

Viscosity of Liquid Water and Water Vapor

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It has been well known that the viscosity of liquid water exhibits different behavior from other ordinary liquids. Many empirical equations which were applied to liquid water failed to predict the exact value of the viscosity.

Only significant structure theory of viscosity¹ had fitted the viscosity of liquid water with success by assuming that the solid-like volume was summed up to the mole fraction of the ice mixture. On the other hand, the viscosity of water vapor cannot be calculated successfully by the previous theory and any other viscosity equations which describe the liquid state. Therefore, no theory of viscosity can be applicable both liquid water and water vapor.

According to our viscosity theory,² the viscosity of fluids is expressed as follows

$$\eta = (P_k + P_i) (\rho \beta_T / \gamma)^{1/2} (\pi d^2 \frac{V - V_s}{V} \cdot \frac{N}{V})^{-1} \quad (1)$$

where P_k , P_i , ρ , γ , β_T , d and V_s are the kinetic pressure, the internal pressure, the mass density of fluid, the heat capacity ratios C_p/C_v , the isothermal compressibility, the collision diameter and the solid volume respectively. If we can obtain the experimental values of thermodynamic properties included in Eq. (1), we can calculate the viscosities of various substances for both gases and liquids.

Liquid water has the structure with hydrogen bondings and the hydrogen bonding would be expected to affect the solid volume. The distortion of hydrogen bonding with the increasing temperature may give some decrease of the average van der Waals radius of the molecule.³ Therefore the solid volume of the molecule exhibits some decrease with temperature rise. Thus an empirical formula for the solid volume is assumed as follows.

$$V_s = V_o - 0.000 t^2 \quad (2)$$

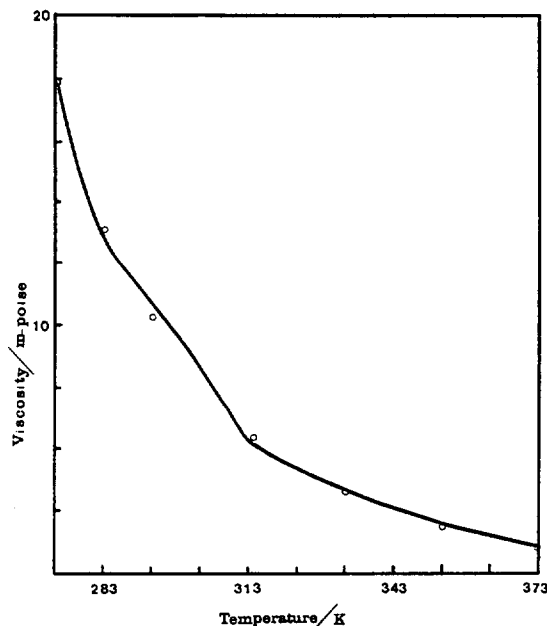


Figure 1. Viscosity of liquid water versus temperature. Solid line: Calculated, Open circles; Observed.

where V_o is the molar volume for the compact state of ice 18.004 cm^3 , t is the Celsius temperature respectively.

Thermodynamic data used in calculation are listed in Table 1.⁴ The collision diameter d is expressed as follows²

$$d^2 = d_o^2 (1 + 1.8 T_b / T) \quad (3)$$

where d_o is the collision diameter at infinitely high temperature 3.018 \AA , T_b is boiling point respectively. The calculated values for liquid water and water vapor at low pressure are compared with the observed data in Figures 1,2 and Table 2. All the calculated values are in good agreements with the observed data for both liquid and gas. We can find that the values of P_k and P_i have the negative sign between 0 and 4°C , and the absolute values of P_k and P_i decrease with the increasing temperature and pressure to some extent. It is because the sign of isobaric thermal expansivity is minus and the thermal expansion coefficient increases with the increasing temperature and pressure. We can easily estimate that only absolute value of P_k and P_i can be contributed for the viscosity. Though we should study still more for the calculation of the viscosity in these regions, we hope we can explain one of the striking anomalies of liquid water^{5,6} that the

Table 1. Thermodynamic Properties of Liquid Water Used in Calculation⁴

| T K | P bar | V $\text{cm}^3 \text{mol}^{-1}$ | $10^3 \alpha_p$ K^{-1} | $10^4 \beta_T$ bar^{-1} | C_p $\text{JK}^{-1} \text{mol}^{-1}$ | C_v |
|----------|------------|--------------------------------------|------------------------------------|-------------------------------------|---|-------|
| 273.15 | 0.006111 | 18.0191 | -0.0685 | 0.5089 | 75.98 | 75.92 |
| 283.15 | 0.012276 | 18.0216 | +0.0878 | 0.4781 | 75.53 | 75.44 |
| 293.15 | 0.023384 | 18.0485 | 0.2067 | 0.4589 | 75.34 | 74.83 |
| 313.15 | 0.073812 | 18.1574 | 0.3853 | 0.4424 | 75.27 | 73.35 |
| 333.15 | 0.19933 | 18.3238 | 0.5232 | 0.4450 | 75.38 | 71.62 |
| 353.15 | 0.47375 | 18.5386 | 0.6412 | 0.4614 | 75.59 | 69.76 |
| 373.15 | 1.01325 | 18.7980 | 0.7503 | 0.4902 | 75.85 | 67.89 |

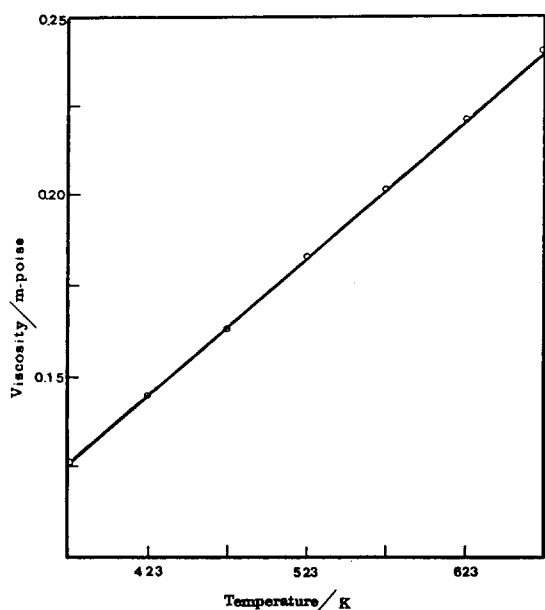


Figure 2. Viscosity of water vapor versus temperature Solid line; Calculated (Values of C_p from Ref. 7), Open circles; Observed.

Table 2. The comparison of calculated and observed viscosities

| T/K | $\eta_{\text{obs.}}^{\text{b}}$ (μpoise) | $\eta_{\text{calc.}}$ (μpoise) | Δ % |
|--------------|---|---|------------|
| Liquid Water | | | |
| 273.15 | 17920 | 17925 | 0.03 |
| 283.15 | 13070 | 12715 | -0.03 |
| 293.15 | 10020 | 10125 | 1.05 |
| 313.15 | 6528 | 6517 | -0.17 |
| 333.15 | 4665 | 4665 | 0.00 |
| 353.15 | 3547 | 3547 | 0.00 |
| 373.15 | 2818 | 2818 | 0.00 |
| Water Vapor | | | |
| 373.15 | 125 | 125 | 0.00 |
| 423.15 | 145 | 145 | 0.00 |
| 523.15 | 183 | 183 | 0.00 |
| 573.15 | 202 | 202 | 0.00 |
| 623.15 | 222 | 221 | -0.45 |
| 673.15 | 241 | 239 | -0.83 |

viscosity near the freezing point decrease with increasing pressure and the explanation for this phenomenon is not clear until now.

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Synthesis of Combination Compounds of Dihydropyridine and m -Blocker

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Combination of two drugs in one compound showing "dual action"¹ has been studied in searching of dual mode of action. H. A. Albrecht *et al.* of Hoffman-La Roche presented the preparation of cephalosporin linked with quinolones to find a broadened antibacterial spectrum². In cardiovascular field the calcium channel blockers and the β -blockers are widely used for treatment the high blood pressure³. Specially the dihydropyridine derivatives (DHP)⁴ in calcium channel blockers and 1-aminopropane-2,3-diol derivatives⁵, such as propranolol, atenolol etc. in β -adrenergic blockers are widely used as cardiovascular drugs. By a combination of those two kinds of drugs in one molecule we would like to see the dual action of antihypertensive activities in the biological system.

Now we report the synthesis of the bifunctional dihydropyridines (5) linked with β -blockers via triazoloyloxy group to find out the dual mode of action in the field of antihypertensive drugs. We chose the benzotriazoloyloxy group as a suitable linker between DHP and aminopropane derivatives because the aromatic moiety has been known as the essential part⁶ in DHP to show the antihypertensive activity and DHP with nitrogen atom at the aromatic ring generally has been accepted to show potency⁷ in calcium channel blocking drugs. Furthermore the different ester groups were chosen aiming for the better activity⁸. In addition the hydroxyl group at the benzotriazole is the best feature to combine two drugs via oxygen which is the common atom in β -blockers⁵.

Two synthetic routes which are shown below were attempted.

The first route is the synthesis of benzotriazolyl aldehyde (3) at the first which has epoxypropanoyl substitution at the aryl skeleton followed by a well known Hantsch reaction⁶ with β -keto ester and amino crotonate to give the DHP derivatives (4). The second route is the synthesis of DHP skeleton (6) first and followed by cyclization of aryl substituents to give the benzotriazole (7), which is condensed with epichlorohydrin to give the compound (4). The first route gave us a low yield of DHP derivatives probably because of the less electron withdrawing power of the triazole group. In other