CONSTRUCTION AND INTERPRETATION OF THE \text{LiCl–LiOH–Density}
THREE-DIMENSIONAL SYSTEM

A. V. Skolunov

Accuracy in determining the density of a ternary solution also brings about accuracy in the quantitative content of one of the components of the solution, making it possible to eliminate thereby more laborious chemical analysis for the other component. An attempt has been made previously to construct nomograms for this ternary system using two methods of expressing concentration: in \% by wt. and in g/liter \cite{1}. Both experimental data proper and also handbook data have been used. The defects of these nomograms — lack of boundaries for stability of solutions and, mainly, complexity in construction \cite{2} — limit their application. Graphs constructed in the coordinates LiCl–LiOH–density, in which the content of the components (C) is expressed in \% by wt. are free from these defects. Such a graph makes it possible to go over easily to other systems for expressing the concentrations of materials in an aqueous solution (Fig. 1).

Let us examine the technique for constructing this graph. In rectangular Cartesian coordinates in the first quadrant (in the upper right to the angle in Fig. 1) from handbook data we construct the linear \text{CLiOH–}$\rho$ dependence; in the second, the \text{CLiCl–}$\rho$ dependence; and in the third quadrant we construct the isotherm for \text{CLiCl–CLiOH} solubility from experimental data from the work of \cite{1}. Using the graphical method, which is usable in constructing a three-dimensional object in three positions: in front, upward, and to the side, points are transferred from the isothermal solubility curve (the third quadrant) into the first quadrant and then into the second. These constructions are particularly easy to carry out on millimeter paper, which brings about high accuracy, on a scale of 1 cm:10 kg/m$^3$ ($\rho$), 1 cm:1\% (C). In the same way, curves are constructed which bound solution stability at 40, 60, and 80°C. Values of $\rho$ for the ternary solution are determined at 20°C.

Let us evaluate the accuracy of the values of $\rho$ determined from the scale of Fig. 1. To do this, we compare them with the values of $\rho$ determined from the empirical formula and by an experimental pycnometric method.

In a number of the ternary solutions prepared, we determined the weight proportions of lithium chloride and lithium hydroxide by potentiometric titration and then we determined values of $\rho$ pycnometrically. Then $\rho$ was calculated in the same solutions. In \cite[p. 395]{3} it was proposed to use for this purpose the so-called modified Ezrokha method:

\[ \lg \rho = \lg \rho_0 + \sum_{i=1}^{n} A_i C_i, \]

where $\rho$ and $\rho_0$ are the density of the solution sought for and of water, respectively, in kg/m$^3$; $A$ is a coefficient, and $C$ is the concentration of the components, in kg/kg. Values of $\rho_0$ and of $A$ are calculated from the regression equations, in which, in turn, it is necessary to calculate the coefficients with allowance for the temperature and, from the table given in \cite[p. 396]{3}, of the specific substance. In the present case, for 20°C we have: $A_{\text{LiCl}} = 0.24517$, and $A_{\text{LiOH}} = 0.48426$.

From Table 1 it is evident that a deviation of $\rho_{\text{eq}}$ from $\rho_{\text{eq}}$ is observed in all solutions, and to a smaller extent for $\rho_{\text{eq}}$ at proportions of LiCl less than 20\% by wt. For binary aqueous solutions of LiCl and LiOH, the value of $\rho$ increases linearly with increase in the weight proportion of the dissolved substance over all the examined range of concentrations (Fig. 1). A priori, we suggest that the ternary solution is a spatially uniform solution in which the intensive quantity which characterizes the mass density $\rho$ is identical in all of its points. This is correct for a solution of a specific composition. Obviously, deviation of the magnitude of $\rho$ from that prescribed by the linear dependence on change in composition is associated with a paired interaction of the anion Cl$^-$ and OH$^-$ or, more accurately, by an alternative effect on water \cite{1,7}. In statistical mechanics of equilibri-

*The operator of partial derivatives along the axes is the Hamiltonian operator: $V = \{\partial/\partial x, \partial/\partial y, \partial/\partial z\}$. Multiplication of this vector operator by the scalar quantity $\rho$ (x, y, z) gives the following: $\nabla \rho = \text{grad} \rho$. A repeated multiplication of grad $\rho$ by $\nabla$ gives: $\nabla \text{grad} \rho = \text{div} \rho$. Operation of div grad $\rho = \nabla (\rho \nabla) = \nabla^2 \rho$ is the Laplace operator. The quantity $\rho$ is identical at all points of the system on the condition that the Laplace equation is satisfied: $\nabla^2 \rho(x, y, z) = 0$.

Translated from Khimicheskie Volokna, No. 5, pp. 27-29, September-October, 1992.
um systems this is called a double partial correlation, which takes account of intermolecular interaction of the given particles at a sufficiently small distance" [4, p. 73], which is also recorded by experimental means. The ice-like structure of the liquid, which is very far from the degree of order of the crystalline lattice [4, p. 317], makes it possible for part of the ions to fill cavities in the structure as the concentration of the solution increases [5]. This leads to an increase in the density of particles \( n \) in a given volume and to a corresponding increase in density of the mass, \( \rho \).

Further, the solubility isotherm curve for LiOH–LiCl at 20°C has a linear character in the range of LiCl proportion in the solution from 0 to 10% by wt. The solubility of LiOH thereupon is 7.0%. Let us recalculate the total concentration of Li\(^+\) ions in this solution as LiCl (10% LiCl, \( \rho = 1.056 \) g/ml; 7% LiOH, \( \rho = 1.074 \) g/ml): \( C_{\text{LiCl}} = 10 \cdot 10^{-3} \cdot 1.056 = 105.6 \) g/liter, where there are 17.2 g-ions/liter as Li\(^+\); \( C_{\text{LiOH}} = 7 \cdot 10^{-3} \cdot 1.074 = 7.52 \) g/liter, where as Li\(^+\) there are 21.7 g-ions/liter; 17.2 + 21.7 = 38.9 g-ions/liter of Li\(^+\), which corresponds to a solution having a molar LiCl concentration of 5.6 moles or 236.3 g/liter (21%).

If the same calculations are performed for other points on the linear section of the isothermal solubility curve at 20°C, we obtain an LiCl concentration of 20-21%. At this concentration, the LiCl solution has a maximum specific electrical conductivity \( \kappa \) and addition of LiOH leads to an increase in \( \kappa \) only in solutions more dilute with respect to LiCl on measuring by a bridge scheme with alternating (1 kHz) electrical current [1]. At the end of the linear section of the isothermal solubility curve, possibly "complete hydration" of the Li\(^+\) ions begins (from the data of [6], all the water is present in the sphere of effect of Li\(^+\) ions at a \( C_{\text{LiCl}} \approx 4.9 \) moles). That is, one can say that in this case the solution is very greatly structured by hydrogen bonds and this structure is balanced by an alternative effect on water of the salt components, which was mentioned above.

Linearity of the solubility isotherm curve in the range 0-10% LiCl may be considered as one of the signs of the presence of free water. The hydration number of the Li\(^+\) ion at an Li\(^+\) content of 21% by wt. in an aqueous solution is 4.5 (at ~30°C), and upon extrapolation to 20°C it is ~4.8 [5]. Thus, about 54% of the water in the solution is present in the first coordination sphere of the lithium ions. With increase in temperature of the ternary solution, not only does the solubility of LiOH increase, but also the linear portion of the solubility isotherm is shortened, which is caused by a more structured solution with hydrogen bonds of the hydroxide ions as compared with Li\(^+\) ions. Thus, at 0°C the range reaches 10.6%; at 40°C, 9.5%; at 50°C, 6% LiCl; and at a higher temperature of the ternary solution, linearity is increasingly less discernible and the scatter of the experimental points becomes ever greater (Fig. 1).

In Fig. 2 the system LiCl–LiOH–\( \rho \) is represented in three-dimensional rectangular coordinates Oxzy. Let us assume that the surface ABCO is a plane, which admits the assumption of additivity in the values of \( \rho \) over the whole range of salt concentrations which bounds the plane. According to the foregoing and the data in Table 1, this assumption is not entirely correct in the region of high LiCl concentrations (equal to or somewhat greater than 20%), due to a decrease in the volume of the solution and as a consequence filling of cavities, which leads to a rise in the density of the number of particles \( n \) ("contraction"). The plane A'B'C'O' is the field of values of \( \rho \) at a temperature of the mixed solution above 20°C. Thereupon, the vector \( \nabla \rho \) does not change, i.e., the gradient at the various temperatures is codirectional with the coordinate axis \( z \). At a solution composition at the point K', for example, which belongs to the plane ABCO, the projection of which lies above the solubility isotherm at 20°C, reduction to this temperature causes supersaturation and the deposition of LiOH·\( \text{H}_2\text{O} \) as a precipitate [1], and to stabilization of a solution composition corresponding to the solution at point K on the AB curve in Fig. 2. Here salting out on cooling of the mixture takes place by a very short path, where \( \rho = \text{const} (\psi = 90°) \). i.e., along the line K'K in Fig. 2.

*The density of the particles (\( n = N/V \)) at the point \( X \) of the solution is determined by some microscopic dynamic function for the corresponding \( n(X) \). In view of the correlation of the effect on a particle at point \( X_1 \), the particles at point \( X_2 \) are \( n_2(X_1, X_2) \). In real systems, the function \( n_2(X_1, X_2) \) differs from \( n(X_1) \cdot n(X_2) \), if the distance \( X_1 - X_2 \) is small.

†The density \( \rho \) of the ternary solution at a given temperature is a function only of composition, i.e., it is determined by the coordinates of a specific M (Fig. 2). A change in the function in the rectangular system of coordinates in an arbitrary direction \( \mathbf{l} = \{ \cos \alpha, \cos \beta, \cos \gamma \} \) appears as follows in partial derivatives:

\[
\frac{\partial \rho}{\partial \mathbf{l}} = \frac{\partial \rho}{\partial x} \cos \alpha + \frac{\partial \rho}{\partial y} \cos \beta + \frac{\partial \rho}{\partial z} \cos \gamma.
\]

The greatest rate of increase in \( \rho \) is determined by the vector \( \nabla \rho = \{ \partial \rho/\partial x, \partial \rho/\partial y, \partial \rho/\partial z \} \) or, in view of (1): \( \partial \rho/\partial l = \nabla \rho \), whence \( \partial /\partial l(M) = |\nabla \rho| \cdot |\mathbf{l}| \cdot \cos \psi \). Obviously, the rate of change in the function is maximum in the case where the angle \( \psi \) between the vectors \( \mathbf{l} \) and \( \nabla \rho \) is equal to 0.