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Note

Viscosity B-coefficients and activation parameters for viscous flow of a solution of heptanedioic acid in aqueous sucrose solution☆

Tong-Chun Bai,* Guo-Bing Yan

Department of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215006, PR China

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Abstract

Viscosity and density data for the system of heptanedioic acid dissolved in aqueous sucrose solution at temperature range from 288.15 to 313.15 K have been measured. The viscosity B-coefficients for heptanedioic acid in aqueous sucrose solution has been calculated. The effect of temperature and sucrose concentration on the B-coefficients is discussed. On the basis of the Feakins equation, the activation parameters ($\Delta\mu_3^{\neq}$, $\Delta H_3^{\neq}$, $\Delta S_3^{\neq}$, $\Delta G_{12}^{0\neq}$, $\Delta H_{12}^{0\neq}$ and $\Delta S_{12}^{0\neq}$) for viscous flow of the solution have been evaluated, together with the Gibbs energy of transfer for the solute from the ground state solvent to the hypothetical viscous transition state solvent ($\Delta G_3^{\neq}(1-1')$). The effect of sucrose concentration and temperature on the activation parameters has been discussed.

Keywords: Viscosity B-coefficients; Activation parameters for viscous flow; Sucrose; Heptanedioic acid; Aqueous solution

Sugar solutions play an important role in the biological and food industries. It is widely recognized that sugars as cosolutes help in stabilizing biological macromolecules. Experimental findings indicate that this action is performed either as a result of direct interactions between them and/or through alteration of the water structure.[1–4] Sucrose has been the subject of structural and theoretical investigations for a long time, and the interest is still very lively. Some researchers are concerned with the solution properties of biological model compounds, for example, the influence of sucrose on solution vapor pressure,[5] ionic interactions,[6] activity coefficients,[7] heat capacities and volumes of transfer.[8] Our interest is in the influence of sucrose on the viscous properties of the solutions of some hydrophobic model compounds. In this work, heptanedioic acid is selected as a model compound of a hydrophobic molecule with dipolar groups. The concentration of sucrose was focused in the range of 0–10 weight percent.

The importance of heptanedioic acid as a model molecule in this work is that the two polar groups are separated by hydrophobic CH_2 groups and that group interaction is connected with the number and structure of CH_2 groups. The hydration of hydrophobic and hydrophilic groups plays an important role in the conformational stability of biopolymers. Characterization of the hydration properties of groups and the medium effect should provide insights into the role of solute–solvent interactions associated with fundamental biopolymer phenomena such as folding–unfolding transitions, ligand interactions, etc. The behavior of the molecules with dipolar groups, such as diols, dicarboxylic acids, and amino acids in solution have attracted the attention of many authors, especially for the investigators on thermodynamic properties of biochemical model compounds.[9–12] Some experimental results[10] indicate that, for molecules with CH_2 groups numbering >4, the thermodynamic properties are of group additivity, and the influence of dipolar groups on nonpolar groups may be neglected.

The measurement of the viscosities of solutions formed the basis of the studies of solute–solvent interactions. Jones and Dole[13] showed that the viscosities of dilute solutions of strong electrolytes could be represented as:

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* Corresponding author.
E-mail address: tcbai@suda.edu.cn (T.-C. Bai).

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$$\eta_{13}/\eta_1 = \eta_r = 1 + \mathrm{A}\sqrt{c_3} + \mathrm{B}c_3 \quad (1)$$

where η_{13} and η_1 are the viscosities of the solution and solvent, respectively, and c_3 is the solute concentration. The A-coefficient takes account of ion–ion interactions and can be calculated from theory. The B-coefficient reflects the effects of solute–solvent interactions on the solution viscosity. For a nonassociated nonelectrolyte, solute 3 dissolved in mixed solvents 1+2 with a fixed concentration, the viscosities of dilute solutions can be represented as:

$$\eta_{123}/\eta_{12} = \eta_r = 1 + \mathrm{B}c_3 \quad (2)$$

where the symbols have the obvious meanings.

The viscosity B-coefficients are important for a number of reasons.[14] Their application in two research areas is interesting. First, B-coefficients are known to provide information concerning the solvation of the solutes and their effects on the structure of the solvent in the near environment of the solute molecules. Second, since some activation parameters of viscous flow can be obtained from B-coefficients,[15] it is possible to analyze the viscous properties on the basis of enthalpy and entropy terms. The values of B-coefficients have been measured for a wide range of electrolytes in aqueous solutions, as well as in mixed organic–aqueous solvents.[14–16] Data are available for molecules such as amino acids and amides in aqueous organic mixed solvent systems.[9,17–19] However, there are fewer reports on the data of hydrophobic solutes in solution-containing sugars.

In the present paper, we report the viscosity and density data for the system of heptanedioic acid dissolved in aqueous sucrose solution at temperatures of 288.15, 293.15, 298.15, 303.15, 308.15 and 313.15 K. The B-coefficients of heptanedioic acid (3) in sucrose (2)+water (1) solvent are obtained. The contribution of solute 3 and solvent 1+2 to the activation parameters, ($\Delta\mu_3^{\neq}$, $\Delta H_3^{\neq}$, $\Delta S_3^{\neq}$, $\Delta G_{12}^{0\neq}$, $\Delta H_{12}^{0\neq}$ and $\Delta S_{12}^{0\neq}$), for viscous flow of the solution have been evaluated. The effect of both temperature and sucrose concentration on the B-coefficients and activation parameters of viscous flow is discussed.

The densities and viscosities of the sucrose+water and heptanedioic acid+water binary solutions are measured and provided in Tables 1 and 2 in the Supplementary Materials on the WEB version of the journal. The comparison between literature data[20] and this work are shown in Fig. 1. The agreement of our results with literature values is good. The densities and viscosities of the ternary solutions, heptanedioic acid (3)+sucrose (2)+water (1) with three fixed sucrose concentrations at different temperatures, are provided in Tables 3 and 4 in the Supplementary Materials on the WEB version of the journal. Since the ionization constant K_a for heptanedioic acid is 3.09×10^{-5} mol dm^{-3} at 298.15 K,[20] and the experimental concentration c_3 is less than 0.2 mol dm^{-3}, the ionization process of heptanedioic acid and the contribution of A-coefficients to η_r were assumed to be negligible. Correlation of η_{123} with c_3 follows a linear relationship, that is, they follow Eq. (2). Here we treat 1+2 as a solvent and heptanedioic acid as a nonelectrolyte solute. The B-coefficients are determined by a least-squares regression method.

Fig. 2(a) and (b) show the effect of temperature and sucrose concentration on B-coefficients. The viscosity B-coefficient originally introduced as an empirical term has been found to depend upon solute–solvent interactions and on the relative size of the solute and solvent molecules. Larger and positive B values indicate a structure making action (hydrophobic and hydrogen bonding actions) of solute on solvents. Wang and co-workers[9] studied the B-coefficients of some amino acids in aqueous urea solution at several temperatures. Their results indicated that the B-coefficient could be considered as a contribution from particular groups of the solute. The values of dB/dT for groups can provide direct evidence regarding their structure making or breaking effect in solution. The values of dB/dT are positive for hydrophilic structural breaking groups. And for a hydrophobic structural making group, its value of dB/dT is negative. In Fig. 2(a), the B coefficient decreases with temperature increase. The dB/dT is more negative. This is an indication in that the effect of hydrophobic groups in heptanedioic acid on solvent structure overcomes the contribution from hydrophilic groups.

The B-coefficients of sucrose in water are larger than the data of heptanedioic acid in sucrose+water mixed solvents, and a negative dB/dT trend was observed. (Data are available in Section 2). This is an indication of structure making action by H-bonding of sucrose on water. In Fig. 2(b), the effect of sucrose on the B coefficient of heptanedioic acid in aqueous solution is shown. In the experimental concentration range, B coefficients increase when water is replaced by sucrose. Heptanedioic acid is acting as a hydrophobic model solute; however, sucrose is acting as a water structure maker by H-bonding.

The density of heptanedioic acid+sucrose+water solution is a linear function of m_3.

$$\rho_{123} = \rho_{12} + \alpha m_3 \quad (3)$$

And the apparent molar volumes V_3^{ϕ} of heptanedioic acid in mixed solvent 1+2 may be estimated by

$$V_3^{\phi} = [1000(\rho_{12} - \rho_{123}) + m_3 M_3 \rho_{12}]/m_3 \rho_{123} \rho_{12} \quad (4)$$

In Eqs. (3) and (4), m_3 is the molality of heptanedioic acid in solution (unit: mol kg^{-1} mixed solvent), ρ_{123} and ρ_{12} represent the densities of the solution (1+2+3) and (1+2), respectively, and M_3 is the molecular weight of

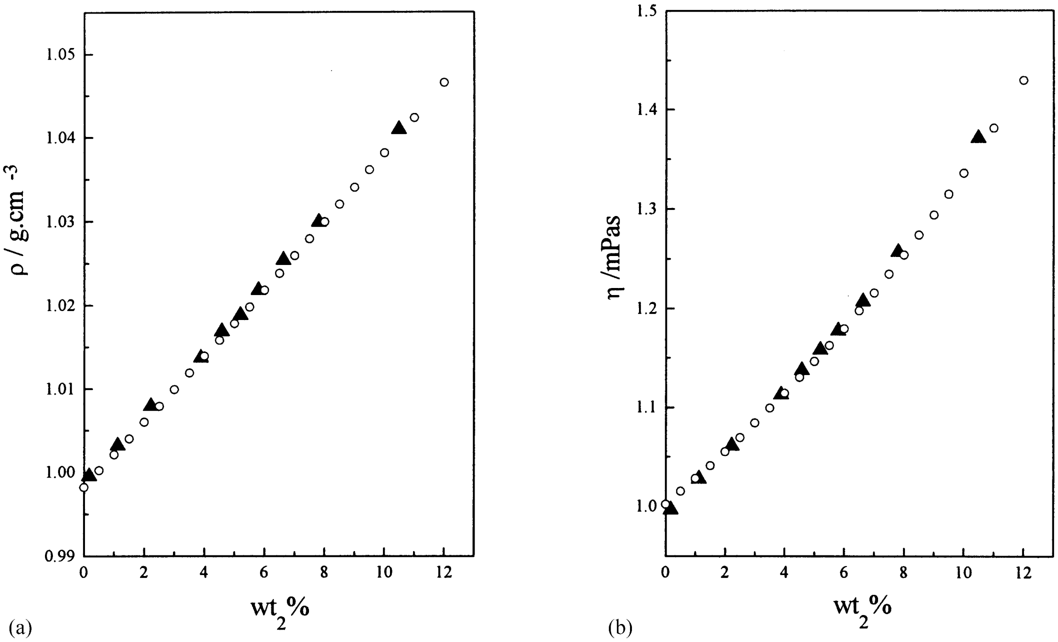

Fig. 1. Comparison between literature and this work. The densities (a) and viscosities (b) of sucrose+water solutions at 293.15 K, ▲, this work; ○, literature.[20]

component 3. The value of α is determined from Eq. (3) by a least-squares regression method. Partial molar volume of solute at infinite dilution, V_3^0, may be estimated by Eq. (5).

$$V_3^0 = M_3/\rho_{12} - 1000\alpha/\rho_{12}^2 \tag{5}$$

The data of V_3^0 and V_{m12} are necessary in calculations of the activation thermodynamic parameters of viscous flow. Where, V_{m12} is the molar volume for sucrose (2)+water (1) solvent.

Eyring and co-workers proposed that the free energy of activation for viscous flow of a pure solvent, $\Delta\mu_1^{0\neq}$,

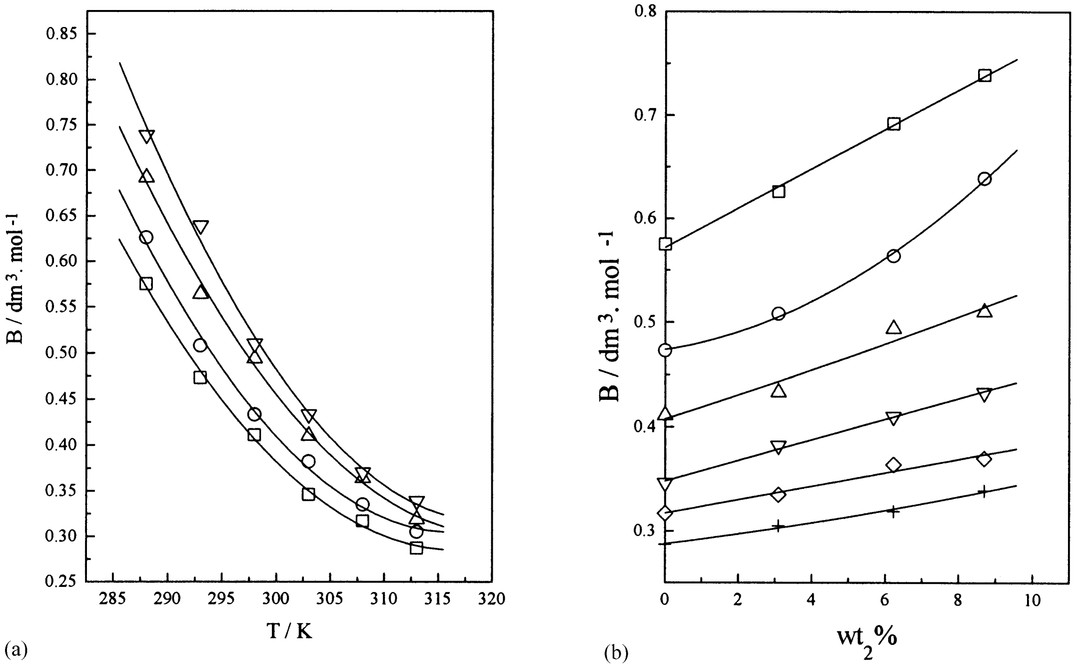

Fig. 2. The B-coefficients of heptanedioic acid in sucrose+water solvents: (a) the effect of temperature for wt$_2$% = □, 0; ○, 3.0926; △, 6.2252; ▽, 8.6931; (b) the effect of sucrose's concentration at □, 288.15; ○, 293.15; △, 298.15; ▽, 303.15; ◇, 308.15 and +, 313.15 K.

could be calculated via

$$\eta_1 = (\mathrm{hN_A}/V_{m1})\exp(\Delta\mu_1^{0\neq}/RT) \tag{6}$$

where $\mathrm{N_A}$ and h are Avogadro's number and Planck's constant, V_{m1} is the molar volume of solvent 1. For solution containing a solute 3 dissolved in pure liquid 1 then they proposed

$$\eta_{13} = (\mathrm{hN_A}/V_{m13})\exp(\Delta G_{13}^{\neq}/RT) \tag{7}$$

where V_{m13} and $\Delta G_{13}^{\neq}$ are respectively the molar volume and the average Gibbs energy of activation for a viscous flow of solution 1+3. In dilute solutions, it may be written

$$\Delta G_{13}^{\neq} = x_1\Delta\mu_1^{0\neq} + x_3\Delta\mu_3^{\neq} \tag{8}$$

Feakins and co-workers[18] showed that if Eq. (1) or Eq. (2) and Eq. (8) are obeyed, then

$$B = (nV_{m1} - V_3^0) + (V_{m1}/RT)(\Delta\mu_3^{\neq} - n\Delta\mu_1^{0\neq}) \tag{9}$$

where the n coefficient is 1 for an undissociated solute, and would be 2 for a fully dissociated univalent electrolyte. In this work, the activation free energy, $\Delta G_{12}^{0\neq}$, for the 1+2 solvent, were calculated from their viscosities, η_{12}, via Eq. (7). The value of $\Delta\mu_3^{\neq}$ for solute 3 in 1+2 solvents was calculated by Eq. (9). In which V_{m1} and $\Delta\mu_1^{0\neq}$ is replaced by V_{m12} and $\Delta G_{12}^{0\neq}$, respectively. The values of $\Delta\mu_3^{\neq}$ are shown in Fig. 3.

If B is known at various temperatures, we can calculate the solute activation entropy from Eq. (10)

$$\mathrm{d}\Delta\mu_3^{\neq}/\mathrm{d}T = -\Delta S_3^{\neq} \tag{10}$$

and the solute activation enthalpy from Eq. (11)

$$\Delta H_3^{\neq} = \Delta\mu_3^{\neq} + T\Delta S_3^{\neq} \tag{11}$$

For sucrose+water binary mixed solvent, the data of $\Delta S_{12}^{0\neq}$ and $\Delta H_{12}^{0\neq}$ were calculated by the same method. In this system, $\Delta G_{12}^{0\neq}$ are linear functions of temperature. The activation entropy $\Delta S_{12}^{0\neq}$ may be considered as approximately constant within the temperature region. The effects of sucrose concentration on the activation parameters $\Delta S_3^{\neq}$, $\Delta H_3^{\neq}$, $\Delta S_{12}^{0\neq}$ and $\Delta H_{12}^{0\neq}$ are shown in Figs. 4 and 5.

There are two contributions to B, as indicated by Eq. (9), the volumetric term and the free-energy term. Comparing Fig. 2(a) and Fig. 3, it can be observed that two curves are much similar in their behavior. This is an indication that the contribution to B mostly from $\Delta\mu_3^{\neq}$. Because the values of $\Delta\mu_3^{\neq}$, $\Delta H_3^{\neq}$ and $\Delta S_3^{\neq}$ are positive, the contribution of $\Delta H_3^{\neq}$ to $\Delta\mu_3^{\neq}$ is greater than $\Delta S_3^{\neq}$.

It can be observed in Figs. 4 and 5 that $\Delta H_3^{\neq} > \Delta H_{12}^{0\neq}$ and $\Delta S_3^{\neq} > \Delta S_{12}^{0\neq}$. The values of $\Delta H_3^{\neq}$ and $\Delta S_3^{\neq}$ increase with the increase in $\mathrm{wt}_2\%$, decrease and approach to the values of $\Delta H_{12}^{0\neq}$ and $\Delta S_{12}^{0\neq}$, respectively with the increase in temperature.

Enthalpy effect indicated that, in the solvation shell, the sucrose–water interaction in the transition state increase with the increase in $\mathrm{wt}_2\%$, decrease and approaches to the state in bulk zone with the temperature increase. This makes the movement of heptanedioic acid in aqueous sucrose solution become more difficult

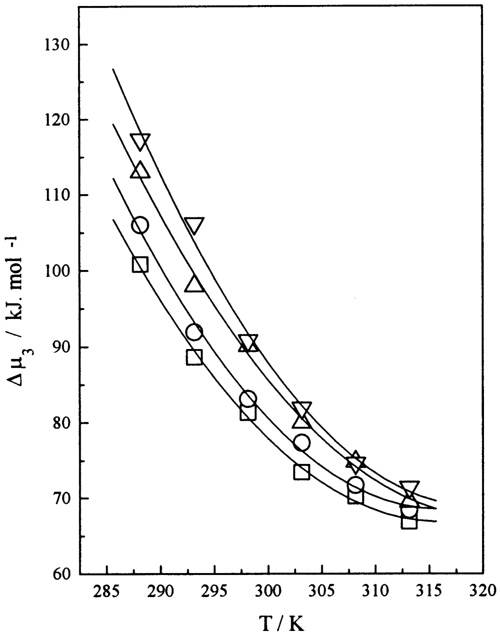

Fig. 3. The values of $\Delta\mu_3^{\neq}$ as a function of temperature in aqueous sucrose solution for $\mathrm{wt}_2\%$: □, 0; ○, 3.0926; △, 6.2252; ▽, 8.6931.

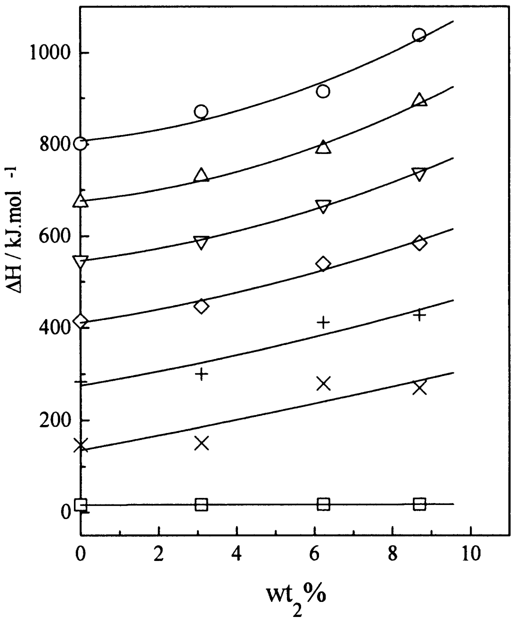

Fig. 4. The activation enthalpy of viscous flow as a function of sucrose mass percent, $\Delta H_{12}^{0\neq}$, □; and $\Delta H_3^{\neq}$ at T: ○, 288.15; △, 293.15; ▽, 298.15; ◇, 303.15; +, 308.15; ×, 313.15 K.

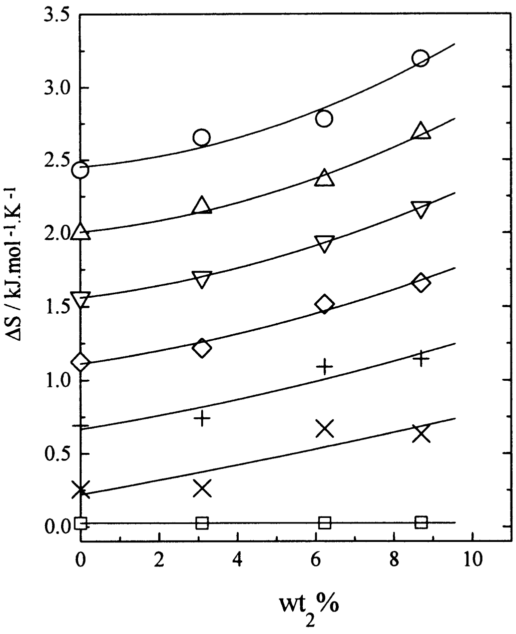

Fig. 5. The activation entropy of viscous flow as a function of sucrose mass percent, $\Delta S_{12}^{0\neq}$ □; and $\Delta S_3^{\neq}$ at T: ○, 288.15; △, 293.15; ▽, 298.15; ◇, 303.15; +, 308.15; ×, 313.15 K.

with wt$_2$% increase and easier with an increase in temperature.

Structure effects are associated with the entropy change of a process. The value of $\Delta S_{12}^{0\neq}$ is associated with structure change of the mixed solvent in the bulk zone, from ground to transition state. A small value of $\Delta S_{12}^{0\neq}$ means that the structure change in this transition process can be neglected. It is also means that there is little change in the H-bonding interaction between sucrose and water when they transfer from ground to transition state. The value of $\Delta S_3^{\neq}$ is associated with the structure change in the solvation shell of a solute 3, from a ground to a transition state. A large positive value of $\Delta S_3^{\neq}$ is an indication in that the structure in the solvation shell in the transition state is of lesser order than for the shell in ground state. With the increase in wt$_2$%, $\Delta S_3^{\neq}$ increases and this makes the movement of heptanedioic acid much easy. The effect of wt$_2$% on $\Delta S_3^{\neq}$ is opposite to that of the effect of wt$_2$% on $\Delta H_3^{\neq}$. The final effect is determined by the enthalpy term. With an increase in temperature, $\Delta S_3^{\neq}$ decreases and approaches to $\Delta S_{12}^{0\neq}$. The solvation shell of a solute approaches to the structure of the solvent in the bulk zone.

In the opinion of Feakins and co-workers,[18] there are two contributions to $\Delta\mu_3^{\neq}$. The first one is thought of as the Gibbs energy of interaction of the solute with a hypothetical transition-state solvent. The effect of the solute on the Gibbs energy of activation of the solvent molecule is, in fact, the difference between the solvation energies of the solute 3 in the ground-state solvent 1 and in the transition-state solvent 1′, or Gibbs energy of transfer, $\Delta G_3^{\neq}(1-1')$, between them. The second contribution to $\Delta\mu_3^{\neq}$ comes from the movement of the solute through its own viscous transition state, $\Delta G_3^{\neq}(3-3')$, thus,

$$\Delta\mu_3^{\neq} = \Delta G_3(1-1') + \Delta G_3(3-3') \tag{12}$$

Also as suggested by Feakins, $\Delta\mu_1^{0\neq}$ (for pure solvent 1) or $\Delta G_{12}^{0\neq}$ (for mixed solvent 1+2) can be used as a common value for $\Delta G_3^{\neq}(3-3')$. Thus the values of $\Delta G_3^{\neq}(1-1')$ may be obtained from $\Delta\mu_3^{\neq} - \Delta\mu_1^{0\neq}$, or from $\Delta\mu_3^{\neq} - \Delta G_{12}^{0\neq}$. The calculated data of $\Delta G_3^{\neq}(1-1')$ are shown in Fig. 6.

According to Feakins, the value of $\Delta\mu_3^{\neq}$ is greater than $\Delta G_{12}^{0\neq}$, that is $\Delta G_3^{\neq}(1-1') > 0$ for net structure makers. This had already been demonstrated experimentally.[9] Values of $\Delta G_3^{\neq}(1-1')$ in Fig. 6 are all positive. This is an indication that heptanedioic acid behaves as a hydrophobic structure maker. This conclusion is consistent with the results deduced from B and dB/dT. The physical meaning of $\Delta G_3^{\neq}(1-1') > 0$ is that, in sucrose+water mixed solvent, the interactions between solute and solvent molecule in the ground state is stronger than that in the transition state. Thus the solute solvation in the transition state is unfavorable in free-energy terms. The value of $\Delta G_3^{\neq}(1-1')$ increases with sucrose concentration. This means the unfavorable interaction between solute 3 and solvent 1 become significant with the addition of sucrose in solution.

In summary, the B-coefficients and activation parameters for viscous flow can be used to obtain informa-

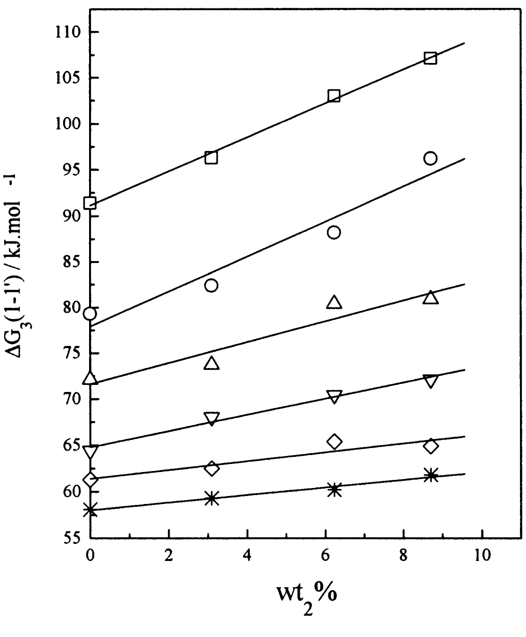

Fig. 6. The data of $\Delta G_3^{\neq}(1-1')$ as a function of sucrose mass percent at T: □, 288.15; ○, 293.15; △, 298.15; ▽, 303.15; ◇, 308.15 and *, 313.15 K.

tion concerning the solvation of the solutes and their effects on the structure of the solvent in the near environment of the solute molecules. Heptanedioic acid is acting as a hydrophobic solute in aqueous sucrose solution, and sucrose is acting as a water structure maker. On the basis of a free-energy study, it can be determined that in the solvation shell of heptanedioic acid, the sucrose–water interaction in the transition state increases with the increase in $\mathrm{wt}_2\%$, and decreases with a temperature increase and approaches to the state in bulk zone.

1. Experimental

1.1. Materials

Sucrose was used as received from Shanghai Chemical Reagent, Inc. Its purity was of analytical grade. Heptanedioic acid, analytical grade, also from Shanghai Chemical Reagent, Inc., was purified by recrystallization from acetone and then dried under vacuum at 393.15 K over 10 h.[21] Both reagents were then stored over P_2O_5 in a desiccator before use. Water was obtained by distilling deionized water from alkaline $KMnO_4$ solution to remove any organic matter.

1.2. Density and viscosity measurement

Mixtures of the desired compositions were prepared by mixing accurately weighed quantities of the material, using a TG328B balance with a precision of ±0.1 mg. Densities were measured with an Anton Paar DMA 602 vibrating tube densimeter. The temperature of the cell was controlled by circulation of water from a water bath with a temperature within ±0.01 K. The densimeter was calibrated by using degassed water and dry air as calibration substances. The estimated error of density measurement is within $\pm 0.00002\ \mathrm{g\ cm^{-3}}$. The kinematic viscosities, v, were measured by means of a suspended level Ubbelohde viscometer. The time of efflux was measured with a digital stopwatch to ±0.1 s. The viscometer was kept in a water thermostat controlled to ±0.01 K. The kinematic viscosity (v) and the dynamic viscosity (η) are given by the following equations:

$$v = Lt - K/t \tag{13}$$

$$\eta = v\rho \tag{14}$$

where t is the efflux time, ρ is the density of solution, L and K are the characteristic constants of the viscometer. The values of the constants L and K were determined by using the density and viscosity values of water and C_6H_6 from literature.[20] The calibration process was carried out in following steps. Measuring the efflux time of water and C_6H_6 in a viscometer at temperature 288.15, 293.15, 298.15, 303.15, 308.15 and 313.15 K, respectively. Using a least-square regression method to fit constants L and K by Eq. (13) for systems of water and C_6H_6, respectively. Two viscometers were used in experiments. Average value of L and K are obtained for each viscometer: (1) $L = 0.007294$, $K = 25.98$; (2) $L = 0.007146$, $K = 23.96$ (η: MPa s; t: s; ρ: $\mathrm{g\ cm^{-3}}$). In all cases, the experiments were performed by using two viscometers at least in 10 replicates for each composition at each temperature, and the results were averaged. The estimated relative standard deviation of replicates for η was ±0.1%.

2. Supplementary material

Numerical data for Figs. 1–6, the data of V_3^0 and V_{m12} (Tables 1–4), have been deposited as Supplementary Material and are available in the WEB version of the journal.

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