

## Solutions of Long Chain Compounds

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### Solutions of Long Chain Compounds

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April 4, 1941

**F**OWLER and Rushbrooke<sup>1</sup> have derived statistically equations for the activities of the constituents of a dilute binary solution, in which the solute molecules are elongated, each occupying twice the volume occupied by a single solvent molecule, with the molecules of the two kinds otherwise so similar that there is no heat of mixing.

Extending their methods to the idealized case of a dilute solution of long chain molecules, each composed of randomly oriented "submolecules," similar in nature and size to one of the solvent molecules, I have derived the following relations:

$$a_1 = N_1^{*1/n} \exp(-k_1 N_2^{*2})$$

$$a_2 = \frac{N_2^*}{k_2^n} \exp\left[2k_1 n \left(N_2^* - \frac{N_2^{*2}}{2}\right)\right].$$

Here,  $a_1$  and  $a_2$  are the activities of solvent and solute,  $N_1^*$  and  $N_2^*$  are related to the mole fractions  $N_1$  and  $N_2$  by the equations

$$N_1^* = \frac{N_1}{N_1 + nN_2} \quad \text{and} \quad N_2^* = \frac{nN_2}{N_1 + nN_2},$$

$n$  is the number of "submolecules" in the solute molecule chain, and  $k_1$  and  $k_2$  are constants, equal to 0.45 and 11, respectively, for a close-packed distribution of solvent molecules and solute submolecules.

These activity equations can, of course, be used to derive expressions for osmotic pressure, freezing point lowering, solubilities, etc. Application to osmotic pressures,

for example, leads to the relation

$$\Pi = \frac{RT}{V_1} (-\ln N_1^{*1/n} + k_1 N_2^{*2}) \\ \approx \frac{RTN_2}{V_1} (1 + k_1 n^2 N_2),$$

where  $R$  is the molal gas constant,  $T$  the absolute temperature and  $V_1$  the molal volume of the solvent. Except for the constant  $k_1$ , this last equation is equivalent (for my hypothetical model) to

$$\Pi \approx \frac{RTN_2}{V_1} [1 + (Q-1)\phi_2],$$

just published by Powell, Clark and Eyring,<sup>2</sup> in which  $Q$  is the number of segments into which the solute molecule is divided and  $\phi_2$  is the volume fraction of the solute in the solution. Their equation was derived by assuming "that the osmotic pressure is determined by the effective mole fraction" and "that the probability of a polymer molecule's moving in segments is a linear function of its environment as expressed by the volume fraction of polymer."

According to the above equations,  $\Pi/c$  increases approximately in proportion to  $c$  (the concentration in g/cc or similar units), a relationship which has been known empirically for some time.<sup>3</sup> On the theoretical side (besides the papers already mentioned), Haller<sup>4</sup> has presented a kinetic interpretation and Meyer<sup>5</sup> has recently discussed the subject from a statistical point of view, but in a qualitative manner.

Details of the present treatment and application to other properties and to real solutions will be given at the Wilder D. Bancroft Colloid Symposium in June.

<sup>1</sup> R. H. Fowler and G. S. Rushbrooke, Trans. Faraday Soc. **33**, 1272 (1937).

<sup>2</sup> R. E. Powell, C. R. Clark and H. Eyring, J. Chem. Phys. **9**, 268 (1941).

<sup>3</sup> H. Mark, *Physical Chemistry of High Polymeric Systems* (Interscience Publishers, New York, 1940).

<sup>4</sup> W. Haller, Kolloid Zeits. **56**, 257 (1931).

<sup>5</sup> K. H. Meyer, Zeits. f. physik. Chemie **B44**, 383 (1940); Helv. Chim. Acta **23**, 1063 (1940).

### Erratum: Spectroscopic Evidence for Hydrogen Bonds: Comparison of Proton-Attracting Properties of Liquids. IV.

(J. Chem. Phys. **9**, 215 (1941))

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April 10, 1941

The captions of Figs. 2 and 3 are interchanged.