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Saturated Ternary Systems. II. Equation of Solubility in a Mixture of Two Solvents

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An equation was worked out for the solubility of a substance in the mixture of two solvents which reads $dM_s/M_s = K \cdot M_x^n \cdot dM_x$, where M_s is the molar fraction of the dissolved matter, M_x is the molar fraction of one of the components of the mixed solvent. From this equation subsequent equations for different magnitude of n were derived and was shown that some other reported equations represent special cases of this equation.

The laws regulating the solubility of solid substances in a mixture of two solvents have been studied for a long time and so far a considerable number of mathematical relations have been derived to interpret the experimentally obtained data. In references¹⁻²³ some of those papers are quoted. However, the equations suggested are very often valid only for those ternary systems for which they were evolved. In addition, at first glance it seems as if these relations differ essentially in their mathematical form as well.

Considering that in formation of the equilibrium of a great number of different saturated ternary systems the same or very similar physico-chemical phenomenon is involved, it can be assumed that it could be formulated by an equation which will be able to satisfy many experimental data regardless of subsidiary processes which may develop during the solving process itself. Many equations derived so far, should appear as special cases of such a generalisation.

Having this in mind we started from the point of view that the change of the solubility M_s (expressed by molar fraction) of a certain substance is dependent on the change of the molar fraction M_x of one of the components of the mixed solvent. Expressed in the form of an equation it would give:

$$\frac{dM_s}{M_s} = K \cdot M_x^n \cdot dM_x \quad (1)$$

Here K represents the constant of proportionality while the exponent n takes into account the fact that the nature of the supposed mathematical dependence could differ considerably.

By integration of the equation (1) we obtain for all finite values of n except for $n = -1$:

$$\ln M_s = \frac{K}{n+1} \cdot M_x^{n+1} + R \quad (2)$$

or for $n = 1$ we get:

$$\ln M_s = K \cdot \ln M_x + R \quad (3)$$

This shows that the expression (2) represents a series of families of exponential curves, while the equation (3) represents the algebraic equation of any order.

If n takes the value 0, the integral (2) acquires the form

$$\ln M_s = K \cdot M_x + R \quad (2a)$$

If we neglect the molar fraction of the solute as a value of a smaller order of magnitude compared with the values of the molar fractions of both components of the solvent, the relation

$$M_x + M_y = 1$$

will be valid. (M_y is the molar fraction of the other component of the mixed solvent). Accordingly, equation (2a) could be written as follows:

$$M_s = M_{s(x)} e^{-K \cdot M_y} \quad (2b)$$

where $M_{s(x)}$ means the solubility in pure solvent x .

From the equation (2b) it can be easily seen that it is valid for the case where the substance is soluble in both components of the mixed solvent because if $M_x = 1$ we obtain $M_s = M_{s(x)}$, while if $M_x = 0$ we obtain $M_s = M_{s(x)} \cdot e^{-K} = M_{s(y)}$.

On the other hand if we take the antilogarithm of the integral (3), it follows that

$$M_s = M_{s(x)} \cdot M_x^K \quad (3a)$$

When $M_x = 1$, M_s becomes $M_{s(x)}$ and when $M = 0$, M_s is equal to 0 and that is equivalent to $M_{s(y)}$ which from it follows that the integral (3) is applicable only for the systems where a substance is soluble exclusively in one of the two components of the binary solvent.

It is evident from the equation (2b) that the constant K could be given in the form

$$K = \ln \frac{M_{s(x)}}{M_{s(y)}} \quad (4)$$

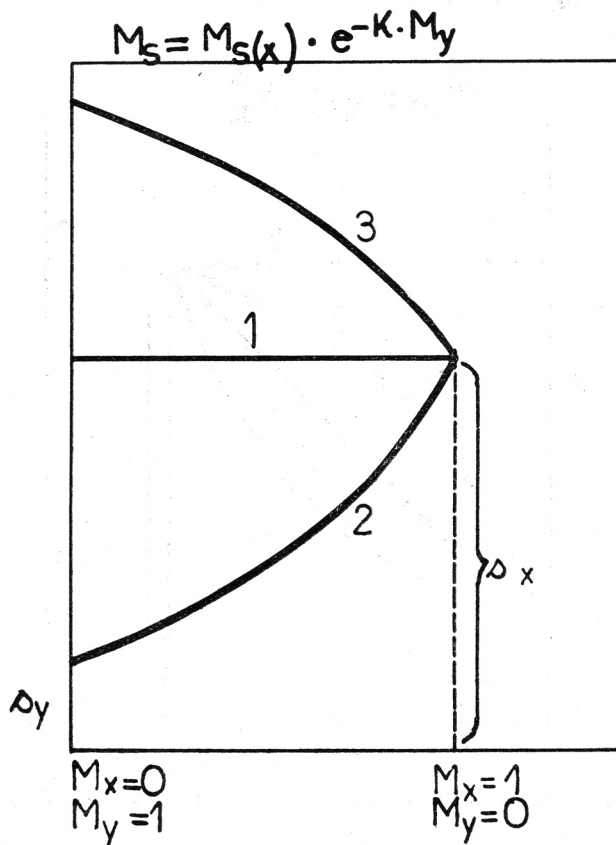
This relation suggests the physico-chemical significance of the constant K :

a) If $M_{s(x)} = M_{s(y)}$ then $K = 0$. — The solubility of the substance is equal in both components of the binary solvent so that no changes happen when their ratio is changed (see the line 1, Fig. 1). In other words, both components of the solvent contribute equally to the solving process,

while no subsidiary processes exist between the components themselves (solvation and the like).

b) If $M_{s(x)} > M_{s(y)}$ then $K > 0$ and $M_s = M_{s(x)} \cdot e^{-K \cdot M_y}$. — The solubility is greater in one of the components (x) of the mixed solvent (see the curve 2, Fig. 1). Since no linear course of the isotherm of solubility exists, it might be supposed that there is some sort of interaction between the components of the solvent itself.

c) If $M_{s(x)} < M_{s(y)}$ then $K < 0$ and $M_s = M_{s(x)} \cdot e^{-K \cdot M_y}$. — The solubility is greater in the second component of the solvent (y) and the nature of the interaction is of a different type (see the curve 3, Fig. 1).



Similarly it could be derived from equation (3a) that

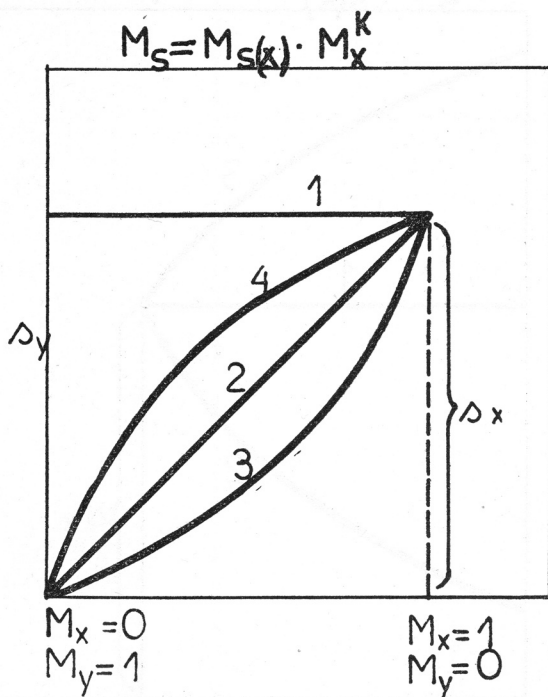
a) If $K = 0$ then $M_s = M_{s(x)} e^{K \cdot M_y}$. — The solubility does not change which means that only one solvent is present (see the line 1, Fig. 2).

b) If $K = 1$ then $M_s = M_{s(x)} \cdot M_x$. A linear change of solubility occurs from 0 to the value of solubility in the pure solvent x (see the curve 2, Fig. 2). This means that the presence of the second component does not change the solubility of the substance in the first component but only dilutes the

latter. The course of solubility isotherme is linear meaning that no interaction takes place between the two components of the solvent.

c) If $K > 1$ then $M_s = M_{s(x)} \cdot M_x^K$. At the beginning the change of solubility is smaller, later on becoming greater than that in case b) (see the curve 3, Fig. 2). This means that with a smaller concentration of the solvent x all its molecules are not available for the solving process but bound in a certain way to the second component of the solvent (solvation). Only when these bonds are saturated the surplus of the solvent x can serve for the solving process itself.

d) If $K < 1$ then $M_s = M_{s(x)} \cdot M_x^K$. — At first the change of solubility is greater, becoming later on smaller than that in case b) (see curve 4, Fig. 2).



The product resulting from the interaction between the components of the mixed solvent helps the solving process of the substance in the pure component x.

From the examples described it can be seen that the equations (2b) and (3a) besides offering a remarkable number of possibilities for an approximation of the isotherms of solubility in binary liquid systems, can also be explained from a physico-chemical point of view.

Furthermore it could be shown that many of the equations cited in literature can be represented after a simple transformation as special cases of the equation (1) or of the integral (2a) or (3), respectively.

Since our equations (2a) and (3) contain only the molar fraction of one of the solvents as a variable on which solubility depends, it is quite natural that only such empiric and theoretically derived equations can be reduced to them which a) do not contain an other variable except this, or b) contain only such variables which are in a known dependence on the molar percentage of one of the two solvents.

Here are a few examples for both kinds of such equations of solubility:

ad a) 1. The equation of solubility after Bodländer² reads in the original notation as follows:

$$W = K \sqrt[3]{S} \quad (5) \quad \text{or} \quad \ln W = \ln K + 1/3 \ln S \quad (5a)$$

Upon inserting our designations for $W = M_x$ and $S = M_s$ and upon solution the ratio we obtain:

$$\ln M_s = 3 \ln M_x - 3 \ln K \quad (5b)$$

When in this equation we substitute $-3 \ln K = R$ and $3 = K$ we obtain our equation (3).

ad a) 2. After Treadwell⁹ the equation in question reads:

$$S = S_0 \cdot C_w^2 \cdot K \quad (6)$$

i. e. in our notation:

$$M_s = M_{s(x)} \cdot M_x^2 \cdot K \quad (6a)$$

By means of logarithms we obtain:

$$\ln M_s = 2 \ln M_x + \ln M_{s(x)} + \ln K \quad (6b)$$

i. e. by contracting the constant values $\ln M_{s(x)} + \ln K = R$ and $2 = K$ we obtain our equation (3).

ad a) 3. Angelescu, Leone and Dumitrescu^{10,12,13} use the following equation:

$$S_c \cdot S_0 = K' \cdot C^P \quad (7)$$

Upon inserting our designations for $S_c = M_s$, $S_0 = M_{s(x)}$, $P = K$, $C = M_x$ and applying the natural logarithm we obtain:

$$\ln M_s = \ln M_{s(x)} - \ln K' + K \cdot \ln M_x \quad (7a)$$

while upon contracting the constants $\ln K' + \ln M_{s(x)} = R$ we obtain our equation (3).

ad a) 4. The equation of solubility after Tamman¹¹ reads:

$$\log (S_0/S) = \lambda \cdot C \quad (8)$$

Upon inserting our designation for $C = M_x$, $S_0 = M_{s(x)}$, $S = M_s$, $\lambda = K$ one can write as follows:

$$\ln (M_{s(x)}/M_s) = K (1 - M_x) \quad (8a)$$

$$\text{or} \quad \ln M_s = \ln M_{s(x)} + K \cdot M_x - K \quad (8b)$$

Upon contracting the constant values $\ln M_{s(x)} - K = R$ we obtain our equation (2a).

ad a) 5. Ahumov's equation^{16,23} reads in its original notation:

$$\log y = \log y_1 + n \cdot \log(1 - x) \quad (9)$$

Upon substitution of our symbols for $y = M_s$, $y_1 = M_{s(x)}$, $x = M_y$ and $n = K$ and after application of the natural logarithms we obtain:

$$\ln M_s = \ln M_{s(x)} + K \cdot \ln(1 - M_y) \quad (9a)$$

If we insert here $\ln M_{s(x)} = R$ and $M_y = 1 - M_x$ we obtain our equation (3).

ad a) 6. Kričevski²¹ brings the following equation:

$$\ln M_s = M_x \cdot \ln s_x + M_y \cdot \ln s_y \quad (10)$$

Upon substitution $M_y = 1 - M_x$ we obtain

$$\ln M_s = M_x \cdot \ln s_x + \ln s_y \cdot (1 - M_x) \quad (10a)$$

resp.

$$\ln M_s = M_x (\ln s_x - \ln s_y) + \ln s_y \quad (10b)$$

If we contract the constant values $\ln s_x - \ln s_y = K$ and $\ln s_y = R$ we obtain our equation (2a).

ad b) 1. The general form of Born's equation²⁴ of solubility in a binary mixture of solvents could be written:

$$\log S_x = \log S_w - K' \left(\frac{1}{D_x} - \frac{1}{D_w} \right) \quad (11)$$

where S_x stands for solubility and D_x is the dielectric constant either of one of the solvents or of the mixture of two solvents, while S_w and D_w are the solubility and dielectric constant of the other solvent (water). In our notation Born's equation reads:

$$\ln M_s = \ln M_{s(y)} - \frac{K'}{D_x} + \frac{K'}{D_y} \quad (11a)$$

In order to reduce also this equation to our equation, we must express the dielectric constant D_x of the solution as a function of the molar fraction M_x . Akerlöf and Short²⁵ showed on a diagram that the dielectric constant of the binary mixture water — acetone is the linear function of the percentage of acetone:

$$D_x = -K'' \cdot M_x + K''' \quad (12)$$

At temperature of 20°C this linear ratio is valid up to circa 60% of acetone in the mixture. If we are allowed to apply the equation (12) also to ternary systems, then Born's equation (11a) will assume in our notation the following form:

$$\ln M_s = \ln M_{s(y)} - \frac{K'}{K''' - K'' \cdot M_x} + \frac{K'}{D_y} \quad (11b)$$

Upon inserting $\ln M_{s(y)} + \frac{K'}{D_y} = R$ we obtain

$$\ln M_s = - \frac{K'}{K''' - K'' \cdot M_x} + R \quad (11c)$$

For those systems where (12) is valid, we can insert into the equation (11c) $M_x = 1 - M_y$ and then we obtain:

$$\ln M_s = - \frac{K'}{K'' - K' + K'' \cdot M_y} + R \quad (11d)$$

Upon contracting $K'' - K' = -K$ there follows

$$\ln M_s = - \frac{K'}{K'' \cdot M_y - K} + R \quad (11e)$$

The same type of equation can be obtained from our equation (2). Namely, if in this equation we insert $n = -2$ we obtain

$$\ln M_s = - \frac{-K}{M_x} + R \quad (2c)$$

If we insert here $K = \frac{K'}{-K''}$ and $M_x = 1 - M_y$ it follows

$$\ln M_s = \frac{-K'}{-K''} \cdot \frac{1}{1 - M_y} = - \frac{K'}{K'' \cdot M_y - K'} + R \quad (2d)$$

By comparing the equation (2d) with above transformed Born's equation (11e) we can observe that both these equations are identical as to their forms, and that they differ only by the notation of a constant in the denominator of the first term.

ad b) 2. The empiric equation of solubility mentioned by Ricci and Davis¹⁸ reads as follows:

$$\log S_x - \log S_w = 3 (\log D_x - \log D_y) \quad (13)$$

If we substitute here also $D_x = -K \cdot M_x + K''$ we obtain

$$\log S_x = 3 \log (K'' - K \cdot M_x) + \log S_w - 3 \log D_y \quad (13a)$$

If in this expression we contract the constants $\log S_w - 3 \log D_y = R'$ and insert $M_x = 1 - M_y$ and $3 = K''$ we obtain

$$\log S = K'' \cdot \log (K'' - K + K \cdot M_y) + R' \quad (13b)$$

and if then we contract $K'' - K = K'$ we obtain in our notation the following equation:

$$\ln M_s = K'' \cdot \ln (K'' + K \cdot M_y) + R'. \quad (13c)$$

The same form of equation can be obtained also from our equation (3):

$$\ln M_s = K \cdot \ln M_x + R \quad (3)$$

Namely, if we insert $M_x = 1 - M_y$ and $K = K''$ and carry out a transformation, we obtain

$$\ln M_s = K'' \cdot \ln (1 - M_y) + R \quad (3b)$$

$$\ln M_s = K'' \cdot \ln \frac{K'' (1 - M_y)}{K''} + R \quad (3c)$$

resp.
$$\ln M_s = K'' \cdot \ln (K'' - K'' \cdot M_y) - \ln K'' + R \quad (3d)$$

After inserting $-\ln K' + K = R'$ it follows:

$$\ln M_s = K'' \cdot \ln(K' - K'' \cdot M_y) + R' \quad (3e)$$

By comparing the equation (3e) with the equation (13c) it can be seen, that they differ only in the notation of a constant in brackets.

It was shown above that many well known solubility equations can be easily transformed to one of the forms of our solubility equation and that they therefore represent its special cases.

This fact allows the supposition that our general equation formulates a widely spread regularity of the equilibrium of the saturated ternary systems. The differences among many solubility equations are only apparent and are caused by the different manner of expressing experimental data.

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IZVOD

Zasićeni ternarni sistemi. II. Jednadžba topivosti jedne tvari u smjesi dvaju otapala

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Izvedena je jednadžba za topivost neke tvari u smjesi dvaju otapala koja glasi: $dM_s/M_s = K \cdot M_x^n \cdot dM_x$ gdje je M_s molarni razlomak otopljene tvari, a M_x molarni razlomak jedne od komponenata miješanog otapala. Od ove jednadžbe izvedene su daljnje jednadžbe za razne veličine n . Pokazano je, da neke iz literature poznate jednadžbe topivosti predstavljaju specijalne slučajeve gore navedene jednadžbe.

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