

## NOTES

*Relation between Vapor Pressure and Internal Pressure in Solutions and Pure Liquids*

By C. V. SURYANARAYANA and  
K. K. JANARDHANAN PILLAI

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Recently Suryanarayana<sup>1)</sup> proposed internal pressure as the basis of a unified theory of solutions. If it should be tenable, several fundamental properties of solutions as well as pure liquids should be explicable on the basis of internal pressure. A search has been made by us if vapor pressure over a liquid, be it pure or a solution, has any relation with the internal pressure. For computing internal pressure, recently Suryanarayana and Govindaswamy<sup>2)</sup> formulated an equation,

$$\Pi = K \cdot \rho^{4\frac{1}{3}} / M^{1/3} \quad (1)$$

based on a relationship pointed out by Young<sup>3)</sup> and Leplace<sup>4)</sup>. In Eq. 1  $K$  is an incomputable constant independent of temperature, whereas  $\Pi$ ,  $\rho$  and  $M$  are internal pressure, density and molecular weight of the medium respectively. Equation 1 is applicable to solutions in the form,

$$\Pi = K \cdot \rho^{4\frac{1}{3}} / (M_1 x_1 + M_2 x_2)^{1/3} \quad (2)$$

where  $x_1$  and  $x_2$  are the mole fractions of the two components, for example in a binary solution, and  $M_1$  and  $M_2$  are respectively the molecular weights. Suryanarayana and Govindaswamy (loc. cit) showed that Eq. 2 is applicable to solutions of nonelectrolytes and fully dissociated electrolytes. The computable part on the right hand sides of Eqs. 1 and 2 has been called the  $\Pi$ -factor. For purposes of comparison of internal pressures a study of the  $\Pi$ -factor must be sufficient and reliable.

Vapor pressure data for electrolyte solutions of sodium carbonate, lithium bromide, nitric acid, hydrochloric acid, sodium sulfate, sulfuric acid, ammonium chloride, sodium chloride, sodium nitrate, sodium hydroxide, potassium

sulfate, sodium iodide, ammonium sulfate and sodium bromide, at least at six temperatures in each case were obtained from the International Critical Tables, Vol. III, 1928. Graphical studies showed that in almost all cases vapor pressure varies linearly with the internal pressure of a solution,

$$P = A - B\Pi' \quad (3)$$

where  $P$  is the vapor pressure,  $\Pi'$  the  $\Pi$ -factor and  $A$  and  $B$  constants. Substituting the  $\Pi$ -factor for pure water in Eq. 3, computed from its density and molecular weight, we can get the vapor pressure  $P$  at a given temperature. Values thus obtained from Eq. 3 agreed excellently with those given in standard tables at all the temperatures tested. The following table gives at 40°C a comparison of vapor pressure values between the standard ones and those obtained from 3 of different salts by substituting  $\Pi'$  of water in the respective equations.

TABLE I. DATA AT 40°C\*

Electrolyte	Vapor pressure of water from the equation mmHg	% deviation from the accepted value
Sodium carbonate	55.25	-0.1266
Lithium bromide	55.14	-0.3254
Nitric acid	55.03	-0.5242
Hydrochloric acid	57.98	+4.808
Sodium sulfate	55.08	-0.4338
Sulfuric acid	57.56	+4.049
Ammonium chloride	54.55	-1.392
Sodium chloride	55.46	+0.253

\* The accepted vapor pressure of water at 40°C is 55.32 mmHg.

Sodium nitrate, bromide, iodide, hydroxide, potassium sulfate and ammonium nitrate solutions give for a plot of vapor pressure versus  $\Pi$ -factor in each case two straight lines intersecting at a point. These can be explained on the basis of 1-1, 1-2 and 2-2 interactions.

The internal pressure of a liquid increases as the temperature decreases. At each temperature probably a quantitative relationship exists between the vapor pressure and internal pressure of a liquid. In expectation of a fundamental relationship between the two, thirty liquids namely, methyl sulfide, diethyl amine, ethyl propyl ether, methyl ethyl ether, cyclohexane, isopropyl isobutyrate, chlorobenzene, methyl acetate, *n*-propyl acetate, benzene, methyl formate, ethyl formate, ethyl acetate, methyl isobutyrate, ethyl sulfide, methyl propionate, ethyl

1) C. V. Suryanarayana, *J. Sci. Ind. Research (India)*, **A20**, 141 (1961).

2) C. V. Suryanarayana and S. Govindaswamy, *Acta Chim. Hung.*, **25**, 341 (1960).

3) T. Young, *Phil. Trans.*, **1**, 65 (1805).

4) P. S. Laplace, "Oeuvres", Vol. IV, 389.

propionate, acetic acid, methyl alcohol, *n*-propyl alcohol, diethyl ether, *n*-pentane, bromobenzene, ethyl alcohol, methyl *n*-butyrate, *n*-propyl formate, acetone, isopropyl alcohol, carbon tetrachloride, and water have been studied. Data of vapor pressure and density for the first six are from International Critical Tables (McGraw-Hill), Vol. III, 1928 and for the rest from Timmermans Physico-chemical Constants of Pure Organic Compounds, Amsterdam, 1950. In almost all cases we found the simple relationship,

$$\log P = A - B/T \quad (4)$$

applicable in almost all cases excepting *n*-propyl formate and water, which require to be explained.

Thus in solutions we observe from Eq. 3 that the vapor pressure varies linearly with internal pressure, whereas in the case of pure liquids the logarithm of the vapor pressure is found to vary as in Eq. 4 linearly with the internal pressure. In the case of solutions, the causative factor that changes internal pressure is the solute concentration whereas in the case of pure liquids it is the temperature. Normally speaking, provided the vapor pressure and the internal pressure are quantitatively related, whatever may be the causative factor that changes the internal pressure, the fundamental relation between the two should remain universal and undisturbed. Invalidation of this expectation and the existence of two types of relations as in Eqs. 3 and 4 signifies a difference in the mechanism of change of internal pressure in the two cases. A detailed study of these and other aspects will be published elsewhere in due course.

*Department of Chemistry  
Mysore University  
Mysore, India*

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