

## DEPENDENCE OF A PROPERTY OF THE LIQUID PHASE ON THE OVERALL COMPOSITION, OBTAINED IN TERNARY SYSTEMS USING DYNAMIC LIQUIDOMETRY

J. EYSELTOVÁ and M. EBERT

*Department of Inorganic Chemistry,  
Charles University, 128 40 Prague 2*

Received February 21st, 1975

On the basis of the correlation law of physico-chemical analysis, a three-dimensional diagram is discussed, which represents the results obtained by dynamic liquidometry (the " $\varphi = f(x)$  diagram"), and its planar projection is proposed. The proposed procedure has been applied to a model system,  $K_2SO_4$ - $MgSO_4$ - $H_2O$ , at 25°C. Simultaneously, the applicability of dynamic liquidometry to systems with congruently and incongruently soluble solvated and unsolvated compounds in the solid phase has been verified.

The study of phase diagrams represents a systematic approach to many problems of preparative inorganic chemistry; the results of such a study are virtually indispensable with systems exhibiting weak interactions among their components. Still, heterogeneous equilibria are not studied very often in inorganic chemistry. This is probably due to the relatively long equilibration times and to the difficulties in selecting analytical methods, which are characteristic of the most common Schreinemakers' method of wet residues<sup>1</sup>.

In order to shorten and simplify the study of phase diagrams in ternary systems containing non-volatile salts A and B and solvent S, a new method, called dynamic liquidometry, has been proposed<sup>2</sup>. This method uses an unsaturated solution of known composition, which is evaporated at the boiling point and at a decreased pressure. Evaporation is interrupted at suitable time intervals, the overall composition of the mixture is determined by weighing and a suitable property of the liquid phase is measured. The values obtained are plotted against the overall composition.

From the breaks on the functional curves obtained, the coordinates of the representative points on the solubility curve and on eutonic and or peritonic nodals of the required phase diagram can be found<sup>3-5</sup>. Moreover, the whole system of functional curves can be employed for graphical analysis of the solid phase<sup>6</sup>. The aim of the present communication is discussion of the shape of the dependence of a liquid phase

\* Part III in the series Heterogeneous Inorganic Systems; Part II: This Journal 36, 3875 (1971).

property on the overall composition in a ternary system and the determination of the relationship of this dependence with the corresponding phase diagram.

## EXPERIMENTAL

The technique of dynamic liquidometry has already been described<sup>2</sup>. As the measured property, the refractive index was employed; its values were measured using an Abbe refractometer thermostatted using a Höppler ultrathermostat. The instrument was calibrated by measuring the refractive index of redistilled water.

Magnesium and potassium sulphates,  $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$  and  $\text{K}_2\text{SO}_4$ , were the products of Lachema, of *p.a.* purity.

## RESULTS AND DISCUSSION

### Graphical Representation

The results of the measurement of a property of the liquid phase in dynamic liquidometry can be treated by the method proposed by Nikurashina and Merclin<sup>4,5</sup> and Zhuravlev and Sheveleva<sup>3</sup>, by plotting the measured values against the solvent content in the mixture. A system of functional curves is thus obtained, from the breaks

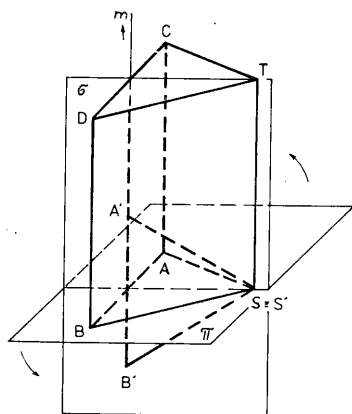


FIG. 1

The Scheme of the Projection of the  $\varphi = f(x)$  Dependence onto a Plane

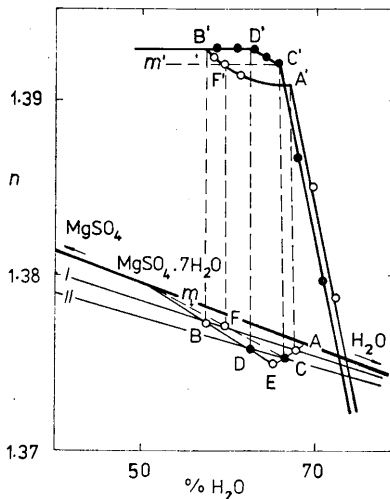


FIG. 2

The Principle of the Determination of the Solubility Diagram Points from the Results of the Measurement of a Liquid Phase Property in a Planar Projection of the  $\varphi = f(x)$  Diagram, Shown on an Example of the  $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$  Crystallization Field

on which the coordinates of the representative points on the solubility curve and on the nodals connecting the eutonic and peritonic points with the representative points of the solid phases in the appropriate solubility diagram can be determined. We dealt in detail with this method of handling measured data and proposed its improvement by introducing a correction of the section shape for the mass of the sample of the liquid phase taken and suggested use of the curves representing the dependence of the measured property of the liquid phase on the mixture composition for graphical analysis of the solid phase<sup>6</sup>.

The dependence of a liquid phase property on the overall composition at a given temperature (termed the " $\varphi = f(x)$  dependence") is a spatial body. Its shape is obtained by constructing perpendicular lines at all points on the composition diagram and plotting the values of the liquid phase property measured in the corresponding mixtures on them at a suitable scale. The  $\varphi = f(x)$  function diagram in the A-B-S system is then limited by the composition diagram, the set of these line segments above its sides AS and BS and the set of the terminal points of the line segments above the remaining area of the composition diagram. On the side opposite the solvent apex, the  $\varphi = f(x)$  diagram is limited by planes perpendicular to the composition diagram

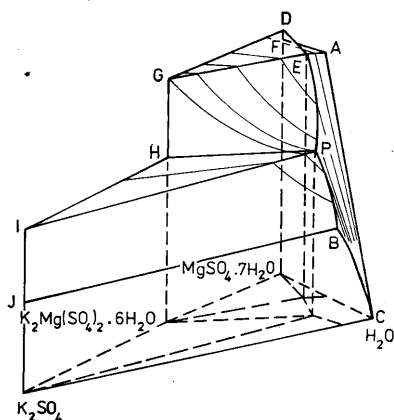


FIG. 3

The Spatial Shape of the  $\varphi = f(x)$  Diagram in the  $K_2SO_4$ - $MgSO_4$ - $H_2O$  System

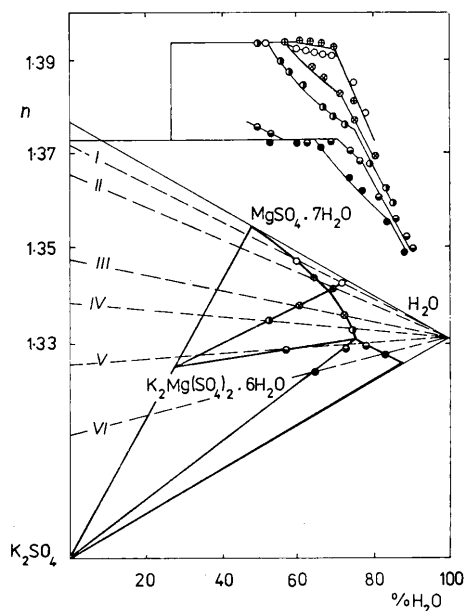


FIG. 4

The Planar Projection of the  $n_{25} = f(x)$  Diagram in the  $K_2SO_4$ - $MgSO_4$ - $H_2O$  System at 25°C

and passing through the connecting lines of the representative points of the individual solid phases. However, these planes themselves do not belong to the  $\varphi = f(x)$  diagram. Systems, in which the solubility curve intersects side AB in the composition diagram, are exceptional (*e.g.* refs<sup>7,8</sup>); in this case the terminal points of the perpendicular lines constructed in all the points of the line segment limited by the liquidus curve on the AN side of the composition diagram also belong to the  $\varphi = f(x)$  diagram.

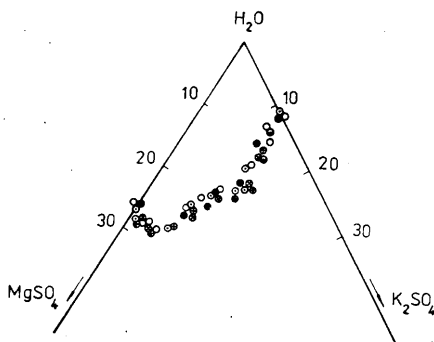
The construction of the  $\varphi = f(x)$  diagram in a plane is shown in Fig. 1. The  $\varphi = f(x)$  diagram is schematically replaced by an enveloping trihedral prism ABCDT. The  $\varphi = f(x)$  diagram is projected on the composition diagram plane,  $\pi$ , and on plane  $\sigma$ , perpendicular to side AB and passing through apex S. The projection in plane  $\pi$  directly yields the solubility diagram for the studied system. The projection in plane  $\sigma$  is a planar diagram  $\varphi = f(x)$  — a system of functional curves  $\varphi = f(\%S)$  with the A/B ratio as their parameter. This type of diagram was discussed earlier<sup>3-6</sup>. If plane  $\pi$  is rotated through 90° along the intercept of planes  $\pi$  and  $\sigma$ , the studied solubility isotherm can be constructed directly in plane  $\sigma$ . This procedure is shown in Fig. 2 on the example of the crystallization field of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  in a  $\text{K}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$  system at 25°C. To each point in the  $\varphi = f(x)$  diagram corresponds, in the solubility diagram, the intercept of the straight line drawn through this point parallel to the  $\varphi$ -axis (*e.g.* B'B in Fig. 2) with the straight line (or curve<sup>6</sup>) representing the corresponding section in the composition diagram (straight lines I, II in Fig. 2).

### The Model System

The results of the study of the model system,  $\text{K}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$  at 25°C, by dynamic liquidometry are summarized in Table I. The three-dimensional shape of the resultant diagram,  $n_{25^\circ} = f(x)$ , is depicted in Fig. 3. The planar projection of this diagram, obtained by the above-described procedure, is shown in Fig. 4. The points of the solubility curve obtained are compared with analogous results by other authors<sup>9-11</sup> in Fig. 5.

FIG. 5  
The Solubility Curve in the  $\text{K}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$  System at 25°C Obtained by Various Authors

● ref.<sup>9</sup>, ○ ref.<sup>10</sup>, ⊙ ref.<sup>11</sup>, ⊖, ⊕, ⊖ the results obtained in the present work.



*Analysis of the  $\varphi = f(x)$  Diagram in the Model System*

Dynamic liquidometry provides a consistent set of data on the liquid and solid phases of the studied system. This fact, which is one of the advantages of dynamic liquidometry over other methods for the study of ternary systems, enables construction of the

TABLE I

The Dependence of the Liquid Phase Refractive Index on the Overall Composition in the  $K_2SO_4$ - $MgSO_4$ - $H_2O$  System at 25°C

Mixture, %			$n_{25^\circ}$	Mixture, %			$n_{25^\circ}$
$K_2SO_4$	$MgSO_4$	$H_2O$		$K_2SO_4$	$MgSO_4$	$H_2O$	
<i>I</i>				<i>IV</i>			
1.0	18.7	80.3	1.3729	14.6	11.0	74.4	1.3769
1.2	21.3	77.5	1.3785	16.6	12.5	70.9	1.3769
1.4	24.3	74.3	1.3857	18.8	14.1	67.1	1.3793
1.6	29.1	69.3	1.3910	21.9	16.6	61.5	1.3841
1.7	31.0	67.3	1.3909	23.7	17.9	58.4	1.3875
1.9	33.7	64.4	1.3912	24.8	18.7	56.5	1.3895
2.0	36.0	62.0	1.3920	27.5	20.8	51.7	1.3931
2.1	37.6	60.3	1.3926	28.2	21.3	50.5	1.3931
<i>II</i>				<i>V</i>			
2.0	17.9	80.1	1.3720	5.7	4.7	89.6	1.3491
2.4	21.4	76.2	1.3798	6.6	5.4	88.0	1.3521
3.0	27.2	69.8	1.3921	7.6	6.4	86.0	1.3551
3.2	28.8	68.0	1.3922	9.9	8.2	81.9	1.3611
3.4	30.8	65.8	1.3928	12.4	10.3	77.3	1.3680
3.6	32.8	63.6	1.3929	13.3	11.0	75.7	1.3690
3.9	35.5	60.6	1.3929	16.9	14.0	69.1	1.3720
<i>III</i>				20.2	16.6	63.2	1.3720
6.0	14.0	80.0	1.3686	25.2	20.7	54.1	1.3732
7.2	17.1	75.7	1.3766	27.1	22.3	50.6	1.3742
8.4	19.8	71.8	1.3819	<i>VI</i>			
9.9	23.3	66.8	1.3861	7.2	3.0	89.8	1.3480
10.4	24.7	64.9	1.3885	9.3	3.9	86.4	1.3522
12.6	30.0	57.4	1.3931	10.9	4.5	84.6	1.3551
<i>IV</i>				16.2	6.8	77.0	1.3615
8.6	6.4	85.0	1.3585	18.2	7.6	74.2	1.3641
9.7	7.3	83.0	1.3622	24.2	10.0	66.0	1.3711
11.7	8.8	79.5	1.3685	26.7	11.3	62.0	1.3720
				31.7	14.4	54.9	1.3722

whole  $\varphi = f(x)$  diagram. According to the correlation law of physico-chemical analysis<sup>12</sup>, the individual areas in this diagram correspond to the individual equilibria in the studied system.

Among the advantages of dynamic liquidometry is, in addition to the possibility of rapid construction of the solubility diagram and a more precise definition of crystallization fields, the obtaining of experimental information on the behaviour of unsaturated solutions, represented *e.g.* in Fig. 3 by area AEPBC. Thus a new possibility arises of constructing the phase diagram and simultaneously studying interactions among the components in the given system in a wide concentration range on the basis of a single measurement. The utilization of the data obtained in dynamic liquidometry for the study of the liquid phase will be dealt with in a separate paper<sup>13</sup>.

In a system containing  $n$  solid phases,  $n$  curved planes correspond to two-phase equilibria between a solid phase and the three-component saturated solution in the  $\varphi = f(x)$  diagram. Their shape is determined by the solubility in the studied system and by the selection of the measured property. From these data the composition of the solid phases can be determined, as described in ref.<sup>6</sup>.

To three-phase equilibria of two coexisting solid phases with their saturated solution correspond  $n - 1$  triangles parallel with the composition diagram plane in the discussed general diagram. Each of these triangles is geometrically identical with the corresponding crystallization field. The distance between these triangles and their distance from the composition diagram is determined by the values of the measured property of the eutonic or peritonic solutions.

The following formations can be distinguished in the  $n_{25^\circ} = f(x)$  diagram of the model system,  $\text{K}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$  at  $25^\circ\text{C}$  (Fig. 3): area AEPBC, corresponding to the refractive indexes of unsaturated solutions, areas ACDE, PEGH and SPIJ, corresponding to the refractive indexes of solutions existing in equilibrium with  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{K}_2\text{SO}_4$ , respectively, and triangles EDG and PIH, depicting the refractive index of solutions existing in equilibrium with two solid phases ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} + \text{K}_2\text{SO}_4$ ).

The results obtained simultaneously verify the applicability of dynamic liquidometry to systems with congruently and incongruently soluble solvated and unsolvated compounds in the solid phase. Fig. 5 indicates that the results obtained by dynamic liquidometry are consistent with those obtained by other authors<sup>9-11</sup>, as was observed during preliminary experiments performed in isolated crystallization fields<sup>2,6</sup>. In the present paper, dynamic liquidometry was applied to a complete system for the first time.

## REFERENCES

1. Schreinemakers F. A. H.: *Z. Phys. Chem.* *11*, 75 (1893).
2. Ebert M., Eysseltová J.: *Chem. Zvesti* *25*, 161 (1971).
3. Zhuravlev E. F., Sheveleva A. D.: *Zh. Neorg. Khim.* *5*, 2630 (1960).
4. Merclin R. V.: *Izv. Biol. Inst. Permsk. Gos. Univ.* *11*, 1 (1937); cited according to ref.<sup>3</sup>.
5. Nikurashina N. I., Merclin R. V.: *Metod Sechenii, Prilozhenie Ego k Izuchenii Mnogofazovogo Sostoyaniya Mnogokomponentnykh Sistem.* Saratov 1969.
6. Ebert M., Eysseltová J.: *This Journal* *36*, 3879 (1971).
7. Ebert M., Grospietch J.: *Chem. Zvesti* *22*, 578 (1968).
8. Ebert M., Muck A.: *Chem. Zvesti* *18*, 285 (1964).
9. Benrath A., Sichelschmidt A.: *Z. Anorg. Allg. Chem.* *197*, 113 (1931).
10. Kurnakov N. S., Schoyket D. N.: *Izv. Sek. Fiz. Khim. Anal. Akad. Nauk USSR* *10*, 310 (1938).
11. van Klooster H. S.: *J. Phys. Chem.* *21*, 513 (1917).
12. Kurnakov N. S.: *Vvedenie v Fizikokhimicheskii Analiz*, p. 27. Izd. Akad. Nauk USSR, Moscow, Leningrad 1940.
13. Ebert M., Eysseltová J.: Unpublished results.

Translated by M. Štulíková.