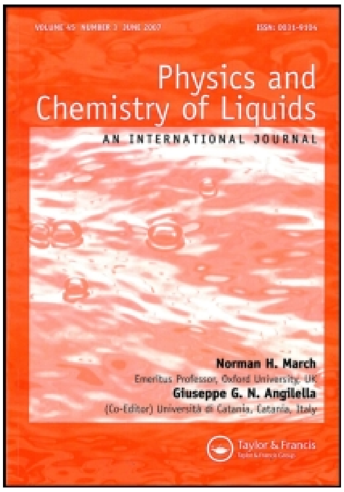

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Solution Solvent Couples Solute Molecules and Enhances Their Internal Tension

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Solution Solvent Couples Solute Molecules and Enhances Their Internal Tension

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A thermodynamic argument is used to show that all colligative properties of a substance 2 (solute) in a solution with a liquid substance 1 (solvent) differ from those of the pure condensed phase of solute precisely as if the internal tension between molecules of solute in the solution was increased by π_2, the osmotic pressure of solute in the solution. It follows from this argument that molecules of solvent serve both to couple the molecules of solute and to enhance the tension in the coupling force between them by an amount π_2. It may be inferred that pressure dependent chemical properties, like all partial molar quantities of the solute, are altered by this enhanced internal tension. A plausible mechanism is proposed by which the internal solute and solvent tensions are enhanced, as required by thermodynamic argument.

INTRODUCTION

When n_2 moles of substance 2 are dissolved in n_1 moles of substance 1, it has been shown by thermodynamic argument that the properties of substance 1 in solution differ from those of pure 1 precisely as if the internal tension in the cohesive force between molecules of substance 1 is increased by the osmotic pressure of substance 1, π_1, Hulett,[1] Hammel.[2] Since $\mu_1(T, p, x_1) = \mu_1^0(T, p - \pi_1)$, it was shown that $\bar{V}_1(T, p, x_1) = \bar{V}_1^0(T, p - \pi_1)$, where μ_1 and μ_1^0 are the chemical potentials and where $\bar{V}_1$ and $\bar{V}_1^0$ are the partial molar and molar volumes of substance 1 in solution and pure substance 1, respectively. These statements are exact for any T, p and x_1 no matter what the compressibility of substance 1 is at any T and p and no matter how π_1 relates to x_1.

The purpose of this article is three-fold: 1) to use the same thermodynamic argument to show that all colligative properties of substance 2 in the solution differ from those of pure condensed phase of substance 2 precisely as if the internal tension between molecules of substance 2 is increased by π_2, 2) to show that molecules of substance 1 serve both to couple the molecules of substance 2 and to enhance the tension in the coupling force between them an amount π_2, the osmotic pressure of substance 2 in the solution and 3) to suggest a plausible mechanism by which the internal solute and solvent tensions are enhanced, as required by thermodynamic argument.

The altered state of substance 2 in a binary solution

When n_2 moles of substance 2 are dissolved in n_1 moles of substance 1, the mole fraction of 2 in the solution is $x_2 = n_2/n_1 + n_2$. Suppose the pressure applied to the solution is increased from p to $p + \pi_2$ at constant T. The chemical potential of substance 2 in the solution will increase an amount

$$\mu_2(T, p + \pi_2, x_2) - \mu_2(T, p, x_2) = \int_p^{p+\pi_2} \overline{V}_2 \mathrm{d}p, \tag{1}$$

where $\overline{V}_2$ is the partial molar volume of substance 2. Now suppose the pressure applied to the pure condensed phase of substance 2 is decreased from p to $p - \pi_2$ at T. The chemical potential of pure substance 2 will diminish an amount

$$\mu_2^0(T, p - \pi_2) - \mu_2^0(T, p) = \int_p^{p-\pi_2} \overline{V}_2^0 \mathrm{d}p, \tag{2}$$

where $\overline{V}_2^0$ is the molar volume of pure 2. If at T a pressure $p + \pi_2$ is applied to the solution and a pressure p is applied to pure 2, then the chemical potentials of substance 2 in solution and pure 2 are the same since π_2 is the osmotic pressure of substance 2, i.e.

$$\mu_2(T, p + \pi_2, x_2) = \mu_2^0(T, p). \tag{3}$$

Likewise, if at T a pressure p is applied to the solution and a pressure $p - \pi_2$ is applied to pure 2, then

$$\mu_2(T, p, x_2) = \mu_2^0(T, p - \pi_2). \tag{4}$$

If now Eq. (3) is combined with Eq. (1) and if Eq. (4) is combined with Eq. (2) and if the resulting equations are summed, it follows that

$$\int_p^{p+\pi_2} \overline{V}_2 \mathrm{d}p = \int_{p-\pi_2}^{p} \overline{V}_2^0 \mathrm{d}p. \tag{5}$$

In other words, no matter what the compressibility of the substance 2 is at any T and p, it follows from Eq. 5 that

$$\overline{V}_2(T, p, x_2) = \overline{V}_2^0(T, p - \pi_2) \tag{6}$$

and that

$$\overline{V}_2(T, p + \pi_2, x_2) = \overline{V}_2^0(T, p). \tag{7}$$

Thus, the chemical potentials and the molar volumes of substance 2 in solution and pure 2 differ precisely as if the internal tension between the molecules of substance 2 in the solution was increased by π_2, the osmotic pressure of substance 2. Furthermore, the other colligative properties of the solute 2 in the solution and of pure 2 differ as if the internal tension between the molecules of substance 2 in the solution was enhanced by π_2.

Dual effects of substance 1 (solvent) on substance 2 (solute)

In a binary solution, n_2 is often very much less than n_1 so that $x_2 \ll 1$ and each molecule of substance 2 is surrounded by many molecules of substance 1. Such a solution will serve to illustrate the dual effects of substance 1 on substance 2, namely to couple the molecules of 2 so that the internal tension in the coupling force between them can be enhanced an amount π_2. The illustration will be made by comparing an equal number and distribution of molecules 2 in the vapor phase and in a solution, Figure 1.

In Figure 1A, pure substance 2 is illustrated in the liquid and vapor phases. The liquid 2 is enclosed in a cylinder with a piston so that a pressure p_2^v can be applied to it. The top surface of the cylinder is porous only to the vapor of substance 2. Neither liquid 2 nor any other substance can penetrate it. The vapor pressure of 2 above the semiporous top surface of the right cylinder

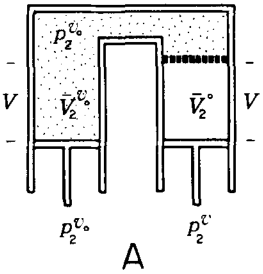

FIGURE 1A. Pure substance 2 is illustrated in liquid phase in the right cylinder at T and applied pressure p_2^v and also in vapor phase at T and p_2^{vo}, where p_2^{vo} is the vapor pressure of liquid 2 at T and p_2^v. The molar volume of pure liquid 2 is $\overline{V}_2^0(T, p_2^v)$ and the molar volume of pure vapor 2 is $\overline{V}_2^{vo}(T, p_2^{vo})$. The volume $V = n_2^0\overline{V}_2^0$ where n_2^0 is the moles of liquid 2 in the right cylinder.

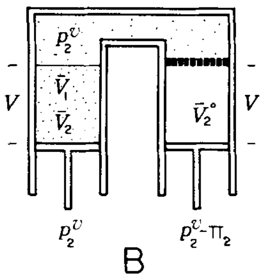

FIGURE 1B As in 1A, n_2^0 moles of pure liquid 2 is in the right cylinder at T, but the applied pressure is now $p_2^v - \pi_2$. Substance 2 is also in vapor phase in equilibrium with pure liquid 2 at T and $p_2^v - \pi_2$ and in equilibrium with n_2 moles of substance 2 dissolved in n_1 moles of liquid substance 1 in the left cylinder at T and p_2^v. n_2 in the solution was chosen to equal the number and distribution of molecules of 2 in an equal volume of vapor 2 in Figure 1A, i.e. $n_2 = n_2^{vo}$ where n_2^{vo} is the moles of pure vapor in volume V. Both n_2^0 and V are the same in Figure 1A and 1B. π_2 is the osmotic pressure of substance 2 in the left cylinder where also $V = n_1 \overline{V}_1 + n_2 \overline{V}_2$. Since $\overline{V}_2^0(T, p_2^v - \pi_2) > \overline{V}_2^0(T, p_2^v)$, V in the right cylinder is slightly larger than V in the left cylinder.

and in the left cylinder is p_2^{vo} and is in equilibrium with the vapor pressure of liquid 2 at T and an applied pressure p_2^v. In the left cylinder of Figure 1A, there are n_2^{vo} moles or n_2^{vo} A molecules of vapor 2 in a volume V, where A is Avagadro's number. The molar volumes of the vapor and liquid phases of pure 2 are designated $\overline{V}_2^{vo}(T, p_2^{vo})$ and $\overline{V}_2^0(T, p_2^v)$, respectively, as they are both functions of T and the applied pressures.

In Figure 1B in the left cylinder, again there are $n_2(=n_2^{vo})$ moles of substance 2 distributed at random in a volume V. However, interspersed between molecules of 2 are n_1 moles of substance 1 so that a binary solution of volume V contains n_2 moles of 2 dissolved in n_1 moles of 1. The partial molar volume of substance 1 is designated $\overline{V}_1(T, p_2^v, x_1)$ and that of substance 2 is designated $\overline{V}_2(T, p_2^v\ x_2)$, indicating that both are functions of T, the applied pressure and the mole fractions x_1 and x_2 respectively. Note that $\overline{V}_2$ is the partial molar volume of 2 in solution and is very much less than the molar volume of the vapor of 2, i.e. $\overline{V}_2 \ll \overline{V}_2^{vo}$. In the right cylinder of Figure 1A $V = n_2^0 \overline{V}_2^0$, whereas in the left cylinder in Figure 1B $V = n_1 \overline{V}_1 + n_2 \overline{V}_2$ where the volume V is the same in both cylinders. The molecules of 2 in V have the same distribution in the left cylinders in Figure 1A and 1B and the same velocity distribution. However, their mean free path is much less in Figure 1B due to frequent collisions with the large number of molecules 1.

The question to be considered here is: in what ways do the presence of molecules 1 alter the properties of molecules 2? That is, how do molecules 2 in the left cylinders of Figures 1A and 1B differ? In the first place, it is evident that the molecules of 1 profoundly alter the equilibrium vapor pressure of substance 2, that is $p_2^v \ll p_2^{vo}$. It is equally clear that equilibrium between the vapor of 2 and the liquid phase of substance 2 in the right cylinder is achieved only by greatly reducing the pressure applied to pure substance 2 from p_2^v to $p_2^v - \pi_2$. The vapor pressure of substance 1 is assumed to be zero so that it exerts no pressure on the solution or the pure liquid 2 in Figure 1B. Also, if $p_1^v = 0$, the molecules of 1 will not dissolve in the pure liquid 2 so that a pressure $p_2^v - \pi_2$ applied to liquid 2 in the right cylinder and a pressure p_2^v applied to the solution in the left cylinder will insure equilibrium between the vapor of substance 2 and substance 2 in the two cylinders. This assumption simplifies the argument without affecting the conclusion.

The changes in the equilibrium properties of substance 2 both in pure liquid 2 and in solution are depicted in Figure 1B and again in Figure 2. Figure 2 is a modification of Figure 1B in only one respect. The solution in the left cylinder is separated from pure liquid 2 by a rigid membrane permeable only to molecules of 2. To establish equilibrium between the pure 2 below the membrane and molecules of 2 in the solution above the membrane, a pressure $p_2^v - \pi_2$ must be applied to the former, as illustrated. The pressure π_2 is, of course, the osmotic pressure of substance 2 in the solution and is induced by the n_1 moles of substance 1.

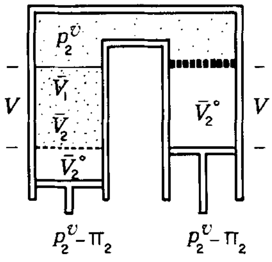

FIGURE 2 V, n_2^0, $\bar{V}_2^0$, n_1, $\bar{V}_1$, n_2, $\bar{V}_2$, p_2^v and π_2 are identical to the corresponding values in Figure 1. Figure 2 differs from Figure 1B in only one respect, pure liquid 2 is below a semipermeable membrane separating it from the solution above. The membrane is permeable only to molecules of 2 so that $p_2^v - \pi_2$ must be applied to the pure liquid 2 below the membrane to maintain equilibrium between liquid 2 and the solution.

The chemical potential of pure liquid 2 below the membrane is diminished by changing the pressure applied to it from p_2^v to $p_2^v - \pi_2$, i.e.

$$\mu_2^0(T, p_2^v - \pi_2) - \mu_2^0(T, p_2^v) = \int_{p_2^v}^{p_2^v - \pi_2} \bar{V}_2^0 \mathrm{d}p. \tag{2a}$$

Obviously, since the substance 2 above the membrane is in equilibrium with liquid 2 below the membrane, their chemical potentials must equal, i.e.

$$\mu_2(T, p_2^v, x_2) = \mu_2^0(T, p_2^v - \pi_2). \tag{9}$$

Substituting Eq. (9) into Eq. (2a), the chemical potential of substance 2 in the solution subject to its own vapor pressure is less than that of pure 2 subject to an applied pressure p_2^v by the amount

$$\mu_2(T, p_2^v, x_2) - \mu_2^0(T, p_2^v) = \int_{p_2^v}^{p_2^v - \pi_2} \bar{V}_2^0 \, \mathrm{d}p. \tag{10}$$

The vapor pressure of pure liquid substance 2 below the semipermeable membrane in Figure 2 is also exactly equal to the vapor pressure above the solution with which substance 2 in solution is in equilibrium, namely, p_2^v. In every respect, no matter what the compressibility of liquid 2 is at any T and p, no matter what x_2 is, no matter how π_2 relates to x_2 and no matter how substance 1 does it, substance 2 in the solution in Figures 1B and 2 is altered by the presence of substance 1 exactly as if the tension between the molecules of substance 2 in the solution was enhanced by π_2. It is exactly as if: 1) there was an adhesive force between each molecule of substance 2 and the more abundant molecules of substance 1 surrounding it, and 2) the internal tension induced in this adhesive force between molecules of 2 and 1 was π_2 more than the internal tension in the cohesive force between molecules of pure liquid 2 at T and p_2^v.

In Figure 1A the $n_2^{vo}A$ molecules in volume V are in thermal motion and are moving at random with a mean energy of about $3/2kT$ per molecule, where k is Boltzmann's constant. There may be very little cohesion between the distantly separated molecules, so that the pressure, p_2^{vo}, they exert on the walls of the vessel of volume V containing them is approximately that calculated from van der Waal's equation of state. In Figure 1B the behavior of the same number of molecules of substance 2 dispersed throughout the same volume has been profoundly altered by the molecules of substance 1. The molecules of 2 in solution no longer behave as in the vapor phase but as if they are in a liquid phase in which they are coupled to one another and as if the tension in the coupling force was increased by π_2. The only features the molecules of 2 have in common in solution and in vapor phase are the same random distribution and the same velocity distribution. In a sense, then, molecules of substance 1 have three effects on molecules of substance 2. They enable the molecules of 2 to be randomly distributed throughout the solution as they couple the molecules of 2 and enhance the tension in the coupling force between them.

A plausible mechanism for enhanced internal tension

A purely thermodynamic argument has been used to deduce changes in the attractive or coupling forces of adhesion and cohesion between molecules in a solution. The rigor of the thermodynamic argument is not lessened by the fact that it is independent of the kinetic theory of molecules in liquid phase. The lower chemical potential of species i in a solution, its partial molar volume and all its colligative properties can be attributed to a greater tension between its molecules by π_i even when the kinetic theory can not describe with equal rigor the mechanism by which the other molecules in the solution do it. The nature of the coupling forces between molecules determines such properties as density, compressibility, thermal coefficient of expansion, surface tension, specific heats at constant pressure or volume, thermal conductivity, index of refraction and viscosity but these forces are not easily described. No pressure dependent intensive property including partial molar quantities of the several species in a solution can be described simply and rigorously. Nor is there a simple, exact relationship between π_i and x_i, the mole fraction of species i in the solution ($x_i = n_i/\Sigma n_j$). Nevertheless, the thermodynamic argument requires the concept that the tension between molecules of species i, τ_i, in a solution is greater than the tension in pure liquid i, τ_i^0, by π_i, i.e.

$$\tau_i - \tau_i^0 = \pi_i \tag{11}$$

for all x_i between 0 and 1. Furthermore, the molar free energy of species i is lowered by increased stress in the coupling force between molecules of i regardless of whether the coupling force is adhesive or cohesive. But, Eq. (11) is as far as thermodynamics can go and the mechanism by which τ_i exceeds τ_i^0 must be sought in kinetic theory.

The internal tension, τ_i^0, between molecules of species i in pure liquid phase may be viewed as the consequence of 1) a cohesive force between its molecules, 2) an internal pressure due to the change of momentum of its molecules at the liquid boundary and 3) an externally applied pressure, p. We can expect the internal pressure to be proportional to RT and inversely proportional to the molar volume $\overline{V}_i^0$. All the molecules in the liquid are in random motion with a mean energy and mean velocity depending on the absolute temperature. Those that are at or near the liquid boundary, with a component of velocity perpendicular to and moving toward the boundary, will be elastically reflected from the boundary with the same velocity component. The rate of change of momentum of all such molecules at or near a unit area of boundary is the internal pressure due to the thermal motion of the liquid molecules. For molecules that all remain monomeric, the internal thermal pressure will be proportional to n_i^0RT/V. This internal pressure is due both to the fact that molecules are in random, thermal motion and to the fact that they are reflected elastically at the boundary by the cohesive force between them. The internal thermal pressure induces the internal tension in cohesive force between the molecules. Its magnitude will be the internal thermal pressure divided by the fraction of the surface that is species i, $n_i^0RT/V \div n_i^0\overline{V}_i^0/V$, minus the applied pressure p. Thus,

$$\tau_i^0 = \frac{n_i^0RT}{V} \div \frac{n_i^0\overline{V}_i^0}{V} - p$$

or

$$\tau_i^0 = \frac{RT}{\overline{V}_i^0} - p. \tag{12}$$

Of course, the internal tension will be less than this if molecules of i tend to cluster into dimers, trimers or polymers at the boundary of liquid i. The tendency to cluster may also be a function of T, p and other molecular species that may be present.

In a solution the internal pressure is due to the random, thermal motion of all molecules. Each molecule of all species in a solution is coupled by cohesive and adhesive forces of attraction to all other molecules. At or near the boundary of the solution, all molecules moving toward the surface are elastically reflected away from the surface with the same component of velocity perpendicular to the surface. The rate of change of momentum of these reflected molecules is a thermal force which stresses the coupling forces between molecules. This thermal force per unit area of boundary surface is an internal thermal pressure. Each species contributes to the thermal pressure in proportion to its concentration, so its contribution to the total thermal pressure is n_iRT/V and the total thermal pressure is $\Sigma n_jRT/V$, where the solution volume $V = n_1\overline{V}_1 + n_2\overline{V}_2 + \cdots + n_j\overline{V}_j$. This assumes only that each molecule is a monomer and moves randomly with respect to all other molecules.

The internal thermal pressure is opposed by the internal tension between molecules of the solution. Each molecular species opposes this total internal thermal pressure by the tension between its molecules, and the tension in species i is τ_i. Since all molecules are coupled by attractive forces between them, each species must oppose the entire thermal pressure. This statement may, at first, be difficult to comprehend so let us consider the magnitude of τ_i for two hypothetical assemblage of molecules before assessing τ_i for species i in the real solution. In all cases, the molecules of species i are presumed to have the same random distribution throughout the volume of the assemblage. First, if the molecules were not coupled by attractive forces between them, then, of course, the thermal pressure they exert would have to be opposed by the walls of the vessel that contains them and τ_i for species i would be 0. Second, if only the molecules of species i were coupled by a cohesive force between them and if there were no adhesive force between molecules of species i and molecules of all other species, then the thermal pressure exerted by species i, n_iRT/V, would be opposed by tension in the cohesive force between its molecules so that species *i* would exert no pressure on the wall of the container. The magnitude of τ_i in this hypothetical case would have to be the same as in pure *i*, that is, τ_i would have to be the force exerted by molecules of *i* on a unit surface area of solution boundary divided by the fraction of the surface consisting of species *i*. The fraction of the surface and the fraction of the volume that is occupied by molecules of *i* are the same, namely, $n_i \bar{V}_i/V$. Thus, for this hypothetical case for which only molecules of *i* are attracted to each other, τ_i would have to be $n_i RT/V \div n_i \bar{V}_i/V$ or $\tau_i = RT/\bar{V}_i$, as in pure liquid *i*. In this case, the thermal pressure by molecules of all other species would have to be opposed by the containing walls and their molecules would not affect the tension between molecules of species *i*.

Now, in a real solution, all molecules are strongly coupled to one another so that the attractive force between molecules of species *i* must oppose not only the thermal pressure by molecules of *i*, $n_i RT/V$, but also the thermal pressure by all other molecules. Thus, in a solution it is as if each species opposes the entire thermal pressure.[3] As in the second hypothetical case above, species *i* constitutes a fraction of the boundary surface, $n_i \bar{V}_i/V$. Since tension in the attractive force between molecules of species *i* is the total force species *i* opposes divided by its cross sectional area, it follows that

$$\tau_i = \frac{\Sigma n_j RT}{V} \div \frac{n_i \bar{V}_i}{V}, \tag{13}$$

when no external pressure *p* is applied to the solution. If the external pressure applied to the pure liquid *i* is also 0, the τ_i in Eq. (13) exceeds τ_i^0 in Eq. (12) so that at the same *T*,

$$\pi_i = \tau_i - \tau_i^0 = \frac{\Sigma n_j RT}{n_i \bar{V}_i} - \frac{RT}{\bar{V}_i^0}. \tag{14}$$

In a binary solution,

$$\pi_1 = \frac{RT n_2}{\bar{V}_1 n_1} + \left(\frac{1}{\bar{V}_1} - \frac{1}{\bar{V}_1^0}\right) RT; \tag{15}$$

and

$$\pi_2 = \frac{RT n_1}{\bar{V}_2 n_2} + \left(\frac{1}{\bar{V}_2} - \frac{1}{\bar{V}_2^0}\right) RT. \tag{16}$$

Since the condensed phases of all species are more or less compressible, so that $\bar{V}_1 > \bar{V}_1^0$ and $\bar{V}_2 > \bar{V}_2^0$, the second term in Eqs (15) and (16) will be negative. The second term of Eq. (15) may be negligible when $n_2/n_1 \ll 1$, i.e. if π_1 is only a few bars pressure. On the other hand, when $n_2/n_1 \ll 1$, then

$n_1/n_2 \gg 1$ and π_2 will be many kilobars and the second term in Eq. (16) will not be negligible even if the condensed phase of species 2 is only slightly compressible.

For example, in a one molal aqueous solution of ethanol at 20°C, Eq. (15) may be used to compute the osmotic pressure of the water assuming that all molecules in the solution are monomers. Compressibility is defined as $\kappa_1^0 = -\mathrm{d} \ln \bar{V}_1^0/\mathrm{d}p$. For water at 20°C from 0 to π_1, κ_1^0 will be about 45.91×10^{-6} bar^{-1} and equal to $(\Delta\bar{V}_1^0/\bar{V}_1^0)/\pi_1$. Since $\bar{V}_1(T, 0) = \bar{V}_1^0(T, -\pi_1)$, then $\bar{V}_1(T, 0) = \bar{V}_1^0(T, 0) + \Delta\bar{V}_1^0$ or

$$\bar{V}_1 \cong \bar{V}_1^0(1 + \kappa_1^0\pi_1). \tag{17}$$

Combining Eqs. (15) and (17), for this 1 molal aqueous solution of ethanol,

$$\pi_1 = 24.305 - 1.418 = 22.887 \text{ bar},$$

since $\bar{V}_1^0 = 18.048$ cm^3/mole and $\bar{V}_1 = 18.067$ cm^3/mole at 20°C or 293.16°K and applied pressure $p = 0$. The percent ethanol in a 1 molal aqueous solution is 4.404% by weight for which its osmolality is 0.981 osm/KgH_2O and its osmotic pressure at 20°C will be 23.911 bars. This experimental value for the osmotic pressure of a 1 molal ethanol solution at 20°C is based on its melting point depression. The value of π_1 calculated from Eq. (15) may be too low because we assumed all molecules were monomers. In fact, water tends to form polymers.[4] It would seem plausible to attribute the difference between 23.911 bars and 22.887 bars to a greater tendency for pure water to form polymers than for water in the ethanol solution to polymerize. This effect would diminish τ_1^0 rather more than τ_1 and π_1 would be greater than calculated by Eq. (15).

In this example, again assuming that all molecules of the solution are monomers, Eq. (16) and a relationship like Eq. (17) for the ethanol, $\bar{V}_2 \cong \bar{V}_2^0(1 + \kappa_2^0\pi_2)$, may be used to calculate the enhanced internal tension between molecules of ethanol. Thus,

$$\pi_2 = 10753 - 224 = 10529 \text{ bar},$$

where $\bar{V}_2^0 = 58.357$ cm^3/mole, $\kappa_2 = 109.8 \times 10^{-6}$ bar^{-1} and $\bar{V}_2 = 125.823$ cm^3/mole. There has been no experimental determination of the melting temperature of ethanol in this solution nor of the vapor pressure of pure ethanol at an applied pressure of -10.5 kilobar at 20°C. However, the vapor pressure of the ethanol in a 1 molal aqueous solution corresponds to an internal tension of the magnitude indicated.

Enhanced intramolecular tension may be inferred

A pure protein is typically crystalline. Nevertheless, the argument is roughly applicable; so that π_2 for a typical 0.001 molar protein solution would be roughly a megabar. A tension of this magnitude, transmitted to within the molecule by the tension in the adhesive force between the protein and its surrounding water, would surely alter its chemistry relative to the chemistry of pure protein. To express this implication differently, the colligative and chemical properties of a protein in a 0.01 molar solution of protein would be the same as in a 0.001 molar solution of the same protein when 100 kilobar pressure is applied to the former and 1 megabar pressure is applied to the latter.

Only if the aggregate of atoms in the molecules of substance 2 is colloidal or smaller in size, will it be subjected to an intramolecular tension of π_2, i.e. molecules of 2 must be able to move randomly. If an aggregate of atoms greatly exceeds a colloidal size, the aggregate can no longer exhibit Brownian motion and it no longer behaves as if dissolved in the solution; although it may be surrounded by solution, it is not in solution.

CONCLUSIONS

In a binary solution, molecules of species 2 and molecules of species 1 are coupled to one another by adhesive and cohesive forces so as to maintain the solution in a liquid phase. Molecules of 2 behave exactly as if the tension in the attractive force between them is enhanced an amount π_2 by molecules of 1. Similarly, molecules of 1 behave exactly as if the tension between them is enhanced an amount π_1 by molecules of 2. The thermodynamic argument used to derive these conclusions is not influenced by the nature of the adhesive force between dissimilar molecules 1 and 2 or by the nature of the cohesive force between similar molecules of 1 or molecules of 2. Nevertheless, the thermodynamic argument requires a mechanism by which the internal tension is enhanced between molecules of 1 and is enhanced between molecules of 2.

A mechanism is proposed whereby the tension between molecules of species i is enhanced by the thermal motion of all species contained in the solution. If the solution has a free surface, it is there that the tension is enhanced and is transmitted by coupling forces to all molecules of species i in the solution. If another surface of the solution is a membrane permeable to only species i and if pure species i is on the other side of the membrane, then the enhanced tension, π_i, in species i in the solution will draw pure species i through the membrane unless a pressure $-\pi_i$ is applied to the pure species i. This mechanism emphasizes the importance of the mole fraction x_i at the free surface without regard for what x_i may be at the membrane. Thus, the osmotic pressure and the vapor pressure of species i is determined by its concentration at the free surface and not the concentration at the membrane. These facts were confirmed experimentally (Scholander and Perez;[5] Hammel and Scholander[6]) by measuring the osmotic pressure of a colloidal solution in an osmometer in which the membrane was permeable to water but not to the colloid. The colloidal suspension was ferro fluid and each colloidal particle was a magnetic dipole. With a magnetic field gradient, the particles could be forced to move toward or away from the free surface and away from or toward the membrane opposite the free surface. Both the transient and the steady state colloid osmotic pressure of the solution increased as the colloidal particles were forced to move toward the free surface and away from the membrane, and vice versa. Also, in a gravity field, if the colloidal particles differed in density from the solvent water, the osmotic pressure was shown to be determined by the colloidal concentration at the free surface and not the concentration at the membrane (Scholander and Perez[7]).

For any intensive partial molar property of species i in a solution, $\bar{Z}_i$, which is altered by pressure, we may conclude that

$$\bar{Z}_i(T, p + \pi_i, x_i) = \bar{Z}_i^0(T, p) \tag{18}$$

or

$$\bar{Z}_i(T, p, x_i) = \bar{Z}_i^0(T, p - \pi_i), \tag{19}$$

where π_i is the enhanced internal tension of species i in the solution and where $\bar{Z}_i$ and $\bar{Z}_i^0$ are the partial molar and molar values of Z_i in the solution and in the pure condensed phase, respectively. $\bar{Z}_i$ may be the chemical potential, partial molar volume or partial molar entropy (μ_i, $\bar{V}_i$ or $\bar{S}_i$) of species i in the solution while μ_i^0, $\bar{V}_i^0$ or $\bar{S}_i^0$ are the molar values of the same property of pure species i.

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3. The internal tension between molecules of each species of the j species in a solution is not analogous to the tension in each strand of j strands of wire in a cable subjected to a force F applied along the axis of the cable and in a direction to cause tension in the cable. Each strand of the cable does not oppose the total force F even if each strand were of differing materials with differing elastic moduli Y_i and differing cross sections a_i. Assuming no coupling between

strands, i.e. no friction between strands, a force f_i will be applied to strand i. The strain, dl/l, will be the same for all strands in the cable so that the stress τ_i in each strand will differ, depending on Y_i, such that

$$\tau_i = \frac{f_i}{a_i} = Y_i \frac{dl}{l}$$

and such that

$$F = \sum f_j.$$

Combining these equations, $F = \sum a_j Y_j(dl/l) = \sum a_j \tau_j$. If all j strands had the same a and Y, then $F = ja\tau_i$ and the tension in each strand would be $\tau_i = F/ja$. In this case the tension in the cable would be the same as the tension in each strand since the cross section of the cable $A = ja$. Clearly, molecular species in a solution differ from strands in a cable. The molecules are all coupled so that each species must oppose the entire thermal pressure exerted at the surface of the solution and the strain for each species differs from that of all other species in the solution.

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