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PREPRINT I

The Use of Liquid Densities as a New Technique for Determining Liquid Immiscibility Phase Boundaries¹

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Abstract—Liquid densities can be used to determine the immiscibility phase boundaries of any liquid systems which display these regions, including alloys. The densities are determined by the Archimedean method. Using an automatic recording balance, dynamic density measurements can be made as a function of temperature. Inflections in the curves occur at the onset of immiscibility. Density-composition isotherms can also delineate these phase boundaries where they intersect the density curve (slope zero) of the appropriate liquid layer. The methods are applied to the isomyl alcohol-glycerol and phenol-water systems. Results are compared to other methods of determining the boundaries. The limitations and accuracies of these techniques and equipment are described.

Introduction

A perusal of a compilation of alloy constitution diagrams² shows rather dramatically that many systems display regions of liquid immiscibility, but the boundaries of these regions have been determined for fewer than five percent of these systems. In the case of organic systems such techniques as light scattering, Tyndall effect or visible opalescence can be used to determine the onset of immiscibility and thus the boundary can be determined conveniently and reliably. Unfortunately, the opacity of molten metals together with the fact that all metallic liquids look alike whether mixed or dissolved, does not allow for the application of these convenient methods for the determination of immiscibility boundaries. The small heats of solution of liquids in liquids, detract from the accuracy of cooling curve methods to delineate immiscibility boundaries. Chemical analysis of samples withdrawn from gravitationally separated layers,

though leading to accurate results, is a difficult and tedious method of investigation. Apparently, based on the few complete immiscibility regions which have been determined, investigators have been discouraged from evaluating them because of the inherent experimental difficulties and uncertainty of the results.

Our general interest in the determination of constitution diagrams, led to the development of a new technique for investigating immiscibility regions conveniently without sacrificing reliability. Of the several successful methods³ used for solid solution studies, the dilatometric approach seemed most suitable for determining immiscibility boundaries. A simple direct method of measuring liquid volumes as a function of temperature is to measure the density of the liquid. This is most conveniently done by the Archimedean method using a modification of the Westphal balance adaptable to high temperature measurements.^{4, 5}

Apparatus

In order to plot density continuously as a function of temperature, an electronic automatic recording balance was constructed from an Ainsworth "Chainomatic" balance using the electronic circuit described and used by Mauer⁶ at the N.B.S. The sinker, suspended from the left balance pan and submerged in the solution, suffers a weight loss which is directly related to the density and volume of the liquid displaced. If the density is desired at any particular temperature the volume of the sinker must be appropriately corrected for that temperature. Any inflections recorded on the density-temperature curve, as a consequence of a phase change, are not shifted by the change of densities due to sinker volume corrections. Sinker volumes range from 2-12 ml the larger volumes preferred since they give a larger weight change per °C due to buoyancy change. The composition of the sinker, fine wire suspension (circa 5-10 mil.) and container for the liquid must be inert with respect to reaction or solubility by the liquid or solution under investigation.

In the course of a run, the automatic adjustment of the balance is plotted on a two-function Brown recorder as a weight function. The e.m.f. output to the recorder was calibrated by placing known weight son the left pan of the balance and noting the magnitude of deflection by the recorder. The weight-millivoltage relationship was found to be linear and

reproducible for all sensitivity and gain adjustments used and well within the limits used for density measurements in this work. It is possible to distinguish on the recorder a weight change of 0.5 mg. This sensitivity is seldom, if ever, needed since with a sinker of 10 c.c. volume this would correspond to a density change of 0.05 mg/c.c.

A temperature fluctuation of 1°C results, on the average, in a density change for metals of circa 1 mg/c.c. Temperature was controlled with a Tagliabue "Celest Ray" controller which was capable of holding samples at a pre-set temperature to within 0.5°C. The temperature control was especially important in obtaining density isotherm data described below in a later section. All thermocouples were calibrated against an N.B.S.—certified Pt-Pt 10% Rh standard thermocouple and are considered reliable to within 1°C. The thermocouples generally used were chromel-alumel.

For absolute densities a surface tension correction for the observed weight loss of the suspended sinker may be necessary. This weight correction is given by: $\omega = 2\pi r\gamma \cos \theta$; where r = radius of the suspension, γ = surface tension and θ = the contact angle. A near maximum value for this correction is on the order of 16 mg for a 5 mil suspension, a large surface tension of 400 dynes/cm and a hypothetical contact angle of 0°. This correction decreases in significance as the volume of the sinker and the density of the metal increases. Thus the 16 mg hypothetical correction reduces to a density error of 0.05% in the case of a 30 g weight loss due to a 10 ml sinker submerged in a metal with a density of 3 g/ml. Of course this effect is further reduced by using finer suspension wires, realistic contact angles and whenever the surface tension is smaller than 400 dynes/cm.

Based on the experience in this laboratory with a variety of metals and alloys the limit of reproducibility of density values with the apparatus described above can be on the average 2 mg/c.c. corresponding to a lower accuracy limit of about one part per thousand and ranging up to about one part per five thousand for the high density (10 g/c.c.) metals.

Experimental

Some typical density-temperature curves which were obtained with this equipment are reproduced in Fig. 1(A) and (B). The breadth of the plots is a function of amplifier noise and sensitivity and in this figure it

amounts to a weight width of about one mg on the average. It should be noted that the recorder traces are actually plots of the weight loss of the sinker which is a function of the density of the liquid and the volume of the sinker. It is for this reason that these recorder traces are referred to as density-temperature plots.

Figure 1(A) and (B) shows reproductions of the density-temperature recorder traces of a 50 mole % isoamyl alcohol-glycerol solution which displays a density discontinuity at the temperature 81°C , corresponding to the onset of immiscibility. For plot (A) the sinker was maintained in the top of the liquid sample. Plot (B) represents two consecutive runs the first of which is a duplicate of (A) whereas in the second run, (B), the sinker was positioned in the bottom of the liquid sample. The second run

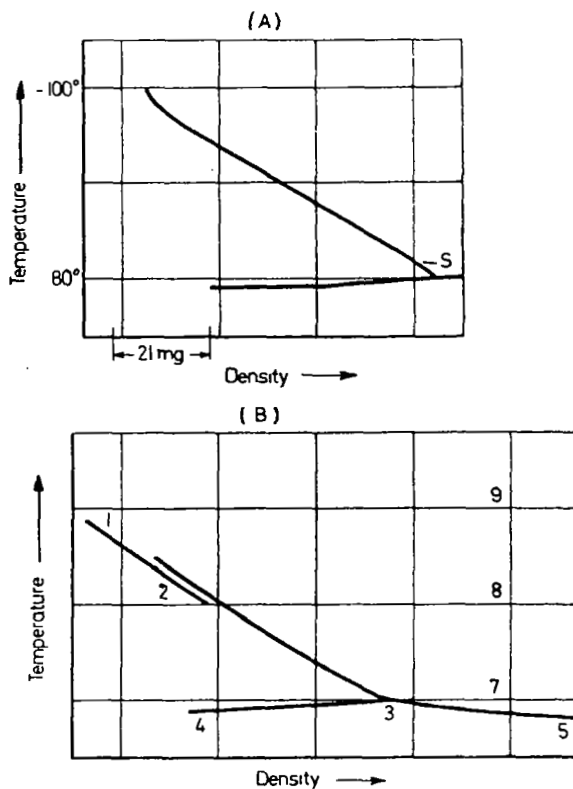


Fig. 1

was begun with the weight function range shifted slightly to the left for the interval (1-2). Superimposition of the two runs began at (2) by shifting the weight function range back to the right to its original value. It is interesting to note that between 2 and 3 the superimposed curves give a trace no wider in pattern than that of the single traces indicating excellent reproducibility by the apparatus. From the point of gravitational separation of the two immiscible liquids at (3), occurring at 80°C, the curve suffers a drastic change in direction towards lower density (4) if the sinker is in the upper region of the sample, whereas the change is toward larger density (5) if the sinker is in the lower region of the sample.

The first evidence of an opalescence (haze), observed perpendicular to a transmitted ribbon shaped light beam, in the samples occurred at (S), a point where the density curve displays a slight slope change. This occurs circa 1°C before the gross slope change (3) at which temperature there was a definite turbidity in the sample. The 1°C lag between gravitational separation and the onset of immiscibility can be reduced by cooling the water bath slower than the rate used in this experiment (circa 2°/minute). In the case of metals it is logical to consider that the small size of their atoms and the large density differences which exist among them compared to the bulky organic molecules and their relatively small density differences, is conducive to a closer approach between the temperatures of the onset of immiscibility and that of gravitational separation. Certainly it is justifiable to consider that these temperatures are within 1° of coincidence and therefore immiscibility boundary point temperatures derived from these observations are within at least 1°C of the correct equilibrium value for the phase diagram.

Density Isotherms

Another approach by which immiscibility boundaries can be deduced, utilizes the density data in the form of density-composition isotherms. The pertinent features which relate the isotherms to the immiscibility boundary are shown in Fig. 2. At temperature T_2 complete solubility exists across the entire composition range and densities determined for a series of selected compositions would result in an isotherm such as shown in the lower part of the figure ranging between the densities ρ_{A2} and ρ_{B2} . The degree and nature of curvature of the isotherm is dependent on the components and their deviation in solution from ideal (Raoult's law) behavior. A second isotherm at the lower temperature T_1 could also

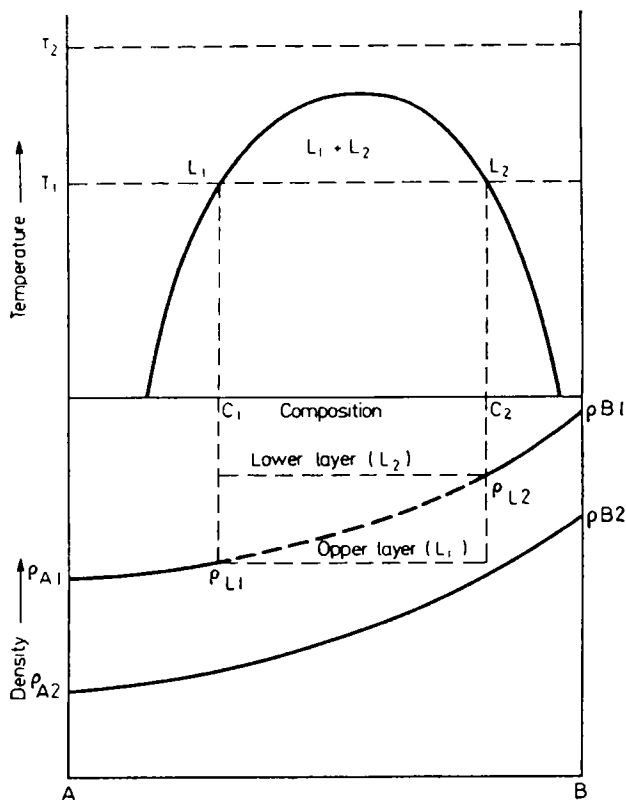


Fig. 2

be constructed similarly and it would range as shown from ρ_{A1} to ρ_{B1} continuously if no immiscibility existed. However, in the case shown here, the dotted section of the curve between compositions C_1 and C_2 cannot be determined for the solution since immiscibility exists between these limits. Within these composition limits two solutions exist which, in this illustration are L_1 (the upper layer) and L_2 (the lower layer). The solutions vary in amount by lever law, between L_1 and L_2 but remain constant in compositions C_1 and C_2 respectively. As a consequence each layer maintains a constant density, ρ_{L1} and ρ_{L2} respectively at T_1 ; regardless of the solution composition selected between C_1 and C_2 .

The experimental procedure involves the determination of a series of density-composition isotherms which cover a sufficient range of compositions on either side of the immiscibility gap in order to establish the

slope and curvature of the isotherms. Additional isotherms can be interpolated for temperatures between and beyond those which were experimentally determined. These interpolations are valid because within even relatively large temperature ranges (e.g. 50°–100°) the coefficient of expansion (or density change with temperature) of a solution is constant for each composition but usually varies from composition to composition. After the isotherms are determined a single composition is selected for further investigation, which falls appropriately within the immiscibility boundary. This is cooled to the temperatures corresponding to each of the isotherm temperatures, and in each case a ρ_{L1} and ρ_{L2} are determined. Since these densities correspond to the constant ρ values depicted in Fig. 2, their composition located on the appropriate isotherm curve, denotes the compositions C_1 and C_2 respectively, which are in equilibrium at this temperature. In this way two composition-temperature points on the phase boundary can be determined at each temperature.

The isotherms can be constructed by selecting density values at the same set of temperatures from a series of ρ - T curves observed for various compositions. They can also be determined, without the use of the automatic recording balance, by using an ordinary balance and measuring density statically at constant temperature. This can be done for a series of compositions whereby their densities are determined at a selected series of temperatures. Another method, which has been followed frequently in this laboratory, consists of holding a specimen at constant temperature and determining its density after each addition of a measured amount of either component A or B to the solution. The latter series of experiments has to be repeated for each isotherm (temperature) which is determined.

Equilibration of samples can be readily checked during static density determinations. When the density is constant with time equilibrium has been reached. It is also important in the determination of ρ_{L1} and ρ_{L2} that the sinker is located exclusively in either L_1 or L_2 . The proper location of the sinker, in each case, is established when slight changes in its elevation do not result in a different density value.

Experimental Results

The glycerol-isoamyl alcohol immiscibility region, Fig. 3, was determined by inflections in density-temperature curves and from density-composition isotherms as described in the previous section. Temperatures

corresponding to density inflections such as (S) in Fig. 1A, are plotted as open circles on the immiscibility boundary representing the onset of immiscibility upon cooling. The boundary values determined from isotherms were obtained for a 50 mole percent solution which cooled and separated into the more dense glycerol-rich and less dense isoamyl alcohol-

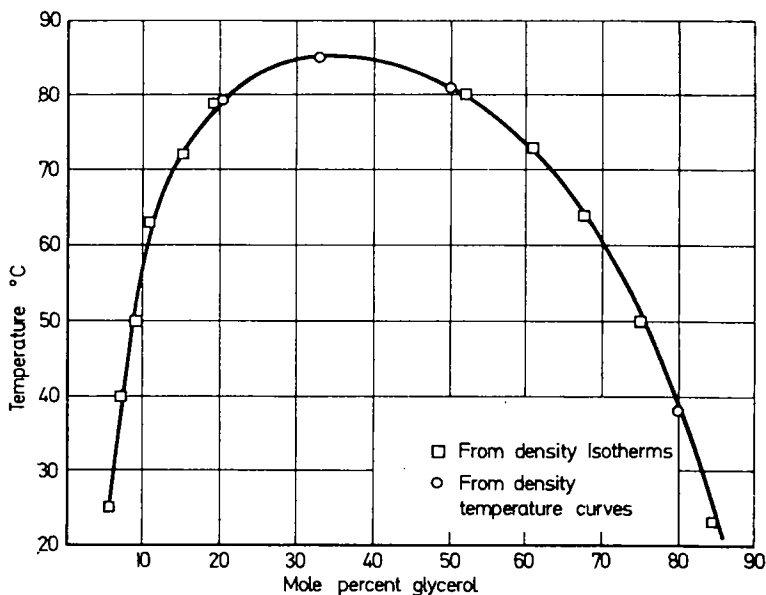


Fig. 3

rich layers. The densities of the glycerol-rich layer were first determined at a series of temperatures. This was followed by a repetition of the experiments for the isoamyl alcohol-rich layer at nearly the same temperatures in each case. This proved convenient because the sinker elevation had to be changed only once instead of each time the temperature was changed.

The agreement between density-isotherm boundary values and density-temperature inflection values is excellent. In the latter case, as indicated earlier in this paper, the agreement with opalescence was also excellent. The consistency between results would certainly argue for the fact that the dynamic measurements give virtually equilibrium results even though temperature is allowed to change with time and not necessarily very slowly.

The Phenol-Water System

This system was also investigated by the density-method and the immiscibility region was determined from density-temperature discontinuities and density-composition isotherms. An 87 mole percent water solution was cooled and equilibrated at various temperatures and the density of the upper (water-rich) layer was determined at each temperature. This was repeated a second time with the sinker in the lower (phenol-rich) layer in order to determine the density of this layer at similar temperatures. The compositions corresponding to these densities were deduced from the isotherms directly or by interpolation.

The temperature composition points are plotted on Fig. 4 and for comparison the data of some other investigators^{7, 8} are also shown. These investigators determined the boundaries by sampling equilibrated layers and subjecting them to chemical and refractometric analysis. The data of Campbell and Campbell⁸ display considerable scatter, especially along the oblique boundary where this is more apt to show up. However the consolute (critical solution) temperatures of the three independent investigators are within 1°C of each other. It has been shown⁹ that consolute temperatures may be raised or lowered by impurities, therefore unless

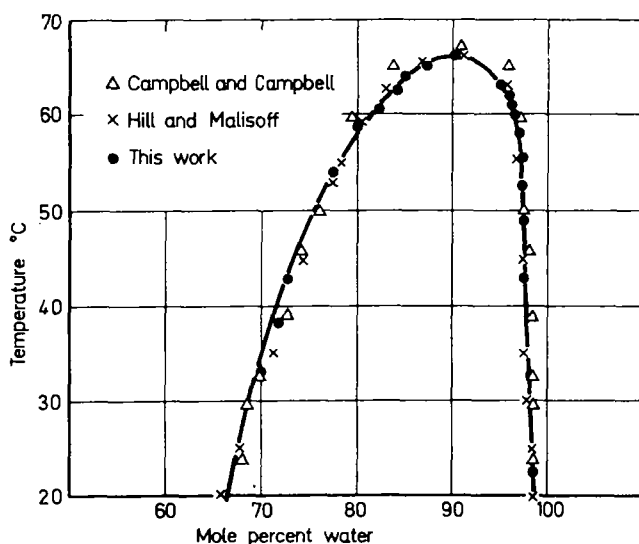


Fig. 4

materials were of comparable purity it would probably be fortuitous if the consolute temperatures of several investigators were in exact agreement.

Discussion of Results and Techniques

In the work reported here with the organic systems no attempt was made to purify the components nor was it the intention to determine the phase boundaries for the sake of improving them. These systems sufficed to test this new approach for the determination of immiscibility boundaries and it is felt that the results adequately demonstrate the reliability of the technique.

Both methods, density-temperature (dynamic) and density-composition (isotherm) should be used. The dynamic method is best suited for the top or "dome" portion of the immiscibility boundary. Solution compositions within this region separate into two widely different compositions with a slight temperature change; therefore the ensuing change in density due to a composition change is very sensitive to temperature variation in this region. The flatter the dome the more dramatic is this effect. The density determination of layers in this region, for the isotherm method, is subject to error if during the equilibration holding time, during which the density is measured, the temperature should fluctuate. This could cause a sufficiently large composition change in the layer, several mole percent for a one degree temperature change would not be unusual, and consequently the density would change accordingly. Matching the erroneously determined density on the density-composition isotherm of the solutions would lead to an erroneous composition point for the boundary at that temperature. This temperature sensitivity is not as pronounced for the determination of the boundary points on the steeply sloped sides of the immiscibility region. Thus the magnitude of composition error due to erroneous densities is greatly reduced. For the reasons cited here it is necessary that reliable thermal control and temperature measurement is necessary whenever layer densities are determined for the selection of composition boundary points from isotherms.

The dynamic method, though well suited for the top dome portion of the boundary, is not the best method for the steep-sided boundary regions for two reasons. First, as in thermal analysis, when a steeply sloping boundary is being evaluated, it is critical that the composition under investigation be known with a high degree of accuracy. To obtain several

points in order to delineate a steeply sloping boundary, requires a series of samples which differ only slightly in make-up composition. A second weakness of the dynamic method for this region stems from the fact that the density inflection, if it occurs, is small. The reason for this can be seen from the lever law application along the steep sloping boundary. The phase which separates from the solution upon crossing the boundary is very different in composition but minute in quantity. The relative amounts of the two phases changes significantly only with a relatively large change in temperature. The steeper the slope the greater is the required temperature change in order to effect a significant composition change. If only a very small amount of the second phase forms then the composition of the original phase can change only slightly, consequently the composition-density effect is slight and may be sufficiently small to avoid reliable detection. This is especially true of organic systems where the densities of the two components do not differ greatly. For example in the phenol-water system the maximum difference between ρ_{L1} and ρ_{L2} is approximately 4%. However, as evident from the study reported here, this proved sufficiently different to allow for the application of the density method to delineate the immiscibility boundary. For metallic systems, where the density differences can be large the separation of only a slight amount of one component can be expected to change the density of a solution sufficiently to cause a significant inflection in the density-temperature trace.

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REFERENCES

1. Abstracted in part from the dissertation of R. C. Faxon submitted to the Chemistry Department of Syracuse University in partial fulfillment of the requirements for the Ph. D. Degree, January, 1966.
2. Hansen, Max, Constitution of Binary Alloys (McGraw Hill Book Co., Inc., New York, 1958), Second Ed.
3. Cahn, R. W., Physical Metallurgy (John Wiley and Sons, Inc., New York, 1965), Chap. 7, pp. 337-362.
4. Loersch, J., and M. S. Thesis, Syracuse University (1965).
5. Kanda, F. A., and King, A. J., A.E.C. Report No. II Contract No. AT30-1-1910, Syracuse University, April 1958.

6. Mauer, F. H., *Rev. Sci. Inst.* **25**, 598 (1954).
7. Hill, A. E., and Malisoff, W. M., *J. Amer. Chem. Soc.* **48**, 918 (1926).
8. Campbell, A. N., and Campbell, J. R., *J. Amer. Chem. Soc.* **59**, 2481 (1937).
9. Rice, O. K., *J. Phys. and Colloid Chem.* **54**, 1303 (1950).