A solution comprises at least two different chemical substances where at least one substance is in vast molar excess. The term ‘solution’ is used to describe both solids and liquids. Nevertheless the term ‘solution’ in the absence of the word ‘solid’ refers to a liquid. Chemists are particularly expert at identifying the number and chemical formulae of chemical substances present in a given closed system. Here we explore how the chemical composition of a given system is expressed. We consider a simple system prepared using water ($\ell$) and urea(s) at ambient temperature and pressure. We designate water as chemical substance 1 and urea as chemical substance $j$, so that the closed system contains an aqueous solution. The amounts of the two substances are given by $n_1 = w_1/M_1$ and $n_j = w_j/M_j$ where $w_1$ and $w_j$ are masses; $M_1$ and $M_j$ are the molar masses of the two chemical substances. In these terms, $n_1$ and $n_j$ are extensive variables.

\[
\text{Mass of solution, } w = n_1 \cdot M_1 + n_j \cdot M_j \quad (a)
\]

\[
\text{Mass of solvent, } w_1 = n_1 \cdot M_1 \quad (b)
\]

For water, $M_1 = 0.018 \text{ kg mol}^{-1}$. However in reviewing the properties of solutions, chemists prefer intensive composition variables.

**Mole Fraction**

The mole fractions of the two substances $x_1$ and $x_j$ are given by the following two equations:

\[
x_1 = n_1 / (n_1 + n_j) \quad x_j = n_j / (n_1 + n_j) \quad (c)
\]

Here $x_1 + x_j = 1.0$. In general terms for a system comprising $i$ chemical substances, the mole fraction of substance $k$ is given by equation (d).

\[
x_k = n_k / \sum_{j=1}^{i} n_j \quad (d)
\]
Hence $\sum_{j=1}^{\infty} x_j = 1.0$. The advantage of the dimensionless mole fraction scale is that in the absence of chemical reaction, the mole fraction $x_k$ of chemical substance $k$ is independent of both temperature and pressure.

**Molality**

For liquid systems, the chemical substance in vast excess is called the solvent whereas the other substances are called solutes. In the urea + water system, water is the solvent if $n_1 >> n_j$. We as observers of the properties of this system draw a distinction between the two substances, identifying urea as the solute. The molality of solute $m_j$ is given by the amount of solute in 1 kg of solvent [1,2].

$$m_j = \frac{n_j}{w_1} \quad (e)$$

Because the molality of solute $j$ is defined in terms of masses of solute and solvent, $m_j$ is independent of temperature and pressure. Hence for precise characterization of the properties of solutes the molality scale is preferred [2].

**Concentration**

The concentration of chemical substance $j$ in a system volume $V$,

$$c_j = \frac{n_j}{V} \quad (f)$$

The latter statement is quite general. However chemists interested in the properties of solutions normally use the term ‘concentration’ with reference to the properties of a solute, substance $j$. Several problems are associated with equation (f). The major problem is that the volume of a solution depends on both temperature and pressure so both these intensive variables should be stated when $c_j$ is quoted. A further problem emerges when there is a need to specify the precise composition of a given solution. Many chemists prepare a solution by dissolving a known mass of solute $j$ in small volume of solvent. The volume of the solution is then ‘made up to the mark’ for a given volume (e.g. 250 cm$^3$). But often chemists do not record precisely how much solvent is used. In these terms we see why the molality is often the preferred composition.
scale for solutions because the amounts of solvent and solute are precisely defined. However when thinking about the properties of solutions, chemists consider the distance between solute molecules rather than their masses. An interesting calculation offers insight into the dependence of intermolecular separation for solutes as a function of solute concentration, $c_j$ [2-4]. As the concentration of the solute (e.g. urea) in an aqueous solution increases so the mean distance between the solute molecules decreases. In the event that the solute is a 1:1 salt (e.g. potassium bromide, KBr), the calculation takes account of the fact that each mole of salt produces, with complete dissociation two moles of solute ions [3,4]. We gain insight into the problem by considering a solution of KBr(aq, 1 mol dm$^{-3}$). The calculated distance between ion centres is 0.94 nm. The radii of these ions are approx. 0.15 nm. The diameter of a water molecule is around 0.4 nm. [5]. So there are relatively few water molecules between the ions at this concentration.

These calculations are important because they indicate how solute-solute distances change on increasing the concentration of solute. [6] Chemists often want to know how solute - solute molecular interactions affect the properties of solutions. [7-11] Certainly the distance between solute molecules is a key consideration in reviewing the properties of solutes in aqueous solutions. The task of understanding the properties of aqueous solutions is usually divided into two parts. For the first part we use the term hydration to describe solute - solvent interactions. We imagine a molecule of solute, chemical substance $j$, in an infinite expanse of solvent and direct attention to the organisation of solvent molecules surrounding each solute molecule, the cosphere. [7] The term hydration number often refers to the number of water molecules contiguous to each solute molecule but the term 'hydration shell' often extends to include solvent molecules outside the immediate sheath.

With increase in solute concentration the mean separation between solute molecules decreases. In responding to the task of understanding the properties of real solutions we define the properties of ideal solutions
In the case of salt solutions, strong and long-range ion-ion interactions contribute to marked deviations from the properties of ideal solutions [11].

Footnotes

[1] \( m_j = \text{[mol kg}^{-1}\text{]} \)


[3] Consider a solution in which each solute molecule is placed at the centre of a cube, edge \( d \) metres. Then distance between solute molecules/m = \( d \)

Volume of one cube/m\(^3\) = \( d^3 \); Volume of \( n_j \) moles of cubes/m\(^3\) = \( n_j \cdot N_A \cdot d^3 \)

where \( N_A \) is the Avogadro constant.

Thus \( V(sln) = n_j \cdot N_A \cdot d^3 \) or \( d = (c_j \cdot N_A)^{-\frac{1}{3}} \)

where \( c_j \) is expressed in mol m\(^{-3}\).

\[
d = \left\{\left[\text{mol m}^{-3}\right] \cdot \left[\text{mol}^{-1}\right]\right\}^{-\frac{1}{3}} = [m]
\]

If \( c_j \) is expressed, as is conventional, in mol dm\(^{-3}\),

\[
d = \left(10^3 \cdot c_j \cdot N_A\right)^{-\frac{1}{3}}.
\]

[4]

<table>
<thead>
<tr>
<th>( c_j/\text{mol dm}^{-3} )</th>
<th>Single Solute</th>
<th>1:1 salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>d/nm</td>
<td></td>
<td>d/nm</td>
</tr>
<tr>
<td>( 10^{-4} )</td>
<td>25.5</td>
<td>20.2</td>
</tr>
<tr>
<td>( 10^{-3} )</td>
<td>11.8</td>
<td>9.4</td>
</tr>
<tr>
<td>( 10^{-2} )</td>
<td>5.5</td>
<td>4.4</td>
</tr>
<tr>
<td>( 10^{-1} )</td>
<td>2.6</td>
<td>2.0</td>
</tr>
<tr>
<td>1</td>
<td>1.2</td>
<td>0.94</td>
</tr>
<tr>
<td>5</td>
<td>0.69</td>
<td>0.55</td>
</tr>
</tbody>
</table>

[5] N. E. Dorsey, Properties of Ordinary Water Substance, Reinhold, New York, 1940. The estimate quoted in the main text is based on the estimates given in Table 15 of this fascinating monograph. The latter
offers information concerning, for example, the load which ice will
support. Apparently, ice having a thickness of 20 cm will support a
battery of artillery with carriages and horses (see p. 458).

[6] Molalities are based on mass, and concentrations on distances.

York, 1953.

[8] H. L. Friedman and C. V. Krishnan, in Water - A Comprehensive
Chapter 1.


[10] One interesting feature is common throughout aqueous chemistry. If
a given water molecule is strongly hydrogen bonded to four other water
molecules, that water molecule exists in a local state which has low
density (high volume). In other words, strong cohesion implies low
density; a pattern contrary to that encountered in nearly all natural
systems (and in human activities); A. Ben-Naim, Chem. Phys. Lett.,
1972, 13, 406. [Exceptions to this statement are found in the structures
of high pressure ice polymorphs - but then there are always exceptions to
general statements.]

[11] The seminal paper in this subject, aqueous chemistry, is probably
that written by J. D. Bernal and R. H. Fowler, J. Chem. Phys., 1933, 1,
515. This paper is remarkable in that despite the subjects covered (i.e.
ice, liquid water and aqueous solutions), the term 'hydrogen-bond' is not
used. The authors refer to the tendency of water to group in 'tetrahedral
coordination'.