

## A COMPOSITE DESCRIPTION OF MIXED SALT SOLUTIONS

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### ABSTRACT

A description of mixed salt solutions is proposed in terms of a composite salt. Equations are developed for mean ionic activity coefficients, practical osmotic coefficients and excess molar Gibbs functions. The treatment is quite general, account being taken of stoichiometric coefficients and charge numbers of each ionic species in the composite salt. The procedures form the basis of a new treatment of the thermodynamic properties of mixed salt solutions.

### INTRODUCTION

The properties [1] of mixed aqueous salt solutions are both interesting and complicated. Thermodynamic treatments of these properties normally follow the well-established procedures in which comparison is drawn with the properties of solutions containing single salts. The properties of a mixed aqueous salt solution containing {KCl + NaBr} are discussed in terms of the properties of two solutions, KCl(aq) and NaBr(aq) at the same temperature and pressure. Although the conventional approach [1] has considerable merit, there are advantages in treating the solutes in a mixed salt solution as part of a single composite salt. In the following section we review a thermodynamic description of this system, developing equations for mean ionic activity coefficients [2], practical osmotic coefficients [2] and excess molar Gibbs functions [3].

### COMPOSITE SALT

#### *Preparation*

An aqueous salt solution is prepared using (a)  $n_1$  moles of water ( $= n_1 \cdot M_1$  kg where  $M_1$  is the molar mass of water); (b)  $n_2$  moles of salt-2,  $\nu_m M^{z(m)+} \nu_x X^{z(x)-}$  where the condition of electrical neutrality requires that

TABLE 1

Composite salt <sup>a</sup>

	Ion			
	$M^{z(m)+}$	$X^{z(x)-}$	$N^{z(n)+}$	$U^{z(u)-}$
Number of moles	$\nu_m \cdot m_2$	$\nu_x \cdot m_2$	$\nu_n \cdot m_3$	$\nu_u \cdot m_3$
Salt solution	$\nu_m \cdot y \cdot m$	$\nu_x \cdot y \cdot m$	$\nu_n \cdot (1-y) \cdot m$	$\nu_u \cdot (1-y) \cdot m$
Salt	$y \cdot \nu_m M^{z(m)+}$	$y \cdot \nu_x X^{z(x)-}$	$(1-y) \cdot \nu_n N^{z(n)+}$	$(1-y) \cdot \nu_u U^{z(u)-}$

<sup>a</sup>  $y \cdot \nu_m M^{z(m)+} + y \cdot \nu_x X^{z(x)-} + (1-y) \cdot \nu_n N^{z(n)+} + (1-y) \cdot \nu_u U^{z(u)-}$ , where  $\nu_i$  and  $z(i)$  are the stoichiometric coefficients and charge numbers respectively of ion- $i$ .

$|\nu_m \cdot z(m)| = |\nu_x \cdot z(x)|$ ; and (c)  $n_3$  moles of salt-3,  $\nu_n N^{z(n)+} + \nu_u U^{z(u)-}$  where the condition of electrical neutrality requires that  $|\nu_n \cdot z(n) = \nu_u \cdot z(u)|$ .

For salt-2 (where mass  $w_2 = M_2 \cdot n_2$ ) molality  $m_2 = n_2/n_1 \cdot M_1$  (1)

For salt-3 (where mass  $w_3 = M_3 \cdot n_3$ ) molality  $m_3 = n_3/n_1 \cdot M_1$  (2)

If the total molality  $m = m_2 + m_3$  (3)

salt mole fraction  $y = m_2/m$  (4)

and  $(1-y) = m_3/m$  (5)

The composition of the salt solution in 1 kg of water (Table 1) leads to the identification of the composite salt "MXNU". Therefore assuming complete dissociation into ions, the total number of moles of ions produced by  $m$  moles of salt in 1 kg of solvent is given by the following equation, leading to the definition of the stoichiometric coefficient  $\nu$

$$\nu_m \cdot y \cdot m + \nu_x \cdot y \cdot m + \nu_n \cdot (1-y) \cdot m + \nu_u \cdot (1-y) \cdot m = \nu \cdot m \quad (6)$$

Hence the stoichiometric number for the composite salt (Table 1)

$$\nu = y \cdot \nu_m + y \cdot \nu_x + (1-y) \cdot \nu_n + (1-y) \cdot \nu_u \quad (7)$$

For a 1:1:1:1 salt at  $y = 0.5$ ,  $\nu = 2$ .

Ionic strength  $I$  is given by

$$I = (m/2) \cdot \left\{ y \cdot \left[ \nu_m \cdot z(m)^2 + \nu_x \cdot z(x)^2 \right] + (1-y) \cdot \left[ \nu_n \cdot z(n)^2 + \nu_u \cdot z(u)^2 \right] \right\} \quad (8)$$

### Activity coefficient

A mean ionic activity coefficient  $\gamma_{\pm}$  for composite salt "MXNU" is defined by the following equation

$$\gamma_{\pm}^{\nu} = (\gamma_{+m})^{y\nu(m)} \cdot (\gamma_{-x})^{y\nu(x)} \cdot (\gamma_{+n})^{(1-y)\nu(n)} \cdot (\gamma_{-u})^{(1-y)\nu(u)} \quad (9)$$

or

$$\begin{aligned} \nu \cdot \ln \gamma_{\pm} = & y \cdot \nu(m) \cdot \ln \gamma_{+m} + y \cdot \nu(x) \cdot \ln \gamma_{-x} \\ & + (1-y) \cdot \nu(n) \cdot \ln \gamma_{+n} + (1-y) \cdot \nu(u) \cdot \ln \gamma_{-u} \end{aligned} \quad (10)$$

In eqns. (9) and (10),  $\gamma_{+m}$ ,  $\gamma_{-x}$ ,  $\gamma_{+n}$  and  $\gamma_{-u}$  are single ion activity coefficients. Thus  $\gamma_{\pm}$  depends on these activity coefficients, the stoichiometric coefficients and the salt fraction. Hence  $\gamma_{\pm}$  characterises the composite salt. The chemical potential of each  $i$ -ion in solution is related to the molality  $m_i$  and activity coefficient  $\gamma_i$  using eqn. (11) (below) where  $\mu_i^{\#}(\text{aq}; T; p)$  is the chemical potential for ion- $i$  in a solution where both  $m_i$  and  $\gamma_i$  are unity at the same  $T$  and  $p$ ;  $m^0 = 1 \text{ mol kg}^{-1}$

$$\mu_i(\text{aq}; T; p) = \mu_i^{\#}(\text{aq}; T; p) + R \cdot T \cdot \ln(m_i \cdot \gamma_i / m^0) \quad (11)$$

Then for the composite salt (Table 1)

$$\mu_j(\text{aq}; T; p) = \mu_j^{\#}(\text{aq}; T; p) + R \cdot T \cdot \sum(i=1; i=4) \nu_i \cdot \ln(m_i \cdot \gamma_i / m^0) \quad (12)$$

where the sum is carried over ions M, X, N and U. Equations (6), (7), (9) and (12) combine to yield the required equation for the chemical potential of a composite salt in solution

$$\mu_j(\text{aq}; T; p) = \mu_j^{\#}(\text{aq}; T, p) + \nu \cdot R \cdot T \cdot \ln(Q \cdot m \cdot \gamma_{\pm} / m^0) \quad (13)$$

where  $\lim(m \rightarrow 0) \gamma_{\pm} = 1.0$  at fixed temperature, fixed pressure and fixed salt fraction  $y$ . By definition (cf. ref. 2)

$$\begin{aligned} Q^{\nu} = & (y \cdot \nu_m)^{y \cdot \nu(m)} \cdot (y \cdot \nu_x)^{y \cdot \nu(x)} \cdot \{(1-y) \cdot \nu_n\}^{(1-y) \cdot \nu(n)} \\ & \cdot \{(1-y) \cdot \nu_u\}^{(1-y) \cdot \nu(u)} \end{aligned} \quad (14)$$

also

$$m^{\nu} = m^{y \cdot \nu(m)} \cdot m^{y \cdot \nu(x)} \cdot m^{(1-y) \cdot \nu(n)} \cdot m^{(1-y) \cdot \nu(u)} \quad (15)$$

$Q$  is dimensionless. Then for the composite salt- $j$ , (Table 1)

$$\mu_j^{\#}(\text{aq}; T; p) = y \cdot \mu^{\#}(\text{“MX”}; \text{aq}; T; p) + (1-y) \cdot \mu^{\#}(\text{“NU”}; \text{aq}; T; p) \quad (16)$$

Here  $\mu_j^{\#}(\text{aq}; T; p)$  is the reference chemical potential of the composite salt in a solution where  $m = 1$  and  $\gamma_{\pm} = 1$ , at constant temperature, constant pressure and fixed salt fraction  $y$ . The latter condition is vital to the definition of  $\mu_j^{\#}(\text{aq}; T; p)$  for composite salts. In terms of a practical osmotic coefficient, the chemical potential of the solvent in the salt solution is given by the following equation where for an ideal solution  $\phi = 1.0$

$$\mu_1(\text{aq}; T; p) = \mu_1^{\star}(1; T; p) - \phi \cdot \nu \cdot R \cdot T \cdot m \cdot M_1 \quad (17)$$

*Mixed ions*

The solution of a composite salt can be regarded as a solution containing mixed cations and mixed anions. The charge numbers of cations and anions are  $\{y \cdot z(m) + (1 - y) \cdot z(n)\}$  and  $\{y \cdot z(x) + (1 - y) \cdot z(u)\}$  respectively. For each mole of composite salt- $j$ , (Table 1) there are in solution  $\{\nu_m \cdot y + (1 - y) \cdot \nu_n\}$  moles of cations and  $\{\nu_x \cdot y + (1 - y) \cdot \nu_u\}$  moles of anions. The crucial neutrality condition for the composite salt is given by the following equation

$$\begin{aligned} & |[y \cdot z(m) + (1 - y) \cdot z(n)] \cdot [\nu_m \cdot y + (1 - y) \cdot \nu_n]| \\ & = |[y \cdot z(x) + (1 - y) \cdot z(y)] \cdot [\nu_x \cdot y + (1 - y) \cdot \nu_y]| \end{aligned} \quad (18)$$

For a composite salt formed by two 1:1 salts at  $y = 0.5$ , eqn. (18) simplifies to  $|(0.5 + 0.5) \cdot (0.5 + 0.5)| = |(0.5 + 0.5) \cdot (0.5 + 0.5)|$ .

*Excess Gibbs function*

Equations (13) and (17) lead directly to an equation for the excess Gibbs function for a solution in 1 kg of solvent where the molality of the composite salt is  $m$

$$G^E(\text{aq}; T; p; w_1 = 1 \text{ kg}) = \nu \cdot R \cdot T \cdot m \cdot (1 - \phi + \ln \gamma_{\pm}) \quad (19)$$

The apparent simplicity of eqn. (19) masks the fact that  $\nu$ ,  $m$ ,  $\phi$  and  $\gamma_{\pm}$  are functions of salt fraction  $y$  and  $\nu_i$  for ion- $i$ .

## DISCUSSION

The analysis described above was prompted by our interest in the kinetics of reactions in salt solutions [4], and in the treatment of medium effects in kinetics using pairwise Gibbs function interaction parameters [5]. In the latter case we used the procedures introduced by Savage and Wood [6] and hence characterised interactions between added solutes and both initial and transition states [5]. We are anxious to extend this approach to understanding kinetic salt effects [4]. The results of such an analysis will be reported later. But the accompanying treatment requires the development of a model for composite salts along the lines discussed above in order to identify contributing ionic activity coefficients to overall mean ionic activity coefficients. Our interests are based on the possibility of describing contributions to ion-ion interactions in terms of pairwise interaction parameters. In these terms, the excess Gibbs function for a salt solution  $G_m^E(\text{aq}; T; p)$  is given by the sum of electrical and cosphere overlap [7] contributions. If this extrathermodynamic assumption is accepted, the way is clear for derivation

of cosphere interaction parameters from the properties of mixed salt solutions.

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#### REFERENCES

- 1 H.S. Harned and R.A. Robinson, *Multicomponent Electrolyte Solutions*, Pergamon, London, 1968.
- 2 R.A. Robinson and R.H. Stokes, *Electrolyte Solutions*, Butterworth, London, 1968, 2nd. edn. revised.
- 3 H.L. Friedman, *Ionic Solution Theory*, Interscience, New York, 1962.
- 4 J.B.F.N. Engberts, M.J. Blandamer, J. Burgess, B. Clark and A.W. Hakin, *J. Chem. Soc. Faraday Trans. 1*, 83 (1987) 865.
- 5 W. Blokzijl, J. Jager, J.B.F.N. Engberts and M.J. Blandamer, *J. Am. Chem. Soc.*, 86 (1986) 6411.
- 6 J.J. Savage and R.H. Wood, *J. Solution Chem.*, 5 (1976) 733.
- 7 R.W. Gurney, *Ionic Processes in Solution*, McGraw-Hill, New York, 1953.