Computerized Method for the Study of Solubility in Ternary Systems

J. EYSSELTOVÁ, Z. MIČKA, and M. WALZELOVÁ

Department of Inorganic Chemistry, Faculty of Natural Sciences, Charles University, CS-128 40 Prague

Received 22 July 1991

A method has been proposed for the study of solubility isotherms in three-component systems with two salts and a solvent generalizing the geometric-analytical method described earlier. Computational programs have been formed to construct the solubility isotherm and to identify the equilibrium solid phases using the composition of phase complex and the mass of equilibrium solid phase as the input. The computational procedure involves iterative elimination of adhered mother liquor and may be modified to solubility investigation of maximum precision. The method was tested on the K_2SO_4—$MgSO_4$—H_2O system and applied to the study of the solubility isotherm at 25 °C in the glycine—H_2SeO_3—H_2O system. During this application, new compound gly · H_2SeO_3 was synthesized.

In the previous paper [1] different methods of solubility investigation were discussed and the geometric-analytical method for the study of solubility in multicomponent salt systems was proposed and tested. This method is based on a property *vs.* composition diagram [2], using the relative mass of the equilibrium solid phase w_s as the measured property. The relative mass of the equilibrium solid phase has been defined as

$$w_s = 100\ m_s/m_t \qquad (1)$$

where m_s and m_t are the mass of the equilibrium solid phase and the total mass of the components of the system, respectively. The shape of the diagram w_s *vs.* composition was discussed and the eutonic line of intersection has been defined in simple eutonic system as the line of intersection of the plane of the composition diagram with the plane determined by the eutonic point, the points having coordinates (0, 100, 100) and (100, 0, 100) (*i.e.* w_s = 100 in pure salts). The possible use of the eutonic line for further generalization of the method has been stated. The present paper demonstrates such general method of investigation of solubility in ternary system where new compounds are formed.

EXPERIMENTAL

Geometric-Analytical Method in Systems with New Solid Phases Formed

Let us suppose that in a ternary system consisting of two salts A and B and a solvent S a compound $A_xB_yS_z$ is formed, its composition being w_r(A)/% A, w_r(B)/% B, and w_r(S)/% = 100 – w_r(A) – w_r(B). Such formulation covers the cases of solvates of the components (x = 0 or y = 0), anhydrous compounds of the salts (z = 0) as well as solvated compounds ($x \neq 0$, $y \neq 0$, $z \neq 0$). Let us treat that system in the same experimental way as described in [1] with the following modification: instead of washing of the isolated solid phase by a small amount of organic solvent, the crystals are filtered under reduced pressure as intensively as possible, the bottom of the frit is dried by a strip of filter paper and the frit with the material resembling the wet residuum in Schreinemakers' method [3] is weighed (w_s'). Then the frit is placed in a desiccator over a proper desiccant (P_2O_5, silica gel) for 2—3 days and weighed again (w_s''). As it will be shown below, a simple computational way exists to eliminate the mother liquor adhered and calculate the mass of equilibrium solid w_s using the values w_s' and w_s''.

For n experimental points, a set of values w_0(A), w_0(B), w_s' and w_s'' will be found. Using these values, the coordinates of the points of solubility curve and the eutonic intersection line(s) may be calculated. The general set of equations is as follows

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

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

Let us suppose now that we are able to make qualified assumptions about the composition of the equilibrium solid phases formed in the system. Then the respective w_r(A) and w_r(B) may be calculated and eqns (*2*) and (*3*) may be applied directly. If sufficient number of experimental points is at the disposal, a system of branches of solubility curve and the eutonic intersection lines appears.

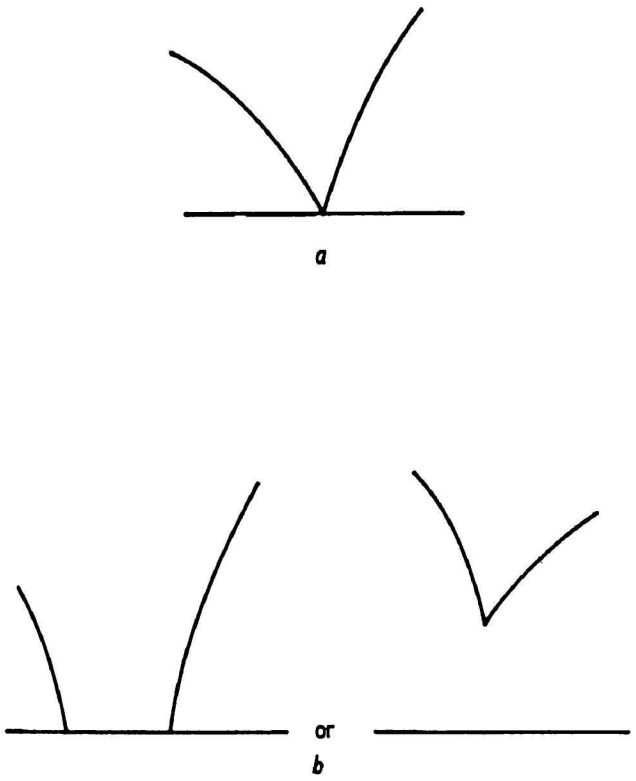

Fig. 1. Schematic depiction of the intersection of solubility curve and the eutonic intersection line. The assumption of the composition of the solid phase is *a*) correct; *b*) incorrect.

The correctness of the assumptions about the equilibrium solid phases composition can be checked graphically as demonstrated schematically in Fig. 1: Each two neighbouring branches of the solubility curve and the corresponding eutonic intersection line intercept mutually all in one point – the respective eutonic point (Fig. 1*a*). Should the choice of the composition of the equilibrium solid phase be erroneous, two points of intersection occur (Fig. 1*b*). This criterion is a simple consequence of the properties of the diagram of the dependence of w_s on the overall composition, which was discussed in paper [1]. These facts have general validity regardless of the number of compounds formed in the system as well as the fact whether the compounds are congruently or incongruently soluble under the experimental conditions of investigation.

Computational Analysis of Solubility Isotherm

Naturally, in most cases no information on the number, composition, and solubility of the compounds formed in the system is available. Preliminary experimental research would mean resigning to the greatest experimental advantage of the method – minimum demands on instrumentation

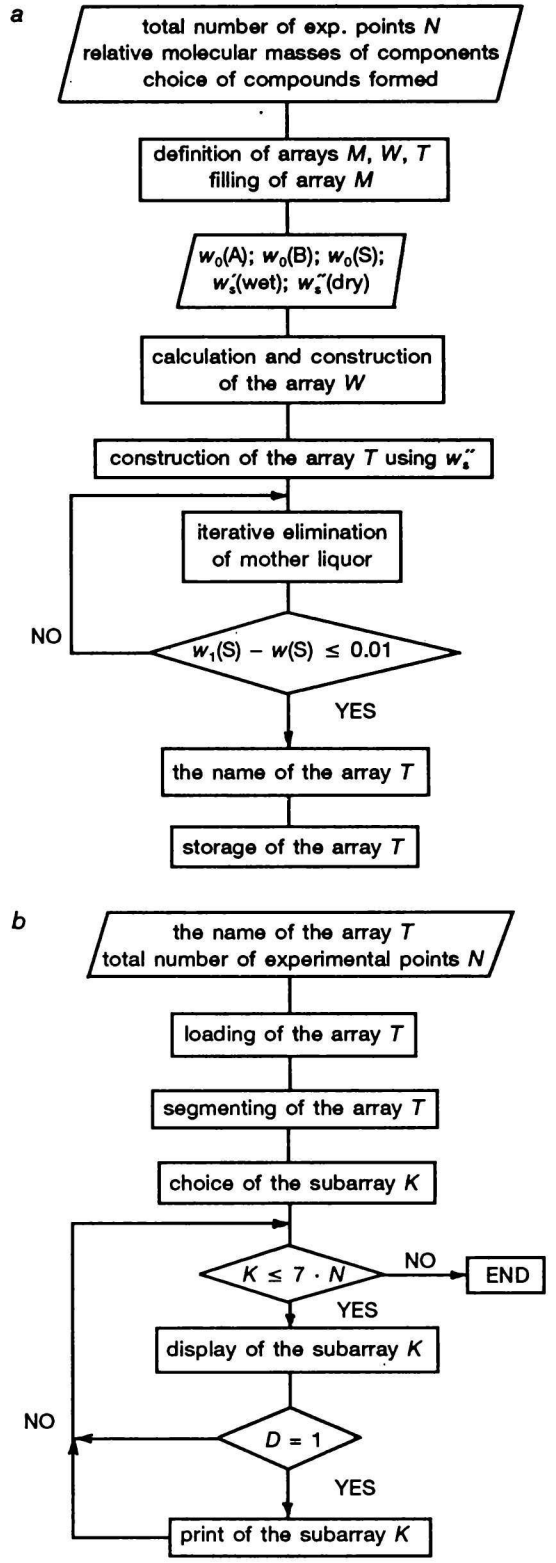

Fig. 2. The chart flows of the programs *a*) GIGANT, *b*) SURVEY.

and no necessity of searching for the analytical methods for the determination of the components in the presence of each other. Fortunately, the problem may be solved with the use of a computer. In our case, a computer TNS was used and all

programs were constructed in its MBASIC. Their chart flows are depicted in Fig. 2.

The computational procedure consists of the following steps:

A. Calculation of the points of tentative solubility curves (program GIGANT);

A1. Input of relative molecular masses of the components and the solvent;

A2. Defining an array M of the dimension 7 7 and filling it by the relative molecular masses of the hypothetical compounds which may be formed in the system.

During the construction of the array M, the composition of the compounds (the relation of the components) may be further altered depending on the character of the problem solved or as a result of unsuccessful first set of calculations.

A3. Input of the number of experimental points n and defining of the following arrays: W having the dimension $n \cdot 3$ and T having the dimension $(6 \cdot n + 7) \cdot 20$;

A4. Input of experimental data: mass of materials in which the components A and B are dosed, mass of the solvent S and the values w_s' and w_s'' in each experimental point. Based on these data, the values w_0(A) and w_0(B) are calculated and the array W filled as follows:

$$W(i, 0) = w_0(\mathrm{A});\ w(i, 1) = w_0(\mathrm{B});\ w(i, 2) = w_s';\ w(i, 3) = w_s'' \text{ for } i = 1 \text{ to } n$$

A5. Calculation of the coordinates of the points of the solubility isotherms or eutonic intersection lines in each experimental point according to eqns (2) and (3), taking w_s'' for w_s and values of w_0(A) and w_0(B) calculated according to the relations

$$w_0(\mathrm{A}) = \frac{100\, x\, M(0, 0)}{M(i, j)} \qquad (4)$$

$$w_0(\mathrm{B}) = \frac{100\, y\, M(6, 0)}{M(i, j)} \qquad (5)$$

for all combinations of i and j from (0, 0) to (6, 6). The coefficients x and y are the stoichiometric mole numbers of the respective compound $A_xB_yS_z$.

A6. Iterative elimination of adhered mother liquor as described later.

A7. Filling of the array T with the coordinates of points of possible solubility curves and its storage on a magnetic medium.

Interpretation of the Results Obtained by the Program GIGANT

As the optimum way of interpretation of the results the interactive treatment of the data was approved. For this purpose a program called SURVEY was developed. This program reloads the array T and divides it into $7 \cdot n$ subarrays having the dimension $7 \cdot 3$. In each subarray, the coordinates of a point of solubility curve, assuming one possible compound (A, A_3B, A_2B, AB, AB_2, AB_3, B) 0- to 6-hydrated as the equilibrium solid phase, are given. Each set of seven subarrays belongs to one experimental point. The individual subarrays may be then displayed on a screen of a computer and either rejected immediately (*e.g.* if all the "concentrations" are negative) or printed. Next interpretation of the data is graphical: in rectangular coordinates w(B) *vs.* w(A) are plotted. Generally, a complicated and difficult to decipher network of points would result. However, it is the concept of eutonic intersection lines as well as general logistics of solubility diagrams that are of substantial use here and make it possible to find the real solubility curve and to determine the composition of solid phases present. The optimum way of examining the set of data starts in the experimental point nearest to one of the binary systems salt—water, where the equilibrium solid is in all probability the respective component or it is some of its solvates. As a rule, this fact approves also in the array T, where only the calculations assuming these solid phases make sense (*i.e.* are positive). With the first point of the solubility branch fixed, the point with the next greater content of the other salt component can be examined with special care on the proper shape of the diagram in the area of eutonic/peritonic point (Fig. 1). As a check, the analytical determination of a component in eutonic solution is highly recommended. Such step-by-step treatment yields finally the whole solubility diagram under consideration.

Iterative Elimination of the Mother Liquor

In the first step, the data in array T are calculated using the value of w_s'' corresponding to the dried solid phase. Then the value w_s is corrected for the amount of mother liquor.

$$w_s = w_s'' - \Delta w$$

where

$$\Delta w = (w_s' - w_s'')w(\mathrm{S})$$

and next calculation of the composition of saturated solution is made. This iteration is repeated until the w(S) values obtained in two consecutive steps differ less than 0.02 %. As a rule, maximum three cycles prove sufficient.

Studied Systems

As a model, the solubility of $K_2Mg(SO_4)_2 \cdot 6H_2O$ in the K_2SO_4—$MgSO_4$—H_2O system at 25 °C was

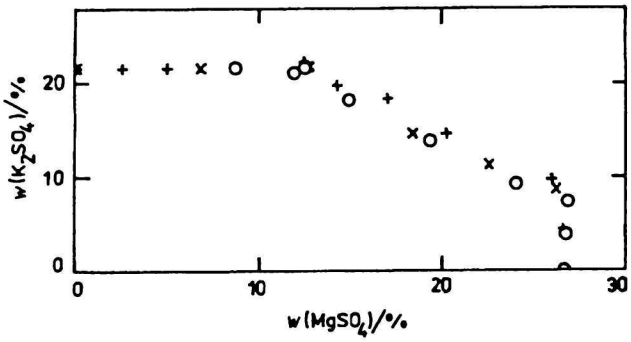

Fig. 3. The solubility curve in the $K_2SO_4-MgSO_4-H_2O$ system at 25 °C. x This paper; O Ref. [4]; + Ref. [5].

studied. In Fig. 3 the results are compared graphically with those of other papers [4, 5]. Then the method was applied on a new system for the first time. As a part of systematic investigation of compounds of amino acids with inorganic salts, the system glycine–H_2SeO_3–H_2O was studied at 25 °C. The samples of the system were prepared by weighing of glycine and SeO_2 (both products of Merck) and water into polyethylene vessels of 20 cm^3 volume. The equilibration lasted for about two weeks. During that time, the samples were shaken periodically on a mechanical shaker. The equilibration was checked by periodic measurement of refraction index of the saturated solution in the reference sample. In the samples having maximum contents of SeO_2 red particles of elemental Se occurred. This partial decomposition of SeO_2 did not influence the shape of the solubility diagram virtually. After equilibration, the solid phase was filtered and the procedure described above was applied. The resulting solubility diagram is depicted in Fig. 4 and the solubility data are summarized in Table 1. According to the solubility diagram, a congruently soluble compound gly · H_2SeO_3 is formed in the system. For this compound w_i(calc.): 38.7 % Se, 6.86 % N, 11.81 % C, 3.43 % H; w_i(found): 38.5 % Se, 6.77 % N, 11.91 % C, 3.44

Table 1. Solubility in the Glycine–SeO_2–H_2O System at 25 °C

Saturated solution w_i/%			Solid phase
Glycine	SeO_2	H_2O	
20.0	0.0	80.0	Glycine
19.09	3.76	77.15	Glycine
20.99	10.97	68.04	Glycine + gly · H_2SeO_3
12.78	19.32	67.90	gly · H_2SeO_3
12.52	18.53	68.94	gly · H_2SeO_3
8.48	31.37	60.14	gly · H_2SeO_3
8.48	54.75	36.76	gly · H_2SeO_3
8.77	75.88	15.35	gly · H_2SeO_3 + H_2SeO_3
8.65	77.23	19.11	H_2SeO_3
0.0	73.0	27.0	H_2SeO_3

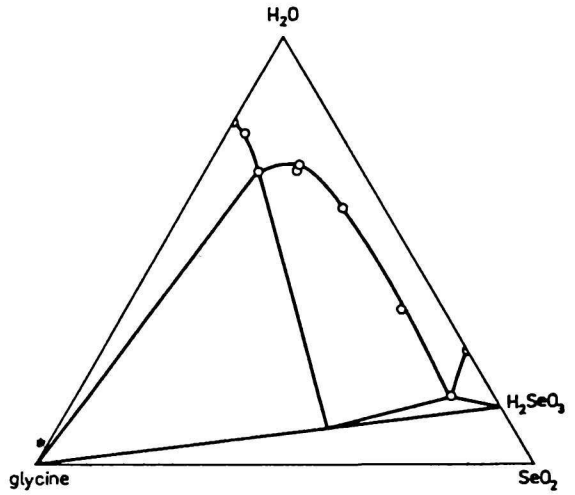

Fig. 4. Solubility in the glycine–H_2SeO_3–H_2O system at 25 °C.

% H. Selenium was determined by iodometric titration, nitrogen was transformed in the form of ammonia by mineralization and then determined according to Kjeldahl. The content of nitrogen, carbon, and hydrogen was determined with the aid of the 240 C Perkin–Elmer apparatus.

DISCUSSION

The results obtained in the $K_2SO_4-MgSO_4-H_2O$ system by the proposed procedure are in very good agreement with the measurements of *Benrath* and *Sichelschmidt* [4] as well as *Kurnakov* and *Shoykhet* [5]. Therefore, the proposed balance method generalizes the applicability of the geometric-analytical method [1] to the systems of any complexity. With the aid of it, a possibility appears to perform routine solubility investigation avoiding chemical analysis.

The method retains all the advantages of the geometric-analytical method such as small consumption of chemicals and low time requirements. Moreover, the condition of good filterability of the equilibrium solid phases loses its importance due to the iterative elimination of the mother liquor. Because of it, the method can be applied even to the systems where the equilibrium solid phase crystallizes in very fine crystals and even relatively greater viscosity of the saturated solution does not prevent the use of the method. As in the case of the geometric-analytical method, the method is not subject to an error larger than common in classical procedures. On the contrary, in special cases the method can easily be adapted for solubility measurements of special precision [6].

In the H_2SeO_3–glycine–H_2O system, an unknown congruently soluble compound gly · H_2SeO_3 was found. According to the result of X-ray

investigation [7] it is monoclinic, $P2_{1/n}$, which denies the possibility of ferroelectricity, otherwise quite frequent in similar compounds of glycine [8–10]. In the analogous H_2SeO_3–alanine–H_2O system, no analogous compound was found [7].

The authors will send the programs on request.

REFERENCES

1. Eysseltová, J. and Kovářová, B., *Chem. Papers 39,* 607 (1985).
2. Eysseltová, J. and Ebert, M., *Collect. Czechoslov. Chem. Commun. 41,* 180 (1976).
3. Schreinemakers, F. A. H., *Z. Phys. Chem. 11,* 75 (1893).
4. Benrath, A. and Sichelschmidt, A., *Z. Anorg. Allg. Chem. 197,* 113 (1931).
5. Kurnakov, N. S. and Shoykhet, D. N., *Izv. Sekt. Fiz. Khim. Anal. Akad. Nauk SSSR 10,* 310 (1938).
6. Eysseltová, J., unpublished results.
7. Walzelová, M., *Thesis.* Charles University, Prague, 1991.
8. Olejnik, S. and Lukaszewisz, K., *Acta Crystallogr., B 31,* 1785 (1975).
9. Pepinsky, R., Okaya, Y., and Jona, F., *Bull. Am. Phys. Soc. 2,* 220 (1957).
10. Matthios, B. I., Miller, C. E., and Remeuka, J. P., *Phys. Rev. 104,* 849 (1956).

Translated by J. Eysseltová

Phase Equilibria in the System LiF–KF–B_2O_3–TiO_2

M. CHRENKOVÁ and V. DANĚK

Institute of Inorganic Chemistry, Slovak Academy of Sciences, CS-842 36 Bratislava

Received 31 October 1991

In the region of the primary crystallization of LiF in the ternary system LiF–KF–B_2O_3 a liquid miscibility gap is formed at the composition from 5 to 23 mole % B_2O_3 in the LiF–B_2O_3 boundary and up to 12 mole % KF in the ternary system. From the thermodynamic analysis of the binary systems it follows that the dissolution of boron oxide in molten lithium fluoride leads to the formation of $Li_2B_4O_7$, while in molten potassium fluoride the compounds KBF_4 and $K_2B_4O_7$ are formed. These compounds are most probably present also in the melts of the ternary system. By addition of TiO_2 into molten LiF or into molten LiF–KF mixtures insoluble Li_2TiO_3 precipitates immediately from the melt. It may be therefore concluded that the rising of the temperature of primary crystallization in the melts of the system LiF–KF–B_2O_3–TiO_2 is due to the formation of Li_2TiO_3 with a relatively high melting point.

The melts of the system LiF–KF–B_2O_3–TiO_2 may be used as the electrolyte in the electrochemical synthesis of titanium diboride, especially when preparing well dispersed powders [1]. The use of this electrolyte is motivated by the effort to exclude special and expensive boron and titanium sources, such as fluoroborates and fluorotitanates, which moreover introduce surplus of alkali fluorides.

The system LiF–KF–B_2O_3–TiO_2 is a considerably complicated subsystem of the quinary reciprocal system Li^+, K^+, B^{3+}, Ti^{4+}//F^-, O^{2-}, in which a number of compounds are formed. The phase equilibria in the system LiF–KF–B_2O_3–TiO_2 have been investigated still unsatisfactorily. The existing phase equilibria studies are as follows.

The phase diagram of the binary system LiF–B_2O_3 was studied in [2, 3], especially in the range of high concentrations of LiF. It was found [3] that two immiscible liquid phases are formed in the composition range 5–23 mole % B_2O_3 with the monotectic temperature of 836 °C and the upper critical temperature of 862 °C at *ca.* 14 mole % B_2O_3. In the system LiF–B_2O_3 a number of chemical reactions between the components may be expected. From the X-ray powder diffraction analysis as well as the IR spectroscopy of quenched melts it follows that $LiBO_2$ and volatile BF_3 is formed up to *ca.* 5 mole % of B_2O_3. At higher amounts of B_2O_3 lithium metaborate polymerizes into tetraborate. The system LiF–B_2O_3 seems to be thus a nonlinear projection of the LiF–$LiBO_2$–B_2O_3 joint.

The binary system LiF–KF is a simple eutectic one with the coordinates of the eutectic point of 49 mole % KF and the eutectic temperature of 492 °C [4].