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Theory of Solutions of High Polymers¹

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Introduction

In recent years it has become increasingly evident that the large deviations from "ideal" behavior shown by solutions of long-chain molecules are due primarily to deviations from ideality of the *entropy* of mixing, rather than to any *heat* of mixing effect, such as is responsible for most deviations in solutions containing only small molecules.

The entropy of mixing of chain molecules with small molecules has been discussed qualitatively by Meyer.² Recently, Flory³ and the writer⁴ have, independently, treated the subject in a quantitative manner, with results which are essentially equivalent.

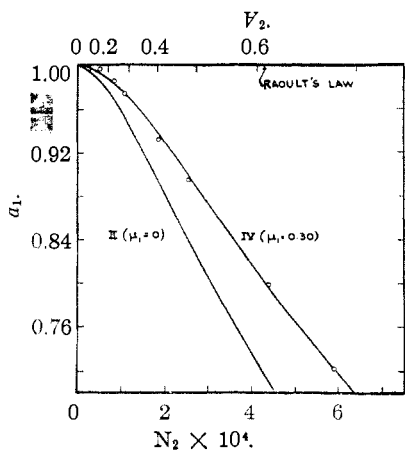


Fig. 1.—Activity as a function of mole fraction for the rubber-chloroform system at 25°. Vapor pressure data by Stamberger⁵; the curves correspond to Eq. 1; $V_2/V_1 = 3644$.

We consider a hypothetical solution consisting of N_1 spherical molecules (Type 1) and N_2 chain molecules (Type 2), each of the latter consisting of n submolecules of the same size as each Type 1 molecule. We assume that there is no volume change on mixing and that the intermolecular energy interactions are not such as to interfere

with the randomness which would result if the heat of mixing were zero. We distribute the Type 1 molecules and Type 2 submolecules among $N_1 + nN_2$ sites, first adding the Type 2 molecules, one submolecule at a time, and then the Type 1 molecules. We count the number of different ways in which each can be added and then multiply these numbers together to obtain the total number of configurations. From the total number of *different* configurations possible, we proceed by well-known methods to the desired equations for the entropy of mixing and the activities of the components.

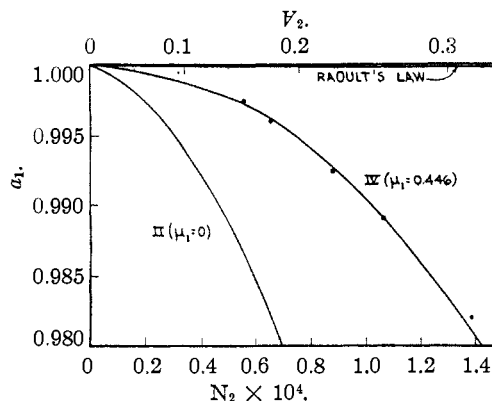


Fig. 2.—Activity vs. mole fraction for the rubber-benzene system at 15–20°. Swelling pressure data by Posnjak.⁶ $V_2/V_1 = 3307$.

Equations for the Activities.—For the logarithms of the activities, we obtain the equations

$$\ln a_1 = \ln V_1 + \left(1 - \frac{\bar{V}_1}{\bar{V}_2}\right) V_2 + \mu_1 V_2^2 \quad (1)$$

and

$$\ln a_2 = \ln V_2 + \left(1 - \frac{\bar{V}_2}{\bar{V}_1}\right) V_1 + \mu_2 V_1^2 \quad (2)$$

with the empirical constants, μ_1 and μ_2 , related by the equation

$$\mu_1 \bar{V}_2 = \mu_2 \bar{V}_1 \quad (3)$$

\bar{V}_1 and \bar{V}_2 refer to the volume fractions⁷ and \bar{V}_1 and \bar{V}_2 to the partial molal volumes of the two components. (With negligible error for our purpose we can assume the partial molal volumes to be equal to the actual molal volumes of the pure

(1) Presented before the Division of Paint, Varnish and Plastics Chemistry at the Memphis Meeting of the American Chemical Society, April 22, 1942.

(2) K. H. Meyer, *Z. physik. Chem.*, **B44**, 383 (1939); *Helv. Chim. Acta.*, **23**, 1063 (1940).

(3) P. J. Flory, *J. Chem. Phys.*, **9**, 660 (1941); **10**, 51 (1942).

(4) M. L. Huggins, *ibid.*, **9**, 440 (1941); *J. Phys. Chem.*, **46**, 151 (1942); *Ann. N. Y. Acad. Sciences*, **41**, 1 (1942).

(5) P. Stamberger, *J. Chem. Soc.*, 2318 (1929).

(6) E. Posnjak, *Kolloidchem. Beihefte*, **3**, 417 (1912).

(7) The new symbol, \bar{V} , is introduced to replace N^* , previously used by the writer⁴ for volume fraction.

components.) The last term in each of Eqs. 1 and 2 takes care of the heat of mixing, deviations from complete randomness of mixing, and other factors.

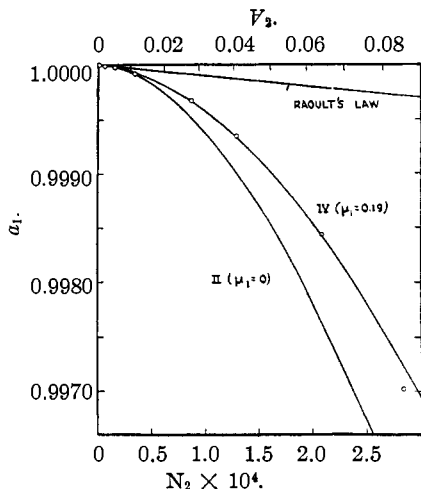


Fig. 3.—Activity vs. mole fraction for solutions of nitrocellulose in acetone at 20°: osmotic pressure data by Duclaux and Wollman⁸; $V_2/V_1 = 330$.

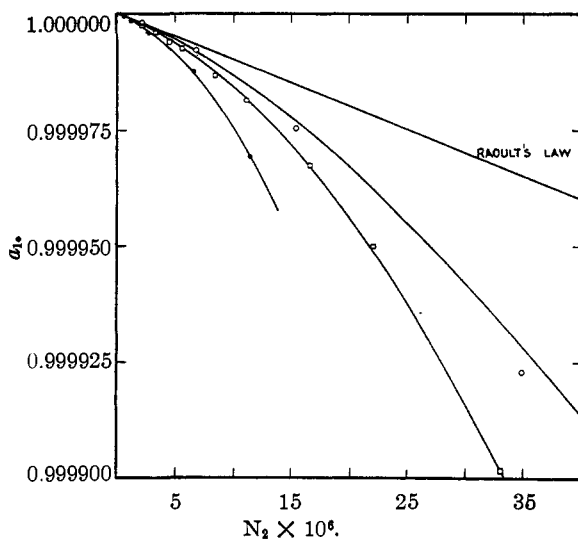


Fig. 4.—Activity vs. mole fraction for solutions of nitrocellulose in acetone: osmotic pressure data on three samples, differing with regard to the degree of nitration, the average chain length, and the temperature. Dots represent data by Dobry⁹ ($\mu_1 = 0.265$; $V_2/V_1 = 793$; $t = 22^\circ$). Squares represent data by Schulz¹⁰ ($\mu_1 = 0.300$; $V_2/V_1 = 550$; $t = 27^\circ$). Circles represent data by Duclaux and Wollman⁸ ($\mu_1 = 0.19$; $V_2/V_1 = 330$; $t = 20^\circ$).

For testing the equations just given, we may use activities calculated from vapor pressure, os-

(8) J. Duclaux and E. Wollman, *Compt. rend.*, **152**, 1580 (1911).
 (9) A. Dobry, *J. chim. phys.*, **32**, 50 (1935).
 (10) G. V. Schulz, *Z. physik. Chem.*, **A176**, 317 (1936).

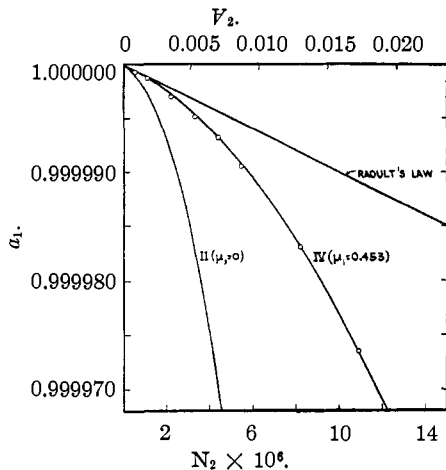


Fig. 5.—Activity vs. mole fraction for solutions of polyethylene oxide in water at 27°: osmotic pressure data by Schulz¹⁰; $V_2/V_1 = 1614$.

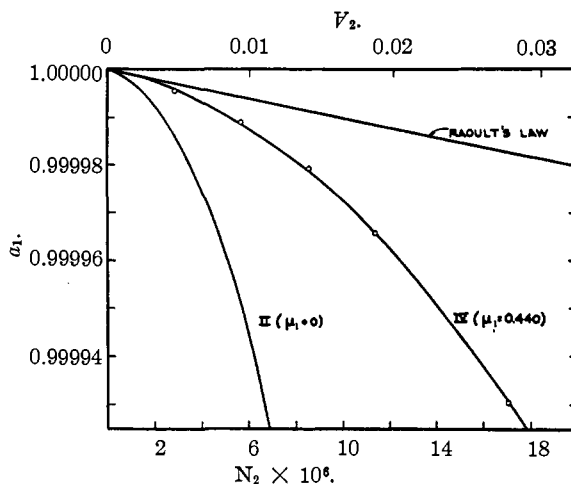


Fig. 6.—Activity vs. mole fraction for solutions of polystyrene in toluene at 27°: osmotic pressure data by Schulz¹⁰; $V_2/V_1 = 1667$.

motric pressure, swelling pressure, boiling point elevation, or other measurements. A thorough survey of the pertinent data in the literature shows the agreement to be excellent, for both short- and long-chain molecules.⁴ This agreement is exemplified by Figs. 1 to 8, in which the activity of the solvent is shown as a function of the mole fraction of the solute for solutions of various long-chain compounds in small-molecule solvents. In each of these figures the straight line represents Raoult's law; the other curves represent Eq. 1 with μ_1 equal to zero (curves II) or an empirical value (curves IV).

Osmotic Pressure.—The osmotic pressure of a solution is related to the activity of the solvent by the equation

$$\Pi = - \frac{RT}{V_1} \ln a_1 \quad (4)$$

R is the gas law constant and T the absolute temperature. Combining this with equation (1), we obtain

$$\frac{\Pi}{V_2} + \frac{RT}{V_1} \left(\frac{\ln F_1}{V_2} + 1 \right) = \frac{RT}{V_2} - \frac{RT \mu_1 V_2}{V_1} \quad (5)$$

Since

$$\ln V_1 = -V_2 - \frac{V_2^2}{2} - \frac{V_2^3}{3} - \dots \quad (6)$$

we can write, for dilute solutions (small V_2)

$$\frac{\Pi}{V_2} - \frac{RT V_2^2}{3V_1} = \frac{RT}{V_2} + \frac{RT}{V_1} \left(\frac{1}{2} - \mu_1 \right) V_2 \quad (7)$$

For concentrations in weight fractions (W_2) or in grams of solute per cubic centimeter of solution (C_2), the corresponding equations are

$$\frac{\Pi}{W_2} - \frac{RT d_1^2 W_2^2}{3M_1 d_2^3} \approx \frac{RT d_1}{M_2} + \frac{RT d_1^3}{M_1 d_2^2} \left(\frac{1}{2} - \mu_1 \right) W_2 \quad (8)$$

and

$$\frac{\Pi}{C_2} - \frac{RT d_1 C_2^2}{3M_1 d_2^3} = \frac{RT}{M_2} + \frac{RT d_1}{M_1 d_2^2} \left(\frac{1}{2} - \mu_1 \right) C_2 \quad (9)$$

where d_1 and d_2 are the densities and M_1 and M_2 the molecular weights of the components.

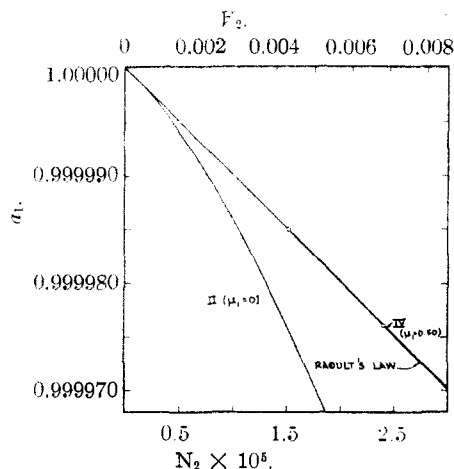


Fig. 7.—Activity vs. mole fraction for solutions of polyvinyl chloride in dioxane at 27°: osmotic pressure data by Staudinger and Schneiders¹¹; $V_2/V_1 = 286$.

Given a set of accurate osmotic pressure values for different concentrations of a given solution, a plot of the quantity represented on the left side of one of these Eqs., 7, 8, or 9, against the concentration (V_2 or W_2 or C_2) should yield a straight line. From its intercept with the axis of ordinates (concentration = 0), one can obtain the mo-

lecular weight of the solute; from its slope one can compute μ_1 .

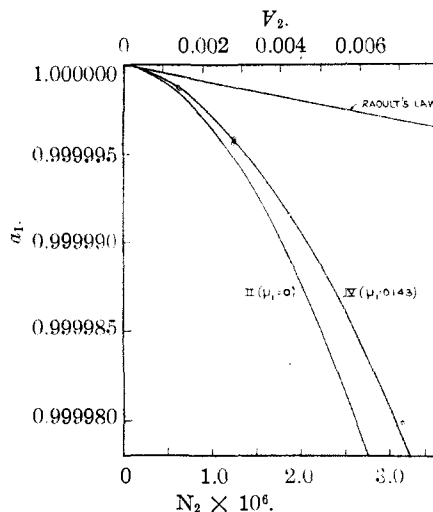


Fig. 8.—Activity vs. mole fraction for solutions of polyvinyl chloride in tetrahydrofuran at 27°: osmotic pressure data by Staudinger and Schneiders¹¹; $V_2/V_1 = 2264$.

The second term on the left side of each of these equations is negligible at most concentrations at which osmotic pressure measurements of solutions of high molecular compounds are made. We thus have a theoretical basis for the well-known¹² rectilinear relationship between Π/C_2 and C_2 (or between Π/W_2 and W_2).

Since μ_1 should be independent of the chain length of the solute molecules—assumed to be alike in other respects—the slopes of the lines obtained for a series of fractions of a given type of polymer should all be equal. On the other hand, a change of either the solvent or the type of solute (e. g., from a nitrocellulose of a certain degree of nitration to one with a different degree of nitration) should change the slope.

These conclusions are amply borne out by the experimental facts, as shown by Figs. 9 to 13.

Separation of Phases. Gels.—Assuming Eq. 1 to hold, the activity of the small-molecule component, in equilibrium with long-chain molecules having \bar{V}_2/\bar{V}_1 equal to 100 or ∞ , varies with composition as shown in Figs. 14 and 15. If μ_1 is larger than a certain critical value, the calculated curve for activity vs. N_2 (or V_2 or W_2 or C_2) exhibits a minimum and a maximum, indicating a separation of the system into two phases. The critical value of μ_1 depends on the ratio of the partial molal volumes according to the equation

(12) Cf. H. Mark, "Physical Chemistry of High Polymeric Systems," Interscience Publishers, New York, N. Y., 1940, p. 240.

(11) H. Staudinger and J. Schneiders, *Ann.*, **541**, 151 (1939).

$$\mu_1(\text{crit.}) = \frac{1}{2}[1 + (\bar{V}_1/\bar{V}_2)^{1/2}]^2 \quad (10)$$

This dependence is shown graphically in Fig. 16.

the other phase is related to μ_1 and the molal volume ratio according to the following equation, obtained by substituting Eq. 11 into Eq. 1.

$$\ln \bar{V}_1 = \left(\frac{\bar{V}_1}{\bar{V}_2} - 1 \right) \bar{V}_2 - \mu_1 \bar{V}_2^2 \quad (12)$$

If the concentration and intermolecular attractions of the long-chain molecule component are such that the motion of each such molecule is greatly restricted by its neighbors, the solution will have a degree of rigidity—it will have the properties of a gel. The effective molecular weight and molecular volume will be very large, relative to the values for the small-molecule component. Hence

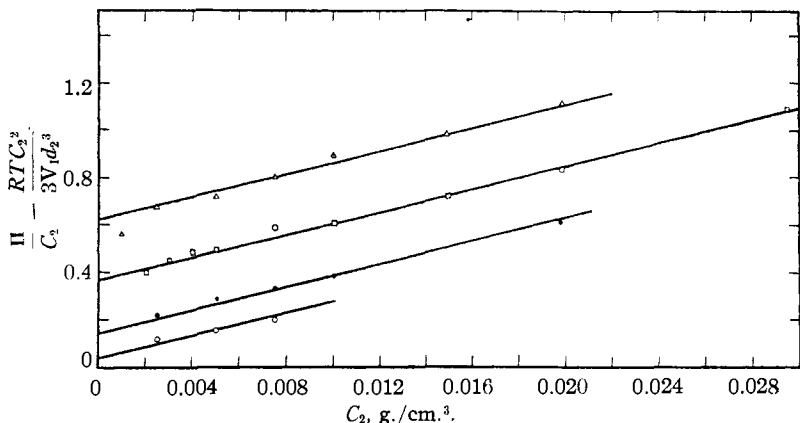


Fig. 9.—Osmotic pressure dependence on concentration for solutions of certain nitrocellulose fractions in acetone at 27°: data by Schulz.¹⁰ The straight lines represent Eq. 9; $\mu_1 = 0.300$.

$$\ln \bar{V}_1 = - \bar{V}_2 - \mu_1 \bar{V}_2^2 \quad (13)$$

We should expect this equation to be applicable to gels in general, since the theoretical derivation of Eqs. 1 and 2 is such that they would be expected to hold as well for flexible *network* molecules as for *chain* molecules.

Figure 17 shows the solubility, as function of μ_1 , of a small-molecule compound in a gel, for effective molal volume ratios (\bar{V}_2/\bar{V}_1) of 100 (Eq. 12) and ∞ (Eq. 13). It can be seen that the composition is very sensitive to the value of μ_1 , but not to the relative sizes of the molecules—unless μ_1 is close to the critical value.

The data of Brønsted and Volqvartz on the swelling of polystyrene in alkyl laurates at different temperatures make it possible to determine the variation of μ_1 with temperature for each of

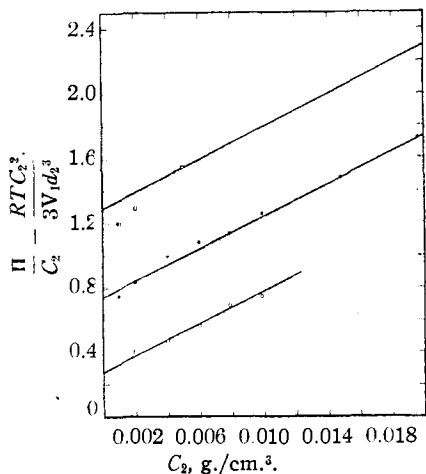


Fig. 10.—Osmotic pressure dependence on concentration for polyethylene oxide fractions in water at 27°: data by Schulz¹⁰; $\mu_1 = 0.453$.

For high molecular solutes, unless μ_1 is very near the critical value

$$a_1 \approx 1 \quad (11)$$

for both phases. One phase is practically pure solvent, in agreement with the experimental findings of Brønsted and Volqvartz,¹³ on the swelling of polystyrene in laurate esters. The composition of

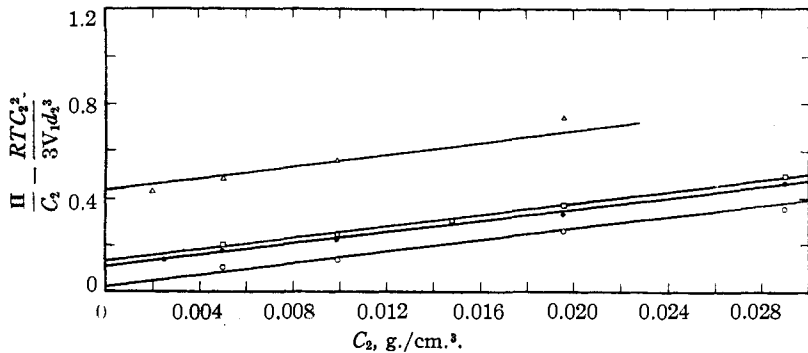


Fig. 11.—Osmotic pressure dependence on concentration for polystyrene fractions in toluene at 27°: data by Schulz¹⁰; $\mu_1 = 0.440$.

(13) J. N. Brønsted and K. Volqvartz, *Trans. Faraday Soc.*, **35**, 576 (1939).

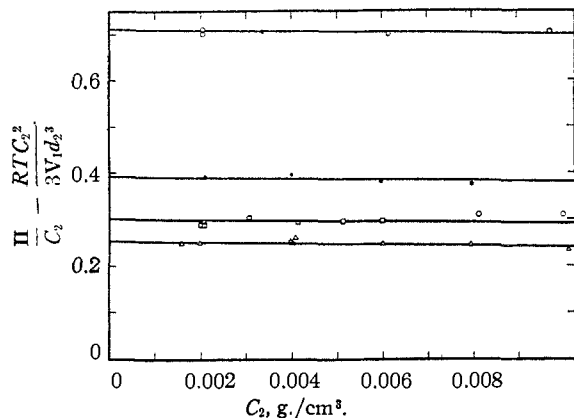


Fig. 12.—Osmotic pressure dependence on concentration for polyvinyl chloride fractions in dioxane at 27°: data by Staudinger and Schneiders¹¹; $\mu_1 = 0.523$.

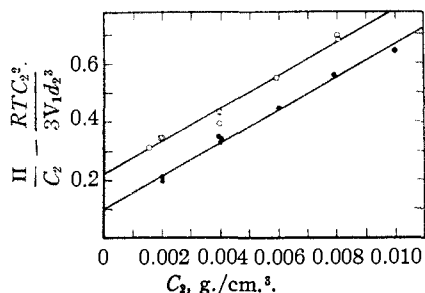


Fig. 13.—Osmotic pressure dependence on concentration for polyvinyl chloride fractions in tetrahydrofuran at 27°: data by Staudinger and Schneiders¹¹; $\mu_1 = 0.143$.

the systems studied. As Fig. 18 shows, the relation

$$\mu_1 = \alpha_1 + \beta_1/T \quad (14)$$

holds, within the probable experimental error. The straight lines in this figure are drawn for a constant value (-0.83) for α_1 , with values of β_1

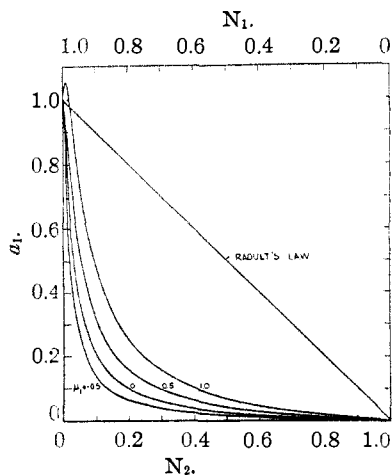


Fig. 14.—Activity vs. mole fraction, according to Eq. 1, for $V_2/V_1 = 100$, with certain values of μ_1 .

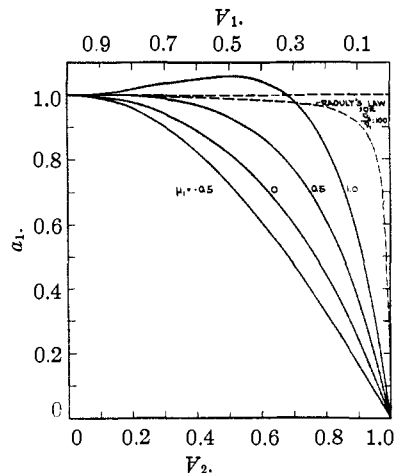


Fig. 15.—Activity vs. volume fraction, according to Eq. 1, for $V_2/V_1 = \infty$, with certain values of μ_1 . The corresponding curves for finite values of the molal volume ratio are lower than those shown; for $V_2/V_1 \geq 100$ the difference is approximately the width of the lines, or less.

varying from 388 for ethyl laurate to 518 for isoamyl laurate. The experimental data, however, are insufficient to establish whether or not the α_1 values really are accurately the same for all of these systems.

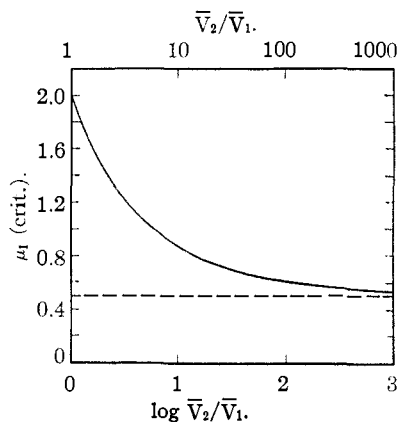


Fig. 16.—Dependence on the molal volume ratio of the critical value of μ_1 for separation of a solution into two phases, according to Eq. 10.

Probably the most important of the terms contributing to μ_1 is the heat of mixing term. From the work of van Laar,¹⁴ Scatchard,¹⁵ and Hildebrand,¹⁶ this term would be expected to be approximately of the form $\bar{V}_1 A_{12}/RT$, where A_{12} is a constant which measures the difference between the average cohesive energy density due to at-

(14) J. J. van Laar, *Z. physik. Chem.*, **A137**, 421 (1928).

(15) G. Scatchard, *Chem. Rev.*, **8**, 321 (1931).

(16) (a) J. H. Hildebrand, *THIS JOURNAL*, **57**, 866 (1935); (b) *Chem. Rev.*, **18**, 315 (1936); (c) "Solubility of Non-Electrolytes," second edition, Reinhold Publ. Corp., New York, N. Y., 1936, p. 73.

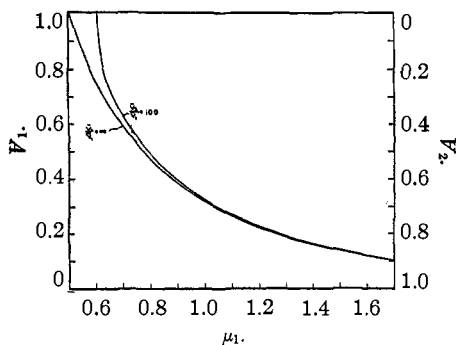


Fig. 17.—Dependence on μ_1 of the composition (volume fraction) of the polymer-rich phase in a two-phase system, for V_2/V_1 equal to ∞ and 100. Except for $\mu_1 \approx \mu_1(\text{crit.})$, the curves agree with Eq. 12.

traction between *like* molecules and that due to attraction between *unlike* molecules. The greater the tendency of like molecules to cluster together, the larger is A_{12} and, in general, μ_1 .

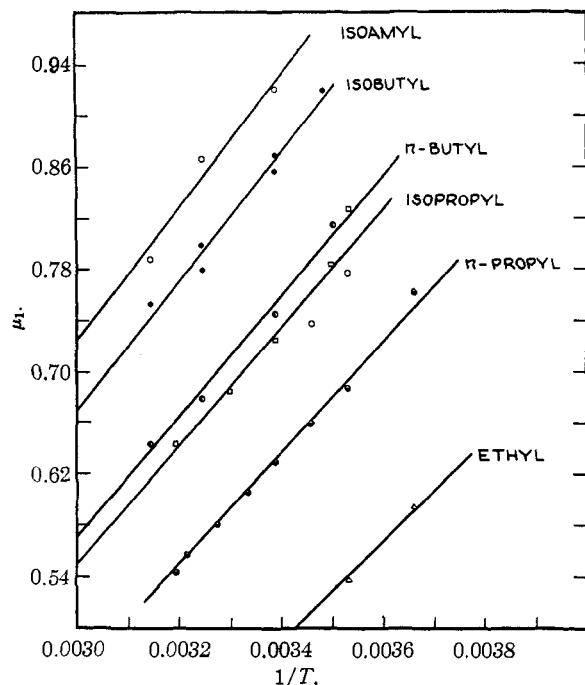


Fig. 18.—Variation of μ_1 with the reciprocal of the absolute temperature, for polystyrene swollen in alkyl laurates. The straight lines represent Eq. 14, with $\alpha_1 = -0.83$ in each case and β_1 equal to 388, 431, 460, 467, 500 and 518 for ethyl, *n*-propyl, . . . isoamyl laurates; data by Brønsted and Volqvartz.¹³

Figure 19 shows that for the alkyl laurates in polystyrene, β_1 is roughly proportional to V_1 (and so to \bar{V}_1). The inexactness of this proportionality is probably attributable in part to variation in A_{12} and in part to the existence of other terms contributing to μ_1 .

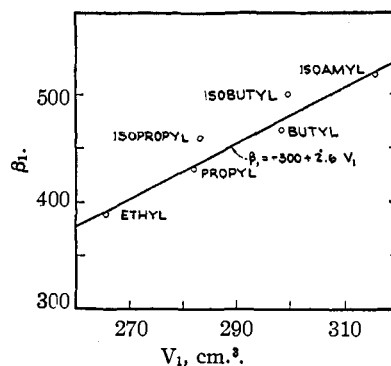


Fig. 19.—Relation between the constant β_1 of Eq. 14 and the molal volume of the small-molecule component, for polystyrene-alkyl laurate gels.¹³

Figure 20 shows the measure of agreement between the experimental polystyrene-laurate gel compositions and those computed from Eqs. (13) and (14).

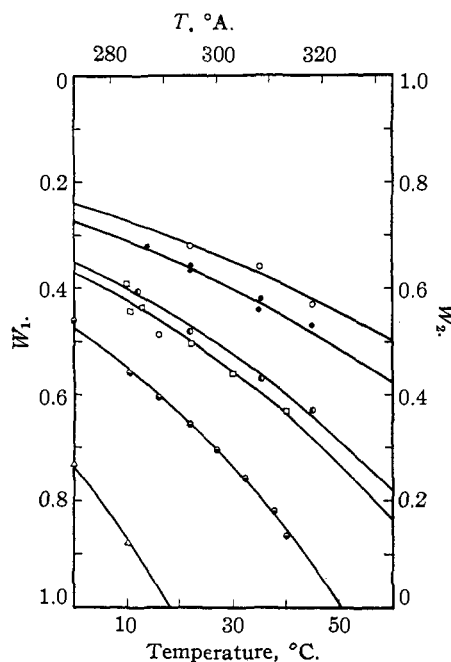


Fig. 20.—Comparison of experimental¹³ compositions of polystyrene-alkyl laurate gels and the theoretical curves corresponding to Eqs. 12 and 14: O, isoamyl; ●, isobutyl; ○, *n*-butyl; □, isopropyl; ⊙, *n*-propyl; △, ethyl.

Solubility of a Polymer in a Small-Molecule Liquid.—For equilibrium between a solid and its (saturated) solution in a liquid, the fugacity of the substance composing the solid must be the same in the two phases. Assuming the heat of fusion (ΔH_f) of the solid not to vary with the temperature between the temperature of the system and the melting point (T_f), the following

relation holds. (Compare Hildebrand's¹⁷ treatment of ideal solutions.)

$$\ln u_2 = -\frac{\Delta H_f}{R} \left(\frac{T_f - T}{TT_f} \right) \quad (15)$$

Combining this equation with Eq. 2 and making the approximation that

$$\mu_2 = \frac{\bar{V}_2}{\bar{V}_1} \mu_1 = \frac{\bar{V}_2 B_{12}}{RT} \quad (16)$$

where B_{12} is a constant independent of temperature, we obtain

$$\ln V_2 = -\frac{\Delta H_f}{R} \left(\frac{T_f - T}{TT_f} \right) - \frac{\bar{V}_2 B_{12} V_1^2}{RT} + \left(\frac{\bar{V}_2}{\bar{V}_1} - 1 \right) V_1 \quad (17)$$

This equation accounts quantitatively (Fig. 21) for the temperature dependence of the solubility of the normal paraffins, $C_{34}H_{70}$ and $C_{60}H_{122}$, in decalin (decahydronaphthalene, $C_{10}H_{18}$). In com-

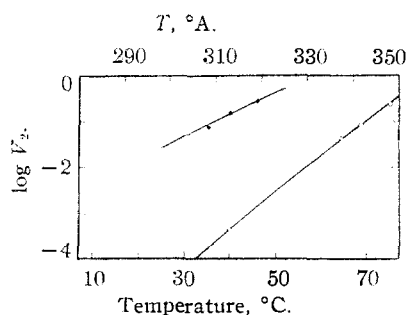


Fig. 21.—Solubility (volume fraction) of n - $C_{34}H_{70}$ and n - $C_{60}H_{122}$ in decalin, as a function of temperature. The curves correspond to Eq. 17, after substitution of Eqs. 18, 19, 20 and 21; experimental data by Meyer and van der Wyk¹⁸: ●, n - $C_{34}H_{70}$, $B_{12} = 1.97$; ○, n - $C_{60}H_{122}$, $B_{12} = 2.66$.

puting the theoretical curves for this figure, we have made use of the thermodynamic relation

$$T_f = \Delta H_f / \Delta S_f \quad (18)$$

and the following empirical expressions:^{19,20,21}

$$\Delta H_f = -1750 + 608.5n \quad (19)$$

$$\Delta S_f = 4.04 + 1.491n \quad (20)$$

$$\bar{V}_2 = V_2 = 26.96 + 16.49n + (29/n) \quad (21)$$

Here, n denotes the number of carbon atoms in the paraffin.

In these systems, the ratio V_2/V_1 is small (3.73 and 6.44), hence it is not surprising that the empirical values of B_{12} are slightly different (1.97 and 2.66) for the two systems. For very long chains

(17) Ref. 16c, pp. 32-34.

(18) K. H. Meyer and A. van der Wyk, *Helv. Chim. Acta*, **20**, 1313 (1937).

(19) W. E. Garner, K. Van Bibber and A. M. King, *J. Chem. Soc.*, 1533 (1931).

(20) M. L. Huggins, *J. Phys. Chem.*, **43**, 1083 (1939).

(21) M. L. Huggins, *This Journal*, **63**, 116 (1941).

which are similar in other respects, B_{12} would be expected to be independent of chain length.

For long chains in general we may make the approximations

$$\Delta H_f = nh_2 \quad (22)$$

$$\Delta S_f = ns_2 \quad (23)$$

and

$$V_2 = nv_2 \quad (24)$$

where h_2 , s_2 and v_2 are heats of fusion, entropies of fusion, and volumes per "monomeric unit" of the chain compound. Then

$$\ln V_2 = -V_1 + n \left[\frac{s_2}{R} + \frac{v_2 V_1}{\bar{V}_1} - \frac{h_2}{RT} - \frac{v_2 B_{12} V_1^2}{RT} \right] \quad (25)$$

If the polymer is not very soluble, V_1 is approximately equal to unity. Then (provided the quantity in brackets in this equation is not close to zero)

$$\ln V_2 \approx n \left(\alpha - \frac{\beta}{T} \right) \quad (26)$$

and

$$V_2 \approx \exp \left[n \left(\alpha - \frac{\beta}{T} \right) \right] \quad (27)$$

where

$$\alpha = \frac{s_2}{R} + \frac{v_2}{\bar{V}_1} \quad (28)$$

and

$$\beta = \frac{h_2}{R} + \frac{v_2 B_{12}}{R} \quad (29)$$

These equations show the dependence of the solubility of a slightly soluble high polymer on the temperature and on other factors.

Further discussion and experimental tests of these solubility relations, together with a treatment of the solubility of polymers in mixed solvents, will be given at a later time.

The writer is glad to express here his indebtedness to Mrs. Dorothy Owen Davis for much help with the calculations and figures for this paper.

Summary

1. Theoretical equations derived for the activities of the components of a solution of chain molecules in a small-molecule solvent are in good agreement with experimental vapor pressure, osmotic pressure, swelling pressure and solubility measurements. A single constant, μ_1 , partly but not entirely due to the heat of mixing effect, must be evaluated empirically.

2. Equations deduced for osmotic pressure as a function of composition account for the known straight-line relationship obtained when the ratio of osmotic pressure to concentration is plotted

against the concentration. For long chains the slope of this line depends on μ_1 , but not on the chain length of the solute molecules.

3. The quantitative relationships derived for flexible chain molecules should also be applicable to flexible network molecules. For values of μ_1 greater than a critical value, the theoretical activity-composition curve indicates separation into two phases. One consists of the nearly pure small-molecule component. The other is usually a gel; its composition depends primarily on the value of μ_1 . From experimental values of equilibrium com-

positions for polystyrene-alkyl laurate gels at different temperatures, μ_1 is a rectilinear function of V_1/T , the ratio of the molal volume of the small-molecule component to the absolute temperature.

4. An equation for the solubility of a solid chain compound in a small-molecule liquid is derived and found to be in agreement with measurements at various temperatures of the solubilities of $n\text{-C}_{34}\text{H}_{70}$ and $n\text{-C}_{60}\text{H}_{122}$ in decalin. Simplified solubility equations, applicable to long-chain polymers, are deduced.

ROCHESTER, N. Y.

RECEIVED APRIL 28, 1942

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

Studies in Dehydrogenation.¹ II. Spirocyclopentane-1,1'-tetralin

BY MEYER LEVITZ² AND MARSTON TAYLOR BOGERT

The investigation of the rearrangement and dehydrogenation of spirocyclohexane-1,1'-indane¹ over a palladium on charcoal catalyst showed the importance of cautious postulation of structure based on the products obtained by dehydrogenation. Thus, a compound thought to be a hydrophenanthrene must be carefully examined if the only proof of its structure is dehydrogenation to phenanthrene, especially if its synthesis can theoretically yield isomeric spiranes.

When passed over Pd-C at 370-375°, spirocyclohexane-1,1'-indane was rearranged and dehydrogenated to phenanthrene while at 400-420° the main product was anthracene. This formation of both phenanthrene and anthracene from a tricyclic spirane has since been applied to the detection of spiranes.³ It therefore appears important to study the action of other spiranes under similar dehydrogenation conditions. The closest isomer to the spirane previously studied is spirocyclopentane-1,1'-tetralin. This compound was therefore passed over the Pd-C catalyst in the vapor phase in a new apparatus especially designed to allow this repeated exposure of the hydrocarbon to the catalyst without the necessity of removing it from one end of the apparatus and reintroducing it at the other.

The heating element (A) was a brass tube 16 mm. in diameter and 75 cm. long, wound with

nichrome wire. The closely fitting Pyrex dehydrogenation tube (B), inserted in the heating element, was closed at one end and had a stopcock sealed on the other end for the removal of samples during the dehydrogenation. The temperature inside this tube was checked beforehand with the temperature inside the thermometer well (C) enclosed by the heating coil. T-Tubes (D and D') were sealed on the dehydrogenation tube 7 cm. from each end of the brass tube. Two 3-way stopcocks (E and E') were connected to these T-tubes in such a way that either end of the dehydrogenation tube could be opened to the mercury trap (F) and a bubble counter (G), while the other end was opened to tube (H) leading to the supply of nitrogen or hydrogen. The palladium catalyst was prepared according to the method of Linstead and Thomas.⁴ It was thoroughly mixed with twice its weight of asbestos and packed into the dehydrogenation tube with a space of 8 cm. left at each end as a preheating zone for the compound. The catalyst was changed for each run.

In operation the compound was pipetted into the dehydrogenation tube through (D) while the apparatus was tilted to prevent contact with the catalyst. Washed and dried nitrogen was passed into the apparatus through (H) to displace the air while the temperature was raised to the desired point. During this time stopcock (E) was open to (H) while stopcock (E') led to the mercury trap.

(1) For the first paper in this series see Levitz, Perlman, and Bogert, *J. Org. Chem.*, **6**, 105 (1941).

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(3) Marvel and Walton, *J. Org. Chem.*, **7**, 88 (1942).

(4) Linstead and Thomas, *J. Chem. Soc.*, 1127 (1940).