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Abstract

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SOME REGULARITIES IN THE THERMODYNAMICS OF AQUEOUS-SALT TERNARY SOLUTIONS

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The experimental material on the isopiestic study of ternary aqueous-salt solutions accumulated at the present time makes it possible to extract very useful information about the thermodynamic features of these solutions. As has already been pointed out earlier (⌒1), in the first approximation for 1-1 electrolytes

$$\frac{1}{m} = \frac{1}{m_{10}} y_1 + \frac{1}{m_{20}} y_2 + b y_1 y_2, \qquad [a_w]$$

$$\ln \frac{a_i}{a_{i0}} = K(1-y_i)^2 \ln \frac{1}{a_w} + \ln y_1, \qquad [a_w] \tag{1}$$

where K is a constant quantity, and b is in general a function of the activity of water*. In accordance with the second equation (1), for the activity coefficient one can obtain the equation (see (⌒1))

$$\ln \frac{\gamma_i}{\gamma_{i0}} = \frac{1}{2} K(1-y_i)^2 \ln \frac{1}{a_w} + \ln \frac{m_{i0}}{m}, \qquad [a_w] \tag{2}$$

which, like equations (1), refers to isopiestic conditions. However, the method of using thermodynamics currently adopted is connected with the use of activity coefficients under isomolal conditions. Therefore let us consider the transition from isopiestic conditions to isomolal ones.

The activity of water a_w under isopiestic conditions corresponds to the molality of the binary solution m_{10}. When the composition of the ternary solution is changed under isomolal conditions, the activity of water changes, say, by Δa_w. Let this change correspond to a change of the quantity m_{10} by Δm_{10}. Then one can write

$$\ln \gamma_{10}(m_{10}+\Delta m_{10}) = \ln \gamma_{10}(m_{10}) + \frac{\partial \ln \gamma_{10}}{\partial m_{10}} \Delta m_{10} + \frac{1}{2} \frac{\partial^2 \ln \gamma_{10}}{\partial m_{10}^2} (\Delta m_{10})^2 + \ldots \tag{3}$$

From the first equation (1) we find

$$\frac{m_{10}}{m} = \frac{1 + (m_{10}/m_{20} - 1)y_2}{1 - mby_1y_2}. \qquad [a_w] \tag{4}$$

In accordance with this relation the quantity Δm_{10} is equal to

$$\Delta m_{10} = m\frac{(m_{10}/m_{20} - 1)y_2 + mby_1y_2}{1 - mby_1y_2}. \tag{5}$$

For the transition from isopiestic conditions to isomolal ones, it is necessary in equation (2), instead of $\ln\gamma_{10}$, to substitute its value $\ln\gamma_{10}(m_{10} + \Delta m_{10})$ according to equation (3), with the first term on the right-hand side of this equation to be referred to constant total molality, i.e. $\ln\gamma_{10}(m_{10}) = \ln\gamma_{10}(m)$. Also using equations (4) and (5), from (2) we obtain

$$\lg\frac{\gamma_1}{\gamma_{10}} = A_1m_2 + B_1m_2^2 + \lg\frac{1 + (m_{10}/m_{20} - 1)y_2}{1 - mby_1y_2}, \qquad [m] \tag{6}$$

* In the present work the notation of work (^1) is used without special reservations.

where

$$A_1 = \frac{\partial\lg\gamma_{10}}{\partial m_{10}}\,\frac{m_{10}/m_{20} - 1 + m_1b}{1 - mby_1y_2};$$

$$B_1 = \frac{1}{2}\frac{\partial^2\lg\gamma_{10}}{\partial m_{10}^2}\left(\frac{m_{10}/m_{20} - 1 + m_1b}{1 - mby_1y_2}\right)^2 + K\frac{1}{m^2}\lg\frac{1}{a_w}. \tag{7}$$

If

$$\left(\frac{m_{10}}{m_{20}} - 1\right)y_2 \ll 1, \qquad mby_1y_2 \ll 1, \tag{8}$$

then, expanding the last term on the right-hand side of equation (6) in a series and retaining only the first term of this series, we obtain

$$\lg\gamma_1 = \lg\gamma_{10} - \alpha_{12}m_2 - \beta_{12}m_2^2, \qquad [m] \tag{9}$$

where

$$-\alpha_{12} = A_1 + \frac{1}{2.3}\frac{1}{m}\left(\frac{m_{10}}{m_{20}} - 1\right) + \frac{1}{2.3}b,$$

$$-\beta_{12} = B_1 - \frac{1}{2.3}\frac{1}{m}b. \tag{10}$$

Equations of type (9) were considered in (1), but in that work no rigorous transition from isopiestic conditions to isomolal conditions was made. For calculations by equation (9) it is necessary to know the quantities K and b, which are determined by the thermodynamic characteristics of the ternary solution. All other quantities entering this equation are determined by the properties of binary solutions. In the zero approximation $K = 0$, $b = 0$ (ideal solutions), and only these latter quantities remain in equation (9). Thus, in the zero approximation, equation (9) makes it possible to calculate the activity coefficients of a ternary solution solely on the basis of knowledge of the properties of binary solutions.

Table 1

Illustration of the applicability of assumption (13) to aqueous solutions of hydrochloric acid and alkali-metal chlorides

NaCl	NaCl	NaCl	KCl	KCl	KCl	CsCl	CsCl	CsCl
m_{10}	m_{20}	$\frac{m_{10}}{m_{20}}$	m_{10}	m_{20}	$\frac{m_{10}}{m_{20}}$	m_{10}	m_{20}	$\frac{m_{10}}{m_{20}}$
3.00	3.70	0.811	3.00	4.24	0.708	3.00	4.50	0.667
2.48	3.00	0.827	2.26	3.00	0.753	2.16	3.00	0.720
Average		0.819			0.731			0.694

Analysis of the experimental data, on which we shall not dwell here, shows that real aqueous-salt three-component solutions are very close to ideal ones, i.e., the use of the zero approximation cannot cause a large error. Further, for the calculation one may adopt two more important assumptions.

1. In equation (9) the last term may be neglected, i.e., instead of (9) one may use the equations

$$\lg\gamma_1 = \lg\gamma_{10} - \alpha_{12}m_2, \qquad [m]$$

$$\lg\gamma_2 = \lg\gamma_{20} - \alpha_{21}m_1, \qquad [m] \tag{11}$$

where

$$-\alpha_{12} = \left(\frac{\partial \lg\gamma_{10}}{\partial m_{10}} + \frac{1}{2.3}\frac{1}{m}\right)\left(\frac{m_{10}}{m_{20}} - 1\right),$$

$$-\alpha_{21} = \left(\frac{\partial \lg\gamma_{20}}{\partial m_{20}} + \frac{1}{2.3}\frac{1}{m}\right)\left(\frac{m_{20}}{m_{10}} - 1\right). \tag{12}$$

2. It may be assumed that, in the first approximation,

$$\frac{m_{10}}{m_{20}} - 1 = \text{const.} \tag{13}$$

Table 1 gives data that illustrate this point for solutions of hydrochloric acid and alkali-metal chlorides. The quantity m_{10} in this table denotes the molality of HCl, and m_{20} the molality of the corresponding salt. Literature data were used for the calculations ([2]). We see that in the present case the assumption (13) may be adopted without introducing a significant error.

Taking these two assumptions into account, the coefficients on the right-hand side of equation (11) are constant and, as is easy to see, these equations express the so-called Harned rule ([2,3]).

Table 2 gives a comparison of the values of the coefficients α_{12} and α_{21} calculated by us with values determined directly; these values are taken from the monograph by Harned and Owen ([3]). In the calculations, hydrochloric acid was chosen as the first component. The value of the derivative of the decimal logarithm of the activity coefficient was determined from literature data at a molality equal to 3. These values were determined numerically and proved to be, for HCl, NaCl, KCl, and CsCl, respectively, 0.119, 0.038, 0.004, and −0.007. The values of m_{10}/m_{20} were used from the data in Table 1. In general, the agreement of the calculated values with the experimental ones is quite satisfactory.

Table 2

Comparison of calculated values of the coefficients of equation (11) with experimental values for aqueous solutions of hydrochloric acid and alkali-metal chlorides for a total molality equal to 3

	NaCl	KCl	CsCl
α_{12} exp.	0.031	0.062	0.098
α_{12} calc.	0.050	0.041	0.083
$-\alpha_{21}$ exp.	0.058	0.054	0.041
$-\alpha_{21}$ calc.	0.044	0.056	0.064

Let us consider another example. Calculation by equations (11) for solutions of NaCl–KCl–H_2O at a total molality equal to 4 gives $\alpha_{12} = 0.019$, $-\alpha_{21} = 0.016$ (α_{12} denotes the coefficient on the right-hand side of equation (11) for NaCl, α_{21} that for KCl). Solutions of NaCl–KCl–H_2O have been studied by the isopiestic method ([1]). Calculation taking these data into account in the first approximation gives $\alpha_{12} = 0.023$, $-\alpha_{21} = 0.010$. The values of these coefficients, determined by the direct method ([2]), are respectively 0.024 and 0.009. Consequently, in the present case, calculation in the first approximation gives complete agreement with calculation by the other method. Calculation in the zeroth approximation gives somewhat different results.

The examples given show that, in fact, the zeroth approximation makes it possible to calculate (or at least estimate) the numerical value of the coefficients of Harned's rule solely from data for binary solutions. In this connection, attention should be drawn to the following. The constancy of the quantities α_{12} and α_{21} is determined, as is easy to see, by the possibility of applying the approximate relation

$$\lg\left[1+\left(\frac{m_{10}}{m_{20}}-1\right)y_2\right]\approx\frac{1}{2.3}\left(\frac{m_{10}}{m_{20}}-1\right)y_2, \tag{14}$$

which we used in passing from (6) to (9) (assumption (8)); condition (13) must also be satisfied. The possibility of applying assumptions (14) and (13) can be determined from data for the corresponding binary solutions, if, of course, the dependence of the activity of water on molality is known for them. Such data are available for a large number of binary solutions ([2]). Further, by equation (3) one can also estimate the value of the quantity β_{12} in equation (9), likewise without resorting to experiment. Consequently, by analyzing the dependence of the activity of water and of the activity coefficient of the salt on molality for the corresponding binary solutions, it is possible to establish whether the given ternary solution obeys Harned' s rule or not. If Harned' s rule is obeyed, numerical values of the coefficients α_{12} and α_{21} can be found. If Harned' s rule is not obeyed,

then the corresponding analytical dependence can also be found for the activity coefficients of a ternary solution under isomolal conditions.

Here we have considered only solutions of 1-1 electrolytes. Analogous considerations are also applicable to ternary solutions of any electrolytes.

In conclusion, let us emphasize that, in our opinion, in analyzing the properties of solutions it is more convenient to use isopiestic conditions rather than isomolal ones. In this case simpler relations are obtained (real solutions are close to ideal ones), and there is no need for rather laborious calculations.

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