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Planarity of Mono- and Non-Variant Equilibria as the Colligative Property of Multicomponent Saturated Water Solutions

V. L. Chechulin and S. A. Mazunin

Perm State University, ul. Bukireva 15, Perm, 614990 Russia
phone: (342)2396424, (342)2396303
e-mail: checulinvl@rambler.ru, smazunin@psu.ru

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Abstract—It was found, that in the *n*-component water–salt systems expressed in wt % (baricentral coordinated) the coordinates of compositions of (*n* – 1)-saturated non-variant solution (the eutonics) and (*n* – 2)-saturated solutions lying on the lines of monovariant equilibria are close to a plane (with the accuracy better than 1%). The rule presented is true for a broad class of systems. Taking into account the excessive difficulties of the analysis of systems with the number of components 4 and more this rule significantly facilitates the solution of research and applied problems.

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While using the commonly accepted types of projections the planar representation of investigation results of the multi-component water–salt systems for systems containing 4 or more components is impossible without the loss of a significant part of information. That is why an accurate reversed reproduction of all the array of results from the planar projection of these systems is impossible.

Nevertheless, at the statistic analysis of the composition coordinates on the lines of mono-variant equilibria and in the non-variant points expressed in wt % in the systems of various types the following rule was established:

In the *n*-component water-salt systems coordinates of points corresponding to (*n* – 1)-saturated eutonics and (*n* – 2)-saturated solutions forming the lines of mono-variant equilibrium are close to a plane when n is 4 or more.

This rule is illustrated by many examples of definite systems presented in the table for various types of systems, 4–5-component, simple and mutual.

Analysis of data was carried out by the statistic method of principal components [1] where during the transformation of orthogonal coordinates the space axes are rotated in a manner permitting to minimize the number of dimensions of the space necessary for the presentation of the data array. In some cases for the four-component systems the least squares method was used. It gives analogous results on the planarity of lines of mono-variant equilibrium and non-variant points.

Small number of exclusions from this general rule accompanied by somewhat larger deflection from planarity is connected with the absence of stable diagonals in the four-fold mutual systems, with the formation of the incongruently soluble systems in simple four-fold systems, with the hydrolysis and loss of components in the four-fold, five-fold, simple, and mutual systems.

Theoretical explanation of this rule about the planarity of coordinates of saturated solutions lies probably in degeneracy of the chemical component of interaction of substances in the multi-component saturated solutions and the prevalence of physical interactions in them.

The established rule permits in the course of solving the research problems the prediction of the probable composition of the non-variant eutonic solution and to evaluate experimentally its composition by the simpler use of known methods of investigation of the water-salt systems.

Measure of non-planarity for the data: eutonics and lines of monovariant equilibrium

Water–salt system	Non-coplanarity measure, %
NaCl–KH_2PO_4–$(C_2H_5)_2NH_2Cl$–H_2O at 25°C (2 double eut., 2 double pertion., 2 triple periton)	0.07
NaCl–NH_4Cl–$(C_2H_5)_2NH_2Cl$–H_2O at 25°C [3]	0.55
KCl–Na_2CO_3–K_2CO_3–H_2O at 20°C (formation of congruent chemical compound, 5 double eut., 2 triple eut., 1 triple periton.) [2, 3]	0.79
$NH_4H_2PO_4$–$(NH_4)_2HPO_4$–$(C_2H_5)_2NH_2Cl$–H_2O at 45°C (monotectic type)	0.17
The same (monotectic type), at 40°C	0.16
$NH_4H_2PO_4$–$(NH_4)_2HPO_4$–$(C_2H_5)_3NHCl$–H_2O at 20°C (monotectic type) [3]	0.06
$NH_4H_2PO_4$–NH_4Cl–$(C_2H_5)_2NH_2Cl$–H_2O at 25°C	0.72
$(C_2H_5)_2NH_2Cl$–$NH_4H_2PO_4$–$(NH_4)_2HPO_4$–H_2O at 20°C	0.17
The same, at 25°C	0.13
NaCl–Na_2SO_4–$Na_2CO_3 \cdot 2\,Na_2SO_4$–$H_2O$ at 50°C [2]	0.98
$(NH_4)_2HPO_4$–NH_4Cl–$NH_4H_2PO_4$–H_2O at 20°C [3]	0.45
$NH_4H_2PO_4$–NH_4Cl–$(C_2H_5)_3NHCl$–H_2O at 20°C [3]	0.64
$NH_4H_2PO_4$–$(NH_4)_2HPO_4$–NH_4Cl–$(C_2H_5)_3NHCl$–H_2O at 20°C [3]	0.09
$NH_4H_2PO_4$–$(NH_4)_2HPO_4$–$(C_2H_5)_3NHCl$–H_2O at 60°C (monotectic type) [3]	0.12
$(NH_4)_2HPO_4$–NH_4Cl–$NH_4H_2PO_4$–H_2O at 60°C [3]	0.62
$(NH_4)_2HPO_4$–NH_4Cl–$(C_2H_5)_3NHCl$–H_2O at 60°C [3]	0.96
$NH_4H_2PO_4$–NH_4Cl–$(C_2H_5)_3NHCl$–H_2O at 60°C [3]	0.87
NaCl–KCl–$MgCl_2$–H_2O at 25°C [2]	0.30
$(NH_4)_2HPO_4$–NH_4Cl–Et_2NH_2Cl–H_2O at 20°C	0.42[a]
The same at 25°C	0.41[a]
$NH_4H_2PO_4$–NH_4Cl–$(C_2H_5)_3NHCl$–H_2O at 20°C [3]	0.34[a]
Et_2NH_2Cl–NH_4Cl–$NH_4H_2PO_4$–H_2O at 25°C [3]	0.31[a]
Exclusions (systems without the stable diagonal, with hydrolysis, etc.)	
NaCl–Et_2NH_2Cl–$NaHCO_3$–H_2O at 10°C [3]	1.05
The same at 25°C [3]	0.22
Et_2NH_2Cl–$NaHCO_3$–$Et_2NH_2HCO_3$–$[Et_2NH_2]_2CO_3$–H_2O (CO_2 is isolated and lost) at 10°C [3]	8.35
The same at 25°C (CO_2 is isolated and lost) [3]	4.65
Et_2NH_2Cl–$KHCO_3$–$Et_2NH_2HCO_3$–H_2O at 10°C	1.26
KCl–Et_2NH_2Cl–$KHCO_3$–H_2O at 10°C	5.63
NaCl–Na_2CO_3–$NaHCO_3$–H_2O at 25°C (formation of incongruent chemical substance, 3 double euton., 2 double periton., 2 triple periton., triple euton.) [2, 3]	2.86
$NH_4H_2PO_4$–$(NH_4)_2HPO_4$–NH_4Cl–$(C_2H_5)_3NHCl$–H_2O at 60°C (monotectic type, NH_3 is isolated and lost) [3]	5.46
$(NH_4)_2HPO_4$–$NH_4H_2PO_4$–Et_2NH_2Cl–H_2O (NH_3 is isolated and lost) at 20°C	2.9[a]
$(NH_4)_2HPO_4$–Et_2NH_2Cl–$NH_4H_2PO_4$–H_2O (NH_3 is isolated and lost) at 25°C	2.8[a]

[a] Least squares method is used for construction of plane close to the diagram points.

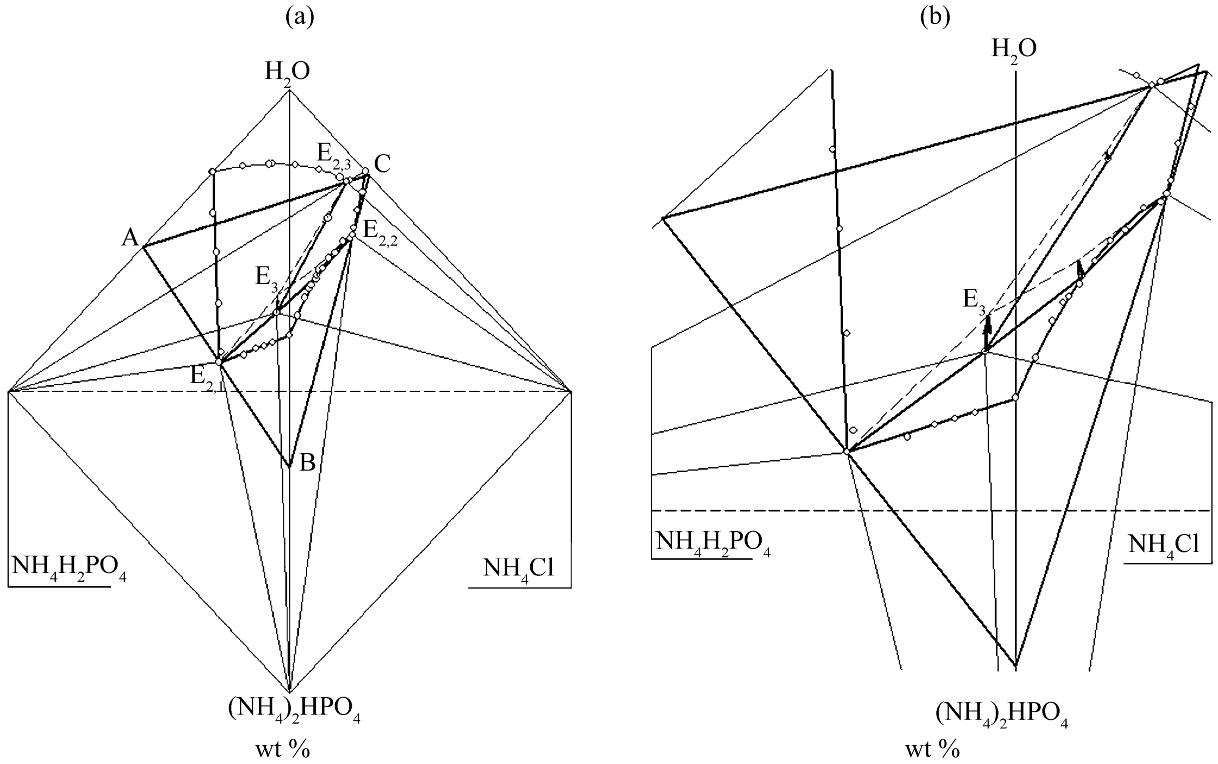

Fig. 1. (a) Plane of optimal projection (ABC) passing through double eutonics and (b) projection of lines of monovatiant equilibrium and triple eutonics on the plane ABC.

Besides the plane corresponding to the statistically obtained solution for the practical use a plane may be applied approximately corresponding to the first one passing through three points most remote from one another and corresponding to (n – 2)-eutonic solutions outlining the systems (see Figs. 1a, 1b).

This plane is the plane of optimal projection of the liquidus surface. It is optimum in the sense that the crystallization fields projected on this plane occupy the largest area. Besides, the existence of such projection of the liquidus surface on the plane permits the evaluation from the coordinates on this plane the starting coordinates of water–salt systems lying in the points of mono- and non-variant equilibrium (what cannot be carried out in the other projections). It facilitates significantly the use of experimental data.

This approach gives a base for constructing the mathematical models for the calculation of compositions and ratio of the equilibrium phases for the arbitrary mixtures of components. This opens the way to the study of the systems with large (theoretically unlimited) number of components.

Hence, the described natural rule characteristic of the multi-component (4 and more) water–salt systems shows mainly physical character of the multi-component saturated solutions. It permits to predict the composition of eutonics in multi-component water–salt systems what facilitates solving the research and applied problems.

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