SOME PROPERTIES OF SOLUTIONS OF LONG-CHAIN COMPOUNDS[1,2]

MAURICE L. HUGGINS

Kodak Research Laboratories, Rochester, New York

I. INTRODUCTION

Much has been written concerning the thermodynamic properties of solutions, yet there has been but little work reported (2, 4, 6, 7, 9, 18) on the dependence of these properties on the sizes of the component molecules and still less dealing with the effect of molecular shape and flexibility. Hildebrand (8, 10), it is true, has dealt with the special case of solutions of rod-like molecules of different lengths; Fowler and Rushbrooke (3) and Chang (1, 2) have treated the case of a solution containing spherical molecules of one kind and elongated double-sized molecules of another; and Meyer (15, 16) and Haller (5) have discussed, primarily in a qualitative manner, solutions of long-chain compounds in solvents composed of small molecules. In this paper, a more quantitative theoretical treatment of such solutions will be described. The procedure is an extension of that given by Fowler and Rushbrooke for their simpler case.

Raoult's law, according to which the activity of each component of a solution is equal to its mole fraction, holds for solutions for which the total heat content does not change as the pure liquid components are mixed, if Δs_M, the entropy change (per mole) on mixing has the value

$$\Delta s_M = R \ln \frac{(N_A + N_B)!}{N_A! N_B!} \tag{1}$$

computed statistically (2) on the assumption of a completely random distribution of the two kinds of molecules in the solution. In equation 1, R is the gas constant per mole and N_A and N_B are the numbers of molecules of the two species.

Deviations from Raoult's law have, quite properly, usually been attributed (7) to differences in the energies of interaction between the different molecular species—i.e., to effects related to the heat of mixing. It seems reasonable, however, that, in solutions of long, flexible chain molecules, deviations in the entropy of mixing from that given by equation 1 may be even more important. This will be shown to be the case.

Time and space will permit only an outline of the procedure and a few of the results to be given here. Details will be presented later.

II. CALCULATION OF THE ACTIVITIES

Let us consider a hypothetical solution containing N_B spherical molecules and N_A chain molecules, each of the latter consisting of n submolecules, equal in size and shape to a single molecule of type B. We assume the volume change on mixing and the heat (or energy) of mixing to be zero. We treat the solution statistically as if it were a *solid* solution, having $N_B + nN_A$ sites for B molecules or A submolecules. The A molecules are first added (hypothetically) one at a time, then the B molecules, counting the number of different ways in which each molecule or submolecule can be added and multiplying these numbers together to obtain the total number of configurations.

Submolecule 1 of A_1 (the first A molecule) can be placed in any of $N_B + nN_A$ sites. Submolecule 2 of this molecule then has a number of alternatives, z, equal to the coördination number. Submolecule 3 has y alternatives, where y equals $z - 1$ if there is complete flexibility at the joint between submolecules 2 and 3. (With actual molecules, y would be expected to differ considerably from $z - 1$. A comparison of experimental and theoretical entropies (12) for gaseous normal paraffins at 25°C. leads to an effective average value for y of about 24 in these compounds.) Submolecule 4 also has y alternatives, as has each of the remaining submolecules of A_1, provided we neglect the blocking of a small fraction of the otherwise possible positions by already placed submolecules of this molecule. (This intramolecular blocking will be taken into consideration in the more detailed treatment; in effect, it merely reduces the average value of y slightly.)

Submolecule 1 of molecule A_2 has $N_B + nN_A - n$ sites available. Submolecule 2 of A_2 has z possible sites, provided submolecule 1 is adjacent to no previously occupied sites; it has $z - 1$ alternatives, if submolecule 1 is adjacent to one previously occupied site; $z - 2$ alternatives, if submolecule 1 is adjacent to two previously occupied sites, etc. The average number of alternatives for submolecule 2 is $z(1 - f_2)$, where f_2 is the chance that any given otherwise available site is already occupied.

·Submolecule 3 (or any other submolecule) of molecule A_2 likewise has $y(1 - f_2)$ alternatives, on the average. In general, for any molecule A_s, submolecule 1 has $N_B + nN_A - (s - 1)n$ alternatives, submolecule 2 has (on the average) $z(1 - f_s)$ alternatives, and each of the $n - 2$ other submolecules has $y(1 - f_s)$ alternatives. (Certain complications, important only for small values of z and y, are here neglected.)

To obtain the number of *different* configurations for the molecules, one must divide the total number of configurations, computed in the manner described, by $N_A!$ and by σ^{N_A}, where the symmetry number, σ, has the value 2 if A is a diatomic or triatomic molecule with both ends alike. For longer chains, σ can be put equal to 1, with but little error.

After the addition of all the A molecules, the remaining sites are filled with the B molecules. These introduce no increase in the number of distinguishable configurations.

The total number of different configurations for the system is computed (for large y and z) to be

$$\Phi = \frac{\left(\dfrac{N_B}{n} + N_A\right)!\,(N_B + nN_A)^{\frac{n-1}{n}N_B}\,n^{N_A}z^{N_A}y^{(n-2)N_A}}{\left(\dfrac{N_B}{n}\right)!\,N_A!\,(N_B)^{\frac{n-1}{n}N_B}\,\exp\left[(n-1)N_A\right]\sigma^{N_A}} \tag{2}$$

The entropy (S) associated with these alternative configurations is given by

$$\frac{S}{k} = \ln \Phi = (N_B + N_A)\ln(N_B + nN_A) - N_B \ln N_B$$

$$- N_A \ln N_A + N_A \ln(z/\sigma) + (n-2)N_A \ln y - (n-1)N_A \tag{3}$$

where k is the Boltzmann constant. Putting $N_A = 0$, we obtain $S_B = 0$ for this entropy in pure liquid B. For pure liquid A, on putting $N_B = 0$, we obtain

$$\frac{S_A}{k} = N_A \ln(nz/\sigma) + (n-2)N_A \ln y - (n-1)N_A \tag{4}$$

The entropy of mixing, divided by k, is

$$\frac{\Delta S_M}{k} = \frac{S - S_B - S_A}{k} = N_B \ln\left(\frac{N_B + nN_A}{N_B}\right) + N_A \ln\left(\frac{N_B + nN_A}{nN_A}\right) \tag{5}$$

The activities of the components of the solution are then

$$a_B = \exp\left[\frac{-\partial(\Delta S_M/k)}{\partial N_B}\right]_{N_A} = \frac{N_B}{N_B + nN_A}\exp\left[\frac{(n-1)N_A}{N_B + nN_A}\right]$$

$$= \frac{N_B}{N_B + nN_A}\exp\left[\frac{(n-1)N_A}{N_B + nN_A}\right] = N_B^* \exp\left[\frac{n-1}{n}N_A^*\right] \tag{6}$$

$$a_A = \exp\left[\frac{-\partial(\Delta S_M/k)}{\partial N_A}\right]_{N_B} = \frac{nN_A}{N_B + nN_A}\exp\left[\frac{-(n-1)N_B}{N_B + nN_A}\right]$$

$$= \frac{nN_A}{N_B + nN_A}\exp\left[\frac{-(n-1)N_B}{N_B + nN_A}\right] = N_A^* \exp\left[-(n-1)N_B^*\right] \tag{7}$$

N_B and N_A denote mole fractions, while N_B^* and N_A^* denote volume fractions. These expressions are mutually consistent with each other, satisfying the well-known Gibbs–Duhem–Margules relationship. For $n = 2$, they agree with the results previously obtained by Chang (1, 2).

Figure 1 shows the variation of the activities (as given by these equations) with the mole fractions and with the number (n) of submolecules in the chain. The deviations from Raoult's law, represented by the straight lines, are seen to be very large for long chains.

The activity equations for small values of y and z differ from equations 6 and 7 chiefly by the substitution of a larger and a smaller number, respectively, in place of $n - 1$ in the exponentials.
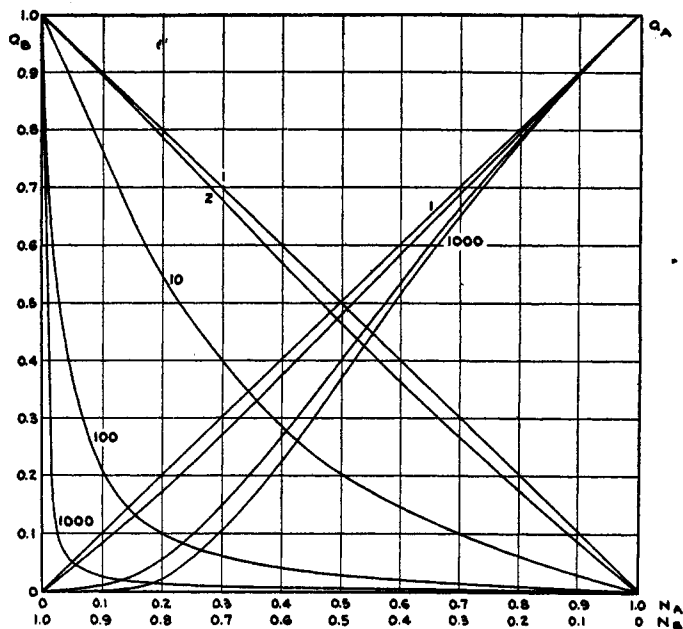
FIG. 1. Variation with mole fraction of the activities of the components for various values of n, indicated by the numbers alongside the curves. (The un-numbered curves for a_A are for $n = 2$ and $n = 10$. The curve for $n = 100$ is practically identical with that for $n = 1000$.)

III. OSMOTIC PRESSURE

The osmotic pressure of a solution is related to the activity of the solvent (B) by the exact thermodynamic equation

$$\Pi = -\frac{RT}{v_B} \ln a_B \qquad (8)$$

v_B is the molal volume of the solvent and T is the absolute temperature. Making use of equation 6, we obtain

$$\Pi = -\frac{RT}{v_B} \left[\frac{n-1}{n} N_A^* + \ln N_B^* \right] \qquad (9)$$

$$\approx \frac{RT}{v_B} \cdot \frac{N_A^*}{n} \left[1 + \frac{n}{2} N_A^* \right] \qquad (10)$$

$$\approx \frac{RT}{v_B} \cdot N_A \left[1 + \frac{n-2}{2} N_A^* \right] \qquad (11)$$

Equation 11 agrees, except for the factor 2 in the final term, with an equation recently published by Powell, Clark, and Eyring (17), which, in the present notation, may be written

$$\Pi = \frac{RT}{v_B} \cdot N_A [1 + (n - 2)N_2^*]$$ (12)

This equation was derived on the basis of the assumptions "that the osmotic pressure is determined by the effective mole fraction,"

$$N_{A,eff} = \frac{N_{A,eff}}{N_B + N_{A,eff}}$$ (13)

rather than the actual 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"—i.e. (for our hypothetical case, in which the volume of a submolecule equals the volume of a solvent molecule),

$$N_{A,eff} = N_A [1 + (n - 2)N_A^*]$$ (14)

The latter assumption seems to the writer highly improbable. Why should a chain molecule become more rigid the more dilute the solution?

As Powell, Clark, and Eyring (and others before them (5, 14)) have shown, there is considerable experimental evidence in favor of an approximately rectilinear relationship between Π/c and c, where c is the concentration in any of the customary units. This relationship follows directly from either equation 11 or equation 12.

From the slopes and intercepts of the Π/c vs. c curves, one can calculate n, and so the average chain length per submolecule. (The "segment lengths" tabulated by Powell, Clark, and Eyring should each be divided by 2, if they are to conform to equation 11 rather than equation 12.) This procedure, however, is based on the assumption that y is large, i.e., that there is a high degree of randomness of orientation at each joint between submolecules. If this is not the case, the calculated value of n will be too small and the computed submolecule length or segment length too large. Moreover, any tendency of the solute molecules to aggregate, e.g., to form clusters of parallel chains, would also tend to decrease the randomness and so the computed value of n, increasing the apparent average length of the submolecule. These effects are doubtless responsible for the apparent segment lengths of ten to fifteen chain atoms in polystyrene and polyethylene oxides, with even larger apparent lengths in rubber and gutta-percha. It is interesting to note, however, that the computed average segment size in various cellulose derivatives corresponds approximately to a single glucose unit, indicating a high degree of randomness of orientation (large y) at each oxygen bridge between the rings.

IV. FREEZING-POINT LOWERING

The lowering of the freezing point of a liquid consisting of small molecules by dissolving in it a substance composed of chain molecules can be treated in much the same way as the osmotic pressure.

The freezing-point lowering (ϑ) is related to the absolute temperature (Θ) of the freezing point of the pure solvent, the heat of fusion (per mole) of the solvent ($\Delta H_f = H_B^0 - H_B^s$), and the activity ($a_B$) of the solvent by the equation

$$\vartheta = -\frac{R\Theta^2}{\Delta H_f} \ln a_B \tag{15}$$

Assuming a_B to be given by equation 6, we have

$$\vartheta = -\frac{R\Theta^2}{\Delta H_f} \left[\frac{n-1}{n} N_A^* + \ln N_B^* \right] \tag{16}$$

$$\approx \frac{R\Theta^2}{\Delta H_f} \cdot \frac{N_A^*}{n} \left[1 + \frac{n}{2} N_A^* \right] \tag{17}$$

$$\approx \frac{R\Theta^2}{\Delta H_f} \cdot N_A \left[1 + \frac{n-2}{2} N_A^* \right] \tag{18}$$

V. SOLUBILITY

Equation 7 for the dependence of a_A on composition and chain length leads to some interesting conclusions regarding the solubilities of long-chain compounds.

For equilibrium between a saturated solution (of A in B) and the pure solid solute (A), the free-energy change is zero. Hence,

$$(\bar{H}_A - H_A^0) + (H_A^0 - H_A^s) - T(\bar{S}_A - S_A^0) - T'(S_A^0 - S_A^s) = 0 \tag{19}$$

Here the four terms are, respectively, the heat of dilution, the heat of fusion, the entropy of dilution (times T), and the entropy of fusion (times T) of the solute. The entropy of dilution we may approximate by the equation

$$\bar{S}_A - S_A^0 = -R \ln a_A \tag{20}$$

where a_A is the activity, given by equation 7, for a solution for which there is no heat of mixing. (In case the intermolecular interactions are such as to diminish markedly the randomness of the mixing, this approximation will not be accurate.)

Each of the other three terms in equation 19 should (11), except for a small end correction, be proportional to n. We can therefore write

$$\frac{(\bar{H}_A - H_A^0) + (H_A^0 - H_A^s) - T(S_A^0 - S_A^s)}{RT} = \kappa_0 + \kappa n \approx \kappa n \tag{21}$$

and so

$$\kappa n \approx -\ln a_A \tag{22}$$

$$\approx -\ln N_A^* + (n-1)N_B^* \tag{23}$$

$$\approx -\ln N_A^* - (n-1)N_A^* + n - 1 \tag{24}$$

Figure 2 shows how, according to equation 24, the solubility (as expressed by N_A^*, the volume fraction of solute in the saturated solution) depends on the chain length (n), for various values of κ. It is seen that the solubility tends to approach either $1 - \kappa$ or zero as the length of the molecule increases, depending on whether κ is less than or greater than unity.
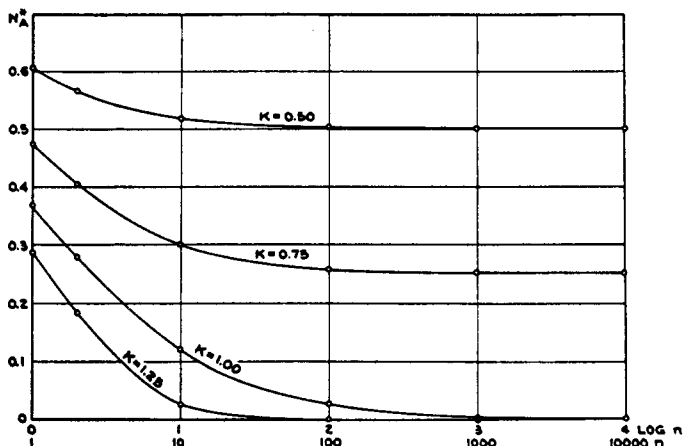

FIG. 2. Variation of solubility (as represented by the volume fraction N_A^*) with chain length, for various values of κ.

A further discussion of solubility, both in single and in mixed solvents, including comparisons with experimental data, is planned for another paper.

VI. SUMMARY

By means of a statistical treatment, equations have been derived for the activities of the components of a solution containing both chain molecules and small (non-chain) molecules. Using these activity equations, relations have been derived and briefly discussed for the osmotic pressure, the lowering of the freezing point, and the solubility of such solutions.

REFERENCES

(1) CHANG, T. S.: Proc. Cambridge Phil. Soc. **35**, 265 (1939).
(2) FOWLER, R. H., AND GUGGENHEIM, E. A.: *Statistical Thermodynamics*. University Press, Cambridge, England (1939).
(3) FOWLER, R. H., AND RUSHBROOKE, G. S.: Trans. Faraday Soc. **33**, 1272 (1937).
(4) GUGGENHEIM, E. A.: Proc. Roy. Soc. (London) **A148**, 304 (1935).
(5) HALLER, W.: Kolloid-Z. **56**, 257 (1931).
(6) HILDEBRAND, J. H.: Chem. Rev. **18**, 315 (1936).
(7) HILDEBRAND, J. H.: *Solubility of Non-electrolytes*, 2nd edition. Reinhold Publishing Corporation, New York (1936).
(8) HILDEBRAND, J. H.: J. Am. Chem. Soc. **59**, 794 (1937).

(9) HILDEBRAND, J. H.: J. Phys Chem. **43**, 109 (1939).
(10) HILDEBRAND, J. H., AND SWENY, J. W.: J. Phys. Chem. **43**, 297 (1939).
(11) HUGGINS, M. L.: J. Phys. Chem. **43**, 1083 (1939).
(12) HUGGINS, M. L.: J. Chem. Phys. **8**, 181 (1940).
(13) HUGGINS, M. L.: J. Chem. Phys. **9**, 440 (1941).
(14) MARK, H.: *Physical Chemistry of High Polymeric Systems.* Interscience Publishers, New York (1940).
(15) MEYER, K. H.: Z. physik. Chem. **B44**, 383 (1939).
(16) MEYER, K. H.: Helv. Chim. Acta **23**, 1063 (1940).
(17) POWELL, R. E., CLARK, C. R., AND EYRING, H.: J. Chem. Phys. **9**, 268 (1941).
(18) SCATCHARD, G.: Chem. Rev. **8**, 321 (1931).

THE SORPTION OF SOLUBLE DYES BY GELATIN[1]

S. E. SHEPPARD, R. C. HOUCK, AND C. DITTMAR

Kodak Research Laboratories, Rochester, New York

The experimental work upon which this communication is based was carried out primarily in connection with certain photographic processes involving the imbibition of dyes.   Neither in detail nor in scope did the investigation consider a number of limitations and factors proper to more complete theoretical study. It was thought, however, that the results obtained offer a useful contribution to the problem of the interaction of dyes with proteins.

No survey will be given of the rather scattered literature upon this subject. A useful, if not complete, bibliography is given in the paper by E. Elöd (6), which covers the subject up to 1932.   Specific references will be noted where pertinent.

The time perhaps has passed when the problem could be discussed in terms of supposedly mutually exclusive theories of physical (electrostatic) adsorption and chemical (stoichiometric) combination.   Actually, it seems that a little less generalization and a greater measure of specific description and discrimination are desirable.   If we have ventured to present these admittedly incomplete studies, it is partly because we have (*1*) compared both acid and basic dyes and (*2*) used both "lime-process" and "acid-process" gelatins.

The significance of the second proviso is as follows: By far the greater number of physicochemical studies with or on gelatin have been made with materials obtained by the alkaline dehairing and plumping of calfskins, followed by washing, neutralization with acid, and extraction with hot water.   Such material has an isoelectric point at pH 4.7 to 5.2 (9, 21) and, apart from minor wrangles