XXII. THE VAPOUR PRESSURE DEPRESSIONS OF AQUEOUS SOLUTIONS OF PHOSPHATE BUFFER MIXTURES AT 20.3°.

BY ARTHUR GROLLMAN¹.

*From the Department of Physiology and Biochemistry,
University College, London.*

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THE difficulties attendant upon the determination of the colligative properties of solutions, at temperatures other than the freezing and boiling points, have prevented the accumulation of data concerning these important physico-chemical functions. The direct measurement of osmotic pressure has been restricted almost entirely to a few organic substances, while accurate determinations of vapour pressure lowerings have been limited owing to the complexity of the methods and apparatus involved in the static and dynamic methods used heretofore. The recent introduction by Hill [1930, 1] of a thermal method for measuring vapour pressure, owing to its simplicity and ease of manipulation compared with the static or dynamic method, renders the determination of such colligative properties relatively easy. The method is particularly useful and accurate for the solution of many chemical problems, furnishing as it does a knowledge of a function whose thermodynamic relationship to other physico-chemical properties is well established.

The common use of Sørensen's [1912] phosphate mixtures as buffer solutions in biochemical work renders a knowledge of their colligative properties of great practical importance. Previous determinations of such properties have been limited to the freezing and boiling points [International Critical Tables, 1928] of solutions of the pure salts, no accurate data being available, even at these temperatures, for mixtures. Such data, therefore, at the suggestion of Mr G. S. Adair, have been obtained and are given below.

The vapour pressure lowerings recorded here were obtained by Hill's thermal method as described in previous papers from this laboratory [Hill, 1930, 1, 2; Margaria, 1930]. The same apparatus and general procedure were used as described elsewhere [Grollman, 1931]. The salts employed were standard "analytical reagents." The primary potassium phosphate (KH_2PO_4) was dried at 110° for a day before use. The secondary sodium phosphate ($\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$) was obtained by exposing $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ to the atmo-

¹ John Simon Guggenheim Memorial Fellow.

sphere, as suggested by Clark [1928]. The various buffer mixtures were prepared according to the usual procedures [Clark, 1928].

The results are given in Table I. Columns 1 and 2 of this table give the

Table I. *The vapour pressures of Sørensen's phosphate buffer mixtures at 20.3°.*

Composition of solution		p_H	NaCl concentration isomolar with solution. Moles per 1000 g. of water	Molar relative vapour pressure lowering
Primary phosphate cc. of $M/15$ KH_2PO_4	Secondary phosphate cc. of $M/15$ Na_2HPO_4			
10.0	0.0	—	0.0637	$3.18 \pm 0.008 \times 10^{-2}$
9.5	0.5	5.589	0.0637	3.18 ± 0.013
9.0	1.0	5.906	0.0639	3.19 ± 0.004
8.0	2.0	6.239	0.0643	3.21 ± 0.016
6.0	4.0	6.643	0.0657	3.28 ± 0.008
4.0	6.0	6.979	0.0680	3.39 ± 0.015
2.0	8.0	7.381	0.0698	3.48 ± 0.010
1.0	9.0	7.731	0.0714	3.56 ± 0.013
0.5	9.5	8.043	0.0737	3.67 ± 0.014
0.0	10.0	—	0.0743	3.70 ± 0.016

composition of the various mixtures investigated. Column 3 shows the p_H of such mixtures, according to Clark [1928]. In column 4 is given the sodium chloride concentration isomolar¹ with the solution in question as found by experiment. Column 5 shows the relative molar vapour pressure lowering as defined by the expression $\frac{p_0 - p}{Mp_0}$, in which p_0 is the vapour pressure of pure water at the temperature of the experiment, p the vapour pressure of the solution, and M the number of moles of solute present per litre of solution. The value of M is constant for the solutions studied and equal to 1/15. It should be noted that the above described mode of expression for the molar relative vapour pressure lowering differs slightly from that usually employed, in which M is expressed in terms of the number of formula weights of solute present per 1000 g. of water. The former mode of expression has been used because buffer solutions are generally expressed in terms of volume concentrations.

The vapour pressure lowerings for pure Na_2HPO_4 and KH_2PO_4 solutions, as given in the table, were obtained by comparison with a 0.064 molar NaCl solution whose molar relative vapour pressure lowering was taken as 3.33×10^{-2} , as previously found [Grollman, 1931]. The data for the mixtures were then obtained by comparison with the Na_2HPO_4 or KH_2PO_4 solutions. The values quoted are the averages of at least four sets of determinations (8 readings) and the probable errors of the mean molar relative vapour pressure lowerings are included in the last column.

It might have been expected that the vapour pressure lowering would be a linear function of the composition of the mixture. This would be the case were no interaction to occur between the constituent salts, *i.e.* were the total

¹ This term is used to describe a solution of the same vapour pressure as a given solution under the same condition of temperature, etc.

ionic activity of the solute to remain constant. This expectation is not fulfilled, as is seen in Fig. 1.

Fig. 1.

Ordinate. The relative molar vapour pressure lowering $(p_0 - p)/Mp_0$, where p_0 is the vapour pressure of pure water, p the vapour pressure of the solution, and M is the number of g. formula weights of solute per litre of solution.

Abscissa. The composition of the solutes expressed as cc. of M/15 Na₂HPO₄ in 10 cc. of the mixture.

It is often assumed in biochemical and physiological work that the colligative properties of mixtures, such as are continually encountered in biological materials, are simple additive properties of the constituents. The inadequacy of this view, even where no apparent interaction occurs between the various solutes (in which case, of course, no such additive relationship would be expected to hold), has been shown elsewhere [Grollman, 1931]. The curve of Fig. 1 emphasises again the extent of the deviation of the colligative properties of a mixture from those anticipated on the assumption of a simple additive relationship between the properties of the mixture and those of its constituents.

The vapour pressure values quoted in the present paper, being functions of the total ionic activities of the solutions, may be utilised in calculations involving expressions for such activities.

SUMMARY.

Data are presented for the vapour pressure depressions of M/15 aqueous solutions of KH₂PO₄, of Na₂HPO₄, and of mixtures of these salts.

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