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Tie Lines in Phase Diagrams for Ternary Liquid Systems

Most laboratory programs in physical chemistry at the undergraduate level include an exercise in the construction of a phase diagram, on triangular coordinate paper, for a ternary liquid system. The experimental method used for this exercise is almost always a titration method in which the endpoint is the appearance (or disappearance) of turbidity when the system changes from one phase to two phases (or vice versa). Such titrations are laborious, and the endpoints are often ill-defined. When the determination of the positions of tie lines is attempted, the method most often prescribed is the titrimetric analysis of aliquots from each phase of a series of two-phase mixtures at equilibrium.

Both parts of the exercise are necessary if the student is to appreciate the way in which the phase diagram represents the variables of the physical system, but if the determination of more than half a dozen points on the binodal curve and one or two tie lines is attempted, the work involved extends beyond the amount which can be accomplished in a normal laboratory session.

The time required to produce a detailed phase diagram may be greatly reduced by adopting refractive index measurements as the analytical tool. Writers of laboratory manuals appear to have neglected this approach, although it was used by Washburn et al.,¹ in 1931 and by earlier workers. The mode of application of refractive index measurements presented here is different from that of Washburn et al., although their paper provided the initial stimulus. Because of the rapidity and precision of refractive index measurements, it is worthwhile introducing students to their use, with some discussion of their advantages and limitations. The method presented in this paper requires the prior preparation of calibration curves, which are supplied to the student.

The Systems Investigated

Several systems were investigated in an endeavor to find one for which this method gave good results. All the systems consisted of two liquids *A* and *B* which were only slightly miscible with each other, and a third liquid *C* which was completely miscible with both *A* and *B*.

The refractive index measurements gave the most accurate analytical figures when the refractive indices of components *A* and *B* were widely different, and that of *C* intermediate in value.

Water and acetic acid were chosen as the components *A* and *C*, and a variety of organic liquids were tested for use as component *B*. As well as the refractive index requirements, satisfactory endpoints in the titrations used in preparation of the calibration curves were necessary.

The final choice was 1,2-dichloroethane. Ordinary laboratory distilled water from an all-glass still, and A.R. glacial acetic acid (99.5% pure) were used without further purification. It may be of some value to note the other compounds tested, with a brief comment on the reasons for their rejection.

Carbon tetrachloride and benzene both behaved satisfactorily, but were not used because of their toxicity. Reagent grade chloroform gave consistent results only when the stabilizing alcohol additive was removed, and it was then difficult to store without the formation of phosgene.

Aniline gave the best titration endpoints in the preparation of the calibration curves, forming milky emulsions with water which cleared sharply when titrated with acetic acid. However, the range of composition giving complete miscibility of all three liquids was large, so that the two-phase area on the triangular diagram was small, and only three or four tie lines could be determined with convenience. Cyclohexane produced the converse problem. The two-phase area filled almost the whole of the triangle, and the turbidity endpoints were difficult.

The final choice, 1,2-dichloroethane, (D.C.E.) was easily purified by distillation, and gave good endpoints when mixtures of water and D.C.E. over a wide composition range were titrated with acetic acid. An additional recommendation is its much lower toxicity² than that of the other chlorinated hydrocarbons tested.

The Preparation of the Calibration Curves

Nineteen mixtures of water and D.C.E. were made ranging in composition from 98.7% by weight of water to 98.9% of D.C.E. The quantities of each liquid were weighed into 150-ml conical flasks, total volumes between 20 and 40 ml being used. The mixtures were titrated with glacial acetic acid while being slowly stirred with a magnetic stirrer. The last disappearance of the water rich phase could be precisely detected because near the endpoints it became a surface film which could be easily seen when the stirrer was switched off. After each titration, the flasks were reweighed, and the refractive index of the solution measured. The titrations were carried out at room temperature (20–21°C), but the refractive indices were measured at 25°C, using an Abbe refractometer thermostatted by water circulated from a water bath.

The weight percentages of water and D.C.E. in the final ternary solutions were calculated, and plotted on a large scale against the refractive index. This gave the curves shown in Figure 1.

The Student Exercise

Students are supplied with photostat copies of the calibration curves, which are a pair of smoothed curves based on the values used to prepare Figure 1.

They are instructed to prepare a series of ten two-phase mixtures with approximate gross compositions as given in the table.

Appropriate volumes of each component are measured into 20-ml separatory funnels, which are weighed after addition. Less accurately, but still satisfactorily, volumes may be measured with burets and converted to weights using the densities of the liquids. The burets should be well flushed with each liquid, and a few ml run out and discarded before measuring out each precalculated volume. This precaution is necessary since quite small changes in the concentration of one component may alter the phase compositions significantly. In particular, systems close to the plait point composition are likely to give anomalous results from this cause. Each mixture is shaken for 5–10 min and then set aside for the two phases to separate.

A drop of the lower layer is run directly from the funnel onto the prism of the refractometer and its refractive index measured. A drop of the upper layer is transferred to the refractometer using a Pasteur pipet. The weight percentages of water and D.C.E. in each phase are then read from the calibration graph, and the results tabulated.

¹ Washburn, E. R., Hnzida, V., and Vold, R., *J. Amer. Chem. Soc.*, 53, 3237 (1931).

² Steere, N. V. (Editor), "Handbook of Laboratory Safety," 1st Ed., Chemical Rubber Co., Cleveland, Ohio, 1967, p. 476.

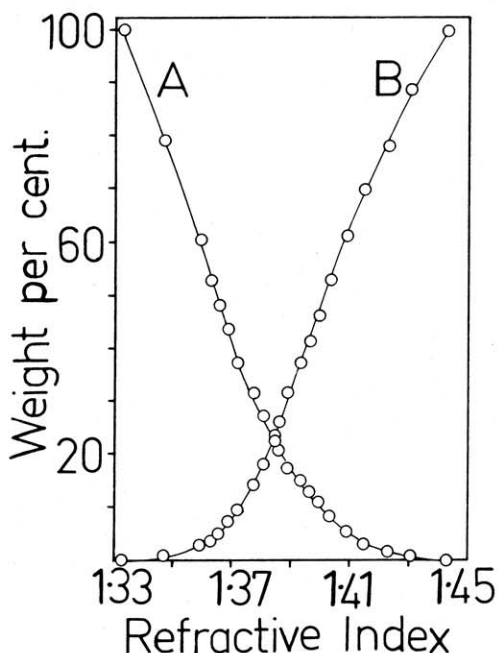


Figure 1. Refractive indices at 25°C of solutions whose compositions lie on the binodal curve of the phase diagram shown in Figure 2, plotted against percentage of two components. Curve A = weight percentage of water and Curve B = weight percentage of D.C.E.

The percentages of the two components in each phase enable the composition of that phase to be represented by a point on triangular coordinates. The points for equilibrium pairs of phases are the ends of the tie line for that system.

When these are all plotted, the phase diagram can be completed by drawing the binodal curve through the points. The gross composition of each system can be calculated from the weights of the three components used and also plotted on the diagram. Each such point should lie on the corresponding tie line. The ends of the binodal curve are fixed on the water axis of the triangle as follows: a) The solubility of D.C.E. in water is given as 0.9 g per 100 g of water at room temperature;³ and b) Water and D.C.E. were shaken together to form a pair of mutually saturated solutions. The refractive index of the D.C.E. rich layer was found to be 1.4428 at 25°C, compared with a value of 1.4430 for pure D.C.E. This very small difference indicates an almost negligible solubility of water in D.C.E., and therefore the left hand end of the curve was taken to the apex of the triangle. The phase diagram produced by this method is shown in Figure 2.

In writing their reports of this exercise, students are asked

To plot the phase diagram on triangular coordinate paper.

To indicate on the phase diagram points which represent systems having zero, one, and two degrees of freedom, and to explain clearly the physical quantities which can be varied if these degrees of freedom are exercised by an experimenter.

As part of the practical work, students make about 5 ml of an approximately 50/50 mixture of water and D.C.E. in a test tube. To this, acetic acid is added slowly and with shaking. In the report, students include a description of the changes observed in this small experiment, and a line is to be drawn on the triangular

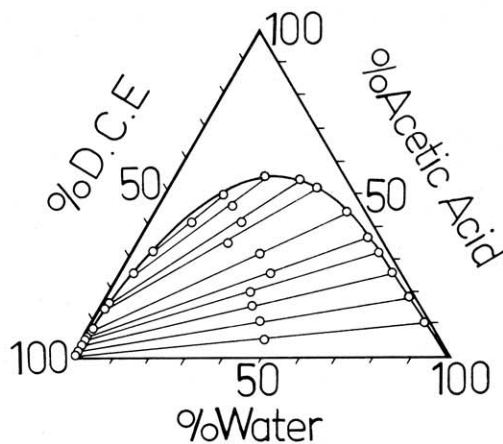


Figure 2. Phase diagram for the system D.C.E.-water-acetic acid at 20-21°C.

Gross Compositions of Two-Phase Three-Component Mixtures of Water, D.C.E., and Acetic Acid

Component	Water	D.C.E.	Acetic Acid
Weight %	50	45	5
	45	45	10
	40	45	15
	40	40	20
	45	40	15
	35	35	30
	25	40	35
	25	35	40
	20	35	45
	10	50	40

diagram representing the changes which occur in the system as the acetic acid is added. These changes are interpreted by means of the diagram.

An additional observation of interest may be made if the funnels containing the ten two-phase systems are arranged in a rack in ascending order of acetic acid content. As the composition of the system changes, the compositions of the phases in equilibrium become more nearly alike. Hence the properties of phases in equilibrium also become more similar. This can be seen by inspection of the refractive index values, and can also be seen with respect to the surface tensions of the two phases. As the surface tensions of the two phases become more nearly equal, the interfacial tension between them becomes lower, and the interfacial meniscus which has a pronounced curvature in the more D.C.E. rich systems, is almost perfectly flat in the systems with higher concentrations of acetic acid. In these cases, the meniscus is also more difficult to see because of the closer values of refractive indices.

Conclusion

It has been found that students who complete this exercise have a good comprehension of the relation of the phase diagram to the physical reality. They are able to interpret three-component phase diagrams with considerable confidence, even for more complex cases. Two students working as a team can easily complete the laboratory work in a three-hour session.

³ Lange, A. L. (Editor), "Handbook of Chemistry," 9th Ed., Handbook Publishers Inc., Sandusky, Ohio, 1956, p. 491.

