Ternary Liquid-Solid Phase Equilibrium

Determination by Physico-Chemical Measurements

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THIS STUDY, one of several (*1-3*), is concerned with development of experimental methods of studying isothermal ternary phase equilibria. A technique for the study of a ternary liquid-solid system by physico-chemical measurements is described. With this method it is unnecessary to determine by analysis the weight per cent of any of the components.

Many of the broad aspects of the approach, such as the underlying theory, nomenclature, pertinent equations, and much of the experimental technique, have been described (*1-3*). The method is given in terms of the system upon which it was tested, KCl-$NaCl$-H_2O at 25° C.

METHOD

Two series of scanning mixtures were prepared. One series extended from the binary KCl-H_2O axis toward increasing concentrations of NaCl; the other series extended from the binary $NaCl$-H_2O axis toward increasing KCl. Both series ultimately reached what later proved to be an invariant region. At this point of the description only those scanning mixtures lying in the two-phase regions are of interest: S_1 to S_5 of the first series and S_6 to S_9 of the second. Each of the scanning mixtures S_1 to S_9 separated into a liquid phase, I_{lUN}, and a solid phase.

Symbols follow those defined previously for liquid-liquid systems (*3*). Thus U originally indicated an upper liquid phase. This symbol may not be applied to liquid-solid systems with the same meaning. The symbols will be maintained, although sometimes with a modified physical significance, to preserve the form of the series of equations in the earlier work. Interpretation in terms of liquid-solid systems should not be difficult.

S_N was prepared so that only a very minor fraction of a solid phase remained. While not a necessity, this will reduce later trail-and-error aspects of the method by allowing the assumption that I_{lUN} and S_N coincide to within approximately 5 weight %. In several instances it was necessary to adjust S_N to a desirable solid-liquid ratio by addition of measured amounts of one or the other of the co-solutes or the solvent. In the present work the decision was based upon visual observation of the equilibrium mixtures. When visual observation is not possible, a crude cooling curve which shows a break at a temperature only slightly above the equilibrium temperature might be used to demonstrate that the desired relationship had been achieved. The initial estimate of a desirable S_N composition may be based upon that found acceptable for that one of the series prepared just previously.

After each S_N reached equilibrium, the property of I_{lUN} used as the basis of the study was measured. The property selected, weight per cent involatile residue, was used in this instance so that the present work might be compared directly with one described previously which had used the same property (*1*). While this property is one from which the weight per cent of one of the components, water, could have been readily obtained, this fact was ignored to maintain the unique approach of the present work. The main advantage of the present method over the previous one (*1*) is that determination by analysis of the weight per cent of any of the components is not required.

Uncertainties in I_{lUN} made it impossible to fix definitely the number of branches to the solubility curve at that point, but the measured property indicated at least two branches with a rather extensive three-phase region. Moreover, as each binary salt-water system is known to contain the anhydrous salt as the solid phase (*4*) two of the possible solid phases in the ternary system were either the anhydrous salts or solid solutions of which one of the components was an anhydrous salt.

On this basis two series of reference mixtures were prepared: R_1 to R_5 in the two-phase region where the solid phase was KCl and R_6 to R_9 where NaCl was the solid phase. Determination of the weight per cent residue of I_{lUN} formed from R_N indicated the presence of only two branches to the solubility curve. For each series of R_N a plot was made relating the composition of R_N to the measured property of its I_{lUN} phase, 1 and 2 of Figure 1. By interpolation of these curves hypothetical R_N which would lie on the same tie lines as the S_N prepared above were determined. This is equivalent to fixing the trace of the tie lines upon which the latter must lie. The trace of the tie lines is represented by 3 and 4 of Figure 1 in terms of the intersection of the tie lines with either the $NaCl$-H_2O or KCl-H_2O axis.

While Figure 1 cannot be used alone to fix the solubility curve, it can be used in establishing the solid phases (*1*), which proved here to be the anhydrous salts. Again to reduce the later trail-and-error aspects of the method, it was advisable to fix the invariant point tentatively by passing through each of two hypothetical R_N the tie line from the solid phase which would be in equilibrium with each of R_N. The intersection of these two tie lines was accepted as the tentative invariant point. Hypothetical R_N were determined by extrapolation of 1 and 2 of Figure 1 to that value of the measured property, found experimentally for S_N which lay in the invariant region.

Solubility curves were now determined by application of the lever rule with the aid of Figure 1. It has been shown (*3*) that, in the present system, if to a weight $g_{I_{lUN}}$ of a mixture I_{lUN} of components A, B, and C there is added a weight g_{J_N} of a working mixture J_N, the composition of the resultant mixture, F_{2N}, may be related to those of the first two by

$$\frac{g_{I_{lUN}} + g_{J_N}}{g_{I_{lUN}}} = \frac{I^A_{lUN} - J^A_N}{F^A_{2N} - J^A_N} \qquad (1)$$

Superscript A refers to the A coordinate in weight per cent of the indicated mixtures. This relationship, which may also be stated in terms of either B or C, fixes the solubility points by procedures already described (*2*). While the operation may be performed by an algebraic approach, application of the method to the present system, in which greater precision was attempted, indicates that the graphical approach is to be preferred.

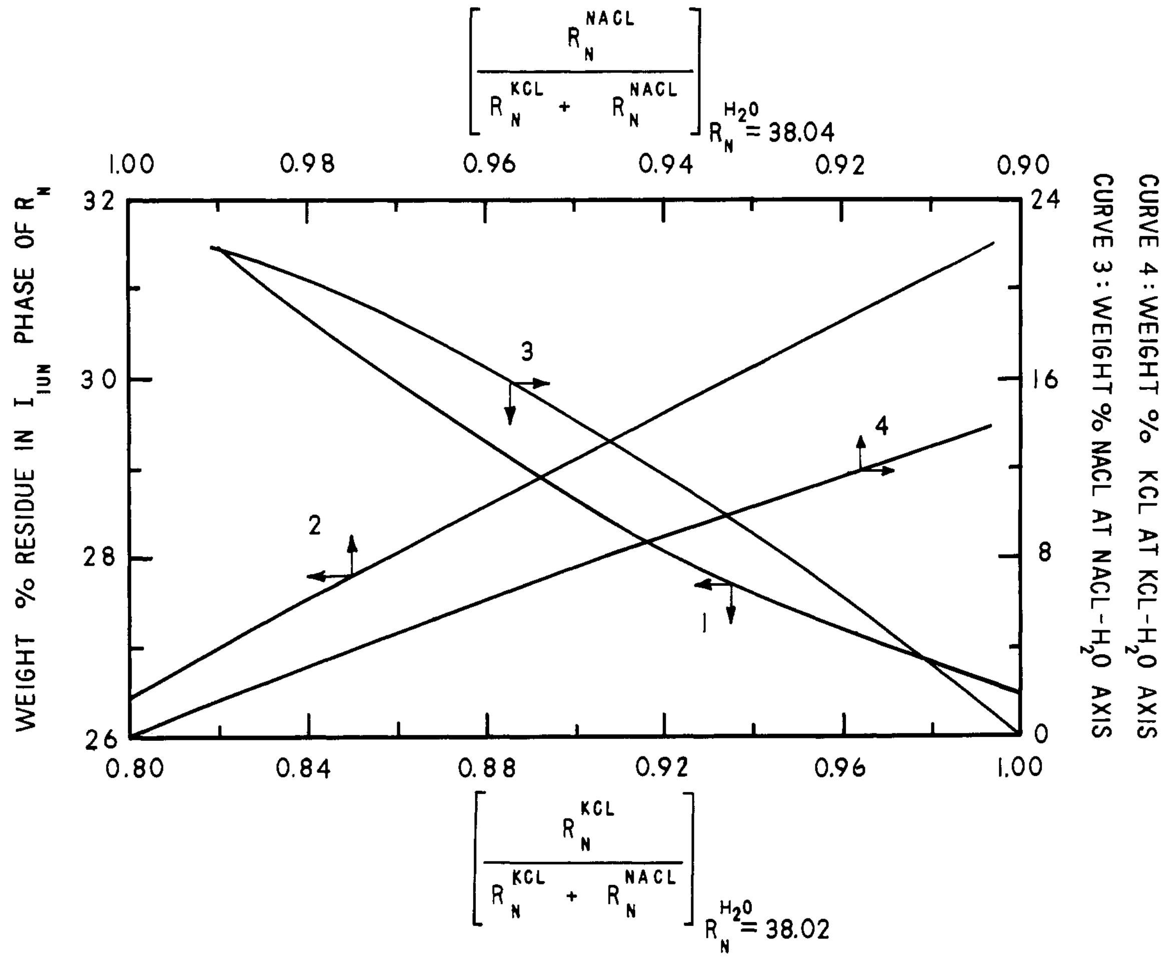

Figure 1. The property of the solution phase of reference mixtures; traces of the tie lines

On this basis the application of Equation 1 to the determination of I_{lUN}^{A} involved a trail-and-error procedure. From J_N a series of straight lines were passed through the tie lines containing F_{2N} and I_{lUN} so as to include the region where the latter was estimated to lie. The intersections of each line emanating from J_N with the two lines established a pair of points tentatively assumed to be the correct F_{2N} and I_{lUN}. If the assumption was correct, the right side of Equation 1 had to agree numerically with the fixed weight relationship of the left side. In the system investigated, convergence on the correct I_{lUN} was approximately linear over the range of weight per cent in I_{lUN} which had to be considered in locating the latter.

Nine points on the solubility curve were determined in this manner, excluding the invariant point. The latter, by this method, must be located by extrapolation of the branches of the solubility curve to their point of intersection (*1*).

RESULTS

The present study and an earlier one of the same system by a different method (*1*) are in agreement. Average deviation of the present results from the best curve is about 1.5 times that of the earlier. The maximum deviation of present data from the best curve is 0.10 weight %. Because of the agreement between the two sets of data, no detailed summary of the present work is presented.

DISCUSSION

Within experimental error data obtained by the present method shows acceptable agreement with results obtained previously. In addition, the difference in precision between the two agrees with the prediction based on analysis of the additional sources of error (*3*) in the present extension of the previous work. The present approach might be profitably applied to many systems which present analytical difficulty.

Practical considerations in application of the present method, in addition to the ones noted previously (*3*), should be mentioned. Worth noting are compositions of resultant mixtures and of working mixtures. The first requires that a mixture to be identified must lie in one or the other of the two-phase regions. This is a trail-and-error feature mentioned above. The second aspect is the practical limitation in the graphical application of Equation 1 due to the scale of commercially available graph paper. The maximum width readily available in linear scale, 50-cm. in 1-mm. divisions, was used, assigning 0.04 weight % per division. With the aid of a mounted reading lens it was possible to distinguish graphically to 0.01 weight %. On this basis the total width of the paper represented 20 weight %, and a given I_{lUN} and J_N could therefore differ by no more than that amount in some one of the components. This aspect would probably not significantly limit the method.

When it was appropriate to proceed with location of the points on the solubility curve it appeared that certainly I_{lU1} and I_{lU2}, and probably I_{lU3}, could be located with resultant mixtures lying in the same two-phase region which contained those I_{lUN} points. This proved to be so, although the first resultant mixture of I_{lU3} lay in the invariant region. I_{lU4} and I_{lU5}, however, both appeared to lie so close to the invariant region that their resultants could be kept in the same two-phase region only by using working mixtures containing only KCl and H_2O. To place the resultant mixture on a usable tie line, however, would have apparently required the use of a weight ratio in Equation 1 which would have caused an excessive extrapolation error. This difficulty was resolved by the use of working mixtures which placed the resultant mixtures in the other two-phase region of the system, where NaCl was the solid phase. The first addition of a working mixture to I_{lU4} appeared from visual observation to give a resultant mixture lying in the one-phase region, which was not usable for application of the method. To bring the latter into the two-phase region, however, it was necessary only to add a small additional measured amount of NaCl. Like considerations applied from I_{lU6} to I_{lU9}, only the first being located by resultant mixtures lying in the same two-phase region containing the former. This effect was caused by the shorter NaCl solubility curve.

When a resultant mixture lies in a two-phase region other than that containing the point located, a larger value of the weight ratio in Equation 1 may be tolerated than that recommended previously (*3*), because the slopes of the concerned tie lines may then be so different that errors of extrapolation are rendered relatively small. Thus in the present study weight ratios greater than 2 gave acceptable results under such circumstances.

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Binary Freezing Point Behavior of Some *N*-Substituted Amides of Palmitic, Stearic, Oleic, and Linoleic Acids

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THE FREEZING point behavior of long chain fatty amides and their binary mixtures is markedly affected by their high degree of association (*8*). The formation of a crystalline equimolar compound in the system stearamide-palmitamide, shown by the freezing point data of Guy and Smith (*2*) might, for example, be attributed to this strong tendency for hydrogen bonding between two amido groups. Association complexes are also involved in the solid-liquid equilibria of the oleamide-linoleamide system (*6*) which exhibits a continuous series of solid solutions.

Mascarelli and Benati (*4*) and Meldrum and Turner (*5*) observed that the substitution of both hydrogens in the amide group eliminated the tendency for association in solution, as indicated by the fact that such derivatives exhibited normal molecular weights. The present report deals with the freezing point data for the binary systems *N*-benzyloleamide–*N*-benzyllinoleamide, *N*-cyclohexyloleamide–*N*-cyclohexyllinoleamide, and *N*-benzylpalmitamide–*N*-benzylstearamide; i.e., for mixtures of compounds in which one of the amido hydrogens has been substituted, and also for the system *N*-stearoylmorpholine–*N*-palmitoylmorpholine, in which both of the amido hydrogens have been substituted.

EXPERIMENTAL

Materials. Highly pure palmitic acid, freezing point, 62.5° C., stearic acid, freezing point, 69.3° C., and oleic acid, freezing point, 16.3° C., were prepared by procedures previously described (*3, 7*). Pure linoleic acid, iodine value (Wijs) 180.3, theoretical 181.0, was obtained from the fatty acids of safflower oil by the urea inclusion method of Swern and Parker (*9*) as modified by Fore, O'Connor, and Goldblatt (*1*). The benzylamine, morpholine, and cyclohexylamine were reagent grade or Eastman Kodak (White Label) products.

Synthesis and Purification of the Substituted Amides. The *N*-substituted amides were prepared by refluxing the pure fatty acid with a 50% excess of amine in the presence of a catalyst using benzene or toluene as an entraining liquid. The preparation of *N*-cyclohexyllinoleamide is typical of the general procedure. A mixture of 28.0 grams (0.1 mole) of linoleic acid, 14.8 grams of cyclohexylamine (0.15 moles), 3 grams of Amberlite IRA-400 resin, and 25 ml. of toluene was refluxed in an apparatus equipped with a stirrer and a Dean-Stark trap until water was no longer evolved. The resin was removed by filtration and the mixture stripped under a stream of nitrogen at reduced pressure. The crude product was dissolved in commercial hexane and passed through a column of Alorco activated alumina (equal parts of Grade F-1, 14- to 30-mesh, and Grade F-20, 80- to 200-mesh) at room temperature or at about 60° C. depending upon the solubilities. After removal of solvent, the product was crystallized six times from absolute methanol. The crude *N*-benzyloleamide and *N*-benzyllinoleamide reaction products were purified by solvent crystallization alone, omitting percolation through alumina.

The resulting *N*-substituted amides were shown by titration to be acid-free and had the following properties (calculated values in parentheses): *N*-Benzyloleamide, f.p., 58.8° C.; I.V. (Iodine Value, Wijs), 68.3 (68.3); C, 80.52% (80.80%); H, 10.90% (11.12%); N, 3.76% (3.77%). *N*-Benzyllinoleamide, f.p., 35.8° C.; I.V., 137.0 (137.3); C, 81.17% (81.24%); H, 10.64% (10.64%); N, 3.73% (3.79%). *N*-Cyclohexyloleamide, f.p., 48.7° C.; I.V., 70.0 (69.8); C, 79.61% (79.28%); H, 12.54% (12.47%); N, 3.84%