HETEROGENEOUS INORGANIC SYSTEMS. II.*

GRAPHICAL ANALYSIS
OF A SOLID PHASE IN DYNAMIC LIQUIDOMETRY

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Dedicated to Professor S. Škramovský on the occasion of his 70th birthday.

The calculation of the total composition in dynamic liquidometry has been made more precise. According to the correlation principle of physicochemical analysis, geometric construction for graphical analysis of a solid phase in a ternary system has been improved. The suggested modification of dynamic liquidometry has been verified using the $Na_2SO_4.10 H_2O$ crystallization field in the Na_2SO_4–$NiSO_4$–H_2O system and the $Cd(ClO_4)_2.6 H_2O$ field in the $Cd(ClO_4)_2$–$HClO_4$–H_2O system at 25°C.

Dynamic liquidometry[1] makes it possible to construct solubility diagrams in systems with salts and a solvent, using measurements of a suitable property of the liquid phase of mixtures whose composition lies on line sections starting from the corner of the solvent. Here, by the mixture is meant a set of one or more condensed phases, produced under given conditions by components of the system concerned. Unsaturated solution of a known composition is used as the start during the investigations. From this solution the solvent is evaporated by boiling under reduced pressure. The evaporation is interrupted at appropriate time intervals, weighing is used to find the total composition and chosen property of the liquid phase is measured. The values found by the measurements are then plotted against total composition at individual experimental points. Merclin[2] showed that from the plots of a liquid phase property against the total composition a liquidus curve and eutonic or peritonic tie-lines, whose points of intersection determine the composition of solid phases and position of eutonic or peritonic points, can be constructed. His method of sections was originally designed to study multiple-phase liquid systems, later it was applied also to systems involving salts and a solvent[3,4].

In dynamic liquidometry, the difference between the composition of a liquid phase and that of the mixture has been as yet neglected, when calculating the total composition. The aim of the present paper is to remove this inaccuracy and utilize further

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the plots of the liquid phase property against total composition for graphical analysis of the solid phase.

EXPERIMENTAL

Sodium sulphate Na_2SO_4 R. G. was a product of firm Lachema. Nickel sulphate hexahydrate $NiSO_4.6 H_2O$ (chem. pure, Lachema) was recrystallized before use and the $NiSO_4$ content was checked by chelatometric titration with chelaton III in ammoniacal solution, murexide[5] being used as indicator. The values obtained varied within 59·5 and 61·0% (58·9% calculated).

Cadmium perchlorate $Cd(ClO_4)_2.6 H_2O$ was prepared by dissolution of cadmium carbonate $CdCO_3$ (chem. pure, Lachema) in 40% $HClO_4$ (R. G., Xenon Lodž). After filtering off excessive carbonate, the solution was evaporated to crystallization. Hygroscopic crystals thus produced were quickly filtered by suction and their $Cd(ClO_4)_2$ content was determined within 67·7 to 73·0% (76·0% calculated) by titrating with chelaton III using pyrocatechol violet[6] as indicator.

The technique of the dynamic liquidometry was described earlier[1]. As a property to be measured, refractive index was again selected. Its values were measured using Abbe refractometer kept at constant temperature with aid of Höppler thermostat. In the $Na_2SO_4-NiSO_4-H_2O$ system, the Na_2SO_4 crystallization field was studied. In the $Cd(ClO_4)_2-HClO_4-H_2O$ system, only a part of the $Cd(ClO_4)_2.6 H_2O$ crystallization field was studied, because of the tension of water vapour being decreased to such an extent in the remaining part of the system that a water-jet pump could not be used for the evaporation.

RESULTS AND DISCUSSION

Calculation of the Total Composition

If the plots of the liquid phase property against composition are to be discussed in detail, it is necessary, after determining the solubility curve, to correct the calculation of the total composition in the region of heterogeneous equilibria according to the liquid phase composition.

The procedure of calculation is schematically presented in Fig. 1 and Table I, where transition from weight G_1 to G_2, or from weight G_3 to G_4 corresponds to the sampling of the liquid phase for the measurements in the mixture whose figuration points X and Y are shown in Fig. 1. The transition from weight G_2 to weight G_3 corresponds to water evaporation at which the figuration point of the mixture is shifted in Fig. 1 from point X towards point Y.

Giving percentual total composition with an accuracy of one decimal place, the correction is necessary if

$$\left| \frac{a_1G_2 - a_2(G_3 - G_4)}{G_4} - \frac{a_1G_2}{G_3} \right| > 1 . 10^{-1} \qquad (1)$$

is valid. The condition (1) follows from Table I and can be modified to

$$[(G_3 - G_4)/G_4G_3] . |(a_1G_2 - a_2G_3)| > 1 . 10^{-1} \qquad (2)$$

The member $(G_3 - G_4)/G_4 G_3$ is the greater, the higher is the weight of the liquid phase sampled. The member $|(a_1 G_2 - a_2 G_3)|$ equals zero in the region of unsaturated solutions. In the region of heterogeneous equilibria, its value is the greater, the more distant is the figuration point of the mixture from the liquidus curve. The correction of the calculation is then necessary for systems having large crystallization fields, in particular if a larger amount of liquid phase is sampled.

The correction described was employed in the $Cd(ClO_4)_2.6 H_2O$ crystallization field in system $Cd(ClO_4)_2-HClO_4-H_2O$ at 25°C (Fig. 2). The sections of the systems turned out to be no longer straight lines in the region of heterogeneous equilibrium; they have tendency to become curved. This phenomenon is characteristic for dynamic liquidometry. The straight-line shape of the section is namely generally maintained in the n-th experimental point inside the crystallization field, provided that

$$\frac{a_1 G_2 - \sum_{i=2}^{n} a_i(G_{2i-1} - G_{2i})}{b_1 G_2 - \sum_{i=2}^{n} b_i(G_{2i-1} - G_{2i})} = \frac{a_1}{b_1} \tag{3}$$
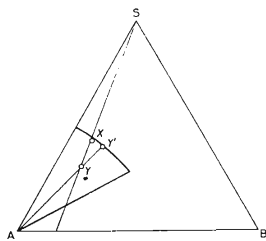
is valid.

Fig. 1

Graphical Representation of Data from Table I

Composition of mixture at individual points: X: $a_1\%$ A, $b_1\%$ B, $[100 - (a_1 + b_1)]$ % S; Y: $a_1 G_2/G_3\%$ A, $b_1 G_2/G_3\%$ B, $[100 - (a_1 + b_1)] G_2/G_3\%$ S; Y': $a_2\%$ A, $b_2\%$ B, $[100 - (a_2 + b_2)]\%$ S.
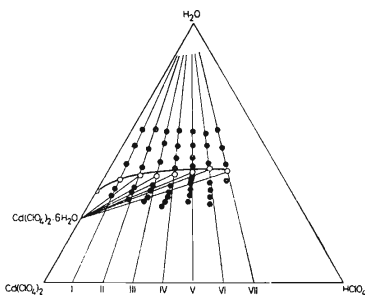

Fig. 2

Solubility in a Part of the $Cd(ClO_4)_2-HClO_4-H_2O$ System at 25°C

● Figuration points of mixtures in which refractive index measurements of the liquid phase were made; ○ points of the solubility curve obtained by dynamic liquidometry; — solubility curve obtained by Lilič and coworkers[10].

TABLE I
Calculation of Composition of a Mixture at Experimental Points of the Section Presented in Fig. 1

Exp. point	Weight of the mixture g	Salt compounds[a] g	Salt compounds[a] %	Solvent g	Solvent %
X	G_1	$0\cdot01\,\alpha_1 G_1$	α_1	$0\cdot01[100 - (a_1 + b_1)]G_1$	$100 - (a_1 + b_1)$
	G_2	$0\cdot01\,\alpha_1 G_2$	α_1	$0\cdot01[100 - (a_1 + b_1)]G_2$	$100 - (a_1 + b_1)$
Y	G_3	$0\cdot01\,\alpha_1 G_3$	$\alpha_1\,G_2/G_3$	$G_3 - 0\cdot01(a_1 + b_1)G_2$	$100 - (a_1 + b_1)(G_2/G_3)$
	G_4	$0\cdot01[\alpha_1 G_2 - \alpha_2(G_3 - G_4)]$	$[\alpha_1 G_2 - \alpha_2(G_3 - G_4)]G_4^{-1}$	$G_4 - 0\cdot01[(a_1 + b_1)G_2\,G\alpha - (a_2 + b_2)(G_3 - G_4)]$	$100 - [(a_1 + b_1)G_2 - (a_2 + b_2)(G_3 - G_4)]G_4^{-1}$

[a] $\alpha = a$ for component A, $\alpha = b$ for component B,

From equation (3) a system of relationships

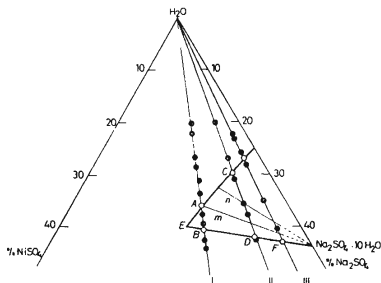$$(b_1 a_i - a_1 b_i)(G_{2i-1} - G_{2i}) = 0$$
$$(i = 2, 3, \ldots, n) \qquad (4)$$

Fig. 3

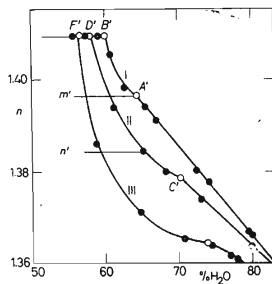Crystallization Field of $Na_2SO_4.10\,H_2O$ in the $NiSO_4$–Na_2SO_4–H_2O System at 25°C

Fig. 4

Plot of Refractive Index of a Liquid Phase against Composition of the Mixture in a Part of the $NiSO_4$–Na_2SO_4–H_2O System, Corresponding to Fig. 3

results as a condition of the straight-line course of the section; this system changes into

$$a_i/b_i = a_1/b_1 \quad (i = 2, 3, \ldots, n) \tag{5}$$

if ultimate amount of the sample has been taken.

This means that sections through the system are in dynamic liquidometry straight lines only if the section is a tie-line at the same time. Any other event provides a curved section. The Merclin method of evaluation the plots of the liquid phase property against the total composition[2] holds also for the case mentioned. Monotony of the section, namely, is sufficient for its application and there is no reason why only linear sections should be considered in the study of heterogeneous systems, as is typical for graphoanalytical method of the sections[3,4].

Graphical Analysis of Solid Phase

The correlation law of physicochemical analysis[7] may be applied also to the plot of the liquid phase property against the total composition. The Merclin construction for the determination of the solid phase composition[2] may be then made more precise in the way described in Fig. 3 and 4 for the $Na_2SO_4.10\,H_2O$ crystallization field in the $Na_2SO_4–NiSO_4–H_2O$ system at 25°C.

If in Fig. 3 the total composition travels along section I between points A and B, the liquidus phase composition passes all points of the liquidus curve between points A and E. In the graph showing the dependence of refractive index upon the total composition (Fig. 4) this part corresponds to branch $A'B'$. Similarly in section II, the part CE of the liquidus curve in Fig. 3 and branch $C'D'$ in the graph in Fig. 4 correspond to the travelling of the total composition along the line segment CD.

Under the part of solubility curve lying between two nonvariant points, the composition of mixtures with equal value of the refractive index of the liquid phase $(m', n'$ in Fig. 4) indicates thus the coordinates of the points of a tie-line $(m, n$ in Fig. 3). By nonvariant points, eutonic and peritonic points are meant and in case of congruently soluble compounds also figuration points of their saturated solutions, which are, of course, nonvariant only in binary systems produced by appropriate compound and water[8].

The tie-lines obtained may be divided into two groups: *1.* Tie-lines starting out from the experimental point on the solubility curve, *e.g. m* in Fig. 3. They are identical with crystallization paths used in the Schreinemakers method of wet residue[9]. $n - 1$ is the number of the tie-lines of this type that can be constructed from the plots of the liquid phase property against composition of the mixtures for n sections passing the same crystallization field. *2.* The tie-lines going merely through points inside the crystallization field *e.g. n* in Fig. 3. Their construction is possible only with use of liquidometry, and from at least two sections under the given solubility curve part arbitrary quantity of them may be virtually constructed.

The solid phase composition is then determined by a common point of inter-section of all the tie-lines obtained. This graphical analysis allows to find composition of the solid phase from the dependence of the measured liquid phase property upon the total composition for two sections intersecting the given part of the solubility curve irrespective of the fact, whether the experimental points attain on them a field of three-phase equilibrium. This provides, in comparison with graphoanalytical method of sections[3,4], new possibility of a more perfect utilization of the plots of the liquid phase property against total composition. If, moreover, value of the measured property of solution simultaneously saturated with two solid phases, *i.e.* eutonic or peritonic solution which limits the given part of the solubility curve, is known at least from one section or comparative experiment, the graphical analysis described here allows even to construct eutonic or peritonic tie-lines and eutonic or peritonic points which are produced by intersection of the former lines. The reason is that the given principles make it possible to extrapolate individual functional curves for this value (see point F' in Fig. 4).

In addition to the points of the solubility diagram, achieved with aid of the procedure described, the solubility curve obtained in the given system by other authors[10] with use of the Schreinemakers method is given in Fig. 2. The consistency of the curve in question with our results confirms that dynamic liquidometry and graphical analysis suggested are applicable to systems with hydrated components in the solid phase.

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