Sedimentation Equilibria of Polydisperse NonIdeal Solutes

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tween which and the solid exceeds the sum of its interactions with an equal number of isolated molecules. The contact angle measures the incongruence of this pattern with that in the normal liquid and at the liquid/vapor interface. Substances completely wettable by water, therefore, are those upon which the pattern of adsorbed water molecules resembles that of the molecules of ordinary water or can fade imperceptibly into it. Incompletely wettable surfaces are not necessarily those which do not adsorb water, but *those on which the pattern is incompatible with that of normal water.* It is highly improbable that this pattern can be identified with that of ordinary ice, since this already exists in water at room temperature, and there is no evidence that contact angles decrease markedly below 4°C. Hysteresis of the contact angle (where real, and not due to contamination) would imply that the adsorbed film can exist in either of two configurations of equal stability.

By the use of a simple technique[10] it has been found possible to build up adsorbed layers of water and of organic vapors on mica to *visible* thickness (from supersaturated vapors) and demonstrate their incongruity with the normal liquids. The differences in behavior between water and such substances as benzene and carbon tetrachloride were too slight to suggest that the more general aspects of the phenomena depend on the hydrogen-bond structure peculiar to water.

Though the heat of adsorption in the outer layers is not necessarily equal to the normal latent heat (with methyl alcohol on charcoal it exceeds it) there are other cases where the difference is small, indicating that the "abnormality" lies in the entropy rather than in the energy of the film.

These observations may be helpful in connection with the theory of *solutions* since they offer suggestions as to the nature of the configurational changes which take place in the near neighborhood of solute molecules.

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Sedimentation Equilibria of Polydisperse Non-Ideal Solutes

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THE interpretation of equilibrium ultracentrifuge data for solutions of extended long chain molecules has been rendered difficult in the past by pronounced deviations from Henry's law at very low concentrations. This difficulty can be overcome by taking account of the deviations from ideality, using thermodynamic data from osmotic pressure measurements.

Consider a column of solution of unit cross section and length dx, in a centrifugal field. At equilibrium, the change in potential energy in moving c_x grams of material through the distance dx to a point where the concentration is $c_x + dc_x$ will be balanced by the work done against the osmotic pressure difference $(\partial p/\partial x)dx$.

Let

$$p = (RT/M_{nx})c_x + b'c_x^2 \tag{1}$$

where $p =$ osmotic pressure, in consistent units and M_{nx} is the number average molecular weight of material at distance x.

Then

$$c_x(1 - \bar{V}\rho)\omega^2 x\,dx = (\partial p/\partial x)dx. \tag{2}$$

Now differentiating (1) and remembering that

$$M_{nx} = \frac{\Sigma_i c_i}{\Sigma_i c_i/M_i},$$

we obtain

$$\Sigma_i c_i \omega^2 x(1 - \bar{V}\rho) = RT\Sigma_i \frac{dc_i}{dx}\frac{1}{M_i} + 2b'\frac{dc_x}{dx}\Sigma_i c_i. \tag{3}$$

This can be considered to be the sum of i equations, so that

$$c_i \omega^2 x(1 - \bar{V}\rho) = \frac{RT}{M_i}\frac{dc_i}{M_i} + b_i'\frac{dc_x}{dx}c_i, \tag{4}$$

where

$$2b'\Sigma_i c_i = \Sigma_i b_i'c_i.$$

It is to be noted that the sedimentation of each species is affected by the presence of the others. It is assumed that $b_i' = 2b'$, as supported by the theory of Scott and Magat[1] and in the absence of evidence to the contrary. Proceeding from this point in a manner similar to that of Lansing and Kraemer[2] expressions for M_{wx} and M_{zx} are obtained, as follows:

$$M_{wx} = \frac{\alpha'Z}{c_x(2Ax - B\alpha'Z)} = \frac{\dfrac{\alpha'B}{2A}\dfrac{Z}{x}}{Bc_x\left(1 - \dfrac{\alpha'B}{2A}\dfrac{Z}{x}\right)} \tag{5}$$

and

$$M_{zx} = \frac{\ln\dfrac{Z_2 x_1}{Z_1 x_2} - \ln\left(\dfrac{1 - \alpha'BZ_2/2Ax_2}{1 - \alpha'BZ_1/2Ax_1}\right)}{A(x_2^2 - x_1^2) - B(c_2 - c_1)}. \tag{6}$$

In these expressions,

$$A = \frac{(1 - \bar{V}\rho)\omega^2}{2RT}$$

$$\alpha' = \frac{1}{Gab\alpha} = \frac{dc/dx}{Z}$$

$$B = \frac{20gb'}{RT},$$

when c_x is measured in g/100 g solution and

$$b' \text{ in } \frac{\text{mm solvent}}{\left(\dfrac{\text{g}}{100\text{ g}}\right)^2}.$$

Experiment	Uncorrected M_z	Concentration g/100 g	R.P.M.	Concentration ratio between ends of cell	Corrected M_w	Corrected M_z
23	95,000	0.108	4700	4	97,000	153,000
24	86,000	0.108	6270	10	107,000	141,000
25	120,000	0.072	6440	10	108,000	150,000

Osmotic pressure M_n	Sedimentation data, corrected M_w	M_z	M_z/M_w	Theoretical M_z/M_w
50,000	104,000	148,000	1.42	1.50

The averaging formula for M_z becomes

$$M_z = \frac{\int_a^b \dfrac{M_{zz}Zdx}{1-\alpha'BZ/2Ax}}{\int_a^b \dfrac{Zdx}{1-\alpha'BZ/2Ax}}.$$

The averaging formula for M_w remains unchanged. Some results obtained with the equilibrium ultracentrifuge for the system polystyrene-carbon tetrachloride are given below in Table I.

The constant B in c.g.s. units for carbon tetrachloride-polystyrene (c_x in g/100 g) was 0.1705×10^{-4}. The molecular weight distribution as calculated from the assumed reaction mechanism gives

$$M_n : M_w : M_z = 1 : 2 : 3.$$

Also it has been found mathematically possible to calculate the differential weight distribution curve of the polymer from one experiment in the equilibrium ultracentrifuge, provided $b_i' = 2b'$. The method is similar to that of Rinde.[3]

However, the calculations are extremely tedious and they are of doubtful accuracy when based on only one experiment. In addition to this the curve will be skewed to a certain extent depending on the difference of b_i' from $2b'$.

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