ANALYTICAL APPLICATIONS OF LIQUID-LIQUID PHASE EQUILIBRIA: ANALYSIS OF BINARY MIXTURES OF CHEMICALLY SIMILAR COMPONENTS

MOHINDER PAL*

Chemistry department, Indian Institute of Technology, New Delhi 110016, India

*Present Address and Address for correspondence- ONGC, 8th Floor, Core-IV, SCOPE Minar, Laxmi Nagar, New Delhi-110092

Summary

A new, simple and rapid method based on the principle of liquid-liquid phase equilibria has been developed for the analysis of binary mixtures of chemically similar organic compounds. The method does not require elaborate instrumentation and can be used to analyse mixtures of members of homologous series. The application of the method has been illustrated by analysing binary mixtures of n-hexane and n-octane where the maximum uncertainty in analysis is about 2%.

Analysis of binary and ternary mixtures of organic compound by phase titration is based on the appearance of a second phase in a homogeneous liquid mixture, giving a turbidimetric end point. In this communication a method is described, based on liquid-liquid phase equilibria, for the analysis of binary mixtures made up of chemically similar organic compounds. Many of these mixtures cannot be analysed by procedures based on chemical reactions because these are usually slow or incomplete, and various interfering consecutive reactions may occur when the system is allowed to proceed to equilibrium. The proposed method is illustrated by its application to the analysis of mixtures of n- hexane and n-octane.

The phase diagram for a ternary system containing one pair of mutually immiscible or only partially miscible components A and B and consolute components C shall be made. If a further substance A’ is chemically similar to A, it will have similar solubility behaviour towards pure B and C. However, the effect of the consolute component on the miscibility of A’ and B will be different from that on the miscibility of A and B, and therefore the binodal curve for the system A-B-C will be different from that for A’-B-C.

For a pseudo-ternary system composed of (A+ A’), B and C, the binodal curve will lie somewhere between the binodal curves for the systems A-B-C and A’-B-C and its locus will depend upon the relative amounts of A and A’ in the mixture.

A ternary mixture A-B-C having the composition represented by the point O in Fig.1 will split into two different phases represented by points L and M (where LM is the tie line). The relative amounts of the two phases are given by the lever rule i.e.

\[
\text{Amount of phase of composition L} = \frac{OM}{OL}
\]

\[
\text{Amount of phase of composition M}
\]

The corresponding ternary mixture A’-B-C defined by O will similarly separate into two phases having the compositions represented by the points L’ and M’, the relative amount being given by the ratio OM’/OL’. It is, therefore, evident that on gradual replacement of A
by A' (i.e. increasing the ratio A'/A) in the pseudo-ternary mixture (A+A')-B-C, the relative amounts of the two phases will move from OM/OL to OM'/OL'. A calibration curve can, therefore, be obtained for the relative amounts of the two phases in the pseudo-ternary mixture (A+A')-B-C as a function of %A/ (%A+%A'). From a knowledge of the binodal curve for the ternary mixture A-B-C and A'-B-C, a position of point O can be computed that will give a large difference between the ratios OM/OL and OM'/OL'. One possible route to obtain optimum precision is to keep OM fairly small, so that the difference (OM'-OM) is much larger than the difference (OL'-OL). The method holds good even when the tie lines for the ternary mixtures A-B-C and A'-B-C are not parallel. The effect of the difference in the slope of the tie lines is taken into account in the calibration curve.

**FIG. 1.** Phase diagram and relative amounts of two equilibrium phases corresponding to the ternary composition at point O for the system A-B-C (——) and A'-B-C(-------)

**EXPERIMENTAL**

**Materials**

Analytical-reagent grade samples of the n-hexane and n-octane were purified by fractional distillation. Laboratory reagent grade acetone was refluxed over potassium permanganate, distilled and stored over anhydrous potassium carbonate. The solvents were fractionally distilled immediately, before use. Distilled water was used throughout.

**Determination of binodal curves for the ternary mixtures A-B-C and A'-B-C**

The binodal curves for the hydrocarbon-acetone-water mixtures were obtained by titrating a set of binary mixtures of hydrocarbon and acetone with water and another set of binary mixtures of water and acetone with hydrocarbon, to a turbidimetric end point. Details of the apparatus, experimental techniques, figures and tables giving data shall be given in full paper.

**Calibration curves**

To obtain the calibration curve, a set of binary mixtures of n-hexane and n-octane covering the entire w/w composition range was prepared. Seven ml of the hydrocarbon mixture, 37 ml of acetone and 6 ml of distilled water were added to the specially designed measuring cylinder (described in full paper) and the mixture was shaken intermittently until thermal equilibrium was obtained. The volumes of the two phases in equilibrium were measured and
a calibration curve of the ratio of the volumes of the two phases against the composition of the binary mixture was drawn.

A set of synthetic mixtures containing both n-hexane and n-octane, having the same volume ratios of acetone, water and total hydrocarbon as those used to obtain the calibration curve, but with different amount of n-hexane and n-octane in the hydrocarbon component, was prepared and subjected to analysis. The volumes of the two phases in equilibrium were measured and the composition of the hydrocarbon mixture read from the calibration curve (calibration curve etc in full paper).

RESULTS AND DISCUSSION

The results obtained for the synthetic mixtures were compared with the actual values and on the whole, the agreement was good. The maximum absolute difference found was 1% for solution rich on n-hexane and 2.2% for solutions rich in n-octane. An examination of the calibration curve reveals that the method will yield more precise results for binary mixtures rich in n-hexane.

Although the illustration of the method has been given by using water and acetone as the components B and C respectively, there are many alternative choices for these components. Their suitability, however, will depend on the nature of the calibration curve obtained, since this governs the precision of the method.