LETTERS TO THE EDITOR

ON THE SURFACE TENSION OF IDEAL SOLUTIONS

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(Received January 24, 1955)

In a recent paper Puchalik (1954) has reported an experimental study on the surface tension of some solutions, made in order to investigate the association processes accompanying dissolving of one substance in another. It seems, however, that the surface tension is influenced by association processes in a very complicated manner and before drawing any conclusions from such a study changes in the surface tension of ideal solutions must be first determined.

For ideal solutions Freundlich (1922) derived an equation based on the additivity of surface tension of pure components. Stachorski's (1928) empirical equation for a solution of two components is

$$\sigma = \frac{\sigma_1 \sigma_2}{\sigma_1(1 - c_1) + \sigma_2 c_1}, \tag{1}$$

where σ, σ_1, σ_2 are respectively the surface tensions of the solution and of its first and second components and c_1 is the molar concentration of the first component. Denoting the molar concentration of the second component by $c_2 = 1 - c_1$, we can easily transform (1) into

$$\frac{1}{\sigma} = \frac{c_1}{\sigma_1} + \frac{c_2}{\sigma_2}, \tag{2}$$

which shows that equation (1) is based on the additivity of reciprocals of the surface tension.

Hammic and Andrew (1929) have assumed that the parachor of an ideal solution

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can be calculated by taking into account the additivity of this constant:

$$P = c_1 P_1 + c_2 P_2 \tag{3}$$

They have determined the parachor P of the solution by measuring the surface tension and the density of a solution of known concentration and comparing P with the value of the parachor calculated from equation (3). The same method was adopted by Puchalik. Thus for determining the parachor of the solution two physical constants have been used, both of which can be influenced by association: the surface tension and the density. It is well known that in non-ideal solutions the density depends considerably on concentration. Because of this fact the method of Hammic and Andrew does not allow us to determine the influence of association on the surface tension. To investigate this influence we have to calculate the surface tension of the solution from the physical constants of pure components only and compare it with the measured value.

An appropriate equation has been obtained some years ago by the author in an unpublished work (Mierzecki 1949)* starting from equation (3). Taking $P = M\sigma^{1/4}/d = V_{mol}\sigma^{1/4}$ (M — molecular weight), we have for an ideal solution of two components

$$\sigma^{1/4} V_{mol} = c_1 \sigma_1^{1/4} V_{mol_1} + c_2 \sigma_2^{1/4} V_{mol_2}. \tag{4}$$

For an ideal solution there is no contraction and therefore

$$V_{mol} = c_1 V_{mol_1} + c_2 V_{mol_2} = c_1 \frac{M_1}{d_1} + c_2 \frac{M_2}{d_2}.$$

Finally

$$\sigma = \left(\frac{c_1 \sigma_1^{1/4} \frac{M_1}{d_1} + c_2 \sigma_2^{1/4} \frac{M_2}{d_2}}{c_1 \frac{M_1}{d_1} + c_2 \frac{M_2}{d_2}} \right)^4 \tag{5}$$

represents the normal behaviour of σ as function of the concentration c.

Puchalik assumes such a function to be given by Szyszkowski's equation (1908): $\sigma = \sigma_0 - b\, ln\, (1 + ac)$ which is valid for aqueous solutions of superficially active substances and contains a and b, two constants different for different substances dissolved. Such solutions can in no way be considered as ideal solutions and cannot therefore serve as basis to draw conclusions regarding association processes.

From equation (5) we see also that one cannot assume that for a given solution the dependence of σ on c is linear and at the same time the parachor is an additive function of the concentrations. Nevertheless Puchalik writes: „Die Kurve für die erstgenannte Lösung (i. e. for the C_2H_5OH — C_6H_6 solution) lässt sich gut durch eine gerade Linie approximieren und bei der gegenwärtigen Genauigkeit der Messungen kann man nicht bestimmt entscheiden, ob die vorhandenen Abweichungen von der Linearität wirklich bestehen" and at the end of his paper we read: „Nur im Falle der

*Dissertation submitted to the Department of Physical Chemistry of the Łódź Institute of Technology in partial fulfilment of the requirement for the degree of Master of Science.

ACTA PHYSICA POLONICA Vol. XIV (1955) Fasc. 4

Aethylalkohol — Benzol Lösungen erweisen sich die Parachore als streng additive Funktionen der Komponenten."

It seems that the exactitude of the contemporary measurement technique of surface tension does not allow Puchalik to determine in an definitive manner either the linearity of the $\sigma = f(c)$ function or the additivity of the parachor. To day it seems also impossible to find out experimentally which of the equations is true: that of Freundlich, equation (2) or equation (5). The values of surface tension of the components of ideal solutions cannot differ strongly and in that case the experimental errors are greater than the differences between the values calculated from these equations.

The problem of the influence of association on surface tension is yet far from beeing solved and it seems that Puchalik is right in stating: „Die endgültige Entscheidung ob man die gewonnenen Resultate zur Unterscheidung der verschiedenen Assoziationsarten verwerten kann bleibt künftigen Untersuchungen vorbehalten."

The author wishes to express his gratitude to Professor A. Dorabialska for permission of publishing some results of his dissertation.

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ACTA PHYSICA POLONICA Vol. XIV (1955) Fasc. 4