Geometric-analytical method for the study of solubility in multicomponent systems

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A geometric-analytical method has been proposed for the study of solubility isotherms in three-component systems with two salts and a solvent, based on the mass balance of the salt components. Equations have been derived from the diagram of the mass of the equilibrium solid phase *vs.* the composition, which can be used for the construction of the solubility isotherm in a system with simple eutonic and for the finding of the eutonic point coordinates in such a system without the use of chemical analysis. The method was tested on the $KCl—KH_2PO_4—H_2O$ system and applied to study the solubility isotherm at 0 °C in the $KCl—K_2H_2P_2O_7—H_2O$ system.

Предложен геометрически-аналитический метод для изучения изотерм растворимости в трехкомпонентных системах двух солей и растворителя. Метод основан на балансе масс солевых компонентов. Выведены уравнения на основании диаграммы зависимости массы равновесной твердой фазы от состава, которые могут быть использованы при построении изотермы растворимости в системе с простой эвтоникой и для обнаружения координат эвтонической точки в такой системе без применения химического анализа. Данный метод был проверен на системе $KCl—KH_2PO_4—H_2O$ и приложен для изучения изотермы растворимости при 0 °C в системе $KCl—K_2H_2P_2O_7—H_2O$.

Construction of a phase diagram of a multicomponent system, or at least the obtaining of a suitable section through such a diagram, is the most complete and thermodynamically consistent description of equilibrium conditions in the studied system and of chemical species that can exist in the system under specified conditions. However, the construction of a phase diagram is usually experimentally difficult.

Consider, for the sake of simplicity, the most often studied three-component condensed systems assuming isobaric conditions. The possible procedures for the study of the appropriate phase diagram can then be classified into those obtaining the liquidus area as a whole in the form of a polytherm and those describing it as a set of isotherms.

The first group is represented by the visual polythermal method of the study of phase diagrams that is widely used mainly by Soviet authors (see *e.g.* [1]). The method is applicable only to systems the equilibrium solid phases of which do not form on cooling supersaturated solutions with a high stability that would interfere in the measurement. The last crystal dissolution method (see *e.g.* [2]), in which supercooling does not interfere, may find more general use in this group of methods. The construction of cooling curves, common in the chemistry of melts, is also principally analogous. This method has not found wide use in the study of systems in which one component — the solvent — has a substantially lower melting point than the remaining components.

The methods of the second group are much more often used for systems containing salts and a solvent. A classical method employs direct determination of the composition of the liquid phase, supplemented by determination of the composition of the equilibrium solid phase, either directly after isolation of the solid phase, or indirectly by various procedures of which the Schreinemakers wet residue method is best known [3]. In these procedures recrystallization of the equilibrium solid phase in a heterogeneous mixture also participates in the equilibration, which on the one hand yields a sufficient number of crystallization centres and on the other hand brings about the danger of the establishment of a pseudoequilibrium with an inhomogeneous solid phase. A principal problem in such study is often difficult choice of the analytical methods for the determination of the system components in the presence of each other.

These analytical difficulties can be overcome in various ways. *Zhuravlev* and *Sheveleva* [4] have developed a graphoanalytical method of sections. In this procedure mixtures are prepared by weighing, the representation points being located on linear sections through a composition diagram. The system is allowed to attain an equilibrium under conditions analogous as in the previous case and a suitable property of the equilibrium liquid phase is measured (*e.g.* the density, refractive index, *etc.*). The shape of the solubility isotherm is then found from breaks on the dependences of the measured property on the composition of the phase complex. This method needs no analysis, but accurate weighing of the mixtures is time-consuming and a large amount of the material is required. Moreover, pseudoequilibria with an inhomogeneous solid phase may also occur.

The dynamic liquidometry [5] uses the idea of obtaining a phase diagram from a study of the properties of the equilibrium liquid phase and simultaneously removes most of the drawbacks of the graphoanalytical method of sections. In this method the solubility diagrams are constructed from measurements of the properties of mixtures the composition of which is varied by gradual isothermal evaporation of the solvent from unsaturated solutions prepared by accurate weighing of the components. The formation of supercooled solutions on the crossing of the solubility curve and the occurrence of metastable phases in the region of heterogeneous equilibria are suppressed mainly by boiling during the evaporation, intense internal stirring and a sufficient number of crystallization centres on the surface of a frit that is part of the apparatus [5]. In connection with this method, a concept of a general property *vs.* composition diagram in ternary systems has been introduced [6] and the relationship between this diagram and the corresponding phase diagram has been discussed.

The present paper demonstrates how the study of the solubility isotherms can be simplified if a property *vs.* composition diagram is used, with the relative mass of the equilibrium solid phase as the measured property. This quantity was measured earlier [7], but only in isomolar series, on the basis of *Tananaev*'s work [8] who followed the volume of the precipitate in precipitation reactions in this way.

Experimental

Properties of the dependence of the mass fraction (%) of the equilibrium solid phase on the composition

If normal lines are constructed in each point of the composition diagram for a ternary system and the value

$$w_s = 100\,\frac{m_s}{m_t}$$

where m_s and m_t are the mass of the equilibrium solid phase and the total mass of all the components of the system, respectively, is plotted on each normal line in a suitable scale, then the terminal points of these segments form a plane the shape of which is schematically depicted in Fig. 1 for the simplest case of an eutonic system with two unhydrated salts A and B and water. In Fig. 1 and in all further geometric-analytical considerations the representation point of water S is located at the origin of the coordinates, the mass fraction of component A (%) being plotted on the x axis and that of component B on the y axis. The plane considered is thus formed of planar part SA'EB', two planes KB'E and LA'E, and triangle KLE.

It can be seen from Fig. 1 that there exists the following correlation between the plane of the dependence of the mass fraction of the solid phase on the composition and the corresponding phase diagram:

1. Planar area SA'EB' located in the $w_s = 0$ plane corresponds to the field of unsaturated solutions.

2. The straight-line planes passing through point L with coordinates {100; 0; 100} for component A and through point K with coordinates {0; 100; 100} for component B correspond to the fields of two-phase equilibria. The line of intersection of these surfaces with plane $w_s = 0$ is the solubility curve in the studied system.

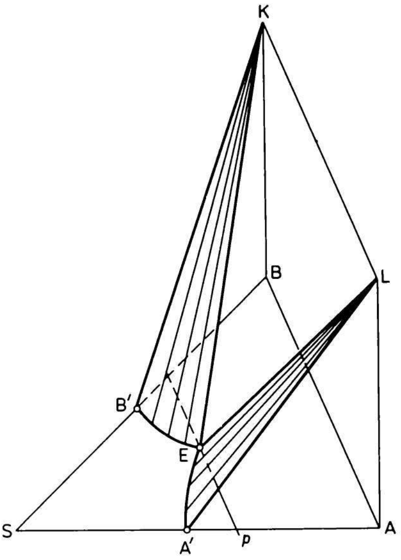

Fig. 1. Schematic representation of the dependence of w_s on the composition in a system with two salts and a solvent, for a case of the eutonic type.

3. Triangle KLE corresponds to the field of three-phase equilibrium and its plane intersects the $w_s = 0$ plane in a straight line p which will be called "the eutonic line of intersection" As can be seen, eutonic point E lies on this line. It must further hold that the eutonic line of intersection is parallel with the line connecting the representation points of the compounds coexisting with saturated solution in the corresponding eutonic (here components A and B).

Derivation of the principal equations

Let an equilibrium solid phase with relative mass w_s be found in a phase complex with composition $w_0(\mathrm{A})$, $w_0(\mathrm{B})$, and $(100 - w_0(\mathrm{A}) - w_0(\mathrm{B}))$. Assume that component A is the equilibrium solid phase in this phase complex. It is evident from Fig. 1 that, if the assumption is true, the coordinates of the corresponding point on the liquidus curve can be found as the coordinates of the point of intersection of the straight line connecting points with the coordinates $\{100;\, 0;\, 100\}$ and $\{w_0(\mathrm{A});\, w_0(\mathrm{B});\, w_s\}$, and the $w_s = 0$ plane. The straight line thus defined will be called "the mantle straight line" The following equations are obtained from analytical geometry for the required coordinates $w(\mathrm{A})$, $w(\mathrm{B})$ of the point on the solubility curve

$$w(\mathrm{A}) = \frac{100(w_0(\mathrm{A}) - w_s)}{100 - w_s} \qquad (1)$$

and

$$w(\mathrm{B}) = \frac{100 w_0(\mathrm{B})}{100 - w_s} \qquad (2)$$

Eqns (*1*) and (*2*) are in this simplest case in agreement with the simple balance of the two components, as can be readily seen.

It can further be demonstrated on the basis of analytical geometry that eqns (*1*) and (*2*) retain their form even if component A is precipitated as a hydrate that is quantitatively dehydrated during drying to the anhydrous component that is weighed. If, on the other hand, component A precipitates as a hydrate containing $w_r(\mathrm{A})$ of substance A and is stable under the drying conditions, then eqn (*1*) assumes the form

$$w(\mathrm{A}) = \frac{100 w_0(\mathrm{A}) - w_s w_r(\mathrm{A})}{100 - w_s} \tag{3}$$

while eqn (*2*) retains its original form.

Consider now the fact that, in the discussed simplest case of a system with simple eutonic and unhydrated solid phases, the point with the coordinates $w_0(\mathrm{A})$; $w_0(\mathrm{B})$ does not lie in the field of two-phase equilibrium but in the neighbouring field of three-phase equilibrium. It can be seen from Fig. 1 that the mantle straight line then lies in the plane of triangle KLE and its intercept with the $w_s = 0$ plane the coordinates of which are again given by eqns (*1*) and (*2*) thus lies on the corresponding eutonic line of intersection.

Principle of the geometric-analytical method for the study of solubility

The following procedure can be proposed for the study of solubility diagrams in three-component systems on the basis of the above facts and the derived relationships: Samples of the system with accurately known initial composition are prepared so that they contain both the liquid and solid phase and cover the whole system composition in sufficiently small intervals (about 10 samples for a simple system). The system is allowed to equilibrate and the equilibrium solid phase is rapidly filtered off in all samples in a preweighed frit crucible. An optimal way of the removal of the adhering mother liquor must be chosen specifically in each case, or found in a model experiment. In the studied systems washing with small amounts of an organic solvent (diethyl ether, heptane, *etc.*), which is immiscible with the liquid phase of the system but is efficient mechanically, was found suitable. The m_s value is found in the individual experimental points after drying.

Starting with the experimental point with the highest content of component A, the results are treated using eqns (*1*) and (*2*) and the intercepts of the mantle straight lines with the $w_s = 0$ plane are plotted graphically. In this way the branch of component A solubility is found, with the eutonic line of intercept passing through the eutonic point that separates the branch of component A solubility from the rest of the diagram. The treatment of the same results starting with the experimental point with the highest content of component B and assuming the presence of component B in the solid phase (the mutual exchange of variables $w(A)$, $w(B)$ and $w_0(A)$, $w_0(B)$ in eqns (*1*) and (*2*)) then yields the branch of component B solubility and the corresponding eutonic line of intersection.

If the assumption of a system with simple eutonic between the components is satisfied, then the two eutonic lines of intersection found are identical and the eutonic point is the common intercept of this straight line and both branches of the solubility curve. If another equilibrium solid phase were formed in the system, in addition to the initial components, the eutonic lines of intersection would not be identical and the further procedure would have to be modified [9]. The eutonic line of intersection thus becomes the principal criterion for the correctness of the assumption made on the quality of the equilibrium solid phase and the starting point for their revision if required; this is schematically depicted in Fig. 2.

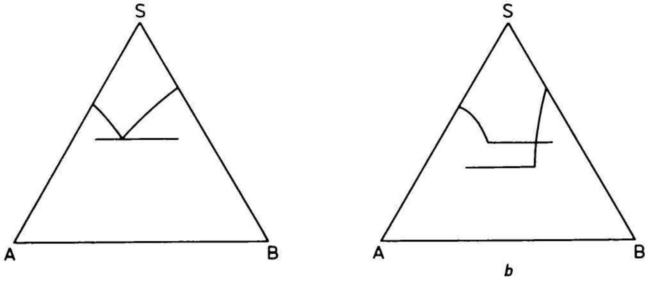

Fig. 2. Scheme explaining the problem of the eutonic straight line.
a) The assumption that the system is of the eutonic type is correct.
b) The assumption that the system is of the eutonic type is incorrect.

Studied systems

As a model system, the solubility diagram was studied in the KH_2PO_4—KCl—H_2O system at 0 °C. The results obtained are summarized in Table 1 and the diagram found is compared with the results of other authors [10, 11] in Fig. 3.

The geometric-analytical method was further used for the study of the $K_2H_2P_2O_7$—KCl—H_2O system at 0 °C. The results obtained are given in Table 2 and the corresponding solubility isotherm is shown in Fig. 4, in comparison with that obtained in the same system at − 8 °C by the Schreinemakers method [12]. As this was the first application of the geometric-analytical method to an unknown system, a control eutonic sample was prepared and analyzed by common methods [12]. The results obtained by the two methods are compared in Table 2.

Table 1

Solubility in the KCl—KH_2PO_4—H_2O system at 0 °C studied by the balance method

Phase complex		w_s/%	Mantle straight line intercept with the $w_s=0$ plane			Assignment
w_0(KCl)	w_0(KH_2PO_4)		w(KCl)	w(KH_2PO_4)	w(H_2O)	
%	%		%	%	%	
29.0	1.00	16.7	22.0	1.2	76.8	KCl branch
28.6	2.10	12.5	21.0	2.4	76.6	eutonic line of intersection
25.6	4.50	8.2	18.4	4.9	76.7	
25.6	6.70	11.8	16.0	7.6	76.6	
12.3	17.8	15.1	14.5	3.6	81.9	KH_2PO_4 branch
8.4	15.7	10.6	9.4	5.5	85.1	
4.1	18.6	10.9	4.6	8.0	87.4	
2.4	19.4	11.1	2.7	9.3	88.0	

The eutonic solution composition obtained graphically (w_i): 2.0 % KCl, 21.4 % KH_2PO_4, 76.6 % H_2O.

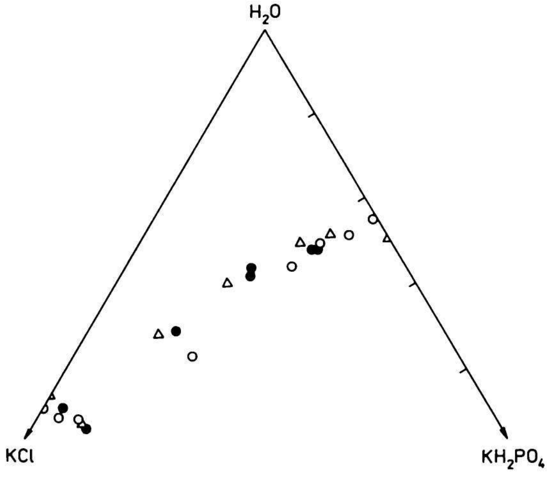

Fig. 3. The solubility curve in the KH_2PO_4—KCl—H_2O system at 0 °C.
△ Our measurements; ○ *Askenasy* and *Nessler* [11]; ● *Brunisholz* and *Bodner* [10].

Table 2

Solubility in the KCl—$K_2H_2P_2O_7$—H_2O system at 0 °C studied by the balance method

Phase complex		w_s/%	Mantle straight line intercept with the $w_s = 0$ plane			Assignment
w_0(KCl) %	w_0(phosph) %		w(KCl) %	w(phosph) %	w(H_2O) %	
24.0	3.78	5.0	20.0	3.98	76.0	KCl branch
24.2	8.34	6.3	19.1	8.90	72.0	
22.6	11.6	6.8	16.9	12.4	70.7	
21.1	19.7	8.5	15.0	17.0	68.0	
20.8	23.8	10.7	11.3	26.6	62.1	
22.2	15.6	9.7	12.6	21.8	65.6	
19.2	28.3	16.7	3.00	34.0	63.0	eutonic line of intersection
12.9	35.6	16.6	15.1	22.2	62.7	
10.5	29.8	4.3	11.0	26.6	62.4	
2.7	46.8	12.6	3.1	39.1	57.8	$K_2H_2P_2O_7$ branch

The eutonic solution composition obtained graphically (w_i): 11.3 % KCl, 26.0 % $K_2H_2P_2O_7$, 62.7 % H_2O.

The eutonic solution composition obtained by the analysis of the liquid phase in the model experiment (w_i): 11.5 % KCl, 25.5 % $K_2H_2P_2O_7$, 63.0 % H_2O.

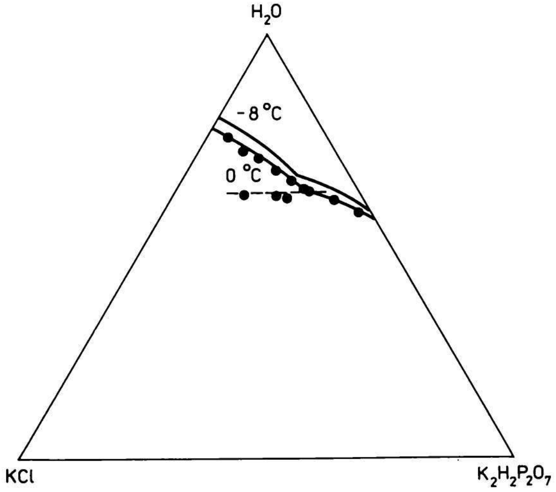

Fig. 4. Solubility in the $K_2H_2P_2O_7$—KCl—H_2O system.

Discussion

The results obtained in the KH_2PO_4—KCl—H_2O system by the proposed procedure are in a very good agreement with the measurements of *Brunisholz* and *Bodner* [10]. The reason for deviations from the results of *Askenasy* and *Nessler* [11] apparently lies in the methods used by these authors for the determination of the system components in the presence of each other. However, the authors did not describe these methods, even though their choice is rather difficult and may significantly affect the accuracy of the results obtained [13].

With the $K_2H_2P_2O_7$—KCl—H_2O system, the geometric-analytical method was used for the first time for an unknown system. The isotherm found corresponds well to that obtained at -8 °C in the same system by the Schreinemakers method [12]. Another fact demonstrating that the geometric-analytical method is not subject to an error larger than that common in classical procedures utilizing chemical analysis is the comparison of the eutonic solution composition found and that obtained in the model experiment.

The method is marked by small demands on instrumentation and small consumption of chemicals. The time requirements are also substantially lower than with other procedures. The applicability is limited by the properties of the test substances. It is evident that the condition for the applicability of the geometric-analytical method is good filterability of the solid phases in the studied system and the possibility to dry them with the formation of defined products. Complexity of the test systems, on the other hand, does not in principle prevent the use of the method. As will be demonstrated in a future communication, the introduction of the property *vs.* composition diagram and the corresponding use of analytical geometry makes it possible to use computing techniques to cope with the problems encountered with complex systems.

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