71. *The Vapour Pressure of Water over Aqueous Solutions of the Chlorides of the Alkaline-earth Metals. Part III. Correlation with Other Physical Properties of the Solutions.*

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This paper presents a critical study of experimental data on certain properties of solutions of the chlorides of the alkaline-earth metals in relation to the vapour pressure, with the special object of correlating the available data at concentrations between 0·1 and 1*M*. If the minima observed in the molecular lowering of vapour pressure for the given salts over this concentration range are real, and also if the theoretical interpretation of the results is correct (Part II, preceding paper, p. 572), corresponding abnormalities may be expected to occur in these properties, *viz.*, freezing-point lowering, viscosity, differential heat of dilution, and specific gravity.

1. *Lowering of Freezing Point.*—The freezing points of aqueous solutions of the chlorides in question have been studied by Arrhenius

(*Z. physikal. Chem.*, 1888, **2**, 496), Loomis (*Ann. Physik*, 1896, **57**, 503; 1897, **60**, 527), and Jones and Chambers (*Amer. Chem. J.*, 1900, **23**, 89). The results of Arrhenius were not sufficiently closely spaced to give precise information, but indicated that the molecular lowering of freezing point passed through a minimum at a concentration between 0·1 and 0·2*M* for solutions of calcium chloride, for which Loomis also found a minimum between 0·1 and 0·7*M*. The work of Jones and Chambers indicated that the molecular lowering of freezing point passed through a minimum in all three cases—for calcium, strontium, and barium chlorides at concentrations of *ca.* 0·1, 0·1, and 0·2*M* respectively.

No modern data appear to exist for the freezing point of solutions of these chlorides over the concentration range 0·1—1*M*; improvements in the experimental method date from 1902 (Hausrath, *Ann. Physik*, **9**, 522), and results obtained before that date cannot be regarded as strictly reliable. During the last few years much attention has been directed towards the freezing-point method in aqueous solution, and precise determinations have been made, more particularly by Lewis and Linhart (*J. Amer. Chem. Soc.*, 1919, **41**, 1952) and by Lange and his collaborators (*Z. physikal. Chem.*, 1930, **149**, 389). Such measurements have been carried out to a previously unparalleled degree of accuracy, but it is surprising that in no case is the highest concentration studied greater than 0·2*M*. This fact makes a quantitative comparison of the available freezing-point data with the vapour-pressure data of less value than it would otherwise be.

The exact thermodynamic relation between these two functions for a given solution was derived independently by Ewan (*Z. physikal. Chem.*, 1894, **14**, 409) and by Dieterici (*Ann. Physik*, 1894, **52**, 263). This relation was used by Dieterici (*ibid.*, 1897, **62**, 616) in connexion with his vapour-pressure results at 0° for solutions of calcium chloride, etc.; and later, Lovelace, Frazer, and Sease (*J. Amer. Chem. Soc.*, 1921, **43**, 102) employed the less accurate formula (ignoring heats of dilution) with solutions of potassium chloride from their vapour-pressure observations at 20°. Dieterici's expression was

$$\log\frac{p_0}{p} = \frac{t}{2{\cdot}303RT_0}\left[\frac{S_0+\bar{L}_0}{T} - \frac{\Delta C_pT_0t}{2T^2} + \frac{\Delta C_pT_0t^2}{3T^3}\right] \quad . \quad (1)$$

and that of Lovelace, Frazer, and Sease (quoted from Washburn, "Principles of Physical Chemistry," 1915, p. 169)

$$\log\frac{p_0}{p} = \frac{\Delta C_p}{R}\log\frac{T}{T_0} - \frac{(S_0-\Delta C_pt)}{2{\cdot}303RT} + \frac{S_0}{2{\cdot}303RT_0} \quad . \quad (2)$$

where T_0 = absolute f. p. of water, T = absolute f. p. of given solution, $t = (T_0 - T)$, S_0 = latent heat of fusion of solvent at 0°, L_0 = differential heat of dilution of solvent, ΔC_p = temperature coefficient of latent heat of fusion.

It is readily shown, however, that formula (1) may be obtained from (2) by expanding $\log T/T_0$ in a power series, retaining the first three terms, and then making the necessary adjustment for the heat of dilution by applying Kirchhoff's equation.

The method employed by Lewis and Randall ("Thermodynamics," 1923, p. 282) in the deduction of the activity of a solid in the neighbourhood of its melting point appears to be based upon the same principles as those of Dieterici, although no mention of his work is made by these authors.

It is evident that either of the above relations could be used to derive the vapour pressure, the freezing-point lowering at a given concentration in a given solution being known. By the application of formula (2), the author has calculated, from the data of Jones and Chambers, in the case of the three chlorides, values of $\log p/p_0$ at 0°, and therefrom p_m, the molecular lowering of vapour pressure. Table I gives the recalculated figures for calcium chloride. Col. 4 contains the values of $\log p/p_0$, col. 5 those obtained experimentally by Dieterici, and col. 6 those of the author. Although there is general agreement in the magnitude of the values of $\log p/p_0$ at concentrations up to $0{\cdot}3M$, yet at higher concentrations the heat of dilution effect becomes somewhat pronounced, the three sets of figures ranging themselves in numerical value according to the temperature of the observations.

Unfortunately, accurate values of the heats of dilution are not available at 0° or below, so the magnitude of the temperature correction cannot be readily determined; the figures for strontium and barium chlorides are therefore not quoted. The corresponding calculations using formula (1) (but ignoring the heat of dilution for the reason given) have also been carried out; the results are practically identical with those obtained by using formula (2). In each case it follows clearly, however (see Table I, col. 7), that if a minimum exists in the molecular lowering of freezing point, a corresponding minimum will be exhibited at the same concentration by the molecular lowering of vapour pressure.

These results, therefore, indicate that the freezing-point and the vapour-pressure measurements agree in showing the existence of corresponding abnormalities in the solutions, and also in the relative disposition of the minima in the case of the three salts, but the concentrations at which these abnormalities occur are not identical. However, it seems probable that at lower temperatures the minimum in the molecular lowering of vapour pressure might be displaced in

TABLE I.

Values of $\log p/p_0$ for aqueous solutions of calcium chloride recalculated from the freezing-point data and compared with the vapour-pressure data.

Soln. No.	M.	t.	$\log p/p_0$.			p_m, recalc.
			Recalc., 0°.	Observed.		
				Dieterici, 0°.	Author, 25°.	
1	0·102	0·508°	−0·00213°	—	—	1·137
2	0·153	0·752	−0·00316	—	—	1·124
3	0·204	1·012	−0·00423	−0·0039	−0·0045	1·127
4	0·255	1·267	−0·00530	—	−0·0056	1·129
5	0·306	1·537	−0·00648	−0·0057	−0·0060	1·150
6	0·408	2·104	−0·00889	−0·0079	−0·0072	1·179
7	0·510	2·681	−0·01134	−0·0101	−0·0092	1·200
8	0·612	3·348	−0·01414	−0·0123	−0·0114	1·244

the direction of lower concentration. Such an idea is confirmed by the fact that Dieterici's vapour-pressure results for calcium chloride (*loc. cit.*) indicate a minimum value for p_m between 0·1 and 0·2M, compared with the minimum found by the author at 0·34M (Part II). The correlation of viscosity and vapour-pressure data, discussed in the following section, also indicates that the minima found in the " molecular viscosity increment " are displaced in the direction of lower concentrations with fall in temperature.

The minimum in the molecular lowering of freezing point may also be explained along the lines suggested in Part II (p. 572), *i.e.*, by assuming that it is produced through dissociation of complex water molecules, if it is considered that the solution–ice equilibrium temperature at each concentration may be regarded as a temperature such that the pressure of water vapour over the ice is equal to that over the solution. Such a conception transforms the problem into one of vapour pressure only, and consequently is capable of the same treatment as employed in Part II.

2. *Viscosity.*—A study of previous work on the viscosity of aqueous solutions of the chlorides of the alkaline-earth metals reveals the fact that measurements made prior to 1904 cannot be accepted over the concentration range which is particularly important in the present connexion (*viz.*, 0·1—1M), since earlier workers did not apply corrections of fundamental importance to their experimental data (compare Grüneisen, *Wiss. Abh. Phys. Tech. Reichsanstalt*, 1904, **4**, 237). Since 1904, however, sufficient accurate measurements have been made to establish with some degree of certainty the change in viscosity with concentration over the crucial concentration range.

Grüneisen determined the viscosity of aqueous solutions of calcium chloride at 18°. Following this author, one may express the results obtained in terms of the " molecular viscosity increment," which may be regarded as a measure of the departure of any given solution from normal behaviour. This magnitude may be given in the form

$$V = (\eta - 1)/M \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where η is the relative viscosity (water = 1) determined experimentally, and M the molality.

The molecular viscosity increment is evidently in the nature of a deviation coefficient, and as such is comparable with the molecular lowering of vapour pressure. In cases where strict proportionality between increase of viscosity and concentration is observed, the molecular viscosity increment will be a constant.

Grüneisen's experimental figures for calcium chloride at 18° are quoted in Table II, together with one result of Sprung (*Ann. Physik*, 1876, **159**, 19; but see p. 578) at a higher concentration in order to indicate the further course of the curve: the molecular viscosity increment passes through a minimum at a concentration between 0·25 and 0·5M, and thereafter increases rapidly with increasing concentration (the concentrations have been recalculated as molalities from the original figures, which were given as g.-equivs. per litre). This result corresponds closely with the author's figures for calcium chloride, where the curve connecting the molecular lowering of vapour pressure and molality passes through a minimum at 0·34M.

The only reliable determinations for strontium chloride since 1904 are those of Schneider (*Diss.*, Rostock, 1910); his results are also quoted in Table II, the values of M and $(\eta - 1)/M$ having been recalculated from his data. In this case also the molecular viscosity increment passes through a minimum value, at a concentration of *ca.* 0·3M, at which concentration the author's vapour-pressure data indicate a minimum in the molecular lowering of vapour pressure.

TABLE II.

Values of the relative viscosity and "molecular viscosity increment" for aqueous solutions of the chlorides of the alkaline-earth metals.

$CaCl_2$, data of Grüneisen for 18°; $SrCl_2$, data of Schneider for 18°; $BaCl_2$(1), data of Schneider for 18°; $BaCl_2$(2), data of Jones and Dole for 25°.

	η (observed).				$(\eta - 1)/M$ (calculated).			
			$BaCl_2$.				$BaCl_2$.	
M.	$CaCl_2$.	$SrCl_2$.	(1).	(2).	$CaCl_2$.	$SrCl_2$.	(1).	(2).
1·00	1·320	1·3081	1·2666	1·2804	0·320	0·308	0·267	0·283
0·50	1·1501	1·1400	1·1207	1·1289	0·3002	0·280	0·241	0·259
0·25	1·0751	1·0663	1·0611	1·0643	0·3004	0·265	0·244	0·258
0·10	—	1·0289	1·0282	1·0270	—	0·289	0·282	0·270
0·05	1·0167	1·0157	1·0132	1·0147	0·334	0·314	0·264	0·295

A corresponding parallelism is shown by the results of Schneider (*loc. cit.*) at 18°, and also by the recent figures of Jones and Dole, (*J. Amer. Chem. Soc.*, 1929, **51**, 2950) at 25°, for barium chloride. The results are shown in Table II. (The values quoted for 0·5*M* and 1·0*M* are obtained by slight adjustment by interpolation, since the actual concentrations used by Jones and Dole were 0·497*M* and 0·9913*M* respectively.)

The figures of Schneider at 18° indicate a minimum at a concentration of approximately 0·5*M*, while Jones and Dole state (*loc. cit.*, p. 2958) that the molecular viscosity increment passes through a minimum at 0·4*M*, which corresponds exactly with the author's result for the molecular lowering of vapour pressure. In their discussion of the results, Jones and Dole do not stress the implications of this minimum value, but transform their results into terms of fluidity (*i.e.*, reciprocal of viscosity), which is more simply treated analytically (*e.g.*, the molecular fluidity decrement does not pass through a minimum value). However, such a mode of treatment certainly does not dispose of the existence of the minimum value of the molecular viscosity increment, particularly in view of the author's result on the closely related property of vapour pressure.

The minima in the molecular viscosity increment are also capable of explanation on the basis of the molecular aggregation of water. Applebey (J., 1910, **97**, 2000) suggested that addition of a salt to water may diminish the viscosity through producing a depolymerisation of trimeric to monomeric water molecules. If this is so, the effect would not be expected to be so notable as that on the vapour pressure, since the total viscosity is not due solely to the monomeric water molecules, as in the case of the vapour pressure, but to all the entities present in the liquid phase. An increase in the number of simple water molecules, thus produced, would presumably not exert such an important influence upon this property of the solution. Such an idea is in agreement with the experimental results.

There is evidence that a temperature effect exists in the molecular viscosity increment minimum, corresponding with that suggested in connexion with the molecular lowering of vapour pressure. For instance, Merton (*ibid.*, p. 2454) found with solutions of cæsium nitrate that the minimum occurred at 0° at a concentration of 0·1*M*, whereas at 25° it occurred at 0·3*M*.

3. *Heats of Dilution at Relatively Low Concentrations.*—Richards and Dole (*J. Amer. Chem. Soc.*, 1929, **51**, 794) determined the integral heats of dilution for calcium and barium chlorides at dilutions ranging from 50 to 12,800 mols. of water per mol. of salt, corresponding with molalities of 1—0·004*M* approximately, and Lange

and Streeck (*Z. physikal. Chem.*, 1931, **152**, 1) obtained similar values for the chlorides of calcium, strontium, and barium over the concentration range 0·1—0·0001*M*.

Both the above investigations show positive values for the integral heat of dilution for barium chloride over the concentration range studied up to 0·5*M*. Comparing these results with those of Stearn and Smith at higher concentrations (*J. Amer. Chem. Soc.*, 1920, **42**, 18), one finds that according to these authors the differential heat of dilution is negative and diminishes in magnitude with fall in concentration. Positive values for the differential heat of dilution, however, are found by Lange and Streeck at concentrations up to 0·1*M*. A change of sign therefore appears to occur in the heat of dilution for barium chloride at a concentration between 0·8*M* (the lowest concentration studied by Stearn and Smith) and 0·1*M* (the highest studied by Lange and Streeck). This matter is not discussed more fully in the present work, since the theoretical implications are somewhat obscure (see, *e.g.*, Bjerrum, *Trans. Faraday Soc.*, 1927, **23**, 446; Richards and Dole, *loc. cit.*, p. 802), but there is evidence that the differential heat of dilution shows a parallelism with the other properties of the solution previously discussed.

The fact that for calcium and strontium chlorides the integral heat of dilution is positive throughout renders it impossible to discuss even qualitatively any change in this magnitude corresponding with that for barium chloride.

4. *Specific Gravity.*—Of the available data at room temperature on aqueous solutions of calcium chloride, those of Pickering (*Ber.*, 1894, **27**, 67, 1379), Jones (*Pub. Carnegie Inst., Washington*, 1907), Heydweiller (*Ann. Physik*, 1909, **30**, 873), and Wade (J., 1899, **75**, 254) do not attain the requisite accuracy, whereas those of Macgregor (*Chem. News*, 1887, **55**, 3), and of Cameron and Robinson (*J. Physical Chem.*, 1910, **14**, 1569), while attaining a high degree of accuracy, are concerned with solutions which are too dilute for the present purpose.

The accurate determinations of Buchanan (*Trans. Roy. Soc. Edin.*, 1914, **49**, 1) cover a wide concentration range, and the paper includes an analytical study of the data obtained; there is, however, no evidence as to the existence of any abnormality over the concentration range 0·1—1*M*. As a result of precision measurements on the alkali chlorides and a study of all the available data, Baxter (*J. Amer. Chem. Soc.*, 1911, **33**, 901; 1916, **38**, 70) concluded that the phenomena involved are highly complex, that no adequate explanation of the cause of the volume changes has yet been proposed, and that the part which the polymerisation of water plays in the change is uncertain, since it is associated with other effects acting in a contrary direction. It is therefore to be expected that no conclusive information could be furnished by measurements of specific gravity in the case of the chlorides of the alkaline-earth metals, and such a view is confirmed by the results of Buchanan.

Summary.

A study of data on freezing-point lowering, viscosity, and differential heat of dilution shows that the anomalous behaviour of the salts studied in regard to the vapour-pressure lowering in aqueous solution is also exhibited by these related properties of the solutions. For the first property, a quantitative thermodynamic correlation is made within the limitations of the available data. No evidence is forthcoming of any corresponding abnormalities in the specific gravity.

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