

increases, until in the case of lignoceric acid, for which the part of the chain projecting above the IdP molecules has a length of about 19 Å, it is sufficient to effect complete condensation even in the presence of IdP molecules.

It may be noted that also in other systems formed by flexible long chain molecules and rosin acid molecules, the relative lengths of the molecules play an important part. In solutions of binary mixtures of rosin acid soap and fatty acid soaps, mixed micelle formation occurs when the fatty acid soaps are sodium myristate and laurate, but not in the case of sodium palmitate and oleate⁶.

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Self-diffusion and Viscosity in Liquids

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In this preliminary communication some problems connected with self-diffusion and viscosity in liquids are treated using a modified kinetic theory. The molecules of a liquid are assumed to move in jumps between equilibrium positions by passing across a potential barrier, ΔF . For a pure liquid in thermodynamic equilibrium, the

mole flow from left to right through a unit area normal to the x -direction, is given by

$$\text{Flow}_{x \rightarrow} = v \cdot c / 6 \quad (1)$$

where c is the concentration in moles/cm³. The velocity of the molecules v is equal to $p \cdot \lambda$, where λ is the mean distance between successive equilibrium positions and p is the number of jumps per sec for which an exponential expression should be used. The mole flow may then be written

$$\text{Flow}_{x \rightarrow} = D \cdot c / \lambda \quad (2)$$

where $D = p\lambda^2/6$ is the coefficient of self-diffusion. In equilibrium the same flow takes place in the opposite direction and the net flow is zero.

If there is a concentration gradient and D is independent of $c(x)$, the net rate of flow becomes

$$\text{net Flow} = \frac{\partial}{\partial c} \text{Flow}_{x \rightarrow} \cdot \Delta c = D \cdot \frac{dc}{dx} \quad (3)$$

since $\Delta c = \lambda \cdot dc/dx$, and Ficks law is obtained.

The diffusion of a group of n arbitrary molecules in the liquid is then considered. The vectorial displacement of the group centroid, when each molecule in the group has made an independent jump, is given by

$$\bar{\lambda}_n = \frac{1}{n} \sum_1^n \bar{\lambda} \quad (4)$$

The average numerical value of $\bar{\lambda}_n$ for a large group, or a large number of small groups, is

$$\lambda_n = \frac{1}{\sqrt{n}} \cdot \lambda \quad (5)$$

The flow of such groups in equilibrium (cf. eqs. (1) and (2)) is then

$$\text{Flow}_{x \rightarrow} = D_n \cdot c_n / \lambda \quad \text{with } D_n = \frac{p \cdot \lambda^2}{6 \cdot \sqrt{n}} \quad (6, 7)$$

The activation energy of a solute molecule (or ion) in water, is supposed to be due to the formation of hydrogen bonds between this and the water molecules, the solute molecule being able to establish a certain maximum number n_s of hydrogen bonds according to its molecular structure. Only a fraction of these hydrogen bonds are established at any time, and this fraction is continually changing. It is postulated that the diffusion coefficient of the solute molecule is equal to the diffusion coefficient of the surrounding group of n_s water molecules. If Eyring's expression for p is used, the diffusion coefficient becomes

$$D_{n_s} = \frac{\lambda^2}{6 \cdot \sqrt{n_s}} \cdot \frac{kT}{h} \exp(\Delta F_s/RT) \quad (8)$$

where n_s is the maximum number of hydrogen bonds for a solute molecule, and ΔF_s is the activation energy of these bonds.

In other liquids n_s may be the coordination number and ΔF_s the activation energy of exchange of one of the neighbouring solvent molecules. When the ΔF_s values of two ions are equal, the simpler equation

$$D_{n_1} \cdot \sqrt{n_1} = D_{n_2} \cdot \sqrt{n_2} \quad (9)$$

may be used to interpret experimental data.

Conductivity and viscosity. The conductivity of ions at infinite dilution is obtained from eq. (8) by partial differentiation with respect to ΔF_s ,

$$\text{net Flow} = 2 \cdot \frac{\partial}{\partial \Delta F_s} \text{Flow}_{x \rightarrow} \cdot \Delta(\Delta F_s) \quad (10)$$

where

$$\Delta(\Delta F_s) = N \cdot z \cdot e \cdot V \cdot \lambda \quad (11)$$

and Nernst's law is obtained:

$$\Lambda_{\infty}^{\pm} = D_n \cdot \frac{F^2 \cdot z}{RT} \quad (12)$$

This derivation of Nernst's law assumes that the electric field causes only a differential change in the free energy of activation, this being the foundation of Ohm's law in the present model for a liquid. The importance of this argument lies in the possibility of deriving similar relationship for other properties of a liquid.

The laminar flow in a liquid is proportional to the applied tangential force

$$K = \eta \cdot dv/dz \quad (13)$$

where η is the coefficient of viscosity and dv/dz the velocity gradient normal to the moving layers. The unit of viscosity, the poise, is defined with reference to flow through a centimeter cube, when the top layer moves with a constant velocity v_0 of 1 cm/sec relative to the bottom layer. If this centimeter cube is considered as being divided into molecular layers, and the flow represented as a diffusion of these layers under the influence of an external force K , then the diffusion coefficient of a layer is given by eq. (8) with $n = \frac{1}{2} (N/V_M)^{2/3}$ as only one side of the layer resists the flow, cf. eq. (5). The net flow is given by eq. (10) with

$$\Delta(\Delta F) = N \cdot \eta \cdot \lambda \cdot dv/dz \quad (14)$$

From macroscopic considerations the flow is equal to

$\frac{v_0}{2} \cdot c$ and the equation

$$\frac{1}{\eta} = \frac{4 \cdot \sqrt{2} \cdot N^{2/3} \cdot V_M^{1/3} \cdot D}{RT} \quad (15)$$

is obtained, where D is the coefficient of self-diffusion for the liquid.

Applications. By assuming a common value of the entropy of activation, eq. (8) yields the following n -values of some simple ions based on $n\text{H}_2\text{O} = 4$, $\text{NH}_4^+ 11.6$; $\text{Cl}^- 12.1$; $\text{K}^+ 11.9$; $\text{Na}^+ 15.0$; $\text{Ag}^+ 11.2$; $\text{NO}_3^- 21.7$; $\text{Ac}^- 18.8$; $\text{Ox}^{2-} 37.0$; $\text{Ca}^{2+} 33.9$; $\text{Ba}^{2+} 33.9$; $\text{SO}_4^{2-} 29.1$;

Values of Λ_{∞} taken from Handbook of Chem. and Physics. Log D/T plotted against $(1/RT)^2$ over the temp. range 50–156° C.

Possible ionic structures are $\text{K}^+ \cdot 4 \text{H}_2\text{O}$, $\text{NO}_3^- \cdot 6 \text{H}_2\text{O}$, $\text{SO}_4^{2-} \cdot 10 \text{H}_2\text{O}$. Ca^{2+} appears to have a double layer of H_2O molecules.

Comparison of the diffusion coefficients of silicate¹, phosphate², vanadate¹ and chromate ions³, with the corresponding Me_2O_7 -ions gives n_s/n_1 -values close to 1.50 which agrees well with a number of 4 or 6 oxygen-atoms, respectively, interacting with the solvent molecules. The corresponding values $n_3/n_1 = 1.99$ and $n_4/n_1 = 2.56$ for the more complex vanadate ions indicate the open tetrahedral structures V_3O_{10} and V_4O_{15} .

Coefficients of self-diffusion calculated from viscosity data using eq. (15) agree with experimental coefficients of self-diffusion for the following liquids, water⁴, heavy water⁴, mercury⁵, ethyl bromide⁶ and benzene⁶; the calculated values of alcohols⁷ are lower due to the effect of deuterium on the hydrogen bonds in these liquids when an alcohol-d is used as tracer. This effect is large in methyl and ethyl alcohol, small in *n*- and *t*-propyl alcohol and almost disappears in *n*- and *t*-butyl alcohol.

A more detailed report on these matters will be given elsewhere.

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