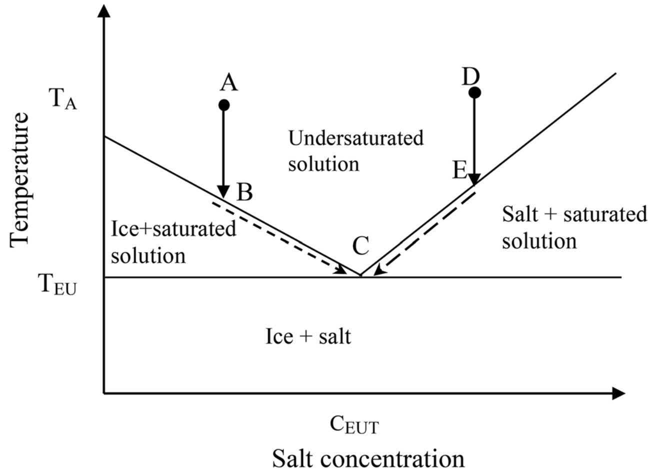

Figure 14.1 Modified phase equilibrium diagram of a binary system. Adapted from the MSc report of Willem Van der Tempel (TU Delft) with permission from Professor Geert-Jan Witkamp.

The principle of operation of EFC is best explained using a phase equilibrium diagram shown in Figure 14.1.

The freezing point of water decreases with increasing solute concentration. Cooling a hypoeutectic aqueous solution (*i.e.* more dilute than the eutectic) from point A to sub-freezing temperatures results in the crystallization of ice. The crystallization of ice causes the salt concentration to increase, thus depressing the freezing point. Further cooling results in the crystallization of more ice at progressively lower temperatures, moving the system along the line BC, until the system is saturated with the salt at the eutectic temperature. Further reduction of the temperature to sub-eutectic values causes the simultaneous crystallization of ice and salt. Thermodynamically, this occurs at a constant composition until the entire solution is recovered as separate solids.

Likewise, cooling an undersaturated hypereutectic mixture (starting at point D) to temperatures below the solubility line will result in a solution that is supersaturated in salt. The crystallization of salt dilutes the solution and the system moves along the line DC if cooling is continued. The point identifying the system characteristics on the phase diagram moves towards the eutectic point and the system is once again saturated in both ice and salt once this point is reached.

This example has illustrated a binary system. However, real brines are usually multicomponent in nature. These systems are more complicated than binary systems since multiple solutes interact with each other[12] and the solvent, thus altering the thermodynamic behaviour of the system. The solubility and activity of species, as well as eutectic parameters of systems often change in the presence of other species.