PHYSICAL CHEMISTRY

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1963

SovietRxiv

Abstract

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ACTIVITY OF ALKALI-METAL AND AMMONIUM CHLORIDES IN AQUEOUS SODIUM CHLORIDE SOLUTION

(Presented by Academician V. I. Spitsyn, May 29, 1963)

The McKay—Perring differential equation for ternary solutions

$$\left(\frac{\partial \ln a_i/a_{i0}}{\partial \ln a_w}\right)_{y_i} = \frac{1}{0.018}\left[\frac{1}{m_{i0}} - \frac{1}{m} - (1-y_i)\frac{\partial(1/m)}{\partial y_i}\right] a_w, \tag{1}$$

where m is the total molality of the salts; a_i and a_{i0} are the activity of the salt of the i-th component in the ternary solution and in the corresponding binary salt—water solution at water activity a_w; m_{i0} is the molality of the salt of the i-th component in the corresponding binary salt—water solution; and y_i is the mole fraction of the salt of the i-th component, calculated without allowance for water, makes it possible to determine the activity a_i relative to a_{i0}, if the dependence of the total molality of the salts under isopiestic conditions is known.

We studied aqueous solutions of sodium chloride with the chlorides of lithium, potassium, rubidium, cesium, and ammonium under isopiestic conditions at 25°. It was found that, to a first approximation, the dependence of the total molality on composition under isopiestic conditions can be described by the equation

$$\frac{1}{m} = \frac{1}{m_{10}}y_1 + \frac{1}{m_{20}}y_2 + by_1y_2, \quad [a_w] \tag{2}$$

where b is a certain quantity, constant under isopiestic conditions. The dependence of this quantity on the activity of water is determined by the equation

$$b = A + Ba_w, \tag{3}$$

where A and B are constants. Figure 1 shows the agreement of equation (3) with our experimental data. It follows from this figure that

$$b = -0.0163 + 0.027a_w \quad \text{for solutions NaCl—LiCl—H}_2\text{O},$$
$$b = 0.0188 - 0.035a_w \quad \text{for solutions NaCl—KCl—H}_2\text{O},$$
$$b = 0.0288 - 0.058a_w \quad \text{for solutions NaCl—RbCl—H}_2\text{O},$$
$$b = 0.0306 - 0.074a_w \quad \text{for solutions NaCl—CsCl—H}_2\text{O}.$$

For solutions of NaCl—NH_4Cl—H_2O, the value of b is small ($\cong -0.001$), and therefore it does not seem possible to determine its dependence on the activity of water, since the experimental errors in determining the value of b are quite substantial here.

Substituting (2), (3) into (1), after integration we obtain

$$\ln \frac{a_i}{a_{i0}} - \ln \frac{a_i^*}{a_{i0}^*} = -\frac{1}{0.018} \left[A \ln a_w + B(a_w - 1)\right] (1 - y_i)^2, \tag{4}$$

where a_i^* and a_{i0}^* are the activities of the salt of the i-th component in an infinitely dilute solution. This equation can be simplified if we take into account the approximate relation

$$\ln a_w \cong a_w - 1, \tag{5}$$

which is valid for water activities close to unity. Then

$$\ln \frac{a_i}{a_{i0}} - \ln \frac{a_i^*}{a_{i0}^*} = -K \ln a_w (1 - y_i)^2, \tag{6}$$

where

$$K = \frac{1}{0.018}(A + B). \tag{7}$$

Calculation from the data given above gives, for solutions of LiCl, KCl, RbCl, and CsCl, values of K respectively equal to $+0.59$, -0.90, -1.62, and -2.41.

Figure 2 shows the dependence of the quantities A and B in equation (3) and of the quantity K on the radius of the ion forming, with sodium chloride and water, the solution. The ionic radii are taken from Ref. [2]. The dashed straight line marks the radius of the sodium ion. We see that the value of the quantity B is satisfactorily described by a straight line whose equation is

$$B = 0.106(0.97 - r). \tag{8}$$

For NaCl–NH_4Cl–H_2O solutions, the quantity b, and consequently also the quantity K, have small values. In accordance with the relationships shown in

Fig. 1. Agreement of equation (3) with experimental data

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Fig. 2. Dependence of the quantities A, B in equation (3) and of the quantity K on the ion radius

Figure 2: Fig. 2. Dependence of the quantities A, B in equation (3) and of the quantity K on the ion radius

Fig. 2, this means that in the $NaCl—NH_4Cl—H_2O$ solution the ionic radius of sodium is close to the radius of the ammonium ion.

Fig. 1. Agreement of equation (3) with experimental data

Fig. 2. Dependence of the quantities A, B in equation (3) and of the quantity K on the ion radius

Equation (6) is based on equation (2), which assumes the constancy of the quantity b under isopiestic conditions. This condition is not exactly fulfilled for all systems. Figure 3 shows the dependence of the quantity b on composition for $NaCl—CsCl—H_2O$ solutions. The experimental points clearly lie on a straight line not parallel to the abscissa axis, i.e., here the quantity b under isopiestic conditions cannot be taken as constant. A similar picture (though less clearly expressed) is also given by the systems $NaCl—KCl—H_2O$ and $NaCl—RbCl—H_2O$. Calculation shows that

$$b = 0.0168 - 0.028\,a_w + 0.0027\,y_1 \tag{9}$$

for the $NaCl—KCl—H_2O$ system,

$$b = 0.0354 - 0.068\,a_w + 0.0044\,y_1 \tag{10}$$

for the $NaCl—RbCl—H_2O$ system,

$$b = 0.0132 - 0.054\,a_w + 0.0100\,y_1 \tag{11}$$

for the $NaCl—CsCl—H_2O$ system, and in the general case

$$b = k_1 + k_2 a_w + k_3 y_1. \tag{12}$$

Substituting equations (2), (12) into (1), after integration and transformations taking (5) into account, we obtain

$$\ln \frac{a_1}{a_{10}} - \ln \frac{a_1^*}{a_{10}^*} = -\frac{1}{0{,}018}(k_1 + k_2 + 2k_3 y_1) y_2^2 \ln a_w;$$

Fig. 3. Dependence of the quantity b on composition for solutions NaCl—CsCl —H_2O: 1—$a_w = 0{,}8227$, 2—$a_w = 0{,}8433$, 3—$a_w = 0{,}8739$, 4—$a_w = 0{,}8941$, 5—$a_w = 0{,}9080$.

Figure 3: Fig. 3. Dependence of the quantity b on composition for solutions NaCl—CsCl—H_2O: 1—$a_w = 0{,}8227$, 2—$a_w = 0{,}8433$, 3—$a_w = 0{,}8739$, 4—$a_w = 0{,}8941$, 5—$a_w = 0{,}9080$.

$$\ln\frac{a_2}{a_{20}} - \ln\frac{a_2^*}{a_{20}^*} = -\frac{1}{0{,}018}(k_1 + k_2 - k_3 + 2k_3y_1)y_1^2 \ln a_w. \tag{13}$$

It can be shown that if the entropy of mixing of a ternary solution does not depend on dilution, then the left-hand side of equations (4) and (13) will be proportional to the partial potential energy of formation of the solution under isopiestic conditions. Then the total potential energy of formation of a ternary solution from the corresponding binary solutions under isopiestic conditions will be proportional to

$$\Delta E \sim K \ln\frac{1}{a_w} \cdot y_1y_2 \tag{14}$$

in the case of equation (4), and

$$\Delta E \sim (k_1 + k_2 + k_3y_1) \ln\frac{1}{a_w} \cdot y_1y_2 \tag{15}$$

in the case of equation (13). Analogous relations hold in the formation of binary homodynamic solutions (equations of the theory of regular solutions, empirical Margules equations). Thus, under isopiestic conditions the formation of a ternary solution from binary solutions proceeds in accordance with the regularities of binary homodynamic solutions.

Fig. 3. Dependence of the quantity b on composition for solutions NaCl—CsCl —H_2O: 1—$a_w = 0{,}8227$, 2—$a_w = 0{,}8433$, 3—$a_w = 0{,}8739$, 4—$a_w = 0{,}8941$, 5—$a_w = 0{,}9080$.

Let us consider some features of ternary solutions within the limits of applicability of equation (4). We represent the activity of the salt of the i-th component in the case of 1—1 electrolytes by the equations

$$\ln a_i = \ln m_i + \ln m + 2\ln\gamma_i; \tag{16}$$

$$\ln a_{i0} = 2\ln m_{i0} + 2\ln\gamma_{i0};$$

$$\ln a_i^* = \ln m_i^* + \ln m^*; \qquad \ln a_{i0}^* = 2 \ln m_{i0}^*. \tag{17}$$

Then

$$\ln \frac{a_i}{a_{i0}} - \ln \frac{a_i^*}{a_{i0}^*} = 2 \ln \frac{m}{m_{i0}} - 2 \ln \frac{m^*}{m_{i0}^*} + 2 \ln \frac{\gamma_i}{\gamma_{i0}}. \tag{18}$$

Suppose that in an infinitely dilute solution the van’ t Hoff law is valid; for 1—1 electrolytes this leads to the relation $m_{i0}^* = m^*$. Combining (18), (4), we obtain

$$\ln \frac{\gamma_i}{\gamma_{i0}} = \ln \frac{m_{i0}}{m} - \frac{1}{2} K \ln a_w (1 - y_i)^2. \tag{19}$$

Equation (2) can be transformed:

$$\frac{m_{i0}}{m} = 1 + \beta_i (1 - y_i) + b m_{i0} y_i (1 - y_i), \tag{20}$$

where

$$\beta_1 = \frac{m_{10}}{m_{20}} - 1, \qquad \beta_2 = \frac{m_{20}}{m_{10}} - 1. \tag{21}$$

Applying the approximate relation

$$\ln \frac{m_{i0}}{m} \simeq \beta_i (1 - y_i) + b m_{i0} y_i (1 - y_i), \tag{22}$$

we write equation (19) in the form

$$\ln \frac{\gamma_i}{\gamma_{i0}} = \beta_i (1 - y_i) + b m_{i0} y_i (1 - y_i) - \frac{1}{2} K \ln a_w (1 - y_i)^2. \tag{23}$$

We transform this equation to the final form

$$\begin{aligned} \lg \gamma_1 &= \lg \gamma_{10} - \alpha_{12} m_2 - \beta_{12} m_2^2; \\ \lg \gamma_2 &= \lg \gamma_{20} - \alpha_{21} m_1 - \beta_{21} m_1^2, \end{aligned} \tag{24}$$

where

$$\begin{aligned} \alpha_{12} &= -\frac{1}{2.3} \frac{1}{m} (\beta_1 + b m_{10}); \qquad & \alpha_{21} &= -\frac{1}{2.3} \frac{1}{m} (\beta_2 + b m_{20}); \\ \beta_{12} &= \frac{1}{2.3} \frac{1}{m^2} \left(b m_{10} + \frac{1}{2} K \ln a_w \right); \qquad & \beta_{21} &= \frac{1}{2.3} \frac{1}{m^2} \left(b m_{20} + \frac{1}{2} K \ln a_w \right). \end{aligned} \tag{25}$$

Calculations show that, for the systems studied by us, $\alpha_{12} > \beta_{12}$, $\alpha_{21} > \beta_{21}$. Therefore equations (24) may be written in the approximate form

$$\begin{aligned} \lg\gamma_1 &= \lg\gamma_{10} - \alpha_{12} m_2; \\ \lg\gamma_2 &= \lg\gamma_{20} - \alpha_{21} m_1. \end{aligned} \tag{26}$$

Equations (24) and (26) apply to isopiestic conditions. If the isopiestic conditions are close to isomolal ones, then equations of the type (24) and (26) may also be applied to isomolal conditions. Then equation (26) will express Harned' s empirical rule, while equation (24) will express corrections to Harned' s rule (3). Thus, in our opinion, the meaning of the constants in Harned' s rule acquires a distinct physical content.

In conclusion, we note that the regularities indicated here were also observed for other systems studied by us. The systems NaCl—LiCl—H_2O, NaCl—KCl—H_2O, and NaCl—CsCl—H_2O were studied earlier (4–6). However, for the calculations carried out in the present work, the literature data were insufficient.

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Received
27 V 1963

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Note: Figure translations are in progress. See original paper for figures.

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