The Vapour Pressure of Lithium Nitrate–Potassium Nitrate–Water Mixtures containing 5—75 Mole % Water[1]

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ALTHOUGH it has been pointed out repeatedly that progress towards understanding the behaviour of concentrated aqueous electrolyte solutions requires understanding of the fused-salt end of the concentration scale, there have been no systematic studies of the transition region between aqueous salt solutions and molten salts.[2] Recently we showed that a quasi-lattice model of molten salt solutions could be extended to explain successfully the dependence on water content and on temperature of the association of dilute solute ions, Cd^{2+} and Br^-, in molten lithium nitrate–potassium nitrate containing 0—56 mole % water.[3] In the extended model, water molecules were treated as ligands competing with bromide ions for sites in the co-ordination sphere of the cadmium ions. Other workers have measured vapour pressures of water dissolved in molten alkali nitrates (or solubilities of water in molten alkali nitrates) at concentrations of water below 1 mole %.[4] The solubility of water in molten nitrates was found to be proportional to the vapour pressure, indicating a simple dissolution process. On the other hand, the solubility of water in alkali silicates and in alkali borate melts containing alkali oxides was reported to be proportional to the square root of the water vapour pressure, suggesting an acid–base reaction on dissolution.[5] Similar behaviour was suggested by the reaction of water with molten lithium fluoride–beryllium fluoride mixtures.[6]

In order to investigate further the state of water dissolved in alkali nitrate melts, we have measured the vapour pressure of solutions of water in equimolar lithium nitrate–potassium nitrate at water concentrations between 5 and 75 mole % and at temperatures between 119 and 150°. Our measurements over this extended range of concentrations were made by a modified differential transpiration method[7] with the saturator containing pure water maintained at a lower temperature (64·60 ± 0·02°) than the saturator containing solution (119—150°). Corrections for the Poynting effect, for the solubility of nitrogen in the melt, and for deviations from ideality of the water vapour–carrier gas (nitrogen) mixtures were never greater than 0·3 mm. The reproducibility of the measurements was ±0·5 mm.

Figure 1 shows the vapour pressures as a function of temperature and water content to 50 mole % water [$R(H_2O) = 1$]. The remarkable linearity of plots of vapour pressure against *mole ratio* (moles of water per mole of nitrate) of water (*not* mole fraction) is noteworthy. A plot of the logarithm of the Henry's Law constants calculated from these data against the reciprocal of the absolute temperature falls on the same straight line as the results of Bertozzi[4] at 230—265° and corresponds to a heat of vaporization of 10·1 ± 0·2 kcal./mole compared to the calculated value of the heat of vaporization of pure water at 135° of 9·30 kcal./mole. The decrease of vapour pressure with increasing proportions of lithium ion to potassium ion may be interpreted as reflecting the preferential hydration of the lithium ions.

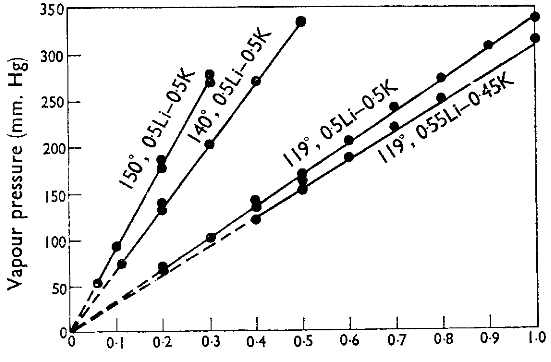

FIGURE. *Vapour pressure of* $LiNO_3$–KNO_3–H_2O

The observed linearity obviously cannot persist to much higher water contents, since the vapour pressure must be asymptotic to the vapour pressure of the pure water as $R(H_2O)$ becomes infinite. The compositions of mixtures boiling (p = 1 atm.) at 119°, 130°, 140°, and 150°, respectively, were 72, 62, 53, and 45 mole % water, and these points no longer fell on the straight lines of the Figure. These data indicate that departures from linearity in the mole ratio of water occur for values of $R(H_2O)$ between 1·0 and 2·5 at 119°, between 0·5 and 1·1 at 140°, and between 0·3 and 0·8 at 150°.

The quasi-lattice model, which was consistent with results for the competition between hydration and association equilibria of Cd^{2+} and Br^-,[3] and with the near additivity of molar volumes in these melts,[8] predicts linearity of the vapour pressure in the mole fraction of water rather than the mole ratio. Plots of the vapour pressures against mole fraction of water are linear only up to about 20 mole % water ($R = 0·33$). A model which does predict linearity of the vapour pressures in the mole ratio of water, but is not consistent with the volumetric properties and association equilibria in lithium nitrate–potassium nitrate–water mixtures, is a "site" or "interstitial" model, with solute particles randomly distributed on "sites" whose number is proportional to the number of solvent particles.[9]

Additional measurements in this concentration range for this and other systems may provide the basis for a model which can explain the above results and can be extended to more dilute salt solutions. The experimental details, results of measurements at other salt compositions, and extension of the quasi-lattice model will be presented in a forthcoming Paper.

This work was supported by the U.S. Atomic Energy Commission, under contracts with the Union Carbide Corporation and the University of Maine.

(*Received, November 16th,* 1967; *Com.* 1244.)

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[1] Based on a Ph.D. dissertation submitted by T. B. Tripp to the University of Maine, Orono, Maine, 1967.

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