Notes

CHROM. 4752

A rapid method of determining isothermal vapour–liquid equilibria

Several articles have appeared in the literature on the determination of vapour–liquid equilibria by gas chromatography[1-5]. WICHTERLE et al.[4,5] have designed an all-glass isothermal vapour–liquid equilibrium cell which is attached directly to the gas chromatograph. With the aid of this cell it is possible to determine these equilibria much more rapidly and with very much smaller samples than by the classical distillation methods. Partial pressures have also been determined by the same means[5].

We have found an even simpler method of determining isothermal vapour–liquid equilibria. The system involves the use of a lockable gas-tight syringe and an ampoule fitted with a silicone rubber septum. The results obtained are in good agreement with those obtained by WICHTERLE AND BOUBLIKOVA[5].

Apparatus

The equilibrium vessel used in this work was made by sealing off the bottom end of a Quickfit* ST 10/2T sleeve to give an ampoule having a screw thread at its upper end which can be sealed with a silicone rubber septum by means of the plastic screw cap supplied with the Quickfit sleeve. Such ampoules are also commercially available.

The sampling device is a 1 ml series A Pressure-Lok** gas syringe. This syringe is claimed to be pressure tight to 250 p.s.i. and can be sealed by twisting the needle. This permits a sample of vapour to be drawn into the syringe and locked in it prior to withdrawing the needle from the ampoule. However, as the syringe is at ambient temperature there is a tendency for part of the vapour to condense, so that it is not possible to inject the vapours directly into the gas chromatograph. To overcome this difficulty a small quantity of solvent was placed in the syringe prior to sampling. The vapours are dissolved in the solvent and the solution was then analysed.

Procedure

Approximately 1 ml of the mixture whose isothermal vapour–liquid equilibrium is to be determined is placed in the ampoule together with a small Teflon coated magnet. The ampoule is sealed with a silicone rubber septum by means of the plastic screw cap. As the latter has a relatively large orifice it is advisable to place a washer having a small central hole above the septum to keep it from being blown out in the event of pressure build-up. The sealed ampoule is placed vertically in a thermostatted bath so that it is almost totally immersed and the contents stirred magnetically.

A quantity of 0.1 ml of a solvent (preferably with a higher boiling point than the materials to be analysed) is placed in the 1 ml Pressure-Lok syringe, in the following manner:

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* Quickfit and Quartz Ltd., Stone, Staffordshire, Great Britain.
** Catalog No. 010033, Precision Sampling Corp., Baton Rouge, La., U.S.A.

The needle of the Pressure-Lok syringe is removed by unscrewing the locking mechanism and withdrawing the needle from the Teflon plug at the bottom of the syringe. The plunger is set slightly above the 0.1 ml calibration mark, the syringe inverted and 0.1 ml of the solvent injected into the syringe through the hole in the Teflon plug with the aid of another syringe. The needle is now replaced with the syringe still inverted and the syringe locked. This method of loading the syringe prevents contamination of the needle with solvent and therefore avoids any possibility of contaminating the sample in the equilibrium cell.

When the ampoule and its contents have reached the desired temperature the needle of the syringe is forced through the septum into the vapour space of the test tube, the needle allowed to warm up and the plunger raised to the 0.8 ml graduation mark. This creates a vacuum in the syringe and on opening the locking device vapours are drawn into the syringe. The needle is left open for a few seconds, relocked and withdrawn. The syringe is shaken thoroughly so that the vapours dissolve in the solvent and the contents are then ejected into a small test tube and analysed in the usual manner by gas chromatography. The solvent peak is of course not involved in the calculations; it must, however, be well separated from the other peaks.

As initially there is a tendency for liquid to condense on the cold needle it is advisable to penetrate the septum at an angle so that if a drop of liquid forms at the tip of the needle it can be removed by touching the needle tip on the ampoule wall.

Discussion and results

As it is only necessary to determine the ratio of the components, the volumes of solvent and vapour taken are not critical. Nor is it necessary to remove air from the ampoule. This can, however, be done by freezing the ampoule contents and penetrating the septum with a needle attached to a vacuum line.

The results for n-hexane–toluene at 70° obtained by this method using m-xylene

TABLE I

VAPOUR–LIQUID EQUILIBRIUM DATA OF THE n-HEXANE-TOLUENE SYSTEM AT 70°

x_1	y_1
0.000	0.000
0.083	0.292
0.169	0.533
0.258	0.558
0.352	0.677
0.449	0.736
0.548	0.799
0.654	0.837
0.764	0.906
1.000	1.000

as solvent are given in Table I and plotted together with those obtained by WICHTERLE AND BOUBLIKOVA[5] in Fig. 1.

An attempt to determine partial pressures by the use of a solvent containing an internal standard proved unsuccessful. Although the amount of solvent in the
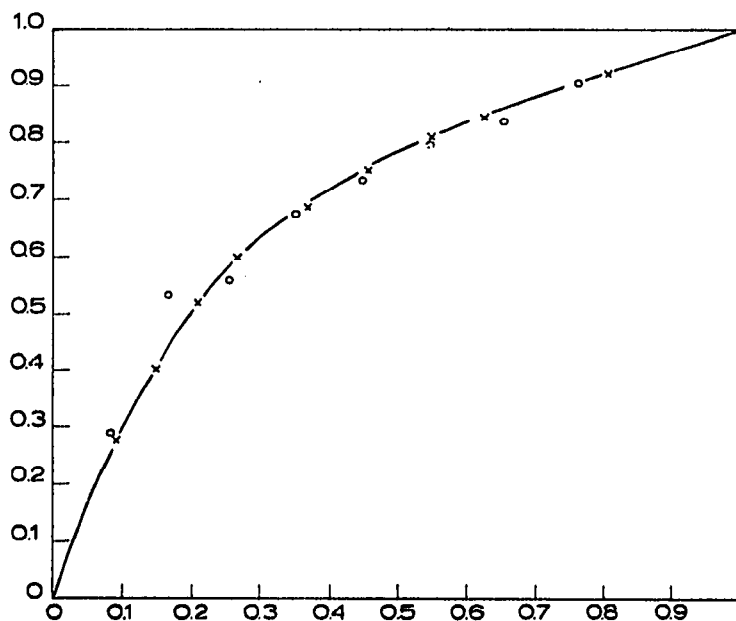
Fig. 1. x–y diagram of n-hexane–toluene system at 70°. ◯, This work; ×, results obtained from ref. 5.

syringe can be measured accurately the volume of vapour sampled cannot be determined. The fact that the syringe is at ambient temperature and that it contains a solvent for the vapours causes vapour to condense in the syringe during the sampling. As a result the volume of vapour that enters the syringe is larger than the volume set by the piston of the syringe.

This system is therefore only suitable for the determination of the relative vapour composition but for this purpose it is much simpler than the equilibrium cell used by WICHTERLE AND BOUBLIKOVA[5].

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Received March 25th, 1970