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Theoretical considerations on the Melander Effect

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(*Received 21 April 1955*)

ABSTRACT. Melander effect has been critically examined from the theoretical point of view. Heats of vaporisation of sodium chloride from its solutions as ions, have been calculated. The values obtained are too high to favour any appreciable escape of NaCl from the solution into the air.

1. Introduction

Wright (1939, 1940) proposed that the atmospheric condensation nuclei chiefly consisted of salt particles, predominantly of sodium chloride, coming into the air from sea water. Simpson (1939) is inclined to believe that if sodium chloride or any other salt comes into the air from sea water they must do so only through spray droplets. But the rate of production of spray droplets necessary to account for the cloud condensation of the whole atmosphere amounts to a fictitious figure of about 10^1 per sq. cm per second according to his computation. He believed this figure to be improbable. Wright attempted to meet Simpson's objections in the light of Melander's (1897) observations that glass slides exposed over warm (not boiling) sodium chloride solution developed salt stains which he attributed to salt particles which might have escaped from the solution in the course of evaporation of the solvent. Obviously, Wright was of the opinion that sea salts would come out from the surface of sea water by evaporation and could thus form the condensation nuclei. He was not, however, quite explicit in stating the mechanism by which the salts would leave the aqueous environment but the implication was to some sort of evaporation process leading to the expulsion of certain amount of salt into the space above to form the condensation nuclei.

Lodge, Mc Donald and Baer (1954) checked the Melander effect both theoretically and experimentally and pointed out that from theoretical considerations Melander effect can have hardly any meteorological importance. From their experimental result they came to the conclusion that observations made by Melander regarding the formation of salt stains on a glass slide might be the result of some contamination which might have occurred for lack of sufficient precautions. From theoretical considerations these workers were of the opinion that the amount of heat necessary for the escape of NaCl from the solution would be 880 cal per gm and they calculated that the amount of NaCl crossing unit area was of the order of 10^{-24} gm per sq. cm per sec. They, however, indicate that if the hydration of ions were considered this value would be still less, and would be inadequate to account for the cloud condensation.

In the present report the energy of activation necessary for the escape of NaCl from sea water has been recalculated on the basis of the actual ionic state in which NaCl is present in the sea water, with due consideration to the hydration of the ions and the effect of the ionic atmosphere in the solution.

2. Calculation

The average NaCl content of sea water amounts to about 2·8 per cent and of other salts to 0·7 per cent approximately. These other salts include $MgCl_2$, Na_2SO_4 etc, of which $MgCl_2$ may be regarded as the second most abundant salt. These salts being all strong electrolytes are fully ionised in solution. These ions are again hydrated. One Na^+ ion is associated with 4 molecules of H_2O, and one Cl^- ion having only 3 molecules as inferred from transport number measurements

(Ulrich 1933). Individual ions are again surrounded by other ions all statistically distributed forming an ionic atmosphere in which the oppositely charged ions are in excess (Glasstone 1949). Inspite of the binding of the ionic atmosphere the central ion and other ions have certain degrees of freedom of movement as a result of which the probability for the simultaneous escape of Na^+ and Cl^- ions is small.

Let us, however, assume that the escape of one Na^+ ion from the solution is always associated with the corresponding escape of one Cl^- ion, thus producing electroneutrality of the solution and calculate the energy necessary for the escape of one gm mole of NaCl (58·5 gm) from its aqueous solution (sea water). We shall consider below the energies far 1 gm ion of Na^+ and for 1 gm ion of Cl^- separately in the first instance.

(*a*) *Energy for the escape of* Na^+ *ions*

Na^+ ions present in solution as $Na^+, 4H_2O$ may escape into the air as gaseous Na^+ ions according to the following mechanism. The hydrated ion first escapes into the air from the solution after being detached from the ionic atmosphere. Afterwards the ion releases its water of hydration and may become anhydrous*. The process may therefore be regarded as taking place in three stages— (*i*) The release of Na^+ from the ionic atmosphere, (*ii*) escape of the hydrated ion from the bulk of the solution and (*iii*) release of the water of hydration. All the processes are assumed to take place at the standard temperature of 25°C

Energy in stage (*i*)—The attractive potential due to the ionic atmosphere at the central Na^+ ion is given by $(-Z_i\varkappa E/D)$ where Z_i is the valency of the central ion, E the electronic charge, $\varkappa$ the reciprocal of the thickness of ionic atmosphere and D the dielectric constant of the medium (here the solvent water). The value of $\varkappa$ is given by—

$$\frac{1}{\varkappa} = \left(\frac{DT}{\Sigma C_i Z_i^2} \times \frac{1000k}{4\pi E^2 N} \right)^{\frac{1}{2}}$$

where k is the Boltzmann's constant and equals $1 \cdot 38 \times 10^{-16}$ ergs per °C. Taking the dielectric constant D of the solution as approximately equal to that of pure water which amounts to 78·6 at 25°C

$$\frac{1}{\varkappa} = \frac{4 \cdot 31 \times 10^{-8}}{(\Sigma C_i Z_i^2)^{\frac{1}{2}}} \text{ cm}$$

This ionic atmosphere whose potential at the central ion is given above attracts the Na^+ ion with charge E on it with an energy $-Z_i E^2 \varkappa/D$, since the potential refers to unit charge. The negative sign refers to the attractive energy which must be overcome in order to get away. The attractive energy is, therefore,

$$\frac{Z_i E^2 \varkappa}{D} = 1 \times (4 \cdot 80 \times 10^{-10})^2 \times \frac{(\Sigma C_i Z_i^2)^{\frac{1}{2}}}{4 \cdot 31 \times 10^{-8}} \times \frac{1}{78 \cdot 6}$$

where Z_i = valency of Na^+ ion $=1$, E the electronic charge $= 4 \cdot 80 \times 10^{-10}$ e.s.u. and $D = 78 \cdot 6$. The energy can be calculated if we find out the value cf $(\Sigma C_i Z_i^2)^{\frac{1}{2}}$.

In sea water NaCl content amounts roughly to 2·8 per cent and other salts to about 0·7 per cent only. These other salts include $MgCl_2$, Na_2SO_4 etc, and we shall regard all other salts present as $MgCl_2$ which will however render the calculation approximate but will give us an idea about the order of

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* Any other mechanism for the escape of Na^+ ion from solution into air may be assumed but the energy change in the process will be the same since the initial stage (*viz.*, any hydrated Na^+ ion in solution) and the final stage (a dehydrated Na^+ ion in air) are the same

magnitude. We are, however, justified in a way in this approximation as $MgCl_2$ is the second abundant salt in sea water next to NaCl only.

Hence, concentration of NaCl (in moles per litre)$=0{\cdot}48$ molar, yielding concentration of Na^+ ions $=$ concentration of Cl^- ion $= 0{\cdot}48$ gm ions each. Concentration of $MgCl_2=0{\cdot}075$ molar yielding $0{\cdot}075$ gm ions of Mg^{++} and $2 \times 0\ 075(=0{\cdot}15)$ gm ions of Cl^- ions.

So,

$$\Sigma C_iZ_i^2 = (0{\cdot}48 \times 1^2 + 0{\cdot}48 \times 1^2 + 0{\cdot}075 \times 2^2 + 0{\cdot}15 \times 1^2) = 2{\cdot}82$$

$\therefore\ (\Sigma C_iZ_i^2)^{\frac{1}{2}} = 1{\cdot}68$ and the attractive energy

$$= \frac{(4{\cdot}8\times 10^{-10})^2\times 1{\cdot}68}{4{\cdot}31\times 10^{-8}\times 78{\cdot}6} \text{ erg for } 1\ Na^+ \text{ ion.}$$

For 1 gm ion of Na^+, the attractive energy

$$= \frac{6{\cdot}03\times 10^{23}\times(4{\cdot}8\times 10^{-10})^2\times 1{\cdot}68}{4{\cdot}31 \times 10^{-8} \times 78{\cdot}6} \text{ ergs/gm-ion} = 1642 \text{ cal.}$$

This energy must be absorbed by 1 gm ion of Na^+ in order that it may escape from the ionic atmosphere of the sea water.

Energy in stage (ii)—Since the Na^+ ion is in combination with 4 molecules of water (Ulrich 1933), the hydrated Na^+ion in solution essentially behaves as a cluster of water molecules with one Na^+ ion imbedded in it, so far as Van der Waal's attraction is concerned. So the escape of 1 gm ion of Na^+ from solutions is equivalent to escape of 4 gm moles of water from its own environment. This will involve work against internal pressure to the extent of 498 cal/gm of water*. Therefore for 4 gm moles of water the energy necessary amounts to $4 \times 18 \times 498=35{,}856$ cal.

Energy in stage (iii)—From the literature we find that $Na + aq = Na^+, aq$ and $\triangle H=$ —57,279 cal, *i.e.*, there is evolution of 57,279 cal of heat when 1 gm ion of Na^+ gets in contact with $54{\cdot}3$ moles of water. In the present case the water of hydration is only 4 moles. Hence a hydrated Na^+ ion may be regarded as a more concentrated solution of Na^+ ion in water. Hence the integral heat of solution will be still greater. But since the integral heat does not change very much in concentrated solutions we shall make a further approximation here in assuming $Na^+, 4H_2O$ has the same heat effect (*viz.*, —57,279 cal) as $Na^+, 54{\cdot}3\ H_2O$.†

So the total heat to be supplied to one gm ion of Na^+ (23 gm of Na) to enable it to escape from the sea water amounts to an algebraic sum of these and equals (1642+35,856+57,279) to 94,777 cal.

(*b*) *Energy for the escape of Cl^- ions*

Stage (i)—In a similar manner the energy for escape from the ionic atmosphere on the part of the Cl^- ion amounts to 1642 cal (absorption).

Stage (ii)—Energy necessary for the escape of the hydrated ion (with 3 molecules of H_2O) amounts to $3\times 498\times 18=26{,}892$ cal (absorption).

Stage (iii)—Energy necessary for getting rid of the water molecules amounts to 40,030 cal (absorption) and the total energy necessary for the release of one gm ion of Cl^- comes to a total of 68,834 cal.

(*c*) *Energy for the escape of 1 gm ion of Na^+ and Cl^- each*

Hence to set free 1 gm ion of Na^+ and 1 gm ion of Cl^- as free anhydrous ions from the sea water to the atmosphere, the energy necessary amounts to $94{,}777+68{,}834 = 163{,}611$ cal (absorption). Whence for 1 gm of NaCl the absorption of heat amounts to $2{\cdot}80\times 10^3$ cal (approx.).

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* This amount (498 cal) is the internal latent heat of vaporisation of water and goes to overcome the Van der Waal's attractive force. The pressure—volume energy involved in vaporisation of 1 gm mole of water is 41 cal only and the two together amount to the usual latent heat of vaporisation of 539 cal/gm.

†In accepting this approximation we are erring on the side of moderation. Actual heat effect will be somewhat higher than this value.

The activation energy necessary for the vaporisation of the Na^+ and Cl^- ions from an aqueous solution having approximately the same composition as that of sea water is thus quite high. A high concentration of NaCl in air cannot therefore be expected from the sea water. In fact judging from the above figures it is not difficult to see that the probable concentration of Na^+ and Cl^- ions will be much lower than that suggested by Lodge, Mc Donald and Baer (1954). Thus we consider the hypothesis that salt nuclei for the formation of clouds owe their origin from evaporation of salts from the sea water is unconvincing.

In the following table (Table 1) heats of formation of Na^+, Cl^-, NaCl molecules etc are all given (National Bureau of Standards, U.S.A.). From these, heats of formation of NaCl molecules and crystalline NaCl in the solid states can be easily calculated.

TABLE 1

Substances	Heat of formation in k. cal at 25°C	Substances	Heat of formation in k.cal at 25°C
Na^+(g)	+ 146·015	NaCl(aq)	—97·302
Na^+(aq): m=1	— 57·279	Cl^- (g)	—58·30
NaCl(g)	— 43·5	Cl^-(aq)	—40·023
NaCl(S)	— 98·232		

3. Conclusion

From results of the above calculation we conclude that large scale vaporisation of sea salts does not appear to be possible in view of the high activation energy necessary for the escape of Na^+ and Cl^- ions.

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