

## Thermodynamics of high temperature electrolyte solutions: Vapour-liquid equilibrium

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**Abstract** - Two procedures have been employed to calculate from experimental data the value at infinite dilution of the distribution ratio of electrolyte between the liquid and vapour phases in equilibrium,  $K_D^\infty$ . For aqueous NaCl and KCl,  $K_D^\infty$  shows the expected asymptotic behaviour when the critical point of the solvent is approached. The thermodynamic evidence suggests that in the range 573 to 643 K the values of  $K_D^\infty$  are dominated by a single species. The results were compared to the predictions of cluster theory. Theory indicates that ions in the vapour phase are strongly associated into neutral clusters, the dominant species changing with temperature. In this first report of our work we discuss various alternatives to resolve this apparent discrepancy.

### INTRODUCTION

During the last decade very valuable information about the behaviour of electrolytes over wide ranges of  $(p, T, c)$  has been obtained from theoretical and molecular simulation studies, and from experimental studies. This vast information should enable a thorough description of the thermodynamics of electrolyte solutions including phase equilibria and critical behaviour. The possibility of describing the liquid-vapour equilibrium in aqueous electrolyte solutions is of interest because it would afford a means of predicting the electrolyte concentration in the vapour phase, a quantity which has important practical implications, but is difficult to measure directly.

Theoretical and simulation studies have analyzed liquid-vapour equilibrium in molten salts using the restricted primitive model (RPM). The thermodynamic properties of ionic fluids having ions of charge  $q$  and diameter  $\sigma$  depend, according to the RPM, upon two reduced variables, the reduced temperature,  $(T^*)^{-1} = q^2/\epsilon kT\sigma$ , and the reduced density,  $\rho^* = \rho\sigma^3$ . In molten salts the two phases in equilibrium have different reduced densities, but are at the same reduced temperature. For the case of binary electrolyte solutions, the vapour and liquid phases in equilibrium do not have the same  $T^*$  since the dielectric constant,  $\epsilon$ , is different in each phase. Fig. 1 is a plot of temperature, solvent density and  $T^*$  for an aqueous (1:1) electrolyte having  $\sigma = 0.425$  nm. It may be seen that the reduced temperature of the liquid phase decreases with increasing  $T$  due to the strong effect of temperature and density upon the dielectric constant of water. The difference between the reduced temperatures in the liquid and vapour phases in equilibrium implies that interionic interactions should also be different. Furthermore ions will conventionally have different standard chemical potentials in the two phases, the difference, which is very large, has to be taken into account to enable the description of phase equilibrium in electrolyte solutions. This is a complication for the theoretical description of liquid-vapour equilibrium when compared to the case of pure ionic fluids (molten salts), *i.e.* it will require the inclusion of a Born-type term. Nevertheless the study of liquid-vapour equilibrium in electrolyte solutions appears as an important step worth exploring to establish the possibility of a thorough description of ionic fluids, covering molten salts as well as electrolyte solutions.

The present work is based upon the results of the study of vapour-liquid equilibrium carried out by Khaibullin and Borisov (ref. 1) for NaCl and KCl aqueous solutions, and upon the thorough survey and critical analysis of the NaCl aqueous system made by Bischoff and Pitzer (ref. 2). The infinite dilution distribution ratio of salt between the vapour and liquid phases in equilibrium was calculated and compared to the predictions of the RPM employing Larsen's equation of state (ref. 3) for the liquid ionic phase and the cluster theory of electrolytes (ref. 4,5) for the vapour phase.

### THERMODYNAMIC INFORMATION

Isothermal values of the ratio of the concentrations of salt in the two fluid solvent phases in equilibrium,  $K_D = y/x$ , where  $y$  and  $x$  are the mole fraction of electrolyte in the vapour and liquid phases respectively, were calculated at different  $x$  and extrapolated to  $x \rightarrow 0$  in order to determine  $K_D^\infty$ .

Pitzer and coworkers (ref. 6,7) have proposed an equation of state for NaCl aqueous solutions from which, in principle, it is possible to calculate all thermodynamic properties. However, the authors reported two different sets of parameters which were originated in a different evaluation of the same data. In order to avoid introducing problems which may arise in the mathematical processing of the data, we decided to employ directly the experimental data of Khaibullin and Borisov (ref. 1) and those reported in the critical compilation of Bischoff and Pitzer (ref. 2). The latter only deals with NaCl solutions. For each temperature the ratios of the analytical equilibrium concentrations in the liquid and vapour phases were plotted as a function of pressure and extrapolated to the solvent vapour pressure to obtain  $K_D^\infty$ . Only data for liquid phase concentrations smaller than  $2 \text{ mol dm}^{-3}$  were used; the lower experimental concentration was about  $0.1 \text{ mol dm}^{-3}$ , so that the concentration range covered is rather narrow. Due to the very low concentration of electrolyte in the vapour phase, the values of  $K_D^\infty$  have a sizable uncertainty.

To complement this information we have used an alternative procedure which allows the calculation of  $K_D^\infty$  from the change of total pressure with composition. This procedure has proved very useful in the description of the distribution ratio of volatile solutes in aqueous solutions (ref. 8). Based upon the general relations of Gibbs-Konowalow it is possible to derive an expression for the ratio of concentrations in both phases in equilibrium (ref. 9), which for infinite dilution yields,

$$(K_D^\infty)^{-1} = 1 - \frac{V_1(g) - V_1(l)}{RT} \left( \frac{\partial p}{\partial y} \right)_{T,\sigma}^\infty, \quad (1)$$

where  $V_1$  is the solvent molar volume in the corresponding phase. An analogous expression may be obtained exchanging  $x$  for  $y$ , but then the quantity  $(\partial p/\partial x)_{T,\sigma}^\infty$  appears in eq (1). The latter is to be preferred when volatile solutes are studied while eq (1) is better suited to deal with nonvolatile solutes, *i.e.* when  $K_D^\infty$  is very small. Eq (1) could not be used for KCl since the data were not sufficiently abundant to allow extrapolation of  $(\partial p/\partial y)_{T,\sigma}$  to infinite dilution.

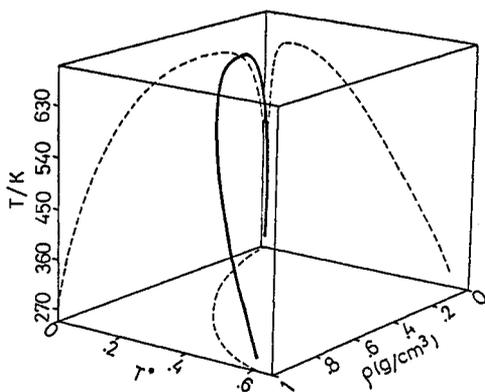


Fig. 1.  $(T, T^*, \rho)$  diagram for (1:1) electrolyte of 0.425 nm diameter.

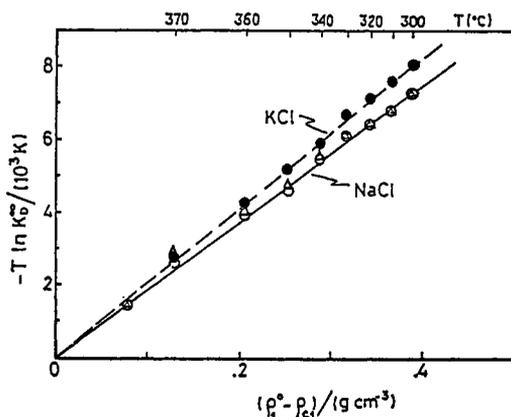


Fig. 2.  $T \ln K_D^\infty$  against  $\rho_1^*$  for NaCl ( $\circ$  employing eq(1),  $\Delta$  extrapolating  $(y/x)$ ) and KCl ( $\circ$ ).

Eq (1) relies also upon the results of phase diagram studies and for aqueous NaCl the values of  $(\partial p/\partial y)_{T,\sigma}^\infty$  were obtained from the same sources as the analytic concentrations in both phases. However the two types of information were processed in a different manner to get  $K_D^\infty$ , so that the agreement between the two sets of  $K_D^\infty$  for NaCl aqueous solutions shows the thermodynamic consistency of the data and gives more confidence to the values employed in this work.

It has recently been shown (ref. 10) that close to the solvent critical point the expression

$$T \ln K_D^\infty = A(\rho_1^0 - \rho_{c1}) \quad (2)$$

should be valid. This relation has been verified for volatile solutes (ref. 8,10) where, unexpectedly, it was found to extend at least 150 K away from the critical point of the solvent. The asymptotic linear relation should be valid for the distribution of *any* solute between vapour and liquid phases. Figure 2 shows that for NaCl and KCl, the calculated values of  $\ln K_D^\infty$  also obey eq (2). The linear behaviour was verified down to 573 K, which is the lowest temperature we have studied. Below this temperature  $K_D$  becomes too small and its uncertainty too large to give useful information. The slopes of the straight lines in Fig. 2 are  $-18\,692$  and  $-20\,704$   $\text{K}\cdot\text{cm}^3\cdot\text{g}^{-1}$  for NaCl and KCl respectively, which reflects the fact that KCl is less volatile than NaCl. The values of the slopes are within a 10 % of those given by the equations of state proposed by Pitzer and coworkers (ref. 6,7). Due to the low  $T^*$  of the vapour phase, it might be expected oppositely charged ions would be associated, as discussed in (ref. 6). However the linearity observed for  $T \ln(K_D^\infty)$  suggests that, within the experimental concentration and temperature ranges, there are no major changes in the nature of the dominant species present in the two fluid phases, and that the dominant species appears to be the same in water and in steam (ref. 10).

## THEORY AND MODEL CALCULATIONS

The theoretical methods which are usually applied to (dense) electrolyte solutions at ambient temperature rely on the use of integral equations. The two approximations more frequently and successfully employed are MSA and HNC. The first, being a linearized version of Ornstein-Zernike equation, cannot deal with ion pairing except by the *ad hoc* incorporation of this concept. HNC is better suited to deal with stronger ion-ion interactions leading to ion-pair formation, but HNC has a severe limitation (ref. 11) and cannot be used when  $(T^*)^{-1} > 7$ . Thus these integral equations are not suitable to describe the liquid-vapour equilibrium in electrolyte solutions. Only an extension of cluster theory could be deemed satisfactory (ref. 4,5).

The behaviour of RPM fluids over wide ranges of  $T^*$  has been studied by Larsen with Monte Carlo methods (ref. 3). He obtained an equation of state for the ionic fluid as a function of the reduced temperature for different values of the reduced density. In a study of liquid-vapour equilibrium in ionic melts, Gillan (ref. 5) showed that Larsen's equation of state describes correctly for the high density fluid phase, but fails to describe the properties of an RPM fluid having the reduced density typical of the vapour. Gillan applied an ionic cluster model to the vapour phase, calculating the free energy of cluster formation with the Monte Carlo method. Pitzer and Schreiber (ref. 12) have added the contribution of intercluster interactions using MSA. The overall result of this procedure is summarized by an expression of the partition function of the ionic fluid which is divided into two factors giving, respectively, intercluster and intracluster contributions to the Helmholtz energy. From this it is possible to calculate the concentration of the different clusters in the vapour phase.

Gillan's cluster method (ref. 5) is similar to that developed by Tani and Henderson (ref. 13,14) to deal with (2:2) electrolytes. A group of ions forms a cluster when all of them are at a distance not greater than  $R = 2\sigma$  from at least one other ion of that cluster. Ions having no other ion within a sphere of radius  $R$  of its centre are assumed to be free. Clusters are restricted to a maximum of six ions, and only neutral and singly charged clusters are considered to contribute significantly. For the present case, where the reduced temperature in the vapour phase is so low, there are no practical differences between Gillan's definition of a cluster and that inspired on Bjerrum's concept of ion pairing (ref. 14). Moreover, for such low  $T^*$  cluster partition functions do not depend significantly on the particular value chosen for  $R$ .

In order to describe liquid-vapour equilibrium in aqueous electrolytes we have employed the following procedure: the configurational chemical potential in the liquid phase having  $c^1$  moles of NaCl per  $\text{dm}^3$ , is given by,

$$\mu_{\pm}(l) - \mu_{\pm}^{\ominus}(T^*(l)) = RT \ln\left(\frac{c^1}{c^{\ominus 1}} \gamma_{\pm}(l)\right). \quad (3)$$

The mean activity coefficient was calculated employing Larsen's equation of state. For the vapour phase the total partition function was replaced by the maximum term of the sum over the number of particles in that phase (ref. 5,13). The maximization procedure yields for the reduced number density of particles of a cluster with  $s$  anions and  $t$  cations (ref. 12,14),

$$\rho_{s,t}^* = \lambda^{s+t} Q_{s,t} T^*(g) G(\eta_c) [F(\Gamma_c)]^{(s-t)^2}, \quad (4)$$

where  $\lambda$  is the Lagrange multiplier used to find the condition of maximum for the total partition function,  $Q_{s,t}$  is the intracluster partition function,  $G$  and  $F$  give the intercluster contribution due to hard-sphere interactions among

clusters with a packing fraction  $\eta_c$  and to electrostatic interactions, respectively, where  $(\Gamma^c)^{-1}$  is the MSA parameter equivalent to the ionic atmosphere radius. To calculate  $Q_{s,t}(T^*(g))$  we have used Gillan's expressions for the reduced temperature dependence of the internal energy of the clusters and integrated them to obtain the intracluster partition functions. The Lagrange multiplier is related to the chemical potential in the vapour phase by,

$$\ln \lambda = \beta[\mu_{\pm}(g) - \mu_{\pm}^{\ominus}(T^*(g))]. \quad (5)$$

For each temperature two concentrations of NaCl in the vapour phase,  $c^{\oplus}$ , were calculated from the values of  $K_D$  corresponding to 0.1 mol dm<sup>-3</sup> (experimental) and 0.01 mol dm<sup>-3</sup> (extrapolated) concentrations in the liquid. These were used to calculate with the set of eq (4) the values for  $\rho_{s,t}^*$  and  $\lambda$  in the vapour phase. Subtracting eq (3) from eq (5) under the condition of liquid-vapour equilibrium, we obtain,

$$\Delta \ln \lambda = \beta[\mu_{\pm}^{\ominus}(T^*(l)) - \mu_{\pm}^{\ominus}(T^*(g))]. \quad (6)$$

This quantity is related to the difference in the work necessary to charge the ions in the two fluid phases. Thus, direct information about the difference of standard chemical potential of ions is obtained from the concentration distribution ratio.

TABLE 1: Activity Coefficients of aqueous NaCl at 573 K.

$m$ mol kg <sup>-1</sup>	$c$ mol dm <sup>-3</sup>	$\gamma_{\pm}$ (EXP)		$\gamma_{\pm}$ (CALC)
		LR	MMM	$\sigma = 0.35$ nm
0.001	$0.712 \cdot 10^{-3}$	0.916	0.916	0.917
0.01	$0.713 \cdot 10^{-2}$	0.774	0.774	0.775
0.02	$1.43 \cdot 10^{-2}$	0.707	0.707	0.713
0.05	$3.57 \cdot 10^{-2}$	0.603	0.602	0.601
0.10	$7.16 \cdot 10^{-2}$	0.518	0.516	0.515
0.20	0.1437	0.434	0.430	0.434
0.50	0.3624	0.332	0.324	0.350
1.0	0.7309	0.266	0.256	0.311

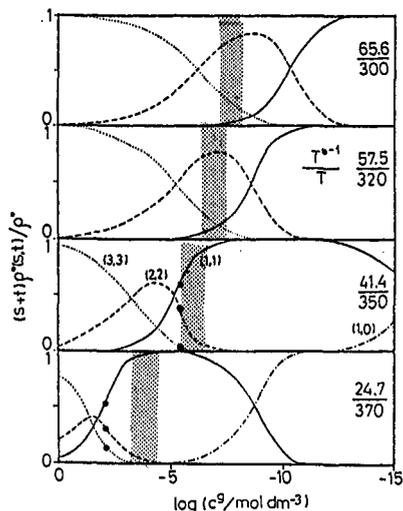


Fig. 3. Fraction of ions in species  $(s, t)$  present in the vapour phase.  $\circ$ : calculated ref. 5.

The ionic diameter  $\sigma$  was fixed at the value necessary to fit with Larsen's equation the activity coefficient data of aqueous NaCl at 573 K reported in the compilation of Pitzer *et al.* (ref. 15). The reported activity coefficients were transformed into MacMillan-Mayer reference (ref. 16). Table 1 illustrates the performance of Larsen's equation for  $\sigma = 0.35$  nm, where it is observed that agreement is quite good up to 0.2 mol dm<sup>-3</sup>. For higher concentrations the agreement is poorer, which may reflect the fact that NaCl does not have ions of equal size as required by the RPM which is the basis of Larsen's equation. This difference should be more important at higher concentrations. The effect of intercluster interactions has been found to be completely negligible for the concentrations existing in the vapour phase.

The values of the properties of water were taken from the compilation of Schmidt (ref. 17), and the formulation of Uematsu and Franck (ref. 18) for  $\epsilon$ .

## RESULTS

The correctness of this calculation procedure was established by reproducing the results for RPM fluids reported by Larsen (ref. 3), Pitzer and Schreiber (ref. 12) and Gillan (ref. 5). Speciation in the vapour phase for the four temperatures 573, 593, 623 and 643 K, was calculated as a function of the molar concentration of electrolyte in steam. Fig. 3 reports the fraction of ions in each cluster as a function of  $c^{\oplus}$ . The hatched areas in the graphs correspond to the values of  $c^{\oplus}$  which are in equilibrium with liquid electrolyte of concentrations between 0.1 and 0.01 mol dm<sup>-3</sup>. Fig.

3 also shows the speciation found by Gillan (ref. 5) for vapour in equilibrium with an RPM molten salt, the curves reproduce exactly these values. According to the present calculation, at high  $T^*(g)$  the dominant species in the vapour phase is the (1,1) cluster. As  $T^*(g)$  decreases, the (2,2) clusters become relatively more important. Only at very low  $T^*$  and high  $c^s$  does the (3,3) cluster concentration becomes significant. The concentration of charge-bearing clusters is negligible under all the conditions shown in Fig. 3, except for the single ions at high  $T^*$  and low  $c^s$ . According to cluster theory, the difference in the relative populations of the vapour phases in equilibrium with molten salt and with aqueous electrolyte at a given  $T^*$ , is only due to the higher ionic concentration present in the liquid and vapour phases of the molten salt.

## DISCUSSION

The distribution of species illustrated in Fig. 3 indicates that, according to cluster theory, in the experimental range employed to determine  $K_D$  free ions would make a negligible contribution ( $\ll 1\%$ ) to  $c^s$ , with the (2,2) species being dominant below 613 K and the (1,1) cluster above that temperature. In their study of the equation of state of NaCl in water, Tanger and Pitzer (ref. 6) considered that the main species in the vapour was the associated pair. However, as mentioned before, the fact that we found that  $K_D^\infty$  complies with eq (2) would imply that the same species dominates in both fluid phases and that this species does not change significantly over the studied temperature range.

It is interesting to analyze the conductivity data for aqueous NaCl (ref. 19) obtained over wide  $(p, T)$  ranges, since it should provide a direct indication of the amount of free ions present in steam. We have determined the degree of dissociation of NaCl from the dissociation constant extrapolated to the appropriate density and temperature. The calculated degree of dissociation is not very sensitive to temperature probably because an increase in temperature increases the density of steam (increasing dissociation) and  $c^s$  (decreasing dissociation). The net effect produces a degree of dissociation which does not vary too much with temperature. A conservative estimate yields 0.05 and 0.20 for the degrees of dissociation of NaCl in the vapour in equilibrium with the liquid electrolyte solution in the range 0.1 to 0.01 mol dm<sup>-3</sup>. There are small, but not negligible and 30 times greater than the largest degree of dissociation predicted by cluster theory. It is interesting to mention that Turner (ref. 20) has suggested that the concentration of free ions in steam is greater than expected.

In order to clarify this issue, it is important to analyze the applicability of the RPM to ions dissolved in the solvent vapour phase. The procedure employed to calculate the binary equilibrium with the RPM also yields the difference in standard chemical potentials of the ions due to the different  $T^*$  prevailing in each phase (*cf.* eq (6)), which is related to the difference in the work necessary to charge the ions in each phase. Table 2 gives in the second column the values of  $\Delta \ln \lambda$  obtained from the calculation procedure and the values calculated with the Born equation for ions of 0.35 nm of diameter in the third column. As noted by Wood and coworkers (ref. 21) the Born charging process, when applied to ions in the vapour phase or in the liquid phase close to the critical point of the solvent, should take account of the enhanced compressibility of the bulk phase. If the fluid is compressible the electric field will induce changes in the density close to the ions which in turn will produce an increase in  $\epsilon$ . This effect may be taken into account, in a first approximation, by adding a correction ( $\Delta$ ) to the diameters in the Born equation. We only use a correction for the vapour phase since the effect should be much smaller in the dense phase except for the isotherm of 643 K. Hence,

$$\Delta \ln \lambda = \beta [\mu_{\pm}^{\ominus}(T^*(l)) - \mu_{\pm}^{\ominus}(T^*(g))] = \beta q^2 \left( \frac{1}{\epsilon^l \sigma} - \frac{1}{\epsilon^g(\sigma + \Delta)} \right). \quad (7)$$

The values obtained for ( $\Delta$ ) are recorded in the last column of Table 2. It should be remarked that the corrections are given in terms of a distance only for convenience, so they should not be construed as implying that ions in the vapour phase are larger.

T K	$\Delta \ln \lambda$		$\Delta$ nm
	Gillan	Born	
573	37.73	61.46	0.199
	36.40		0.217
593	32.02	52.89	0.200
	30.78		0.217
623	21.30	35.58	0.185
	20.74		0.196
643	9.83	16.21	0.144

TABLE 2: Differences of standard chemical potential between vapour and liquid phases. (For each temperature the higher row corresponds to  $c^l = 0.1$  mol dm<sup>-3</sup> and the lower to 0.01 mol dm<sup>-3</sup>, at 643 K where they coincide.)

The RPM cluster theory gives slightly different values for  $\Delta \ln \lambda$  for different  $c^1$  as illustrated by the two entries reported in Table 2 for every temperature except 643 K. This is an incorrect result of the theoretical treatment. It is doubtful whether the RPM may be applied to an electrolyte solution having vapour-like density, since the strong electrostatic interactions may lead to local inhomogeneity in the distribution of solvent particles. In spite of this argument, we have evaluated the magnitude of the correction due to the compressibility of the fluid, using reasonable assumptions to estimate the compressibility of water vapour having higher densities than that of the saturated solvent vapour. The unrealistic nature of this picture has been already pointed out by Wood *et al.* (ref. 21). We have assumed dielectric saturation is taken into account by the use of a hydrated ionic diameter. The magnitude calculated for the effect of compressibility indicates that if this is taken into account by the Born equation the correct  $\Delta \ln \lambda$  is obtained with  $\Delta = 0$ . It is only worth estimating the order of magnitude of the correction, since the continuum model itself should be put into question if a closer agreement were desired. Rigorously the fluid's compressibility will influence also the values of  $Q_{s,i}$ , however the situation is much more difficult to resolve qualitatively and quantitatively by accounting for this.

It seemed important to evaluate the capacity of the calculation procedure to describe the liquid-vapour equilibrium in a real one-component ionic fluid. We have calculated  $\ln \lambda$  for NaCl with cluster theory using the ionic crystallographic diameters and the value of  $c^s$  corresponding to the experimental vapour pressure in the range 1273 to 1473 K (0.025 to 0.020 in  $T^*$ ). The same quantity was calculated with Larsen's equation. Both values agreed within 1 %, which is considered a satisfactory result. Thus, the procedure based upon an RPM gives a sound description of the vapour-liquid equilibrium in a pure ionic fluid.

We conclude that a single species dominates the value of the extrapolated distribution ratio of electrolyte in the fluid phases in the range 573 to 643 K and that ions in low densities water (*i.e.* steam), interact less strongly than predicted by the RPM. Ions in steam behave as if the reduced temperature were effectively higher than that obtained using the bulk dielectric constant of the vapour. Preliminary calculations of the potential of average force of a pair of ions and a small number of H<sub>2</sub>O molecules suggest that such a contention is correct (ref. 22).

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