

# Activity of water in aqueous systems; A frequently neglected property

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In this *critical review*, the significance of the term ‘activity’ is examined in the context of the properties of aqueous solutions. The dependence of the activity of water( $\ell$ ) at ambient pressure and 298.15 K on solute molality is examined for aqueous solutions containing neutral solutes, mixtures of neutral solutes and salts. Addition of a solute to water( $\ell$ ) always lowers its thermodynamic activity. For some solutes the stabilisation of water( $\ell$ ) is less than and for others more than in the case where the thermodynamic properties of the aqueous solution are ideal. In one approach this pattern is accounted for in terms of hydrate formation. Alternatively the pattern is analysed in terms of the dependence of practical osmotic coefficients on the composition of the aqueous solution and then in terms of solute–solute interactions. For salt solutions the dependence of the activity of water on salt molalities is compared with that predicted by the Debye–Hückel limiting law. The analysis is extended to consideration of the activities of water in binary aqueous mixtures. The dependence on mole fraction composition of the activity of water in binary aqueous mixtures is examined. Different experimental methods for determining the activity of water in aqueous solutions are critically reviewed. The role of water activity is noted in a biochemical context, with reference to the quality, stability and safety of food and finally with regard to health science.

## I Introduction

The Oxford English Dictionary<sup>1</sup> explains the meaning of the word ‘activity’ as (i) the state of being active, the exertion of energy, and (ii) the state or quality of being abundantly active. The underlying message is that ‘activity’ is a dynamic variable, a property changing with time. For the most part this is not the message implied when the term ‘activity’ is used in a description of the thermodynamic properties of solutions and mixtures. Rather Lewis and Randall in their classic monograph<sup>2</sup> published in 1923 refer to the ratio of the fugacities of a

component in solution at two concentrations at the same temperature. One state for the solute is defined as the standard state, using superscript ‘°’, so that the ratio of fugacities ( $f/f^\circ$ ), the relative fugacity is the activity  $a$ .<sup>2</sup>

Originally the term ‘relative activity’ was used with respect to the gaseous state but the word ‘relative’ has been dropped and the concept of activity extended to the properties of solutions and liquid mixtures. Here we explore the definition of activity with respect to water in both aqueous solutions and binary aqueous mixtures. In the case of salt solutions, an extensive scientific literature describes how the activities of water in salt solutions are measured. The thermodynamic properties of solutions are discussed in papers, reviews,

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textbooks and monographs,<sup>3–7</sup> thereby recognising the importance of these systems from academic and industrial viewpoints. Most texts consider in turn the properties of both solute and solvent but centre their attention on the properties of solutes, the solvent being assigned almost a secondary role in the form of a convenient medium in which to disperse solutes. The component in vast molar excess is the solvent and so the frequent neglect of the solvent is somewhat surprising. Here we redress the balance in a broad survey of the physical chemistry of aqueous systems, highlighting the role of the activity of water.

## II Thermodynamic background

In their classic monograph,<sup>2</sup> Lewis and Randall used as the title of chapter XXII a sentence which includes the following words ‘A useful function called the Activity...’. The concept of (thermodynamic) activity was introduced by Lewis almost 100 years ago.<sup>8</sup> This review builds on the insight offered by Lewis concerning the concept of ‘activity’.

At defined temperature  $T$  and pressure  $p$ , the Gibbs energy  $G(\text{mix})$  of a given binary aqueous mixture can be expressed as the sum of products of amounts,  $n_1$  and  $n_2$ , and chemical potentials  $\mu_1(\text{mix})$  and  $\mu_2(\text{mix})$  respectively of the two components; eqn. (1).

$$G(\text{mix}) = n_1\mu_1(\text{mix}) + n_2\mu_2(\text{mix}) \quad (1)$$

Here we identify water as component 1. By dividing eqn. (1) through by  $(n_1 + n_2)$ , we obtain an equation for the molar Gibbs energy of the mixture in terms of the mole fractions of the two components,  $x_1$  and  $x_2$ .

$$G_{\text{m}}(\text{mix}) = x_1\mu_1(\text{mix}) + x_2\mu_2(\text{mix}) \quad (2)$$

Concentrating attention on the properties of water in aqueous systems we write  $\mu_1(\text{mix})$  as  $\mu_1(\text{aq})$ . We confine attention to the properties of liquid mixtures and solutions at ambient pressure which is close to the standard pressure  $p^\circ$ . At fixed temperature  $T$  and pressure, the difference between the chemical potentials

of water(aq) in the aqueous mixture  $\mu_1(\text{aq})$  and pure water( $\ell$ ),  $\mu_1^*(\ell)$  is related to the activity of water,  $a_1$  using eqn. (3) where  $R$  is the gas constant.

$$\mu_1(\text{aq}) = \mu_1^*(\ell) + RT \ln(a_1) \quad (3)$$

From the nearly one-century old<sup>8</sup> eqn. (3), an array of thermodynamic equations has emerged which underlies the measurement and interpretation of water activities. At temperature  $T$  and at equilibrium, the vapour pressure of water above an aqueous mixture (or an aqueous solution) equals  $p_1(\text{aq})$ . At the same temperature the activity of water( $\ell$ ) is unity where the vapour pressure is  $p_1^*(\ell)$ . Hence the activity  $a_1$  in an aqueous mixture (or solution) is given by the ratio given in eqn. (4).

$$a_1 = p_1(\text{aq})/p_1^*(\ell) \quad (4)$$

In the event that the thermodynamic properties of the solution are ideal, eqn. (3) is re-expressed to define the corresponding activity of water,  $(a_1)^{\text{id}}$ .

$$\mu_1(\text{aq};\text{id}) = \mu_1^*(\ell) + RT \ln[(a_1)^{\text{id}}] \quad (5)$$

The chemical potential of water in an aqueous liquid mixture is also related to the mole fraction of water  $x_1$  and a rational activity coefficient,  $f_1$

$$\mu_1(\text{aq}) = \mu_1^*(\ell) + RT \ln(x_1f_1) \quad (6)$$

By definition at all  $T$  and  $p$ ,

$$\lim(x_1 \rightarrow 1)f_1 = 1 \quad (7)$$

Hence from eqns. (3) and (6),

$$\ln(a_1) = \ln(x_1f_1) \quad (8)$$

Further,

$$\ln[(a_1)^{\text{id}}] = \ln(x_1) \quad (9)$$



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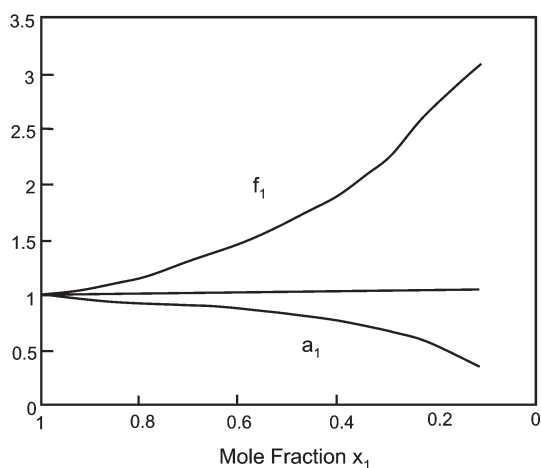
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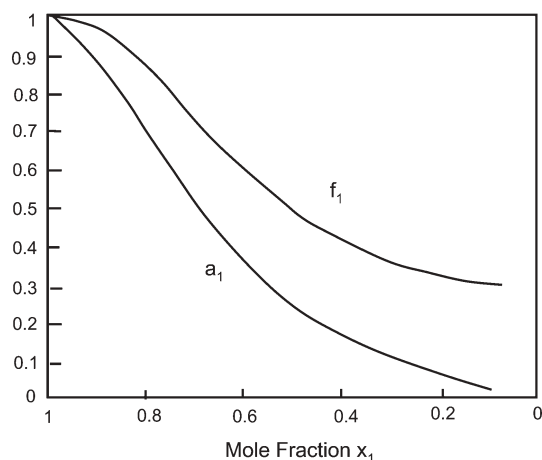
In the case of an aqueous liquid mixture having thermodynamic properties which are ideal, the mole fraction of water is a direct measure of its activity. In other words the standard state, here pure water( $\ell$ ), is the state for which the activity of the component is unity. In the mixture  $x_1 < 1$  and hence the activity  $(a_1)^{\text{id}}$  is also less than unity. Furthermore, the activity  $(a_1)^{\text{id}}$  is not perturbed by changes in temperature, pressure and chemical nature of component 2.

The above set of equations can be rewritten as a description of liquid component 2;  $\mu_2^*(\ell)$  is the chemical potential of the non-aqueous component. In the description of the system under investigation using the term 'mix', the reference chemical potentials  $\mu_1^*(\ell)$  and  $\mu_2^*(\ell)$  are self-consistent. Both activities  $a_1$  and  $a_2$  are unity in the respective reference states. It is important to distinguish between the dependences on mole fraction composition of activity  $a_1$  and rational activity coefficient  $f_1$  for binary aqueous liquid mixtures. At 303.2 K,  $f_1$  for water in sulfolane + water liquid mixtures<sup>9</sup> increases with decrease in  $x_1$  (Fig. 1) whereas  $f_1$  for water in DMSO + water liquid mixtures<sup>10</sup> at 298.2 K decreases with decrease in  $x_1$  (Fig. 2). However for both mixtures (Figs. 1 and 2)  $a_1$  decreases with decrease in  $x_1$ . In other words, mole fraction  $x_1$  is the determining property with respect to the dependence of the activity of water  $a_1$  on mixture composition.

Stewart and Van Dyke<sup>11</sup> indicate that the activity of water is not a useful parameter in the context of discussing chemical reactions in aqueous systems. Professor Ross E. Robertson (University of Calgary) would often express surprise that rate constants for solvolysis of organic solutes in aqueous solution always decrease when an organic co-solvent is added, independently of the nature of the co-solvent. In fact this general pattern can be understood in part if one makes a link (incorrectly) between 'reactivity' and activity of water in binary aqueous mixtures. The general pattern in reactivity emerges from a decrease in mole fraction of water and not from a change in rational activity coefficient of water.



**Fig. 1** Dependences<sup>9</sup> of activity  $a_1$  and rational activity coefficients  $f_1$  of water in sulfolane + water binary mixtures at ambient pressure and 303.15 K.



**Fig. 2** Dependences<sup>10</sup> of activity  $a_1$  and rational activity coefficients  $f_1$  of water in DMSO + water binary mixtures at ambient pressure and 298.15 K.

### III Aqueous solutions; simple solutes

The term 'solution' describes systems where  $n_1 \gg n_2$ . Eqn. (1) is valid if we replace 'mix' by 'aq' for an aqueous solution. In order to make the distinction we change the identifier '2' to the symbol ' $j$ ' where chemical substance  $j$  is the solute. For an aqueous solution where  $n_1 \gg n_j$ ,

$$G(\text{aq}) = n_1\mu_1(\text{aq}) + n_j\mu_j(\text{aq}) \quad (10)$$

However the term 'solute' signals a switch of the description of the second chemical substance. For example, in the case of an aqueous solution containing solute  $j$ , the composition of the solution is expressed in terms of molality  $m_j (=n_j/w_1$  where  $n_j$  is the amount of solute and  $w_1$  is the mass of the solvent). The reason for describing the non-aqueous component as chemical substance  $j$  arises from the fact that the reference state for solute  $j$  is an aqueous solution and not pure substance  $j$ . The Gibbs energy of an aqueous solution prepared using water( $\ell; w_1 = 1$  kg) is given by eqn. (11) where  $M_1$  is the molar mass of water.

$$G(\text{aq}; w_1 = 1 \text{ kg}) = (1/M_1)\mu_1(\text{aq}) + m_j\mu_j(\text{aq}) \quad (11)$$

Although we have changed the description of the system from mixture to solution, eqns. (3)–(9) form the basis of descriptions of the properties of water in aqueous solutions. According to eqn. (8), activity  $a_1$  reflects in an *elegant* fashion the composition of the solution and the extent to which the properties of water differ from those of water in an ideal aqueous solution. In principle, activity  $a_1$  should be compared with  $(a_1)^{\text{id}}$  for a given aqueous solution.

For a solution,  $x_1 < 1$  and  $\ln(x_1) < 0$  meaning that  $(a_1)^{\text{id}} < 1$  such that  $[\mu_1(\text{aq}; \text{id}) - \mu_1^*(\ell)]$  is negative. In other words the solvent is stabilised by adding a solute. This conclusion is quite general, the pattern being the same independent of the nature of the solute.

Eqn. (6) can be re-expressed in terms of the molality of a neutral solute  $m_j$  using eqn. (12) where  $\phi$  is the

practical osmotic coefficient and  $M_1$  is the molar mass of the solvent.

$$\mu_1(\text{aq}) = \mu_1^*(\ell) - \phi RTM_1m_j \quad (12)$$

If the thermodynamic properties of a given solution are ideal, the practical osmotic coefficient is unity. The difference between  $\phi$  and unity for a real solution reflects the impact of solute–solvent interactions on the properties of the solvent *via* the Gibbs–Duhem equation.

Hence a solution for which the thermodynamic properties are ideal,

$$\mu_1(\text{aq};\text{id}) = \mu_1^*(\ell) - RTM_1m_j \quad (13)$$

The difference  $(\phi - 1)$  yields an immediate indication of the extent to which the properties of a given solution are not ideal. In other words, eqns. (12) and (13) describe changes in the chemical potential of pure water( $\ell$ ) upon addition of a simple solute to form either ideal or real aqueous solutions. For a solution containing a single neutral solute  $j$ , molality  $m_j$ ,

$$\ln(a_1) = -\phi M_1m_j \quad (14)$$

Hence for an aqueous solution,

$$\ln(a_1) = -\phi[0.018015 \text{ kg mol}^{-1}]m_j \quad (15)$$

For a solution containing  $i$  solutes,

$$\ln(a_1) = -\phi M_1 \sum_{j=1}^{j=i} m_j \quad (16)$$

Comparison of eqns. (12) and (13) shows that for an aqueous solution  $(a_1)^{\text{id}}$  is simply related to the molality of the solute  $m_j$ .<sup>†</sup> Thus,

$$\ln[(a_1)^{\text{id}}] = -M_1m_j \quad (17)$$

For an aqueous solution the following simple equation is obtained.

$$\ln[(a_1)^{\text{id}}] = -[0.018015 \text{ kg mol}^{-1}]m_j \quad (18)$$

In other words  $\ln[(a_1)^{\text{id}}]$  is a linear function of  $m_j$ , *the same plot being obtained for all solutes*. With increase in  $m_j$ , the solvent is further stabilised. The chemical potential of water( $\ell$ ) is lowered by adding a solute. This conclusion forms the basis of classic studies into the colligative properties of aqueous solutions. For example, this conclusion explains why the freezing point of water falls when a solute is added; see section VIII. In the event that the thermodynamic properties of the solution are not ideal, the form of the plot showing  $\ln(a_1)$  as a function of molality  $m_j$  is characteristic of the solute.

The chemical potential of a simple solute  $j$  in an aqueous solution (at fixed  $T$  and  $p$ ) is related in eqn. (19) to the activity of the solute  $a_j$  which is in turn related to the molality  $m_j$  and activity coefficient  $\gamma_j$ ;  $m^\circ = 1 \text{ mol kg}^{-1}$ .

$$\mu_j(\text{aq};T;p) = \mu_j^\circ(\text{aq}) + RT \ln(a_j) \quad (19)$$

Here

$$a_j = (m_j/m^\circ)\gamma_j \quad (20)$$

By definition, at fixed  $T$  and  $p$ ,

$$\lim(m_j \rightarrow 0)\gamma_j = 1 \quad (21)$$

The reference state for substance  $j$  is a solution having unit molality where the properties of chemical substance  $j$  are ideal; *i.e.* both activity and activity coefficient are unity. Both  $a_1$  and  $a_j$  are dimensionless properties. [In the case of a salt, the activity  $a_j$  is related to the molality using a mean ionic activity coefficient,  $\gamma_{\pm}$ ; see section V.] As a consequence of solute–solvent interactions, the activities  $a_j$  for simple neutral solutes at a common molality depend on the solute.<sup>12,13</sup> For example at a common molality  $5 \text{ mol kg}^{-1}$ ,  $\ln(a_1)$  decreases through the series glycerol ( $-0.096$ ), glucose ( $-0.102$ ) and sucrose ( $-0.131$ ).<sup>12</sup>

The practical osmotic coefficient  $\phi$  for the solvent is related to the activity coefficient  $\gamma_j$  for solute  $j$  using eqn. (22), the link being established by the Gibbs–Duhem equation.

$$(\phi - 1)dm_j/m_j + d\phi = d \ln(\gamma_j) \quad (22)$$

Eqn. (23) is the integral of eqn. (22).

$$\phi = 1 + \frac{1}{m_j} \int_0^{m(j)} m_j d \ln(\gamma_j) \quad (23)$$

Or,

$$\ln(\gamma_j) = \phi - 1 + \int \frac{\phi - 1}{m_j} dm_j \quad (24)$$

Eqn. (23) emerges from the idea that  $\gamma_j$  describes the impact of solute–solvent interactions on the properties of a given solution. If we can formulate an equation for  $\ln(\gamma_j)$  in terms of the composition of a solution, using eqns. (14) and (23) we obtain the activity  $a_1$ .

In general the scientific literature dealing with the properties of aqueous solutions reports practical osmotic coefficients  $\phi$  for a given solution as a function of solute molality (at ambient pressure and fixed temperature). The activity  $a_1$  is, as shown above, simply related to the practical osmotic coefficient. This feature is fortunate on the grounds that the concept of activity of solvent  $a_1$  seems intuitively attractive. Indeed Leffler and Grunwald note the great convenience of combining experimentally derived parameters into activities for both solvent and solute.<sup>14</sup>

Bower and Robinson<sup>12</sup> report the dependence of osmotic coefficient for urea (aq) at 298 K over the range  $0 \leq m_j/\text{mol kg}^{-1} \leq 20.0$ ;  $\phi$  decreases with increase in  $m_j$ . Stokes and Robinson<sup>13</sup> report the dependences of  $\phi$  on solute molality for sucrose(aq), glucose(aq) and glycerol(aq) over the range  $0 \leq m_j/\text{mol kg}^{-1} \leq 7.5$ .

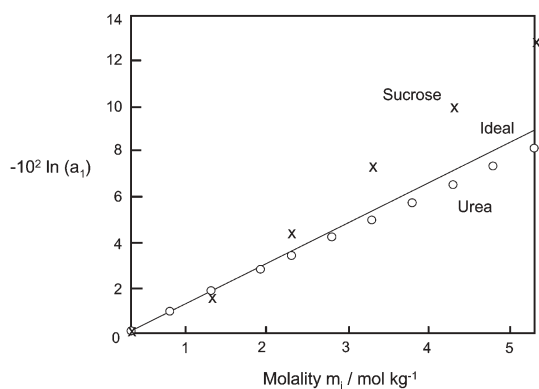
For  $m(\text{urea}) = 4 \text{ mol kg}^{-1}$ ,  $a_1$  equals 0.938 whereas  $(a_1)^{\text{id}}$  equals 0.933. Thus  $(a_1)^{\text{id}}$  is less than unity because the mole fraction of water  $x_1$  is less than unity. However  $a_1 > (a_1)^{\text{id}}$  indicating that at this molality water is at a higher chemical

potential than in the case for a solution where the thermodynamic properties are ideal as a consequence of solute–solute interactions; Fig. 3.<sup>12</sup> On the other hand for the hydrophilic solute, sucrose where  $m(\text{sucrose}) = 4 \text{ mol kg}^{-1}$ ,  $a_1$  equals 0.906 whereas  $(a_1)^{\text{id}}$  equals 0.933 indicating that adding sucrose at this molality to water lowers the chemical potential of water relative to that for a solution having ideal properties; Fig. 3.<sup>13</sup>

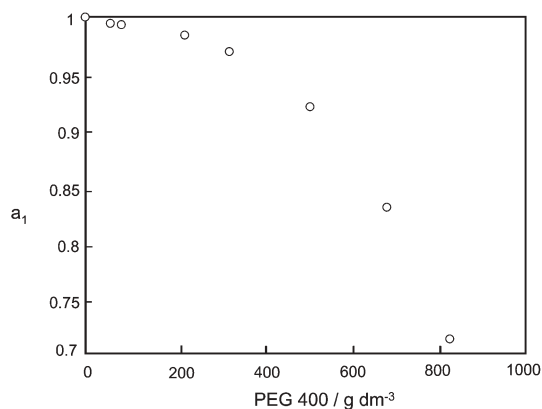
The activities for alkyl ureas(aq) illustrate the modest impact of changes in hydrophobicity of the solute.<sup>15</sup> The dependence of water activity on the mass of PEG(400), a water soluble polymer<sup>16,17</sup> in  $1 \text{ dm}^3$  of solution is illustrated in Fig. 4.

#### IV Aqueous solutions: hydrates of simple solutes

The thermodynamic properties of aqueous solutions are not ideal and hence the activity of water in these solutions is not equal to  $x_1$ . For the most part the difference is attributed to solute–solute interactions which in the case of salt solutions are strong and long range (section V). However for solutions containing neutral solutes the extent to which the properties are not ideal can be discussed in terms of hydrate formation. Thus there are two descriptions of a given solution prepared



**Fig. 3** Dependence of activity of water, expressed as  $\ln(a_1)$ , in aqueous solution at 298.15 K as a function of molality of urea ( $\circ$ )<sup>12</sup> and sucrose ( $\times$ ).<sup>13</sup> Comparison with the corresponding dependence of  $\ln(a_1^{\text{id}})$ .



**Fig. 4** Dependence of water activity on the concentration of PEG(400), a water soluble polymer<sup>16,17</sup> in aqueous solution at 298.15 K.

using  $n_1$  moles of water and  $n_j$  moles of solute  $j$ . In description A there are  $n_j$  moles of solute, chemical substance  $j$ , and  $n_1$  moles of solvent. In description B the solute is hydrated such that there are  $n_j$  moles of solute  $jh \text{ H}_2\text{O}$  and  $(n_1 - hn_j)$  moles of water. At fixed  $T$  and  $p$ , the system is at equilibrium, being therefore at a minimum in Gibbs energy. The Gibbs energy is not dependent on our description of the system;<sup>18</sup> it does not know which description we favour!‡ The activity coefficient  $\gamma_j$  for solute  $j$  using description A is related to the hydration number  $h$  for solute  $j$  by eqn. (25) using description B.

$$\ln(\gamma_j) = 2hn_jM_1 \quad (25)$$

The hydrate model for activity coefficients can be understood in an anthropomorphic fashion. When  $\delta n_j$  moles of solute are added to a solution molality  $m_j$ ,  $h\delta n_j$  moles of water are removed from ‘solvent’ and transferred to the solute. In these terms each solute molecule responds to this increased competition for solvent by other solute molecules and therefore ‘knows’ that there are other solute molecules in the solution. Any communication between solute molecules in solution is reflected in the extent to which  $\gamma_j$  differs from unity.

The theme developed above anticipates a description of solute–solute interactions and hence formulation of equations describing (practical) osmotic coefficients. On this basis we explore links with the hydrate theory of solutions proposed by Scatchard<sup>19,20</sup> in 1921.

In the context of properties of aqueous solutions the role of solute–solute interactions was recognised in the early development of the subject. However the role of solute–solvent interactions was underplayed. Nevertheless many authors developed models for solute–solvent interactions.

A given solution is prepared by dissolving  $n_j$  moles of neutral solute  $j$ , molar mass  $M_j$ , in  $n_1^\circ$  moles of water( $\ell$ ), molar mass  $M_1$ . The molality of solute as prepared is given by eqn. (26).

$$m_j(\text{prepared}) = n_j/n_1^\circ M_1 \quad (26)$$

Then  $\ln(a_1;\text{prepared})^{\text{id}}$  is given by eqn. (17). However in another description of the solution under investigation we envisage that each mole of solute  $j$  is strongly hydrated by  $h$  moles of water. The mass of solvent water  $w_1$  is therefore  $[n_1^\circ - hn_j]M_1$ . Hence the molality of hydrated solute is given by eqn. (27).

$$m_j(\text{hydrated solute}) = n_j/[n_1^\circ - hn_j]M_1 \quad (27)$$

In effect the molality of the solute increases because there is less ‘solvent water’. Hence by analogy with eqn. (17),

$$\ln(a_1;\text{hyd}) = -n_j/(n_1^\circ - hn_j) \quad (28)$$

Therefore for a range of solutions containing different solutes but prepared using the same amount of each solute, the activities of the solvent are a function of the different extents of hydration of the solutes. With increase in  $h$  at fixed  $m_j$ ,  $\ln(a_1;\text{hyd})$  decreases (*i.e.* becomes more negative) indicative of

increasing stabilisation of water in the system by virtue of hydration of a solute.

Recently Zavitsas<sup>21</sup> revived interest in this approach, calculating hydration numbers for both ions and neutral solutes in aqueous solutions. Some reservation must be expressed concerning the conclusion that the hydration number of halide anions is zero, bearing in mind clear evidence from neutron scattering studies<sup>22</sup> concerning the arrangement of water molecules around, for example, chloride anions in aqueous solution.

The Scatchard model<sup>19,20</sup> starts with the following description of aqueous solutions. In solution the mole fraction of (solvent) water is  $x_1$  and the mole fraction of hydrated solute is  $x_j$ .

Then,

$$x_1 + x_j = 1 \quad (29)$$

The mole fraction ratio  $x_1/x_j$  is given by eqn. (30).

$$\frac{x_1}{x_j} = \frac{x_1}{1-x_1} \quad (30)$$

Eqn. (30) forms the basis of a treatment described by Scatchard<sup>19,20</sup> in 1921, over eighty years ago. Scatchard described water( $\ell$ ) as a mixture of hydrols; monohydrols and polymerised water. Scatchard discussed hydration of solutes although not all solutes in a given solution were seen as hydrated to the same extent; *i.e.* a given solution contains various hydrates. However Scatchard envisaged that one hydrate is dominant. Scatchard invoked an assumption called the ‘semi-ideal’ assumption in which mole fraction  $x_1$  on the right hand side of eqn. (30) is replaced by the activity of the solvent, water  $a_1$ ; eqn. (31).

Hence,

$$\frac{x_1}{x_j} = \frac{a_1}{1-a_1} \quad (31)$$

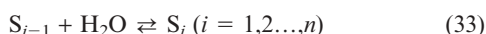
With reference to an aqueous solution prepared using  $m_j$  moles of solute  $j$  in 1 kg of water( $\ell$ ) the difference between the ratios  $[(1.0/0.018015 \text{ kg mol}^{-1})/m_j]$  and  $[a_1/(1-a_1)]$  yields the ‘average degree of hydration’,  $h$  of solute  $j$ .

Then,

$$h = \frac{(1.0/0.018015 \text{ kg mol}^{-1})}{m_j} - \frac{a_1}{1-a_1} \quad (32)$$

Eqn. (32) is Scatchard’s equation describing the amount of water ‘removed’ from the solvent by 1 mol solute  $j$ .

Stokes and Robinson<sup>13</sup> extended the Scatchard analysis using a chemical equilibrium involving solute hydrates. Hydration of a given solute is described by equilibrium constants characterising  $n$ -hydration steps. Solute S, where each mole of solute is hydrated by  $(i-1)$  moles of water, is hydrated to form a solute incorporating  $i$  moles of hydrating water; eqn. (33).



Each step is described by an equilibrium constant,  $K_i$ . So for a solute hydrated by three water molecules there are three equilibrium constants. Stokes and Robinson<sup>13</sup> set  $n$  equal to 11 for sucrose. Stokes and Robinson<sup>13</sup> simplified the analysis by assuming that the equilibrium constants for all hydration steps are equal. The outcome is eqn. (34).

$$\frac{(1/M_1)}{m_j} = \frac{a_1}{1-a_1} + \frac{\sigma}{\Sigma} \quad (34)$$

where

$$\sigma = Ka_1 + \dots + K(a_1)^n \quad (35)$$

and

$$\Sigma = 1 + Ka_1 + \dots + (Ka_1)^n \quad (36)$$

Two interesting parameters,  $n$  and  $K$ , describe the hydration of a given solute  $j$ . Stokes and Robinson<sup>13</sup> described a method of data analysis but modern computer-based methods should lighten the arithmetic drudgery. For sucrose(aq) at 298.15 K Stokes and Robinson<sup>13</sup> estimate that  $n = 11$  and  $K = 0.994$ . For glucose(aq)  $n = 6$  with  $K = 0.786$ . The hydration model based on eqn. (34) has merit in offering a solute–solvent interaction model for real aqueous solutions containing hydrophilic solutes.

In terms of current descriptions of the properties of dilute solutions of neutral solutes the difference between ideal and real properties is understood<sup>23–25</sup> in terms of a pairwise Gibbs energy interaction parameter  $g_{ij}$  using eqn. (37) where  $m^\circ = 1 \text{ mol kg}^{-1}$  and the units of  $g_{ij}$  are  $\text{J kg}^{-1}$ .

$$1 - \phi = -(1/RT)g_{ij}(1/m^\circ)^2m_j \quad (37)$$

Then using eqn. (14), we obtain eqn. (38).

$$\ln(a_1) = -M_1m_j[1 + (RT)^{-1}g_{ij}(m^\circ)^{-2}m_j] \quad (38)$$

Or,

$$\ln(a_1) + M_1m_j = -M_1(RT)^{-1}g_{ij}(m^\circ)^{-2}(m_j)^2 \quad (39)$$

Hence for dilute solutions  $[\ln(a_1) + M_1m_j]$  is a linear function of  $(m_j)^2$ , the gradient of the plot yielding the pairwise Gibbs energy parameter  $g_{ij}$ . If for example,  $g_{ij}$  is positive indicating solute–solute repulsion,  $[\ln(a_1) + M_1m_j]$  decreases with increase in  $m_j$  such that  $\mu_1(\text{aq}) > \mu_1(\text{aq};\text{id})$ . In the event that solute–solute interactions are attractive,  $g_{ij}$  is negative. Hence the difference between the properties of real and ideal aqueous solutions is highlighted by eqn. (39). It is interesting to note that  $(a_1)$  and  $(a_1)^{\text{id}}$  are simply related.

Thus,

$$\ln(a_1) + M_1m_j = \ln(a_1) - \ln(a_1)^{\text{id}} \quad (40)$$

In other words the practical osmotic coefficient is linked to solute–solute interactions and not necessarily to solute–solvent interactions. Thus with respect to aqueous solutions at 298 K

containing alkyl ureas, Barone *et al.* comment<sup>15</sup> on the possible association of solutes but leave open the question of accounting for trends in practical osmotic coefficients; see also comments by Ellerton and co-workers.<sup>26,27</sup> The merit of this model over the Stokes–Robinson approach is the potential for describing solute–solute interactions in terms of attractive–repulsive solute–solute interactions.

The properties of aqueous solutions containing two neutral solutes are interesting. Ellerton and co-workers draw attention to a general equation relating osmotic coefficients and solute molalities.<sup>26,27</sup> Stokes and Robinson<sup>13</sup> show that for a solution containing *i*-solutes, the activity coefficient for solute *k* is given by eqn. (41) where  $m_k$  is the molality of solute. In a solution where solute *k* is the only solute  $\Gamma_k$  is the activity coefficient of solute *k*.

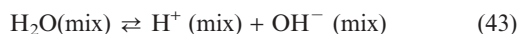
$$\gamma_k = m_k \Gamma_k \left/ \sum_{j=1}^{j=i} m_j \right. \quad (41)$$

Lilley and Tester report<sup>28</sup> the osmotic coefficients for aqueous solutions at 298.15 K containing mixtures of urea and guanidinium chloride, prompted by the fact that such mixed solutions do not have as marked effect on the denaturation of lysozyme than solutions containing just one of these solutes. A quantity  $\Delta(m\phi)$  is defined by eqn. (42) where  $m_{\text{ref}}$  and  $\phi_{\text{ref}}$  are molality and practical osmotic coefficient of urea in a reference solution,  $m_g$  and  $m_u$  being the molalities of guanidinium chloride and urea, practical osmotic coefficients  $\phi_g^\circ$  and  $\phi_u^\circ$  characterising the separate solutions at the same molalities.<sup>28</sup>

$$\Delta(m\phi) = \sum_{j=1} \sum_{i=1} A_{ij} m_g^i m_u^j \quad (42)$$

In the context of aqueous solutions containing two different solutes, Lampreia and co-workers<sup>29</sup> point out the need for clear identification of the standard states used for expressing reference chemical potentials in one-solute and two-solute solutions.

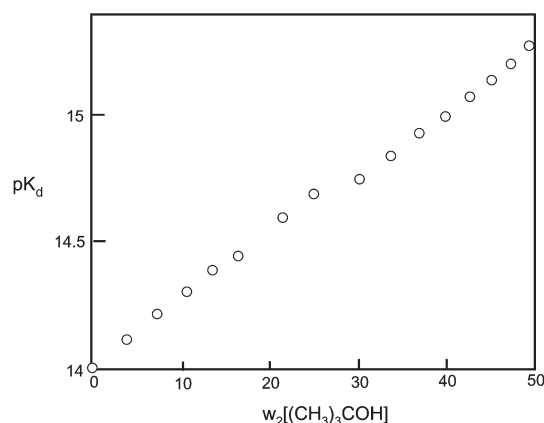
The discussion so far has treated water( $\ell$ ) as an interesting molecular solvent. Nevertheless self-dissociation is an important property of this liquid. A general equation for the self-dissociation of water in binary aqueous mixtures (at fixed *T* and *p*) takes the following form.



Woolley *et al.*<sup>30</sup> describe this equilibrium in several ways. One interesting way uses the following definition of a self-dissociation constant  $K_d$  which takes account of the change in activity of water as co-solvent is added.

$$K_d = c^{\text{eq}}(\text{H}^+)c^{\text{eq}}(\text{OH}^-)(\gamma_{\pm})^2/a_1 \quad (44)$$

$c^{\text{eq}}(\text{H}^+)$  and  $c^{\text{eq}}(\text{OH}^-)$  refer to the equilibrium concentrations;  $\gamma_{\pm}$  is the mean ionic activity coefficient. The activity of water  $a_1$  was calculated from the ratio of the equilibrium partial pressure of water to that of water( $\ell$ ) at the same *T* and *p*. For example, in 2-methylpropan-2-ol + water (Fig. 5) and dioxan + water mixtures,  $pK_d$  increases with increasing organic mole fraction although a decrease is observed when glycol is



**Fig. 5** Dependence<sup>30</sup> of  $pK_d$  for water on mass (%),  $w_2$  (%) of 2-methylpropan-2-ol.

added.<sup>30</sup> The analysis has been extended to DMSO + water mixtures by Fiordiponti *et al.*<sup>31</sup>

## V Aqueous salt solutions

The activity of water in a salt solution is given by eqn. (45).

$$\ln(a_1) = -\phi M_1 \nu m_j \quad (45)$$

Here  $\nu$  is the stoichiometric parameter, the number of moles of ions produced by complete dissociation of one mole of salt *j*; for a 1 : 1 salt  $\nu$  equals 2. For a solution where the thermodynamic properties are ideal,

$$\ln(a_1)^{\text{id}} = -M_1 \nu m_j \quad (46)$$

The stoichiometric factor  $\nu$  in eqns. (45) and (46) shows the impact of salt type on the activity of water. If we confine attention to 1 : 1 salts,

$$\ln(a_1)^{\text{id}} = -2M_1 m_j \quad (47)$$

For a 1 : 1 salt having molality 1.0 mol kg<sup>-1</sup>,  $a_1^{\text{id}} = 0.965$  indicating a modest stabilisation of the solvent, water. Thus for an ideal solution the effect of one mole of 1 : 1 salt is more dramatic than 1 mol non-electrolyte for which  $a_1^{\text{id}} = 0.982$ . With increase in molality  $m_j$ ,  $\ln(a_1)^{\text{id}}$  decreases linearly. With reference to eqn. (45),  $\lim(m_j \rightarrow 0)\phi = 1.0$ . With dilution of a salt solution a plot of  $\ln(a_1)$  against  $m_j$  approaches a linear interdependence.

For a 1 : 1 salt (*e.g.* KBr) in aqueous solution, the chemical potential of the salt is given by eqn. (48).

$$\mu_f(\text{aq}) = \mu_j^0(\text{aq}) + 2RT \ln(m_j \gamma_{\pm}/m^\circ) \quad (48)$$

For a 1 : 1 salt where the thermodynamic properties of the solution are ideal,

$$\mu_f(\text{aq};\text{id}) = \mu_j^0(\text{aq}) + 2RT \ln(m_j/m^\circ) \quad (49)$$

In other words where  $m_j < 1$  mol kg<sup>-1</sup>,  $\mu_f(\text{aq};\text{id}) < \mu_j^0(\text{aq})$ , indicating that the chemical potential of a salt in an ideal

solution is lower than that in the reference solution state for salt  $j$ . If  $m_j > 1 \text{ mol kg}^{-1}$ ,  $\mu_j(\text{aq};\text{id}) > \mu_j^0(\text{aq})$ , indicating that the chemical potential of the salt in an ideal solution is higher than that in the reference solution.

According to the Debye–Hückel limiting law (DHLL), for (very) dilute solutions,<sup>32</sup>

$$\ln(\gamma_{\pm}) = -S_{\gamma}(m_j/m^{\circ})^{1/2} \quad (50)$$

The Debye–Hückel limiting slope for 1 : 1 salts is theoretically expressed<sup>32,33</sup> in terms of eqn. (51) where  $e$  is the elementary charge,  $N_A$  the Avogadro constant,  $\rho_1^*(\ell)$  the solvent density,  $\epsilon_0$  the permittivity of vacuum,  $\epsilon_r$  the relative permittivity of solvent and  $k$  the Boltzmann constant.

$$S_{\gamma} = e^3[2N_A\rho_1^*(\ell)m^{\circ}]^{1/2}/8\pi[\epsilon_0\epsilon_r kT]^{3/2} \quad (51)$$

Using presently recommended values<sup>33</sup> for the properties of water( $\ell$ ), at 298.15 K and ambient pressure,  $S_{\gamma} = 1.1749$ .

In the context of the thermodynamic properties of aqueous solutions, activity coefficients of salts in aqueous solution have received most attention.<sup>34</sup> The scientific literature dealing with osmotic coefficients of aqueous salt solutions contains detailed reports concerning a vast range of salts in aqueous solution including polyvalent electrolytes<sup>35</sup> and alkaline earth metal halides,<sup>36</sup> and information concerning alkylammonium salts,<sup>37–40</sup> trifluoroacetates,<sup>41</sup> lanthanum nitrate,<sup>42</sup> Tris sulfate,<sup>43</sup> nickel chloride,<sup>44</sup> sodium dithionate,<sup>45</sup> calcium chloride,<sup>46</sup> caesium chloride,<sup>47</sup> ammonium thiocyanate,<sup>48</sup> and ammonium bromide.<sup>49</sup>

The impact on practical osmotic coefficients of changing the solvent from water to deuterium oxide has been studied.<sup>50,51</sup> Similar interest has been shown in the practical osmotic coefficients of mixed aqueous salt solutions; *e.g.* alkali metal chlorides + nitrates,<sup>52</sup> mixtures of  $(\text{Pr}_4\text{N}^+\text{Br}^- + \text{Na}^+\text{Br}^-)$ ,<sup>53</sup>  $(\text{NaCl} + \text{MgCl}_2)$ ,<sup>54</sup>  $(\text{NaCl} + \text{Na } p\text{-ethylbenzene sulfonate})$ ,<sup>55</sup>  $(\text{CsCl} + \text{KCl})$ ,<sup>56</sup> alkali metal chlorides,<sup>57</sup>  $(\text{LiCl} + \text{BaCl}_2)$ ,<sup>58</sup>  $(\text{H}_2\text{SO}_4 + \text{MgSO}_4)$ .<sup>59</sup>

A key feature of the DHLL is that charge–charge interactions lead to mutual stabilisation of a salt in solution; *i.e.* a lowering of the chemical potential of the salt.

Further the integral in eqn. (23) for  $\phi$  can be evaluated using the DHLL expression for  $\ln(\gamma_{\pm})$  given in eqn. (50). In this way we obtain eqn. (52) for  $\phi^{\text{dhll}}$ .

$$\phi^{\text{dhll}} = 1 - (S_{\gamma}/3)(m_j/m^{\circ})^{1/2} \quad (52)$$

Robinson and Stokes<sup>4</sup> report extensive tables for osmotic coefficients of aqueous salt solutions at 298.15 K and ambient pressure. For a 1 : 1 salt using eqns. (45) and (52) [with  $S_{\gamma} = 1.1749$  and  $M_1 = 0.018 \text{ kg mol}^{-1}$ ],

$$\ln(a_1)^{\text{dhll}} = -2M_1m_j + [2(S_{\gamma}/3)M_1(m^{\circ})^{-1/2}](m_j)^{3/2} \quad (53)$$

Then  $\ln(a_1)^{\text{dhll}}$  predicts that for a salt solution, molality  $m_j$ ,  $\ln(a_1)$  exceeds that in the corresponding salt solution having ideal thermodynamic properties. In other words the activity of the solvent water is enhanced above that for water in solutions where the thermodynamic properties are ideal; the solvent is

destabilised. For very dilute solutions  $[\ln(a_1)^{\text{dhll}} + 2M_1m_j]$  is a linear function of  $(m_j)^{3/2}$ , independent of the nature of the 1 : 1 salt.

The dependence of  $\ln(a_1)$  on salt molality is summarised in Figs. 6 and 7 for two bromides. One curve shows the dependence predicted for a mixture of two neutral solutes. A second curve shows the calculated dependence of  $\ln(a_1)^{\text{dhll}}$  on molality  $m_j$ .

For alkali metal bromides,  $\ln(a_1)$  at a given molality is less than required by  $\ln(a_1)^{\text{dhll}}$  indicating the operation of a stabilising effect on the solvent, this effect decreasing through series, LiBr, NaBr, KBr. In the latter case  $\ln(a_1)$  for KBr is close to  $\ln(a_1)^{\text{dhll}}$  up to at least  $0.05 \text{ mol kg}^{-1}$ . If the pattern described for neutral solutes is taken as indicative, the overall pattern reflects the more hydrophilic nature of  $\text{Li}^+$ , relative to  $\text{Na}^+$  and then  $\text{K}^+$ . In fact this conclusion is supported by the pattern shown by the tetra-alkylammonium bromides where with an increase in hydrophobic nature of the cation,  $\ln(a_1)$  increases at a given molality,  $\ln(a_1)$  exceeding  $\ln(a_1)^{\text{dhll}}$ , Fig. 7.

The opposing effects of added salt and solvent is an example of Gibbs–Duhem compensation in the context of the properties of a solution. However for other than very dilute salt solutions, eqn. (50) is inadequate. For more concentrated salt solutions we write the following modified Debye–Hückel

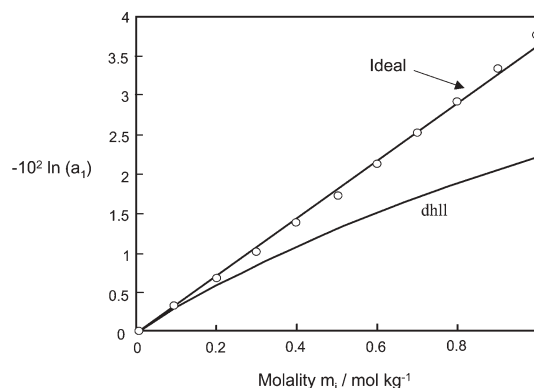


Fig. 6 Dependence of  $\ln(a_1)$  on salt molality for LiBr(aq) at 298.15 K and ambient pressure.<sup>4</sup>

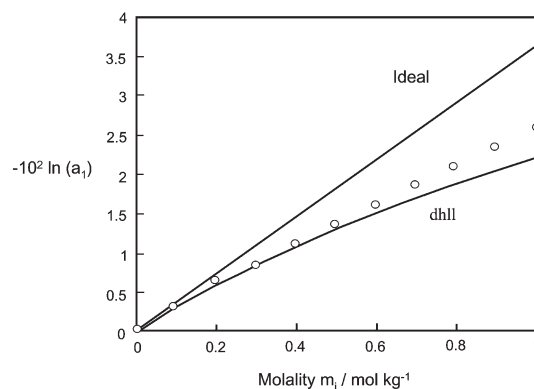


Fig. 7 Dependence of  $\ln(a_1)$  on salt molality for tetra-n-butylammonium bromide(aq) at 298.15 K and ambient pressure.<sup>40</sup>



equation.

$$\ln(\gamma_{\pm}) = -S_j(m_j/m^\circ)^{1/2} + (2g_{\pm}/3RT)(m_j/m^\circ) \quad (54)$$

Here  $g_{\pm}$  is an ion–ion interaction parameter characteristic of salt  $j$  in aqueous solutions at defined  $T$  and  $p$ . Then using eqn. (23),

$$\phi = 1 - (S_j/3)(m_j/m^\circ)^{1/2} + (g_{\pm}/3RT)(m_j/m^\circ) \quad (55)$$

For a range of 1 : 1 salts at a common  $m_j$ ,  $\phi$  reflects the impact of the interaction parameter  $g_{\pm}$ .<sup>24</sup>

## VI Aqueous salt solutions; natural waters

Most natural waters are aqueous solutions containing more than one salt. Seawater is the natural water which occurs in vast amounts but river, lake, rain and ground waters are also important.<sup>60</sup> Attention has recently been given to aerosols which comprise aqueous salt solutions<sup>60</sup> and to the seasonal change in composition of seawater in coastal areas.<sup>61</sup>

A model of oceanic water comprising the six major seawater ions ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) is an aqueous solution containing four salts with total molality around 6.0 mol  $\text{kg}^{-1}$ . Natural waters, however, become very concentrated multi-component salt solutions if subjected to intense evaporation. High ionic strengths are attained in hypersaline waters thus produced, as in the case of the Dead Sea.

The ionic strength  $I$  of a solution containing  $k$  different ions is defined by eqn. (56).

$$I = \frac{1}{2} \sum_{i=1}^k m_i z_i^2 \quad (56)$$

Here  $m_i$  and  $z_i$  are, respectively, the molality and charge number of ion  $i$ . If a solution contains only 1 : 1 salts, its ionic strength equals the total salt molality. However in all other cases the ionic strength exceeds the total salt molality.

The simple treatment of salt solutions outlined in the previous section is not applicable to salt solutions of great complexity as encountered in Nature. Nevertheless one would like to relate the properties of aqueous solutions containing, for example, sodium chloride and magnesium sulfate to the properties of the two separate single salt solutions. The task is more difficult in the case of solutions containing mixed-valence type salts and mixtures of salts with a common ion. Khoo<sup>62</sup> elegantly summarised the earlier attempts (and their shortcomings) to treat these complexities. The contributions made by Guggenheim<sup>63</sup> and Scatchard<sup>64</sup> are notable.

The way forward was to envisage an aqueous salt solution as comprising solute ions in water( $\ell$ ).<sup>65</sup> The modern approach was developed by Pitzer.<sup>66–68</sup> Pitzer<sup>66</sup> expressed the excess Gibbs energy of an aqueous salt solution containing ions  $i, j, k$  prepared using 1 kg of water( $\ell$ ) in the form of eqn. (57).

$$G^E(\text{aq}; w_1 = 1 \text{ kg})/RT = f(I) + \sum_i \sum_j \lambda_{ij}(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk}(I) m_i m_j m_k \quad (57)$$

In eqn. (57)  $f(I)$  describes long-range charge–charge interactions including the DHLL, and is a function of the ionic strength  $I$ , temperature, pressure and solvent properties. Short-range interactions between the ions are described by pairwise  $\lambda_{ij}$  and  $\mu_{ijk}$  virial coefficients. Third order virial coefficients  $\mu_{ijk}$  are important although their dependence on ionic strength can be ignored. Because  $\lambda_{ij} = \lambda_{ji}$  and  $\mu_{ijk} = \mu_{jik} = \mu_{ikj}$  the number of virial coefficients is reduced. Further triplet interactions between all ions of the same sign need not be taken into account.

We are primarily interested in the practical osmotic coefficient  $\phi$  of a salt solution as a measure of the activity of solvent water. With

$$\phi = 1 - [RT \sum_i m_i]^{-1} (\partial [n_1 G^E(\text{aq}; w_1 = 1 \text{ kg})] / \partial n_1)_{T, p, n(i)} \quad (58)$$

Then<sup>67,68</sup>

$$\phi = 1 - [\sum_i m_i]^{-1} \{ [f'(I) - f(I)] + \sum_i \sum_j [\lambda_{ij}(I) + I \lambda'_{ij}(I)] m_i m_j + 2 \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k \} \quad (59)$$

In this theoretical expression for the practical osmotic coefficient,  $f'(I)$  and  $\lambda'_{ij}(I)$  are ionic strength derivatives of, respectively,  $f(I)$  and  $\lambda_{ij}(I)$ .

However individual ion parameters, such as  $\lambda_{ij}$  and  $\mu_{ijk}$ , are not directly accessible to experiment. Therefore Pitzer developed more complicated equations for salt and mixed salt solutions.<sup>68</sup> In other words Pitzer's equations, although possessing a theoretical basis, become at least in part empirical.<sup>7,69</sup> On the other hand, the corresponding equations have been developed for a large range of aqueous salt solutions.<sup>5,60,68</sup>

Using the electroneutrality condition for a solution of a single salt MX for which  $v = v_M + v_X$ , eqn. (59) can be recast as eqn. (60).<sup>68</sup>

$$\phi = 1 + [z_M z_X] f^\phi + (2v_M v_X / v) B_{MX}^\phi m_{MX} + [2(v_M v_X)^{3/2} / v] C_{MX}^\phi m_{MX}^2 \quad (60)$$

The experimentally measurable parameters  $f^\phi$ ,  $B_{MX}^\phi$  and  $C_{MX}^\phi$  are defined as follows.

$$f^\phi = [f'(I) - f(I)]/I/2 \quad (61)$$

$$B_{MX}^\phi = \lambda_{MX}(I) + I \lambda'_{MX}(I) + (v_M / 2v_X) [\lambda_{MM}(I) + I \lambda'_{MM}(I)] + (v_X / 2v_M) [\lambda_{XX}(I) + I \lambda'_{XX}(I)] \quad (62)$$

$$C_{MX}^\phi = [3/(v_M v_X)^{1/2}] (v_M \mu_{MMX} + v_X \mu_{MXX}) \quad (63)$$

Hence parameters  $f^\phi$  and  $B_{MX}^\phi$  depend on the ionic strength of the solution..

The extended form of the Debye–Hückel term  $f^\phi$  was shown statistically to be accurately described by eqn. (64) in which  $b$  is a universal parameter, 1.2  $\text{kg}^{1/2} \text{mol}^{-1/2}$ .

$$f^\phi = -A_\phi I^{1/2} / (1 + bI^{1/2}) \quad (64)$$

In the latter equation,  $A_\phi$  has been called<sup>70</sup> the Pitzer–Debye–Hückel limiting law slope and is simply related to  $S_\gamma$  [(cf. eqn. (51))] as follows.

$$A_\phi = (1/3)S_\gamma(m^\circ)^{-1/2} \quad (65)$$

The dependence of  $B_{MX}^\phi$  on ionic strength is described by eqn. (66) where  $\alpha$  equals  $2.0 \text{ kg}^{1/2} \text{ mol}^{-1/2}$  for most salts, including mixed-valence type salts but not for 2 : 2 salts.

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha I^{1/2}) \quad (66)$$

In summary, the practical osmotic coefficient and hence the activity of water in most single-salt solutions can be described up to high salt concentrations in terms of three adjustable parameters,  $\beta_{MX}^{(0)}$ ,  $\beta_{MX}^{(1)}$  and  $C_{MX}^\phi$  which are characteristic of a given salt MX at fixed temperature and pressure

For 2 : 2 salts, such as the seawater component  $\text{MgSO}_4$ , an extra exponential term has to be added to eqn. (66).<sup>68</sup> For mixed-salt solutions Pitzer<sup>68</sup> defined additional like-sign ion-interaction terms  $\Phi_{MM}$ ,  $\Phi_{XX}$ ,  $\psi_{MM'X}$  and  $\psi_{MXX'}$ , which are different combinations of respectively, virial coefficients  $\lambda_{ij}$  and  $\mu_{ijk}$ . The advantage of these new parameters is that they can be estimated using experimental data for mixed salt solutions with a common ion. Thus together with parameters for single salt solutions, a complete description of the practical osmotic coefficients for complex aqueous mixtures is achieved in terms of the Pitzer model. In the case of seawater, it is possible to introduce a considerable simplification. Because NaCl accounts, on a mole basis, for about 90% of the dissolved salts in seawater, the magnitudes of mixed salt terms  $\Phi_{ij}$  and  $\Psi_{ijk}$  are small. Therefore the activity of water in seawater is approximately given by the activity of water in NaCl(aq) having the same ionic strength.

An extremely important subject with an extensive literature concerns the activity of water in strongly acidic and basic media where the definition of reference states in terms of composition variables raises enormous problems as discussed by Cox.<sup>71</sup>

## VII Binary aqueous mixtures

A given binary liquid mixture<sup>72–74</sup> is prepared (at fixed  $T$  and  $p$ ) by mixing  $n_1$  and  $n_2$  moles of liquids  $\ell_1$  and  $\ell_2$  respectively. Then

$$x_1 = n_1/(n_1 + n_2); x_2 = n_2/(n_1 + n_2) \quad (67)$$

Also

$$\mu_1(\text{mix}) = \mu_1^*(\ell) + RT \ln(x_1 f_1) \quad (68)$$

and

$$\mu_2(\text{mix}) = \mu_2^*(\ell) + RT \ln(x_2 f_2) \quad (69)$$

At all  $T$  and  $p$ , for  $i = 1$  and  $2$ ,

$$\lim(x_i \rightarrow 1) f_i = 1 \quad (70)$$

Here  $\mu_1^*(\ell)$  and  $\mu_2^*(\ell)$  are chemical potentials of the two pure liquids at the same  $T$  and  $p$ ;  $f_1$  and  $f_2$  are rational activity coefficients. These (rational) activity coefficients, as shown by eqn. (70), approach unity at opposite ends of the mixture composition range. Thus for the aqueous component, as  $x_1$  approaches unity (at the same  $T$  and  $p$ ) so  $f_1$  approaches unity.

The change in pattern is illustrated by the properties of water(1) and ethanol(2) liquid mixtures<sup>75</sup> at 303.15 K. At one composition extreme,  $x_1 = 0.9957$ ,  $f_1 \cong 1$  and  $a_1 = 0.996$  with  $x_2 = 0.0043$ ,  $f_2 = 4.0191$  and  $a_2 = 0.017$ . At the other extreme,  $x_1 = 0.0185$ ,  $f_1 = 2.408$  and  $a_1 = 0.044$ ;  $x_2 = 0.9815$ ,  $f_2 \cong 1$  and  $a_2 = 0.982$ . Thus as  $x_1$  approaches zero, the chemical potential of water in the binary system approaches ‘minus infinity’. The latter accounts for the difficult problem of removing the last traces of water from another liquid. If across the whole composition range (at all  $T$  and  $p$ ) both  $f_1$  and  $f_2$  are unity, the thermodynamic properties of the liquid mixture are ideal.

By analogy with eqn. (8) the activities  $a_1(\text{mix})$  and  $a_2(\text{mix})$  of the two components are given by  $(x_1 f_1)$  and  $(x_2 f_2)$  respectively.

In the mixtures

$$a_1(\text{mix}) = x_1 f_1 \quad (71)$$

$$a_2(\text{mix}) = x_2 f_2 \quad (72)$$

Hence for both components, with  $i = 1, 2$ ,  $\lim(x_i \rightarrow 1) a_i(\text{mix}) = 1$ . Moreover the activity of water in the aqueous mixture is related to the excess molar Gibbs energy of mixing,  $G_m^E$ .§ Thus,

$$\ln[a_1(\text{mix})] = \left[ \frac{G_m^E}{RT} + \frac{x_2}{RT} \frac{dG_m^E}{dx_1} \right] + \ln(x_1) \quad (73)$$

We note that

$$\ln[a_1(\text{mix})] = \ln(f_1) + \ln(x_1) \quad (74)$$

Eqn. (73) yields a method of obtaining the activities of both components in a given mixture granted  $G_m^E$  has been obtained as a function of liquid mixture composition. An important task is to fit the dependence of  $G_m^E$  on  $x_2$  to an equation in order to calculate the derivative  $dG_m^E/dx_2$  at required mole fractions. The Guggenheim–Scatchard<sup>76</sup> (also called the Redlich–Kister<sup>77</sup>) equation is one such equation, having the following general form.

$$G_m^E = x_2(1 - x_2) \sum_{i=1}^{i=k} A_i(1 - 2x_2)^{i-1} \quad (75)$$

$A_i$  are coefficients obtained from a least-squares analysis of the dependence of  $G_m^E$  on  $x_2$ . Eqn. (75) clearly satisfies the condition that  $G_m^E$  is zero at  $x_2 = 0$  and at  $x_2 = 1$ .§ In fact very accurate and extensive data are required to justify the use of four or more empirical  $A_i$  parameters. Nevertheless, using these parameters, the dependence of activity  $a_1 (=x_1 f_1)$  on mixture composition is readily obtained.<sup>7</sup>

In fact the first term in the G-S equation has the following form.¶

$$X_m^E = x_2(1 - x_2)A_1 \quad (76)$$

According to eqn. (76),  $X_m^E$  is an extremum at  $x_2 = 0.5$ , the plot being symmetric about the line from  $X_m^E$  to  $x_2 = 0.5$ . In fact for most systems the  $A_1$  term is dominant. Eqn. (75) fits the dependence with a set of contributing curves which all pass through points,  $X_m^E = 0$  at  $x_1 = 0$  and  $x_1 = 1$ . The usual procedure involves fitting the recorded dependence using increasing number of terms in the series, testing the statistical significance of including each further term.

Although eqn. (75) has been applied to many systems and although the equation is easy to incorporate into computer programs using packaged least-squares and graphical routines, the equation suffers from several disadvantages. In fact eqn. (75) is ill-suited for representing skewed data and clearly unable to describe an experimental excess molar property showing a sigmoidal-shaped composition dependence. Thus different empirical equations have been proposed, which are more flexible than eqn. (75). Here we refer to the square-root relationship of Missen and co-workers<sup>78</sup> and to the function proposed by Ortega,<sup>79</sup> respectively eqns. (77) and (78).

$$X_m^E = x_2(1 - x_2) \sum_{i=1}^{i=k} B_i x_2^{(i-1)/2} \quad (77)$$

$$X_m^E = x_2(1 - x_2) \sum_{i=1}^{i=k} C_i \{x_2/[x_2 + D(1 - x_2)]\}^{i-1} \quad (78)$$

However the need for these equations is more likely to arise while fitting excess molar enthalpies<sup>80</sup> and excess molar volumes<sup>80,81</sup> than excess molar Gibbs energies.<sup>80</sup>

With reference to these equations (*e.g.* eqn. (75)) as one incorporates a further term in the series, (*e.g.*  $A_j$ ) estimates of all the previously calculated parameters (*i.e.*  $A_2, A_3, \dots, A_{j-1}$ ) change. For this reason orthogonal polynomials have been increasingly favoured especially where the appropriate computer software is available. The only reservation is that derivation of explicit equations for the required derivative  $dG_m^E$  is not straightforward. The problem becomes rather more formidable when the second and higher derivatives are required. The derivative  $d^2G_m^E$  is sometimes required in calculations concerning the properties of binary liquid mixtures.

If the coefficients  $A_2, A_3, \dots$  in eqn. (75) are zero,

$$G_m^E = x_2(1 - x_2)A_1 \quad (79)$$

and

$$dG_m^E/dx_2 = (1 - 2x_2)A_1 \quad (80)$$

With reference to the Gibbs energies and coefficient  $A_1$ ,

$$\ln(f_1) = (A_1/RT)[x_2]^2 \quad (81)$$

$$\ln(f_2) = (A_1/RT)[1 - x_2]^2 \quad (82)$$

Eqns. (81) and (82) are often called the two-suffix Margules equations.<sup>7</sup> In fact the equation reported by Jost *et al.*<sup>82</sup> has this form.

Rather than using the Redlich–Kister equation, recently attention has been directed to the Wilson equation<sup>83</sup> written in eqn. (83) for a two-component liquid mixture.

$$G_m^E/RT = -x_1 \ln(x_1 + A_{12}x_2) - x_2 \ln(x_2 + A_{21}x_1) \quad (83)$$

Then, for example

$$\ln(f_1) = -\ln(x_1 + A_{12}x_2) + x_2 \left( \frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{A_{21}x_1 + x_2} \right) \quad (84)$$

The Wilson equation forms the basis for two further developments which use the concept of local composition to account for non-randomness. These approaches are described as the NRTL (non-random, two liquid) equation<sup>7,83</sup> and the UNIQUAC (universal quasi-chemical theory) equation.<sup>7</sup> Based on the latter equation, the UNIFAC (universal function activity coefficient) method has been developed for the calculation of activity coefficients using group contributions.<sup>7</sup>

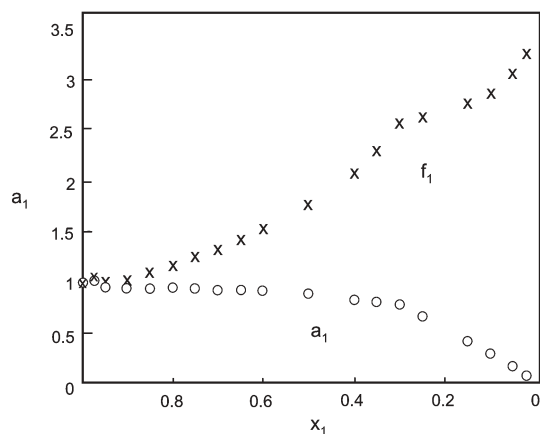
For most binary aqueous mixtures  $G_m^E$  is a smooth function of water mole fraction  $x_1$  with an extremum near  $x_1 = 0.5$ . Rarely for a given mixture does the sign change across the mole fraction range although this feature is not unknown.<sup>84,85</sup> However changes in sign of  $H_m^E$ ,  $TS_m^E$  and  $V_m^E$  are common.

Nevertheless the task of accounting for the properties of binary aqueous mixtures is awesome. For this reason even more than 30 years later the classification introduced by Franks<sup>86</sup> has considerable merit which forms the basis for an analysis of the dependence of the activities of the components on composition. A distinction is drawn between typically aqueous (TA) and typically non-aqueous (TNA) binary aqueous mixtures based on the thermodynamic molar excess functions,  $G_m^E$ ,  $H_m^E$  and  $TS_m^E$ . TA mixtures are complicated. Nevertheless these mixtures are often used as solvents for synthetic and mechanistic studies.

For many binary aqueous liquid mixtures where the non-aqueous component is, for example, a monohydric alcohol the pattern shown by the molar excess thermodynamic parameters is  $G_m^E > 0$ ;  $|TS_m^E| > |H_m^E|$ . This summary of excess molar properties defines TA mixtures.  $G_m^E$  is positive because the excess molar entropy of mixing is large in magnitude and negative in sign. In these terms the mixing is dominated by entropy changes. The excess molar enthalpy of mixing is smaller in magnitude than either  $G_m^E$  or  $TS_m^E$  but exothermic in water-rich mixtures.

The word ‘typically’ in the description stems from the observation that this pattern in thermodynamic variables is rarely shown by non-aqueous systems. Also in 1968 when the classification<sup>86</sup> was proposed, most binary aqueous liquid mixtures seemed to follow this pattern. Among the many examples of this class of system are aqueous mixtures formed by ethanol,<sup>75</sup> 2-methyl propan-2-ol<sup>87</sup> and cyclic ethers including tetrahydrofuran.<sup>88</sup> In the water-rich mixtures, the dominant feature effect is a dramatic negative  $T \cdot S_m^E$  producing a large (positive)  $G_m^E$ .

The activity of water in 2-methyl propan-2-ol + water mixtures<sup>87</sup> at 298.15 K (Fig. 8) decreases from 1.0 at  $x_1 = 1.0$  to 0.064 at  $x_1 = 0.02$ . Over the short range,  $1.0 \geq x_1 \geq 0.945$ ,



**Fig. 8** Dependence of the activity of water  $a_1$  and its activity coefficient  $f_1$  on mole fraction of water  $x_1$  in 2-methyl propan-2-ol mixtures at 298.15 K. Activities calculated from the dependence of excess molar Gibbs energy of water on  $x_1$  are summarised in Table 1 of ref. 87.

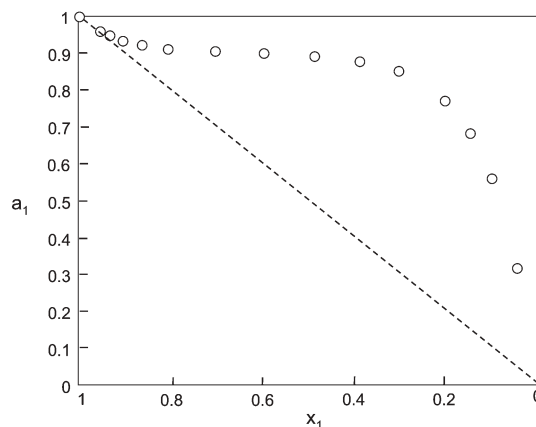
the pattern in activity  $a_1$  is close to  $a_1^{\text{id}}$ . For  $x_1 < 0.40$  the activity  $a_1$  reflects a clustering of alcohol molecules.

An important characteristic of TA mixtures is a tendency towards and in some cases actual decrease in liquid miscibility with increase in temperature. At ambient  $T$  and  $p$ , the mixture 2-methylpropan-2-ol + water is miscible (but only just!) in all molar proportions. The corresponding mixtures prepared using butan-1-ol and butan-2-ol are partially miscible. TA systems are therefore often characterised by a lower critical solution temperature (LCST). In fact nearly all examples quoted in the literature of systems having an LCST involve water as one component; *e.g.* LCST = 322 K for 2-butoxyethanol + water<sup>89</sup> and 298.8 K for 2-isobutoxy-ethanol.<sup>90</sup> This tendency to partial miscibility is often signalled by the properties of the completely miscible systems.

For the group of binary aqueous mixtures classified<sup>86</sup> as typically non-aqueous positive (TNAP),  $G_m^E$  is positive. An example of such a mixture is 'water + acetonitrile'.<sup>91–93</sup> The positive  $G_m^E$  reflects endothermic mixing across nearly all the mole fraction range. These mixtures have a tendency to be partially miscible with an upper critical solution temperature, UCST. For aqueous mixtures the composition at the UCST is often 'water-rich'. For acetonitrile + water, the UCST is 272 K. The positive  $G_m^E$  and endothermic mixing are attributed to disruption of water–water hydrogen bonding by added MeCN. Thus the activity of water  $a_1$  exceeds that in the corresponding ideal mixture;<sup>91</sup> Fig. 9.

Several binary aqueous mixtures combine thermodynamic patterns for both TA and TNAP systems to produce a closed miscibility loop; *e.g.* 1-propoxypropanol-2-ol (UCST = 171.7 °C; LCST = 34.5 °C) and 2-propoxypropan-1-ol (UCST = 162.0 °C, LCST = 42.8 °C).<sup>94</sup>

By way of contrast, for typically non-aqueous negative (TNAN) mixtures,  $G_m^E$  is negative because there is strong inter-component interaction which also produces exothermic mixing. Examples of this class are the mixtures, at 298.15 K, water + DMSO,<sup>10,95,96</sup> and water + H<sub>2</sub>O<sub>2</sub>.<sup>97</sup>



**Fig. 9** Dependence of activity of water  $a_1$  on mole fraction of water  $x_1$  in MeCN + water mixtures.<sup>91</sup>

The distinction between binary aqueous mixtures formed by 2-methylpropan-2-ol and by acetonitrile described above is based on thermodynamic properties. Support for this distinction is provided by mass spectra of aqueous solutions.<sup>98</sup> The mass spectra of water( $\ell$ ) show prominent peaks corresponding to the cluster  $\text{H}^+(\text{H}_2\text{O})_{21}$ . For water + methanol mixtures (molar ratio 100 : 1 respectively) a series of clusters is observed containing 21 molecules (*i.e.* ratios 1–20, 2–19, and 3–18 methanol to water) indicating that the interaction is substitutional whereas for MeCN + H<sub>2</sub>O systems, clusters containing 21 water molecules are observed leading to the description 'additional mixing'. We recall in this context the X-ray spectra of clathrate hydrates<sup>99</sup> and the controversy around the question whether or not these structures exist in solution.

The complexity in the properties of binary aqueous mixtures carries over to the properties of solutes in these systems and to the kinetic of reactions in these mixed solvents.<sup>100</sup>

## VIII Activity of water, determination

We noted in Section II how for binary liquid mixtures, the determination of partial vapour pressures  $p_1$  as a function of mixture composition yields using eqn. (4) the corresponding dependence of activity  $a_1$ . By way of contrast the activities of water in aqueous solutions containing involatile solutes are determined using several methods.<sup>101</sup>

Robinson and Stokes<sup>4</sup> describe three general methods based on vapour pressures for measuring the activities of water in aqueous solutions; (i) the direct static method, (ii) the dynamic method and (iii) the isopiestic method.

The key property is the ratio of the partial vapour pressure of water above a given solution to the vapour pressure of water( $\ell$ ) at the same temperature; eqn. (4).

In the direct static method described by Gibson and Adams,<sup>102</sup> the vapour pressure of water  $p_1^*(\ell)$  and the difference  $\Delta p$  between vapour pressures of solvent and solution were measured using a manometer filled with butyl phthalate ( $\ell$ ). The vapour pressure of the pure solvent  $p_1^*(\ell)$  was measured. A number of stopcocks were used to connect in turn the manometer to flasks containing water( $\ell$ ) and the solution. Hence  $p_1^*(\ell)$ ,  $\Delta p$  and the ratio  $\Delta p/p_1^*(\ell)$  were obtained

for a given salt solution. The results were expressed in the form of the dependence of the ratio  $(a_1/x_1)$ , (where  $a_1$  and  $x_1$  are activity and mole fraction of water respectively) as a function of the molality of salt,  $m_j$ , Fig. 10. This ratio corresponds to the rational activity coefficient of water in the aqueous solution,  $f_1$  where  $a_1 = x_1 f_1$ . A similar procedure is described by Taylor and Rowlinson in their determination of the activity of glucose(aq).<sup>103</sup>

Shankman and Gordon<sup>104</sup> improved the method and procedures in a determination of the activity of water in sulfuric acid(aq) at 298.15 K over the range  $0 \leq m_j/\text{mol kg}^{-1} \leq 22.63$ , the activity of water falling remarkably to 0.0538. The experimental results were analysed using eqn. (85) where  $p_1^*(\ell)$ ,  $p_1(\text{aq})$  and  $\Delta p$  are three experimentally measured pressures.

$$\frac{2p_1(\text{aq})}{p_1^*(\ell) + p_1(\text{aq}) + \Delta p} = \frac{2p_1(\text{aq})}{p_1^*(\ell) + p_1(\text{aq}) + p_1^*(\ell) - p_1(\text{aq})} = \frac{2p_1(\text{aq})}{2p_1^*(\ell)} = a_1 \quad (85)$$

This procedure starting with the term on the LHS of eqn. (85) minimises the impact of experimental error on the calculated activity  $a_1$ .

Apelblat and co-workers directly measured vapour pressures using an isoteniscope<sup>105</sup> and hence obtained osmotic coefficients for citric acid(aq),<sup>106</sup>  $0.5 \leq m_j/\text{mol kg}^{-1} \leq 8.0$  over the temperature range  $298.15 \leq T/\text{K} \leq 318.15$  and the same technique to examine the properties of DL-malic acid(aq) and L(+)-tartaric acid(aq)<sup>107</sup> and of thorium nitrate(aq).<sup>108</sup>

Taylor and Rowlinson<sup>103</sup> measured the difference in vapour pressures of water( $\ell$ ) and glucose(aq) and expressed  $\ln(f_1)$  as a quadratic function of the square root of the mole fraction of glucose.

The dynamic method described by Bechtold and Newton<sup>109</sup> involves passing a dry inert gas (*e.g.* air) through successively water( $\ell$ ), a desiccant, an aqueous solution of an involatile solute and, finally, a second desiccant. A detailed diagram showing the apparatus is given in reference 109. During the course of each experiment, the desiccants gain mass,  $m_0$  and  $m_1$  respectively from water( $\ell$ ) and the solution. The vapour pressures of the two liquids are  $p_1^*(\ell)$  and  $p_1(\text{aq})$ .  $B_0$  and  $B_1$

are the total pressures at the end of the saturators filled with water and solution.

Hence,

$$\frac{p_1^*(\ell) - p_1(\text{aq})}{p_1(\text{aq})} = \frac{m_0[B_0 - p_1^*(\ell)] - m_1[B_1 - p_1^*(\ell)]}{m_1 B_1} \quad (86)$$

Then knowing  $p_1^*(\ell)$ , the ratio  $p_1(\text{aq})/p_1^*(\ell)$  yields the activity  $a_1(\text{aq})$ ; Fig. 11.

In a rather different approach developed by Stokes,<sup>110</sup> a solution at 298.15 K is allowed to come into equilibrium with water( $\ell$ ) at a known different temperature,  $T_1$ . Hence the vapour pressure of water in the solution  $p_1(\text{aq})$  at 298.15 K equals  $p_1^*(\ell)$  at temperature  $T_1$  which is available from standard data sources.

In another approach, activities of water in saturated aqueous salt solutions are measured using an evaporimeter<sup>111</sup> which was originally developed to measure rates of evaporation from solid surfaces; *e.g.* skin. This technique has been used to measure vapour pressures of saturated aqueous salt solutions (*e.g.*  $\text{BaCl}_2$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{K}_2\text{CO}_3$  and  $\text{ZnSO}_4$ ) over a range of temperatures; *e.g.* 283 to 313 K; Fig. 12. Apelblat<sup>111,112</sup> has shown that good agreement is obtained using this technique with previously published

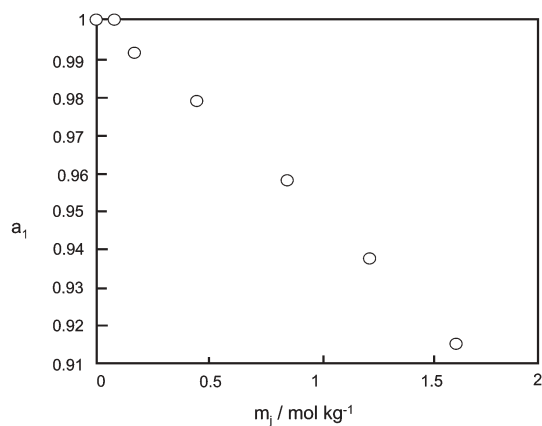


Fig. 11 Activity of water in  $\text{BaCl}_2(\text{aq})$  at 298.15 K.<sup>109</sup>

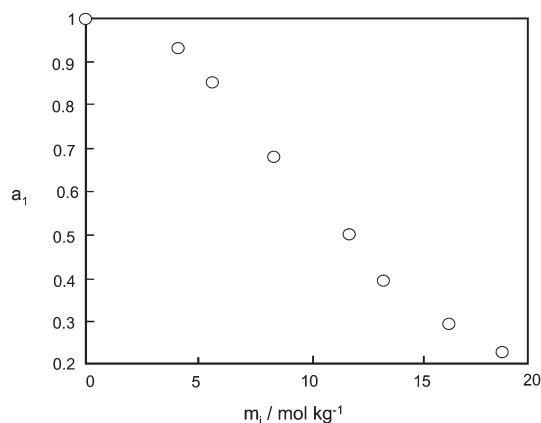


Fig. 10 Activity of water<sup>102</sup> in  $\text{LiCl}(\text{aq})$  at 298.15 K.

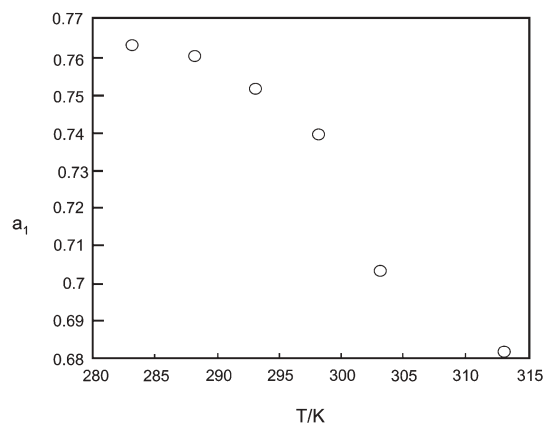


Fig. 12 Activity of water<sup>111</sup> in saturated  $\text{NaNO}_3(\text{aq})$  as a function of temperature  $T$ .

data for extensive ranges of salt solutions; *e.g.* KBr(aq) and ZnSO<sub>4</sub> (aq).

In another recent development differences between vapour pressures of solvent and solution are measured using differential capacitance manometry.<sup>113</sup> The precision of this method was convincingly demonstrated<sup>114</sup> in a study of the vapour pressure of ice between 194.7 and 271.7 K.

Despite this extensive range of techniques for measuring the activity of water in aqueous solutions, the 'method of choice' seems to be the 'beautifully simple'<sup>115</sup> isotonic method,<sup>59,116,117</sup> more frequently called the 'isopiestic method'. Analysis of the experimental results presents a challenge as detailed by Clarke and Glew.<sup>118</sup>

The term 'iso-piestic' was suggested by Bousfield<sup>119</sup> in 1917 to identify a condition where solutions have the same vapour pressure at the same temperature. Bousfield described experiments in which weighed amounts of different salts are placed in small glass containers. The latter are held in a closed thermostatted desiccator which also holds a small amount of water(*l*) which is continually replenished. The sample cells contained for example the salts KCl, NaCl, LiCl and KNO<sub>3</sub>. These salts spontaneously hydrate by uptake of water from the vapour phase. The sample cells in the experiment reported were weighed daily for three months. The results provided estimates of the hydration of salts. Interestingly the paper is heavily criticised in the published discussion. Clearly the critics did not understand what Bousfield was reporting. Only later was the importance of the ideas underlying this simple experiment recognised.

The impact of the experiments reported by Bousfield has been dramatic, the technique being extensively refined. In current applications, dishes holding aqueous solutions stand in a copper block (ensuring good thermostating) within a partially evacuated desiccator which is rocked gently. The dishes are weighed periodically, each dish reaching eventually a constant weight indicating that the solutions are in thermodynamic equilibrium. In other words the chemical potentials and hence activities of water in the solutions are equal. One of the dishes contains a standard where the activities of the solution are known. NaCl(aq) is often used as isopiestic reference system.<sup>117</sup>

The isopiestic technique has been used to study many aqueous salt solutions,<sup>59,116,117</sup> including methanesulfonic acid(aq)<sup>120</sup> and phthalic acid.<sup>121</sup> An extensive literature describes the results of studies using the isopiestic technique into the properties of mixed salt solutions;<sup>59,116,122</sup> *e.g.* mixed amino acids(aq).<sup>58</sup> Interestingly osmotic coefficients measured using the isopiestic technique for ternary mixtures (HClO<sub>4</sub> + NaClO<sub>4</sub> + LiClO<sub>4</sub>)(aq) can be predicted using osmotic coefficients for the three binary solutions.<sup>123</sup> Using the isopiestic technique, Covington *et al.*<sup>57</sup> showed that the cross-square rule for enthalpies of mixing can be extended to excess Gibbs energies.

Within the context of microbiological investigations, an agar dish isopiestic method can be used to control the water activity of solids.<sup>124</sup>

The key limitation of the techniques examined above arises from the fact that the partial vapour pressure of the solute must be negligibly small. So for example the isopiestic

technique is applicable to aqueous solutions containing hydrophilic solutes (*e.g.* sucrose) but not to aqueous solutions containing hydrophobic solutes (*e.g.* ethanol).

The classic interest in the properties of solvents in solutions (*cf.* activities of solvent) was closely linked to measurement of osmotic pressures, depression of freezing point and elevation of boiling point; *i.e.* the colligative properties of solutions.

Classically, the colligative properties of non-ionic solutions were used to determine the molar masses of solutes. Key dates are around the late nineteenth century when the connection was made between depression of freezing point and lowering of vapour pressure. The fact that the depression of freezing point of a liquid is a function of the molar mass of the solute was noted by Watson (1771) and Blagden (1788). Russell<sup>125</sup> has described how Beckmann designed a thermometer to measure precisely the difference in freezing point of solutions and the solvent. In the application of cryoscopic techniques, a common assumption is that the thermodynamic properties of the solution are ideal. If the properties of a given aqueous solution are determined to a significant extent by solute–solute interactions, a determined molar mass for the solute will be in error. Effectively a complete analysis of cryoscopic data requires a satisfactory description of solute–solute interactions. Indeed modern mass spectrometric techniques make redundant measurement of the colligative properties of solutions in determination of the molar masses of solutes.

The key equation concerning, for example, depression of freezing point emerges from the Schroder–van Laar equation; *e.g.* eqn. (22.5) in ref. 3. The depression of freezing point  $\theta$  is defined by  $(T_1^\circ - T)$  where  $T_1^\circ$  is the freezing point of the pure solvent. Taking account of the dependence of the standard enthalpy of fusion  $\Delta_f H^\circ$  on temperature in terms of the standard isobaric heat capacity of fusion  $\Delta_f C_p^\circ$  the activity of water  $a_1$  is related to  $\theta$  using eqn. (87).

$$-\ln(a_1) = \frac{\Delta_f H_1^\circ}{RT_1^\circ} \frac{\theta}{T_1^\circ} + \left( \frac{\Delta_f H_1^\circ}{R} - \frac{\Delta_f C_{p1}^\circ}{RT_1^\circ} \right) \frac{\theta^2}{(T_1^\circ)^2} \quad (87)$$

If the established values for  $\Delta_f H^\circ$ ,  $\Delta_f C_p^\circ$ ,  $R$  and  $T_1^\circ$  are used, eqn. (87) simplifies to eqn. (88) with  $\Delta T = T_1^\circ - T$ .

$$\log(a_1) = -4.207 \times 10^{-3}(\Delta T/K) - 2.1 \times 10^{-6}(\Delta T/K)^2 \quad (88)$$

Apelblat *et al.*<sup>126</sup> confirm that  $a_1$  calculated using eqn. (88) agrees with  $a_1$  calculated from relative pressures,  $[p_1(\text{ice}; T)/p_1(\text{water}; T)]$ ; see for example<sup>127</sup> a study of sodium tetraborate(aq) and sodium carbonate(aq). Another method is described by Lilley and Scott<sup>39,128</sup> in which the freezing point depression  $\theta$  is related to the practical osmotic coefficient using eqn. (89) where  $\lambda = 1.860 \text{ kg K mol}^{-1}$  and  $b = 4.0 \times 10^{-4} \text{ K}^{-1}$ .

$$\theta(1 + b\theta) = 2\lambda m_1 \phi \quad (89)$$

In a detailed study of aqueous salt solutions containing four amides<sup>129</sup> an extended polynomial relating  $\theta$  and salt molality was used.

## IX Activities of water in foodstuffs

Away from the more traditional concerns of chemists, an important scientific literature comments on the activity of water in the context of biochemistry and of the very important industry concerned with food stuffs.<sup>130–133</sup>

Scott<sup>134</sup> identified the importance of water activity and microbial growth on foodstuffs; *e.g.* chilled beef. Hartel reviews the problem of the freezing of water in, for example, ice cream.<sup>135</sup> The importance of water activity in sensory crispness and mechanical deformation of snack products is discussed by Katz and Labuza.<sup>136</sup> Water activity is an important variable in fungal spoilage of food.<sup>137,138</sup>

Crucially important in this context are publications produced by the National Institute of Standards and Technology.<sup>139</sup> Thus Part 114 refers to water activity as a measure of the free moisture in a food product as the ‘quotient of the water vapour of the substance divided by the vapour pressure at the same temperature’; *cf.* eqn. (4) above. This is not the place to summarise these regulations. Nevertheless it is interesting to note that pickles have a water activity greater than 0.85 and a pH  $\leq$  4.6. Another section refers to ‘Commercial sterility which is achieved ... by control of water activity ... which renders food free of microorganisms capable of reproducing...’

## X Biochemistry, life and health sciences

Enzyme activity in organic media is sensitive to the amount of residual water. As an extension of this observation Bell and co-workers<sup>140</sup> analyse enzyme activity of an immobilised lactase in binary aqueous mixtures, drawing a comparison with the dependence of water activity,  $a_1$  on mole fraction composition. However across a range of mixtures, plots of  $a_1$  against mole fraction composition do not identify a strong link with high maximum reaction velocity for enzyme activity; *cf.* the Michaelis–Menten equation.

‘Are we alone?’ The quest for evidence of life somewhere in the rest of the universe attracts enormous attention. In the accompanying discussion, a key piece of evidence for such life would be the discovery of water( $\ell$ ) on a planet circling another ‘sun’. Thus many authors including Albert Szent-Györgyi, recognise that water( $\ell$ ) is the ‘matrix of life’; *i.e.* water( $\ell$ ) is associated with life processes.

Indeed an enormous scientific literature describes the rates and mechanisms of, for example, enzyme-catalysed reaction in aqueous solutions and the accompanying theories of hydrophobic interactions. The aim is to understand the chemistry of life processes in, for example, the unit cell. Nevertheless recently emphasis has changed to a consideration of the impact of molecular crowding on rates of reactions in a unit cell.<sup>141–146</sup>

In a unit cell, water is held between proteins or lipid bilayers and so the properties of water in these systems probably differs from those of water( $\ell$ ).<sup>144</sup> Consequently the activity of water in these systems is probably quite different from that in more conventional solutions. An interesting question concerns the extent to which the kinetics of enzyme-catalysed reactions in these crowded systems differ from those in conventional aqueous solutions. Recently the effect of adding polyethylene

glycol PEG400 on the kinetics of trypsin-catalysed hydrolysis of *p*-nitrophenyl ethanoate has been studied. Remarkably the rate constant  $k_{\text{cat}}$  changes by less than a factor of three despite a change in the concentration of water from 55 to 38 mol dm<sup>-3</sup>, with roughly a 10% decrease in water activity.<sup>16,17</sup> A similar pattern is observed for the Diels–Alder reaction between 1,4-naphthoquinone and cyclopentadiene. The conclusion is that there is clear merit in drawing consideration of water activity into the analysis of biochemically important reactions.

Grant discusses in a fascinating review<sup>147</sup> the considerable literature describing organisms capable of living in environments where the ‘activity’ of water is low; *e.g.* hypersaline environments such as the Dead Sea. Here we have placed quotation marks around the word ‘activity’ because the meaning used by Grant differs from that used here. Rather the activity of water is defined as the ratio  $[n_1/(n_1 + n_j)]$ , the mole fraction of water where  $n_j$  is the amount of salt. It would be interesting to explore the impact of the thermodynamic activity in the context of the subject discussed by Grant.<sup>147</sup>

Finally we comment on a phenomenon related to water activity, namely human perspiration. A normal adult loses approx.0.5 dm<sup>3</sup> of water each day, more if the person is engaged in heavy work or under emotional stress (*e.g.* writing an article for *Chemical Society Reviews*). The vapour pressure gradient adjacent to the surface of skin is measured using in one method an organic-polymer dielectric sensitive to humidity.<sup>148</sup> One application is directed towards water-loss by new-born infants placed in incubators.

## XI Summary

Activities of water in aqueous solutions have been in general ignored despite their thermodynamic basis and the interesting insight they provide into the properties of aqueous solutions. We have looked at several topics in solution chemistry to show how the role of activities of water in aqueous solutions can be investigated and understood.

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## Notes and references

† A given solution is prepared using  $n_1$  moles of water, molar mass  $M_1$ , and  $n_j$  moles of a solute  $j$ , molar mass  $M_j$ . Mass of solute =  $n_j M_j$  Mass of solvent =  $n_1 M_1$  Then,

$$x_1 = \frac{n_1}{n_1 + n_j} = \frac{1}{1 + (n_j/n_1)} \quad (\text{a})$$

But  $m_j = n_j/(n_1 M_1)$ ; or,  $n_j/n_1 = m_j M_1$ .

Then

$$x_1 = \frac{1}{1 + (m_j M_1)} \quad (\text{b})$$

From eqn. (a),

$$\ln[(a_1)^{\text{id}}] = \ln\left(\frac{1}{1 + M_1 m_j}\right)$$

Or,  $\ln[(a_1)^{\text{id}}] = -\ln[1 + M_1 m_j]$ . We recall that  $\ln(1 + x) = x - x^2/2 + x^3/3 - x^4/4 + \dots$ . Then  $\ln[(a_1)^{\text{id}}] = -M_1 m_j = -(0.018015 \text{ kg mol}^{-1})m_j$ .

‡ We imagine two open dishes in a partially evacuated chamber at constant temperature,  $T$ . Each dish contains the same amount of a certain solution but we label one dish A and the other dish, B. Further the Gibbs energies are equal because they are the same solutions.

$$G(\text{A}) = G(\text{B}) \quad (\text{a})$$

The vapour pressures of water, chemical substance 1, are the same so that,

$$\mu_1(\text{aq};\text{A}) = \mu_1(\text{aq};\text{B}) \quad (\text{b})$$

For dish A, eqn. (c) holds where  $\mu_j$  is the chemical potential of solute  $j$ .

$$G(\text{A}) = n_1 \mu_1(\text{aq};\text{A}) + n_j \mu_j(\text{aq};\text{A}) \quad (\text{c})$$

For dish B, where we describe the properties of the solution in terms of hydrate formation, eqn. (e) holds where  $\mu_{jh}$  is the chemical potential of solute hydrate  $jh \text{ H}_2\text{O}$  in solution. We note that

$$n_j = n_{jh} \quad (\text{d})$$

$$G(\text{B}) = (n_1 - n_{jh})\mu_1(\text{aq};\text{B}) + n_{jh}\mu_{jh}(\text{aq};\text{B}) \quad (\text{e})$$

Hence from eqns. (a)–(e)

$$n_j \mu_j(\text{aq}) = -n_{jh} \mu_1(\text{aq}) + n_{jh} \mu_{jh}(\text{aq}) \quad (\text{f})$$

Or,

$$\mu_j(\text{aq}) = -h \mu_1(\text{aq}) + \mu_{jh}(\text{aq}) \quad (\text{g})$$

Or,

$$\mu_{jh}(\text{aq}) = \mu_j(\text{aq}) + h \mu_1(\text{aq}) \quad (\text{h})$$

The three chemical potentials in eqn. (h) are related to the composition of the solution. Hence,

$$\begin{aligned} \mu_{jh}^\circ(\text{aq}) + RT \ln[m_{jh} \gamma_{jh} / m^\circ] &= \mu_j^\circ(\text{aq}) + RT \ln[m_j \gamma_j / m^\circ] \\ &+ h \{ \mu_1^*(\ell) - \phi RT M_1 m_j \} \end{aligned} \quad (\text{i})$$

A key step involves an assumption relating the two reference chemical potentials for the solutes and the chemical potential of the pure solvent at the same  $T$  and  $p$ . At all  $T$  and  $p$ , limit  $(m_j \rightarrow 0) \gamma_j = 1.0$  and limit  $(m_{jh} \rightarrow 0) \gamma_{jh} = 1.0$ . In the same limit,  $\phi = 1$ .

Since (cf. eqn. (d)),

$$m_j m_{jh} = 1 - h m_j M_1 \quad (\text{j})$$

Eqn. (k) follows from eqn. (i) provided that  $h$  is independent of  $m_j$ .

$$\mu_0^{jh}(\text{aq}) = \mu_j^0(\text{aq}) + h \mu_1^*(\ell) \quad (\text{k})$$

Hence from eqns. (i) and (k),

$$\ln[m_{jh} \gamma_{jh} / m^\circ] = \ln[m_j \gamma_j / m^\circ] - \{h \phi M_1 m_j\} \quad (\text{l})$$

We assume that the properties of the hydrated solute are ideal. Therefore,

$$\ln[m_j \gamma_j / m^\circ] = \ln[m_{jh} \gamma_{jh} / m^\circ] + \{h \phi M_1 m_j\} \quad (\text{m})$$

Or,

$$\ln[\gamma_j] + \ln[m_j / m_{jh}] = \{h \phi M_1 m_j\} \quad (\text{n})$$

Hence (cf. eqn. (j)),

$$\ln[\gamma_j] + \ln[1 - m_j h M_1] = \{h \phi M_1 m_j\} \quad (\text{o})$$

But according to the standard mathematical operation for dilute solutions (i.e.  $m_j h M_1 < 1$ ),

$$\ln[1 - m_j h M_1] \cong -h m_j M_1 \quad (\text{p})$$

Then,

$$\ln[\gamma_j] = \{h \phi M_1 m_j\} + \{h m_j M_1\} \quad (\text{q})$$

Further for dilute solutions,  $\phi \cong 1$ . Hence,

$$\ln(\gamma_j) = 2 h m_j M_1 \quad (\text{r})$$

§ For the unmixed ‘liquid system’, the Gibbs energy defined here as  $G(\text{no-mix})$  is given by eqn. (a).

$$G(\text{no-mix}) = n_1 \mu_1^*(\ell) + n_2 \mu_2^*(\ell) \quad (\text{a})$$

After mixing the Gibbs energy of the mixture is given by eqn. (b).

$$G(\text{mix}) = n_1 [\mu_1^*(\ell) + RT \ln(x_1 f_1)] + n_2 [\mu_2^*(\ell) + RT \ln(x_2 f_2)] \quad (\text{b})$$

By definition,

$$\Delta_{\text{mix}} G = G(\text{mix}) - G(\text{no-mix}) \quad (\text{c})$$

Hence the Gibbs energy of mixing,

$$\Delta_{\text{mix}} G = RT [n_1 \ln(x_1 f_1) + n_2 \ln(x_2 f_2)] \quad (\text{d})$$

By definition the Gibbs energy of mixing for 1 mol of mixture where the thermodynamic properties are ideal is given by eqn. (e).

$$\Delta_{\text{mix}} G_{\text{m}}(\text{id}) = RT [x_1 \ln(x_1) + x_2 \ln(x_2)] \quad (\text{e})$$

Hence the excess molar Gibbs energy of mixing is given by eqn. (f).

$$G_{\text{m}}^{\text{E}} = RT [x_1 \ln(f_1) + x_2 \ln(f_2)] \quad (\text{f})$$

We differentiate this equation with respect to  $x_1$ ;  $dx_2 = -dx_1$ . Then,

$$\frac{1}{RT} \frac{dG_{\text{m}}^{\text{E}}}{dx_1} = \ln(f_1) + x_1 \frac{d \ln(f_1)}{dx_1} - \ln(f_2) + x_2 \frac{d \ln(f_2)}{dx_1} \quad (\text{g})$$



But according to the Gibbs–Duhem equation, at fixed  $T$  and  $p$ ,

$$x_1 \frac{d \ln(f_1)}{dx_1} + x_2 \frac{d \ln(f_2)}{dx_1} = 0 \quad (\text{h})$$

Then, using eqn. (g),

$$\ln(f_2) = \ln(f_1) - \frac{1}{RT} \frac{dG_m^E}{dx_1} \quad (\text{i})$$

Using eqn.(f),

$$\frac{G_m^E}{RT} = x_1 \ln(f_1) + x_2 \ln(f_2) - \frac{x_2}{RT} \frac{dG_m^E}{dx_1} \quad (\text{j})$$

Or,

$$\ln(f_1) = \left[ \frac{G_m^E}{RT} + \frac{x_2}{RT} \frac{dG_m^E}{dx_1} \right] \quad (\text{k})$$

¶ It is of interest to rewrite eqn. (75) in the following alternative form.

$$G_m^E = x_2(1 - x_2)[A + B(1 - 2x_2) + C(1 - 2x_2)^2 + D(1 - 2x_2)^3]$$

Hence the activity coefficient of water in the binary liquid mixture is given by the following equation.

$$RT \ln(f_1) = ax_2^2 + bx_2^3 + cx_2^4 + dx_2^5 + \dots$$

where  $a = A + 3B + 5C + 7D$

$$b = -4(B + 4C + 9D)$$

$$c = 12(C + 5D)$$

$$d = -32D$$

|| From eqn. (83),

$$\begin{aligned} \frac{1}{RT} \frac{dG_m^E}{dx_1} &= -\ln(x_1 + A_{12}x_2) - \frac{x_1(1 - A_{12})}{x_1 + A_{12}x_2} \\ &+ \ln(A_{21}x_1 + x_2) - \frac{x_2(A_{21} - 1)}{A_{21}x_1 + x_2} \end{aligned}$$

Using eqn. (73) with  $1 - x_1 = x_2$ ,

$$\begin{aligned} \ln(f_1) &= -x_1 \ln(x_1 + A_{12}x_2) - x_2 \ln(A_{21}x_1 + x_2) \\ &- x_2 \ln(x_1 + A_{12}x_2) - \frac{x_1x_2(1 - A_{12})}{x_1 + A_{12}x_2} \\ &+ x_2 \ln(A_{21}x_1 + x_2) + \frac{(x_2)^2(1 - A_{21})}{A_{21}x_1 + x_2} \end{aligned}$$

Or,

$$\begin{aligned} \ln(f_1) &= -(x_1 + x_2) \ln(x_1 + A_{12}x_2) \\ &+ x_2 \left[ \frac{A_{12}x_1 - x_1}{x_1 + A_{12}x_2} - \frac{A_{21}x_2 - x_2}{A_{21}x_1 + x_2} \right] \end{aligned}$$

But  $A_{12}x_1 - x_1 = A_{12}(1 - x_2) - x_1 = A_{12} - (x_1 + A_{12}x_2)$ . Hence,

$$\begin{aligned} \ln(f_1) &= -\ln(x_1 + A_{12}x_2) \\ &+ x_2 \left[ \frac{A_{12} - (x_1 + A_{12}x_2)}{x_1 + A_{12}x_2} - \frac{A_{21} - (A_{21}x_1 + x_2)}{A_{21}x_1 + x_2} \right] \end{aligned}$$

Or,

$$\ln(f_1) = -\ln(x_1 + A_{12}x_2) + x_2 \left[ \frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{A_{21}x_1 + x_2} \right]$$

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