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THERMODYNAMIC FUNCTIONS OF ACTIVATION FOR VISCOUS FLOW OF SOME MONOSACCHARIDES IN AQUEOUS SOLUTIONS

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ABSTRACT

The viscosities of aqueous solutions of some monosaccharides D-pentoses and (D-hexoses) were measured up to 2.5 mol kg^{-1} in the temperature range from 293.15 to 318.15 K. On the basis of Eyring's theory of the transition state, the relations for the thermodynamic functions of activation for viscous flow of binary liquid mixtures, i.e. molar Gibbs free energy, $\Delta^{\#}\overline{G}_{1,2}$, entropy, $\Delta^{\#}\overline{S}_{1,2}$, and enthalpy, $\Delta^{\#}\overline{H}_{1,2}$, and for the partial molar quantities of activation for viscous flow of solute and solvent, respectively, were obtained. Thereby, the dependence of the molar thermodynamic functions of activation for a viscous flow of solution against the solute mole fraction was given as a second-degree polynomial. It was shown that the linear correlation coefficient β_Y, (Y denotes G, H or S), is given by the difference between the partial molar activation parameter of the solute at infinite dilution and the respective molar quantity of the pure solvent. In addition, correlations between the coefficient β_Y and the viscosity coefficient B and/or temperature derivative of the viscosity coefficient B were found. For the solutions investigated, the molar thermodynamic activation parameters for viscous flow were found to be linearly dependent on the solute mole fraction, which means that the partial molar quantities of activation of the solutes are concentration independent.

INTRODUCTION

A number of papers have dealt with the physical chemistry of aqueous solutions of small carbohydrate molecules [1–7]. Nevertheless, it seems that there is no general consensus of opinion about the effects of the structure of the solute and solvent molecules on the physico-chemical properties of these mixtures. In these systems, these are equilibrium mixtures of enantiomeric solute species, predominantly of cyclic forms with different degrees of hydration. Furthermore, these solutes have hydrophilic as well as hydrophobic characters due to the presence of hydrophilic groups (OH and –O–) and hydrophobic groups (CH and CH_2) in the solute molecules. However, the hydrophobic nature of carbohydrate molecules is actually swamped by their overwhelmingly hydrophilic behaviour [8]. In general, the physico-chemical properties of equilibrium mixtures should be regarded as the sum of the individual contribution of all species present. The results obtained,

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therefore, usually reflect the average values of the parameters determined. In addition, it seems worth noting that some physico-chemical properties of the carbohydrate–water system, e.g. partial molar heat capacity [9] and diffusion coefficient [10], could be correlated with the average number of equatorial OH groups in the carbohydrate molecule, as has been shown previously.

This contribution describes the viscosity behaviour of aqueous solutions of some monosaccharides, in which hydration of the solute plays an important role. To achieve a greater insight into the viscous flow of the solutions investigated, the transition-state theory was applied to analyse the relative viscosities of these solutions. The molar contributions of the solute species to the activation parameters for viscous flow of the solutions were analysed in terms of the relative effects of solute on the ground- and transition-state solvent.

EXPERIMENTAL

D-pentoses (D-ribose, D-arabinose and D-xylose, p.a., Fluka A.G.) and D-hexoses (D-fructose, pure, Merck, D-glucose, p.a., Kemika, D-mannose, pure, Chemapol, and D-galactose, p.a., Merck) were dried under vacuo over P_2O_5 at room temperature for several days and used without further purification, except D-mannose, which was recrystallized from methanol.

Viscosity measurements

The viscosities of the solutions were determined with an Ubbelodhe suspended-level viscometer in the concentration range 0.1–2.5 mol kg^{-1} and at temperatures from 293.15 to 318.15 K in 5 K intervals. The absolute viscosities were calculated by means of the equation [11]

$$\eta_{1,2} = C\,d_{1,2}t - \frac{E\,d_{1,2}}{t^2} \qquad (1)$$

where $\eta_{1,2}$ is the absolute viscosity of the solution (kg m^{-1} s^{-1}), $d_{1,2}$ is the density of the solution (kg m^{-3}), t is the flow time (s) and C and E are constants characteristic of the viscometer. The values of $C = (6.489 \times 10^{-6} \pm 9 \times 10^{-9})$ m^2 s^{-2} and $E = (0.114 \pm 0.019)$ m^2 were determined by a least-squares fit to eqn. (1) of the data for the absolute viscosity [12] and density of pure water [13] at six different temperatures and from the experimentally determined flow times. For the investigated systems at various temperatures, the flow time were in the range 180–600 s. For each viscosity determination the flow times was measured at least five times; the average deviation from the mean value was less than 0.1 s. The temperature of the water bath was maintained with an accuracy of 0.05 K.

RESULTS AND DISCUSSION

From transition state theory, the average Gibbs free energy of activation for viscous flow of solution, $\Delta^{\#}\overline{G}_{1,2}$ (J mol^{-1}), at a given temperature and composition is given by [14]

$$\Delta^{\#}\overline{G}_{1,2} = RT \ln\left(\frac{\overline{V}_{1,2}\eta_{1,2}}{hN}\right) \tag{2}$$

where R is the gas constant, T is the absolute temperature, $\overline{V}_{1,2}$ (m^3 mol^{-1}) is the mean molar volume of the solution, h is Planck's constant and N is Avogadro's constant.

On the other hand, the average Gibbs free energy of activation can be given by

$$\Delta^{\#}\overline{G}_{1,2} = X_1\ \Delta^{\#}\overline{G}_1 + X_2\ \Delta^{\#}\overline{G}_2 \tag{3}$$

where X_i is the mole fraction and $\Delta^{\#}\overline{G}_i$ is the contribution of the component i to $\Delta^{\#}\overline{G}_{1,2}$; $i = 1$ (solvent), 2 (solute).

The entropy of activation for the viscous flow of a solution, $\Delta^{\#}\overline{S}_{1,2}$ (J mol^{-1} K^{-1}), can be calculated from the temperature dependence of $\Delta^{\#}\overline{G}_{1,2}$ as

$$\Delta^{\#}\overline{S}_{1,2} = -\left(\frac{\delta\ \Delta^{\#}\overline{G}_{1,2}}{\delta T}\right)_{n_1} \tag{4}$$

where n_1 is the number of moles of solvent, and the enthalpy of activation, $\Delta^{\#}\overline{H}_{1,2}$ (J mol^{-1}), can be calculated via the Gibbs–Helmholtz relation

$$\Delta^{\#}\overline{H}_{1,2} = \Delta^{\#}\overline{G}_{1,2} + T\,\Delta^{\#}\overline{S}_{1,2} \tag{5}$$

As was shown previously [15], the dependence of activation parameters on the solute mole fraction for liquid mixtures can be given by an empirical relation

$$\Delta^{\#}\overline{Y}_{1,2} = \Delta^{\#}Y_1^{\ominus} + \beta_Y X_2 + \gamma_Y X_2^2;\ (Y \equiv G,\ H,\ S) \tag{6}$$

where $\Delta^{\#}Y_1^{\ominus}$ is the activation parameter for the pure solvent, and the coefficient β_Y is defined as

$$\beta_Y = \left(\frac{\delta\ \Delta^{\#}\overline{Y}_{1,2}}{\delta X_2}\right)_{X_2 \to 0} \tag{7}$$

The β_Y coefficients are related through

$$\beta_G = \beta_H - T\beta_S \tag{8}$$

and, analogously, the γ_Y coefficients are related as follows

$$\gamma_G = \gamma_H - T\gamma_S \tag{9}$$

From eqn. (6), the concentration dependence of the activation parameters of solution expressed as $\Delta^{\#}Y_{1,2} \equiv \Delta^{\#}\overline{Y}_{1,2}(n_1 + m)$, can be given by

$$\Delta^{\#}Y_{1,2} = \Delta^{\#}Y_1^{\ominus}n_1 + \left(\Delta^{\#}Y_1^{\ominus} + \beta_Y\right)m + \gamma_Y\frac{m^2}{(n_1 + m)} \tag{10}$$

where m is the molality of the solution (mol kg^{-1}). Thus, the partial molar parameters of activation for viscous flow of a solute, $\Delta^{\#}\overline{Y}_2$, can be calculated from

$$\Delta^{\#}\overline{Y}_2 = \left(\frac{\delta\, \Delta^{\#}Y_{1,2}}{\delta m}\right)_{n_1} = \left(\Delta^{\#}Y_1^{\ominus} + \beta_Y\right) + \gamma_Y \frac{m(2n_1 + m)}{(n_1 + m)^2} \tag{11}$$

and at infinite dilution as

$$\Delta^{\#}\overline{Y}_{2,0} = \Delta^{\#}Y_1^{\ominus} + \beta_Y \tag{12}$$

Thus, it follows from relation (12) that the parameter β_Y may be considered as the difference between the partial molar parameter of activation for viscous flow of a solute at infinite dilution and the respective molar quantity of pure solvent.

From eqn. (11), the partial molar parameters of activation for viscous flow of a solvent, $\Delta^{\#}\overline{Y}_1$, can be calculated from the relation

$$\Delta^{\#}\overline{Y}_1 = \Delta^{\#}Y_1^{\ominus} - \gamma_Y \frac{m^2}{(n_1 + m)^2} \tag{13}$$

obtained via the Gibbs–Duhem relation. Thus, at infinite dilution, as $m \to 0$, eqn. (13) reduces to $\Delta^{\#}\overline{Y}_{1,0} = \Delta^{\#}Y_1^{\ominus}$, i.e. the partial molar parameter of activation for viscous flow of solvent at infinite dilution is equal to the corresponding molar quantity of pure solvent.

The concentration dependence of relative viscosity, η_r, of a non-electrolyte solution can be given by

$$\eta_r = 1 + Bm + Dm^2 \tag{14}$$

where $\eta_r = \eta_{1,2}/\eta_1$, η_1 is the absolute viscosity of pure solvent (kg m^{-1} s^{-1}) and the coefficients B and D are empirical constants characteristic of a given solute–solvent pair. The viscosity coefficient B is considered to reflect mainly the effect of the size and shape of the solute molecule, as well as the solute–solvent interactions, on viscous flow. The viscosity coefficient B may be regarded as

$$B = \lim_{m \to 0} \left(\frac{\eta_r - 1 - Dm^2}{m}\right) \tag{15}$$

On the other hand, the viscosity coefficient D, besides the solute–solute interactions, also induces those solute–solvent interactions which are not included in the viscosity coefficient B.

The relationships among the coefficients β_Y, the viscosity coefficient B and/or its temperature derivative can be obtained in the following way. In eqn. (7), using expression (2) for $\Delta^{\#}\overline{G}_{1,2}$, the following relation for β_G results

$$\beta_G = RT\left(\frac{\delta \ln \overline{V}_{1,2}}{\delta X_2}\right)_{X_2 \to 0} + RT\left(\frac{\delta \ln \eta_{1,2}}{\delta X_2}\right)_{X_2 \to 0} \tag{16}$$

Considering that for diluted solutions the concentration dependence of $\overline{V}_{1,2}$ on X_2 is linear, i.e. $\overline{V}_{1,2} = V_1^{\ominus} + (\overline{V}_{2,0} - V_1^{\ominus})X_2$, where $V_1^{\ominus}$ is the molar volume of pure solvent, and $\overline{V}_{2,0}$ is the partial molar volume of solute at infinite dilution, and taking into account expression (14) for $\eta_{1,2}$, the following relation for β_G is obtained

$$\beta_G = \frac{RT}{M_1}\left[B + d_1^{\ominus}(\overline{V}_{2,0} - V_1^{\ominus})\right] \tag{17}$$

where $d_1^{\ominus}$ is the density of pure solvent (kg dm^{-3}). Thus, from eqns. (12) and (17), for the partial Gibbs free energy of activation for viscous flow of solute at infinite dilution, $\Delta^{\#}\overline{G}_{2,0}$, the following relation results

$$\Delta^{\#}\overline{G}_{2,0} = \Delta^{\#}G_1^{\ominus} + \frac{RT}{M_1}\left[B + d_1^{\ominus}(\overline{V}_{2,0} - V_1^{\ominus})\right] \tag{18}$$

which is the same as that derived previously [16,17].

From the derivative of $-(\delta\beta_G/\delta T)$, the following relation for the coefficient β_S is obtained

$$\beta_s = -RT\left[\frac{1}{M_1}\left(\frac{\delta B}{\delta T}\right) + \left(\frac{\delta \alpha_{1,2}}{\delta X_2}\right)_{X_2 \to 0}\right] - \frac{R}{M_1}\left[B + d_1^{\ominus}(\overline{V}_{2,0} - V_1^{\ominus})\right] \tag{19}$$

where $\alpha_{1,2}$ is the coefficient of thermal expansion of the solution given by

$$\left(\frac{\delta \alpha_{1,2}}{\delta X_2}\right)_{X_2 \to 0} = -\frac{\alpha_1^{\ominus} d_1^{\ominus}}{M_1}(\overline{V}_{2,0} - V_1^{\ominus}) + \frac{d_1^{\ominus}}{M_1}(\overline{E}_{2,0} - E_1^{\ominus}) \tag{20}$$

where $\alpha_1^{\ominus}$ is the thermal expansion coefficient of pure solvent, $\overline{E}_{2,0}$ is the partial molar expansibility of the solute at infinite dilution and $E_1^{\ominus}$ is the molar expansibility of pure solvent.

So, via the Gibbs–Helmholtz relation, the expression for the coefficient β_H is

$$\beta_H = -RT^2\left[\frac{1}{M_1}\left(\frac{\delta B}{\delta T}\right) + \left(\frac{\delta \alpha_{1,2}}{\delta X_2}\right)_{X_2 \to 0}\right] \tag{21}$$

Relations (18), (19) and (21) differ from those given by Tamamushi and Isono [15] for the contributions of $(\delta \ln \overline{V}_{1,2}/\delta X_2)_{X_2 \to 0}$ and $(\delta \ln \overline{V}_{1,2}/\delta T)_{X_2 \to 0}$, respectively. However, these terms cannot be neglected as $\overline{V}_{2,0}$ and $\overline{E}_{2,0}$ significantly differ from $V_1^{\ominus}$ and $E_1^{\ominus}$, respectively.

For the systems investigated, the values of coefficient β_G, given in Table 1, were obtained by the method of least-squares on the basis of eqn. (6), fitting the values of $\Delta^{\#}\overline{G}_{1,2}$ versus X_2. Thereby, the values of $\Delta^{\#}\overline{G}_{1,2}$ were calculated from eqn. (2) using the experimental results of viscosity and density measurements. The density data for the systems investigated will be published elsewhere. As the experimental results of $\Delta^{\#}\overline{G}_{1,2}$ against mole fraction of solute satisfactorily fit relation (6) in linear form, thus, the $\Delta^{\#}\overline{S}_{1,2}$

TABLE 1

Values of coefficients β_G for the aqueous solutions of investigated D-pentoses and D-hexoses in the temperature range studied

Solute	β_G (kJ mol^{-1})					
T (K) =	293.15	298.15	303.15	308.15	313.15	318.15
D-pentoses						
D-ribose	54.9 ± 0.2	54.6 ± 0.1	54.3 ± 0.2	54.0 ± 0.2	53.9 ± 0.2	53.6 ± 0.3
D-arabinose	57.9 ± 0.2	57.5 ± 0.1	57.1 ± 0.1	56.7 ± 0.1	56.5 ± 0.1	56.0 ± 0.1
D-xylose	58.8 ± 0.3	58.3 ± 0.3	57.9 ± 0.3	57.5 ± 0.4	57.2 ± 0.4	56.9 ± 0.4
D-hexoses						
D-fructose	70.5 ± 0.3	70.0 ± 0.2	69.7 ± 0.1	69.3 ± 0.1	69.1 ± 0.1	68.3 ± 0.3
D-glucose	70.6 ± 0.3	70.3 ± 0.3	70.2 ± 0.3	69.8 ± 0.3	69.5 ± 0.4	69.2 ± 0.3
D-mannose	74.6 ± 0.4	74.2 ± 0.4	73.8 ± 0.4	73.4 ± 0.4	72.9 ± 0.4	72.5 ± 0.3
D-galactose	75.9 ± 0.4	75.2 ± 0.3	74.5 ± 0.2	73.9 ± 0.1	73.3 ± 0.2	72.7 ± 0.2

and $\Delta^{\#}\overline{H}_{1,2}$ values are also linearly dependent on solute mole fraction. As the β_G values in the temperature range studied are linearly dependent on temperature, the values of the coefficient β_S, obtained as $-(\delta\beta_G/\delta T)$, are temperature independent. The calculated values of β_S, obtained by the method of least-squares, are given in Table 2. Furthermore, the values of the coefficient β_H, calculated from eqn. (8) are, within experimental errors, temperature independent for each solute. The average values of β_H are given in Table 2. On the other hand, the partial molar parameters of activation for viscous flow of solute and solvent are concentration independent and equal to their values at infinite dilution, due to the fact that $\gamma_Y = 0$ (see relations (11) and (13), respectively). These values for the solutes investigated, calculated via relation (12), are given in Table 3.

TABLE 2

Values of coefficients β_S and β_H for the aqueous solutions of investigated D-pentoses and D-hexoses in the temperature range studied

Solute	β_S (J mol^{-1} K^{-1})	β_H (kJ mol^{-1})
D-pentoses		
D-ribose	51 ± 2	69.8 ± 0.8
D-arabinose	73 ± 2	79.3 ± 0.7
D-xylose	76 ± 2	81.0 ± 1.0
D-hexoses		
D-fructose	75 ± 3	92.4 ± 1.1
D-glucose	56 ± 3	87.0 ± 1.2
D-mannose	85 ± 2	99.5 ± 1.0
D-galactose	126 ± 2	112.8 ± 0.8

TABLE 3

Values of partial molar parameters of activation for viscous flow of D-pentoses and D-hexoses in aqueous solutions at infinite dilution and 298.15 K, together with values of average number of equatorial hydroxyl groups [9] and hydrophobicity [8] of monosaccharide molecules

Solute	$\Delta^{\#}\overline{G}_{2,0}$ (kJ mol^{-1})	$\Delta^{\#}\overline{S}_{2,0}$ (J mol^{-1} K^{-1})	$\Delta^{\#}\overline{H}_{2,0}$ (kJ mol^{-1})	n (e-OH) [9]	Index A [8]
D-pentoses					
D-ribose	63.8 ± 0.1	76 ± 2	86.5 ± 0.8	2.1	33.5
D-arabinose	66.7 ± 0.1	98 ± 2	96.0 ± 0.7	2.5	32.1
D-xylose	67.5 ± 0.3	101 ± 2	97.7 ± 1.0	3.5	31.5
D-hexoses					
D-fructose	79.2 ± 0.2	100 ± 3	109.1 ± 1.1	3.0	
D-glucose	79.5 ± 0.3	81 ± 3	103.7 ± 1.2		27.9
D-mannose	83.4 ± 0.4	110 ± 2	116.2 ± 1.0	3.4	29.0
D-galactose	84.4 ± 0.3	151 ± 2	129.5 ± 0.8	3.5	28.9

The values of $\Delta^{\#}\overline{Y}_1^{\ominus}$ used at 298.15 K are: $\Delta^{\#}G_1^{\ominus} = 9.2$ kJ mol^{-1}; $\Delta^{\#}S_1^{\ominus} = 25$ J mol^{-1} K^{-1} (obtained from the linear dependence of $\Delta^{\#}G_1^{\ominus}$ in the temperature interval from 293.15 to 303.15 K); and $\Delta^{\#}H_1^{\ominus} = 16.7$ kJ mol^{-1}. The values of $\Delta^{\#}G_1^{\ominus}$ at a definite temperature were calculated from the viscosity [12] and density [13] data of pure water.

The results for $\Delta^{\#}\overline{Y}_{2,0}$, given in Table 3, can be accounted for in the following way. It seems that the ground state solvent of water offers little resistance to coordination with carbohydrate molecules. So, it may be assumed that in the systems investigated the hydration process is nearly complete in the ground state. Thus, in the formation of the transition state, bond-breaking, with a decrease in the order, is significant. The $\Delta^{\#}\overline{Y}_{2,0}$ values mainly reflect the effects of solute–solvent bond-breaking in the transition state, along with any effects on $\Delta^{\#}\overline{H}_{2,0}$ and $\Delta^{\#}\overline{S}_{2,0}$ arising from changes in solvent–solvent interactions [18]. For the systems investigated the values of $\Delta^{\#}\overline{G}_{2,0}$ are large and positive and result from positive and unequal values of $\Delta^{\#}\overline{H}_{2,0}$ and $\Delta^{\#}\overline{S}_{2,0}$; $\Delta^{\#}\overline{H}_{2,0} > T\Delta^{\#}\overline{S}_{2,0}$. The relatively high values of $\Delta^{\#}\overline{H}_{2,0}$ may suggest that the enthalpy of activation also contains a contribution from the solvent–solvent bond-breaking arising from the hydrophobic part of the solute molecules [8]. On the other hand, from the values of $\Delta^{\#}\overline{Y}_{2,0}$ listed in Table 3, it may be concluded that the investigated monosaccharides have a structure-promoting effect on water. Consequently, the solute–solvent bonds are stronger than the solvent–solvent bonds and these solutions are more viscous than pure water, $\Delta^{\#}\overline{G}_{1,2} > \Delta^{\#}G_1^{\ominus}$ [18]. In addition, from Table 3, it can be seen that the equilibrium mixtures of anomeric monosaccharide molecules offer different resistances to viscous flow. It seems that within each group of investigated monosaccharides, having nearly the same hydrophobicity, defined as the percent ratio of the total surface area of the hydrophobic groups (CH and CH$_2$) to the total molecular surface area

(Index *A*) [8], the solute with the largest average number of equatorial hydroxyl groups, *n* (e-OH), is the most compatible with the "lattice" structural component of water [9]. In the formation of the transition state, therefore, the bond-breaking is associated with the largest values of partial thermodynamic functions of activation for viscous flow for such a solute. From Table 3, it can be seen that the determined $\Delta^{\#}\overline{Y}_{2,0}$ values, following the order: $\Delta^{\#}\overline{Y}_{2,0}$ (D-ribose) < $\Delta^{\#}\overline{Y}_{2,0}$ (D-arabinose) < $\Delta^{\#}\overline{Y}_{2,0}$ (D-xylose) in the case of D-pentoses, and $\Delta^{\#}\overline{Y}_{2,0}$ (D-fructose) < $\Delta^{\#}\overline{Y}_{2,0}$ (D-mannose) < $\Delta^{\#}\overline{Y}_{2,0}$ (D-galactose) in the case of D-hexoses, support the above assumption.

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