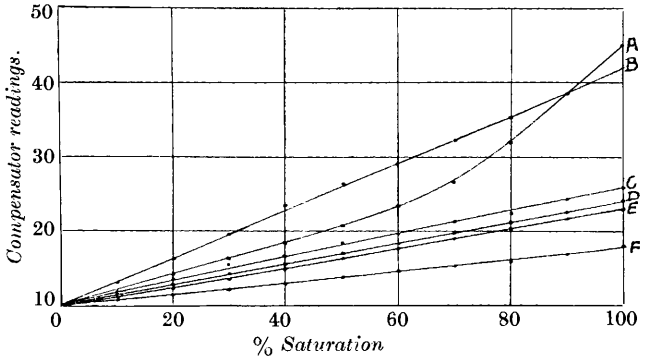
TABLE II.

Compensator readings for % saturation.

Substance.	0.	10.	20.	30.	40.	50.	60.	70.	80.	90.	100
Benzene	10·0	12·0	14·3	16·2	18·5	20·8	23·5	26·5	32·0	38·5	45·0
Camphor	10·0	12·8	16·3	19·8	23·6	26·7	29·0	32·2	35·6	38·7	43·2
sec.-Octyl alcohol	10·0	12·4	14·0	15·5	16·8	18·8	20·0	21·5	22·4	24·5	26·0
Borneol	10·0	11·5	12·8	14·1	15·3	16·7	18·3	19·4	20·8	22·3	24·0
Methyl salicylate	10·0	11·0	12·2	13·5	15·0	16·4	17·9	19·1	20·3	21·6	23·0
Naphthalene......	10·0	11·0	11·5	12·0	12·6	13·7	14·3	14·8	15·5	16·8	18·1

determined the weight of the solute present in it can be found graphically by extrapolation. In practice, it is advisable to prepare one or more dilutions from the solution of known concentration so that there may be a gradual movement of the bands without blurring. Should the graph not be a straight line, a number of weighings would be necessary and the method would lose its merit of simplicity.

FIG. 2.



A. *Benzene*. B. *Camphor*. C. sec.-*Octyl alcohol*. D. *Borneol*. E. *Methyl salicylate*. F. *Naphthalene*.

When a solubility is required at a temperature other than room temperature, a saturated solution is prepared at that temperature and separated off; then, if necessary, a known quantity of water is added so that the solute will remain completely in solution at the temperature of the room in which the readings are taken. The saturated solutions were prepared in stoppered bottles which were rotated in a thermostat with excess of solute for several hours at the required temperature. Table III shows a number of results.

As an indication of the accuracy with which these results could be reproduced, it may be mentioned that a duplicate determination with lead sulphate gave the same value as shown, *i.e.*, 0·032 at 15°,

TABLE III.

[In each case, Solution A_1 was made up as shown in column 2, and Solution A_2 was a two-fold dilution of A_1. These were used for the standardisation, by means of which the concentrations of B_1 (saturated) and B_2 (half-saturated) were deduced from their compensator readings.]

		Compensator readings.					
Substance.	G. of substance in 1000 c.c. of water.	Soln. A_1.	Soln. A_2.	Soln. B_1.	Soln. B_2.	Temp.	Solubility (g. per 1000 c.c. of water).
Naphthalene ...	0·0200	14·0	12·0	14·5		15°	0·022
					14·0	25	0·040
Lead sulphate	0·0250	11·4	10·7	11·8		15	0·032
Borneol	0·5000	18·3	14·3	21·4		15	0·693
					16·2	25	0·740
sec.-Octyl alcohol	1·0407	19·0	14·5	23·5		15	1·508
				21·5		25	1·280

and two additional experiments with borneol gave the following results : 0·697, 0·697 at 15° ; 0·740, 0·734 at 25°.

Water has been used as solvent in these experiments, but the method could be extended to other solvents if they are not too volatile.

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