

Rapid Communication

## Viscosity of aqueous solutions of some alkali cyclohexylsulfamates at 25.0 °C

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### Abstract

The dynamic viscosity of aqueous solutions of cyclohexylsulfamic acid and of its lithium, sodium and potassium salts was measured in the concentration range from 0.02 to 0.70 mol dm<sup>-3</sup> (the potassium salt only up to 0.20 mol dm<sup>-3</sup> because of its poor solubility) at a temperature of 25.0 °C. The data for relative viscosity, which were calculated from the dynamic viscosity, were analysed with the help of the extended Jones–Dole equation and the viscosity coefficients  $A_\eta$ ,  $B_\eta$  and  $D_\eta$  were evaluated. The  $B_\eta$  coefficients of the salts were divided into their ionic contributions and the ionic  $B_\eta$  value for the cyclohexylsulphamic ion was determined. From the viscosity coefficient  $B_\eta$  the partial molar Gibbs energy of activation for viscous flow at infinite dilution was calculated for the investigated solutes and interpreted in terms of relative solute effects on the solvent in the ground and in the transition states. Additionally, the hydration number of the solute was determined and some correlation between the transport properties of solutions of cyclohexylsulphamates and their relative sweetness was found.

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### 1. Introduction

Water is the medium for all sweet taste chemoreception processes (Birch, 2002). According to the three step model of sweet taste chemoreception (Mathlouthi, Bressan, Portmann, & Serghat, 1993), the first step requires that the hydrated molecule reaches the region of sweet receptors in the taste epithelium. Such an accession depends on solution properties, e.g., volumetric properties, but transport properties are also relevant to the kinetics of mouth movement during tasting. Hydration effects are extremely sensitive to the stereochemical details of the solute and are also affected by the molecular configuration (Franks, 2000). Conversely, it is expected that the structure of water would affect the conformation of a sweetener molecule in solution. All these modifications play an important role in the physicochemical properties of the solution and influence the

accession of stimuli to the receptor site and the resulting perception of sweet taste.

According to our knowledge, most of the literature viscosity data are reported for sugar solutions, and surprisingly few viscosity data have been published for aqueous solutions of intense artificial sweeteners at 25.0 °C, especially for electrolytic types of solute (for example Mathlouthi et al., 1993). Therefore this study concentrates on the viscosity properties of aqueous solutions of some alkali salts of cyclohexylsulfamic acid with the aim of elucidating the effect of the individual ionic species on the solution properties and, consequently, on the taste quality.

### 2. Materials and methods

The specifications of the compounds employed, i.e., commercially available cyclohexylsulfamic acid (HCy) and its sodium salt (NaCy), as well as of lithium cyclohexylsulfamate (LiCy) and potassium

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cyclohexylsulfamate (KC<sub>6</sub>), synthesized in our laboratory, were described previously (Rudan-Tasic & Klofutar, 2004).

The investigated solutions were prepared on a molar concentration scale by precise weighing of the solute, to  $\pm 1 \times 10^{-5}$  g (AT201 Mettler Toledo) and dilution with doubly-distilled and boiled water in a calibrated 25.0 cm<sup>3</sup> volumetric flask (Hirschmann).

The solution densities  $d$  were measured at  $(25.00 \pm 0.01)$  °C using an A. Paar digital densimeter (Model DMA 60) with a reproducibility of  $1 \times 10^{-5}$  g cm<sup>-3</sup>. The thermal stability of the measuring cell was controlled by a digital thermometer (DT100-20, A. Paar) to better than  $\pm 0.01$  °C; and the densimeter was calibrated with water (Kratky, Leopold, & Stabinger,) and dry air (Weast, 1974–1975).

The viscosities of aqueous solutions of HC<sub>6</sub> and its salts were determined with an Ubbelohde capillary viscometer at  $(25.00 \pm 0.01)$  °C. The absolute viscosity values were calculated by means of the equation (Cannon, Manning, & Bell, 1960):

$$\eta = Cdt - \frac{Ed}{t^2} \quad (1)$$

where  $\eta$  is the absolute viscosity (i.e., dynamic viscosity) of the solution,  $t$  is the flow time, and  $C$  and  $E$  are constants characteristic of the viscometer. The viscometer constants  $C$  and  $E$  were determined by a least-squares fit to Eq. (1) of the literature data for the absolute viscosity,  $\eta_0$ , and the density of water,  $d_0$  (Riddick, Bunger, & Sakano, 1986), at the respective temperature (i.e., from 20.0 to 45.0 °C in 5 °C steps). The temperature of the water bath was maintained to  $\pm 0.01$  °C and controlled using a precision thermometer (CKT 100, A. Paar). The flow time of the investigated solutions was between 219 and 330 s, and was measured with an accuracy better than 0.1 s. For each solution, the flow time was measured at least ten times. The maximal error of the measured viscosity,  $\partial\eta$ , was  $2 \times 10^{-6}$  Pa s.

### 3. Results and discussion

The viscosity data of the systems investigated are presented in Table 1 as a function of concentration,  $c$  (mol dm<sup>-3</sup>), at 25.0 °C. Besides the dynamic viscosity  $\eta$ , the values of kinematic viscosity,  $v$  ( $v = \eta/d$ ), relative viscosity,  $\eta_r$  ( $\eta_r = \eta/\eta_0$ ), specific viscosity,  $\eta_{sp}$  ( $\eta_{sp} = (\eta - \eta_0)/\eta_0$ ), as well as of reduced viscosity,  $\eta_{red}$  ( $\eta_{red} = \eta_{sp}/c$ ) are presented. It can be seen from Table 1 and from Fig. 1 that the viscosity,  $\eta$ , of the investigated solutions depends on the solute and increases in a non-linear manner with concentration.

The effect of the electrolyte on the flow process of the solution can be explained in terms of Jones–Dole coefficients (1929)

$$\eta_r = 1 + A_\eta c^{1/2} + B_\eta c + D_\eta c^{3/2} + \dots \quad (2)$$

where  $A_\eta$  depends on long-range Coulombic forces,  $B_\eta$  is the viscosity coefficient which is closely related to the ion–solvent interaction (i.e., a function of the size and hydration of the solute) and  $D_\eta$  is a constant which depends on higher terms of the long-range Coulombic forces, on higher terms of the hydrodynamic effect, and on structural solute–solute interactions. As such, the parameter  $D_\eta$  is more complex and it cannot be used unambiguously to obtain information on solute–solute or solute–solvent interactions (Desnoyers & Perron, 1972).

The interaction parameter,  $A_\eta$ , was obtained on the basis of Eq. (2), i.e., from plots of  $(\eta_r - 1)/c^{1/2}$  vs.  $c^{1/2}$ . To obtain a linear relationship (giving the viscosity coefficient  $A_\eta$  at the intercept to the ordinate) only lower concentration ranges were taken into account, i.e., up to 0.50 mol dm<sup>-3</sup> for HC<sub>6</sub>, 0.45 mol dm<sup>-3</sup> for LiC<sub>6</sub> and NaC<sub>6</sub>, and up to 0.18 mol dm<sup>-3</sup> for KC<sub>6</sub>. As a weighting factor, in the procedure of weighted fitting by linear regression, the reciprocal value of the squared term error, i.e.,  $1/[\partial((\eta_r - 1)/c^{1/2})]^2$ , was applied. The  $A_\eta$  coefficients are small and have large standard errors (Table 2), indicating a small ion–ion interaction term,  $A_\eta c^{1/2}$  in Eq. (2). However, the viscosity coefficient  $A_\eta$  was also calculated from the mobility data and solvent properties, on the basis of the Debye–Hückel theory (Crudden, Delaney, Feakins, O'Reilly, & Waghorne, 1986) as

$$A_\eta = \frac{0.2577\lambda^0}{\eta_0(\epsilon_0 T)^{1/2}\lambda_+^0\lambda_-^0} \left[ 1 - 0.6863 \left( \frac{\lambda_+^0 - \lambda_-^0}{\lambda^0} \right)^2 \right] \quad (3)$$

where  $\epsilon_0$  is the dielectric constant of the solvent (Riddick et al., 1986),  $\lambda^0$  is the limiting molar electrolytic conductance of the electrolyte, being an additive property of the respective ionic components, i.e., the limiting molar conductances of cation,  $\lambda_+^0$  (Robinson & Stokes, 2002) and anion,  $\lambda_-^0$ ; for the cyclohexylsulfamic anion, the value  $\lambda_{\text{Cy}^-}^0 = 27.55$  S cm<sup>2</sup> mol<sup>-1</sup> was used (Luci, 2001). The calculated values of the constant  $A_\eta$  (Eq. (3)) are summarized in Table 2.

The viscosity coefficients  $B_\eta$  and  $D_\eta$  were determined by a least-squares analysis of Eq. (2) in the form (Out & Los, 1980):

$$\frac{(\eta_r - 1 - A_\eta c^{1/2})}{c} = B_\eta + D_\eta c^{1/2} \quad (4)$$

where for coefficients  $A_\eta$  the values calculated via relation (3) were used. As an example, Fig. 2 shows the curve of  $(\eta_r - 1 - A_\eta c^{1/2})/c$  vs.  $c^{1/2}$  for sodium cyclohexylsulfamate.  $B_\eta$  and  $D_\eta$  values obtained are also given in Table 2. The relevance of the calculated viscosity parameters was tested by recalculating, by means of their known values, the value of  $\eta_r$  at each concentration

Table 1

Density, dynamic, kinematic, relative, specific and reduced viscosities of aqueous solutions of the investigated cyclohexylsulfamates as a function of the molar concentration at 25.0 °C

| $c$ (mol dm <sup>-3</sup> ) | $d$ (kg dm <sup>-3</sup> ) | $\eta \times 10^3$ (Pa s) | $\nu \times 10^6$ (m <sup>2</sup> s <sup>-1</sup> ) | $\eta_r$ | $\eta_{sp}$ | $\eta_{red}$ (dm <sup>3</sup> mol <sup>-1</sup> ) |
|-----------------------------|----------------------------|---------------------------|---|----------|-------------|---|
| <i>HCy</i>                  |                            |                           |   |          |             |   |
| 0.02502                     | 0.99836                    | 0.899                     | 0.9007  | 1.0101   | 0.0101      | 0.4022  |
| 0.05001                     | 0.99963                    | 0.911                     | 0.9111  | 1.0231   | 0.0231      | 0.4619  |
| 0.07506                     | 1.00090                    | 0.923                     | 0.9227  | 1.0373   | 0.0373      | 0.4976  |
| 0.10004                     | 1.00215                    | 0.934                     | 0.9319  | 1.0491   | 0.0491      | 0.4905  |
| 0.15000                     | 1.00464                    | 0.956                     | 0.9513  | 1.0736   | 0.0736      | 0.4905  |
| 0.20003                     | 1.00711                    | 0.975                     | 0.9676  | 1.0946   | 0.0946      | 0.4732  |
| 0.25001                     | 1.00956                    | 0.994                     | 0.9845  | 1.1164   | 0.1164      | 0.4655  |
| 0.30003                     | 1.01200                    | 1.017                     | 1.0049  | 1.1424   | 0.1424      | 0.4745  |
| 0.35010                     | 1.01443                    | 1.038                     | 1.0233  | 1.1659   | 0.1659      | 0.4741  |
| 0.49996                     | 1.02171                    | 1.105                     | 1.0818  | 1.2416   | 0.2416      | 0.4832  |
| <i>LiCy</i>                 |                            |                           |   |          |             |   |
| 0.02437                     | 0.99843                    | 0.906                     | 0.9079  | 1.0182   | 0.0182      | 0.7478  |
| 0.05174                     | 0.99999                    | 0.916                     | 0.9161  | 1.0290   | 0.0290      | 0.5607  |
| 0.07350                     | 1.00123                    | 0.929                     | 0.9278  | 1.0434   | 0.0434      | 0.5910  |
| 0.10001                     | 1.00273                    | 0.945                     | 0.9428  | 1.0619   | 0.0619      | 0.6193  |
| 0.14985                     | 1.00556                    | 0.971                     | 0.9652  | 1.0903   | 0.0903      | 0.6023  |
| 0.20117                     | 1.00847                    | 1.004                     | 0.9958  | 1.1281   | 0.1281      | 0.6367  |
| 0.25131                     | 1.01131                    | 1.033                     | 0.9958  | 1.1599   | 0.1599      | 0.6364  |
| 0.30214                     | 1.01418                    | 1.064                     | 1.0211  | 1.1952   | 0.1952      | 0.6462  |
| 0.39937                     | 1.01966                    | 1.123                     | 1.0492  | 1.2615   | 0.2615      | 0.6549  |
| 0.50340                     | 1.02551                    | 1.201                     | 1.1014  | 1.3487   | 0.3487      | 0.6927  |
| 0.59869                     | 1.03084                    | 1.277                     | 1.1708  | 1.4341   | 0.4341      | 0.7250  |
| 0.69947                     | 1.03647                    | 1.361                     | 1.2385  | 1.5283   | 0.5283      | 0.7552  |
| <i>NaCy</i>                 |                            |                           |   |          |             |   |
| 0.02502                     | 0.99901                    | 0.904                     | 0.9048  | 1.0153   | 0.0153      | 0.6113  |
| 0.05001                     | 1.00096                    | 0.921                     | 0.9196  | 1.0340   | 0.0340      | 0.6802  |
| 0.07503                     | 1.00292                    | 0.930                     | 0.9277  | 1.0451   | 0.0451      | 0.6004  |
| 0.10001                     | 1.00488                    | 0.948                     | 0.9431  | 1.0646   | 0.0646      | 0.6457  |
| 0.15001                     | 1.00878                    | 0.974                     | 0.9656  | 1.0942   | 0.0942      | 0.6278  |
| 0.19999                     | 1.01267                    | 1.000                     | 0.9880  | 1.1238   | 0.1238      | 0.6191  |
| 0.25004                     | 1.01655                    | 1.031                     | 1.0140  | 1.1579   | 0.1579      | 0.6315  |
| 0.29998                     | 1.02041                    | 1.065                     | 1.0441  | 1.1967   | 0.1967      | 0.6559  |
| 0.35001                     | 1.02428                    | 1.095                     | 1.0694  | 1.2304   | 0.2304      | 0.6583  |
| 0.40002                     | 1.02812                    | 1.135                     | 1.1036  | 1.2745   | 0.2745      | 0.6862  |
| 0.50002                     | 1.03579                    | 1.202                     | 1.1604  | 1.3501   | 0.3501      | 0.7001  |
| 0.60002                     | 1.04341                    | 1.283                     | 1.2292  | 1.4407   | 0.4407      | 0.7345  |
| <i>KCy</i>                  |                            |                           |   |          |             |   |
| 0.02112                     | 0.99883                    | 0.899                     | 0.9001  | 1.0098   | 0.0098      | 0.4654  |
| 0.04023                     | 1.00043                    | 0.906                     | 0.9061  | 1.0182   | 0.0182      | 0.4522  |
| 0.05999                     | 1.00209                    | 0.913                     | 0.9108  | 1.0252   | 0.0252      | 0.4208  |
| 0.09187                     | 1.00477                    | 0.924                     | 0.9194  | 1.0377   | 0.0377      | 0.4100  |
| 0.10111                     | 1.00555                    | 0.929                     | 0.9239  | 1.0436   | 0.0436      | 0.4313  |
| 0.12097                     | 1.00722                    | 0.936                     | 0.9294  | 1.0515   | 0.0515      | 0.4257  |
| 0.13024                     | 1.00801                    | 0.940                     | 0.9321  | 1.0554   | 0.0554      | 0.4255  |
| 0.16011                     | 1.01053                    | 0.952                     | 0.9417  | 1.0690   | 0.0690      | 0.4304  |
| 0.18089                     | 1.01228                    | 0.961                     | 0.9489  | 1.0790   | 0.0790      | 0.4370  |
| 0.19921                     | 1.01385                    | 0.967                     | 0.9538  | 1.0863   | 0.0863      | 0.4330  |
| 0.20879                     | 1.01466                    | 0.974                     | 0.9596  | 1.0936   | 0.0936      | 0.4485  |

and comparing it with the experimental one; the differences were less than 0.0029.

For cyclohexylsulfamic acid, which is not completely dissociated into free ions, the limiting ionic molar coefficients were obtained from the relation (Davies & Malpass, 1964)

$$(\eta_r - 1) - A_\eta F(I) = B_i \alpha c + B_{ip}(1 - \alpha)c \quad (5)$$

where  $\alpha$  is the degree of dissociation of the electrolyte,  $B_i$  is the sum of the corresponding ionic coefficients  $B_+$  and  $B_-$ , and  $B_{ip}$  is the coefficient of the ionic pair and  $I = 1/2 \sum \alpha c z^2$ , where  $z$  is the charge-number of the ion. In Eq. (5) the function  $F(I)$  is given as

$$F(I) = \frac{I^{1/2}}{(1 + I^{1/2}) - 0.2I} \quad (6)$$

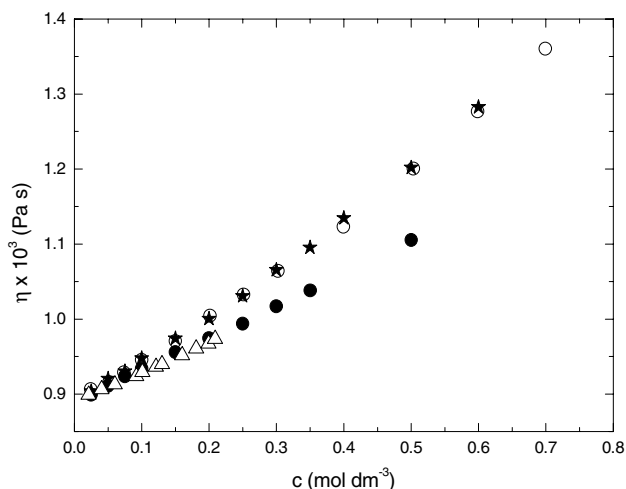


Fig. 1. Concentration dependence of dynamic viscosity for aqueous solutions of cyclohexylsulfamic acid and its alkali salts at 25.0 °C; ○ – LiCy; ★ – NaCy, △ – KCy, ● – HCy.

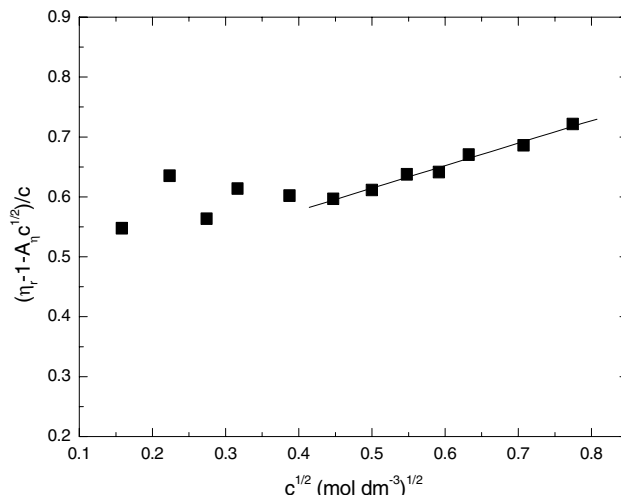


Fig. 2. Relationship between  $(\eta_r - 1 - A_\eta c^{1/2})/c$  and  $c^{1/2}$  for sodium cyclohexylsulfamate at 25.0 °C.

where  $I$  represents the ionic strength of the electrolyte solution. For HCy, whose dissociation constant is known at 25.0 °C ( $K_a = 0.01538 \pm 0.0045$ , Klofutar, Luci, & Abramović, 1999),  $\alpha$  was calculated, and the left-hand side of Eq. (5) divided by  $c$  was plotted against  $\alpha$  for a series of concentrations (up to  $I \approx 0.1 \text{ mol dm}^{-3}$ ); for  $A_\eta$  the theoretically calculated value was used (Table 2). From the satisfactory straight line, the following values of the viscosity coefficients in Eq. (5) were found:  $B_i = (0.343 \pm 0.017) \text{ dm}^3 \text{ mol}^{-1}$  and  $B_{ip} = (0.650 \pm 0.041) \text{ dm}^3 \text{ mol}^{-1}$ . Recalculating  $\eta_r$  via Eq. (5) gives the average difference between the experimental and calculated value of the relative viscosity as  $\pm 0.001$ .

The viscosity coefficient  $B_\eta$  is usually suggested to be a measure of the higher terms of the long-range Coulombic forces, hydrodynamic or size and shape effects, solvation effects and structural effects, and can be interpreted as consisting of two terms (Stokes & Mills, 1965)

$$B_\eta = B_{\text{size}} + B_{\text{solv}} \quad (7)$$

where  $B_{\text{size}}$  is the effect of the solute and  $B_{\text{solv}}$  is the contribution arising from solute–solvent interactions. Thus  $B_{\text{solv}}$

$$B_{\text{solv}} = B_\eta - 0.0025\bar{V}_2^0 \quad (8)$$

Table 2  
Values of the constants in Eq. (2)

| Solute | $A_{\eta(\text{theor})} (\text{mol dm}^{-3})^{-1/2}$ | $A_{\eta(\text{exp})} (\text{mol dm}^{-3})^{-1/2}$ | $B_\eta (\text{dm}^3 \text{ mol}^{-1})$ | $D_\eta (\text{mol dm}^{-3})^{-3/2}$ |
|--------|--|--|---|--------------------------------------|
| LiCy   | 0.011559   | $0.006 \pm 0.015$                                  | $0.486 \pm 0.014$                       | $0.256 \pm 0.028$                    |
| NaCy   | 0.010059   | $0.009 \pm 0.012$                                  | $0.427 \pm 0.013$                       | $0.376 \pm 0.022$                    |
| KCy    | 0.008112   | $0.002 \pm 0.013$                                  | $0.338 \pm 0.013$                       | $0.186 \pm 0.034$                    |
| HCy    | 0.003705   | $0.005 \pm 0.008$                                  |   |                                      |

because, in the ideal case, the coefficient  $B_\eta$  is a linear function of the solute partial molar volume,  $\bar{V}_2^0$  with a slope equal to 0.0025, i.e., the Einstein slope (Desnoyers & Perron, 1972). Such a plot is shown in Fig. 3 for the alkali cyclohexylsulfamates and some other sweeteners in water at 25.0 °C; as expected, the Einstein relation is not obeyed. A positive value of  $B_{\text{solv}}$  (Table 3) would correspond to an overall structure-making effect of the solutes investigated. With the salts of strongly hydrated and strongly electrostrictive ions such as  $\text{Li}^+$  and  $\text{Na}^+$ , the Coulombic-type hydration has opposite effects on  $B_\eta$  and  $\bar{V}_2^0$ , and charge–dipole interactions decrease  $\bar{V}_2^0$  (electrostriction) but increase the effective size of the moving ion. For the potassium salt,  $B_{\text{solv}}$  is close to zero (i.e., neither a “structure-maker” nor a “structure-breaker” but it can be classified as an intermediate type of solute) and because it has the smallest ratio,  $B_{\text{size}}/B_\eta$ , KCy seems to exert less influence on water structure than the other alkali salts or sugars. In general, sugars show similar values for the relative proportions of  $B_{\text{size}}$  and  $B_{\text{solv}}$  in the overall hydrodynamic molar volume,  $B_\eta$  (about 2/3 and about 1/3, respectively, Mathlouthi et al., 1993) and larger differences between artificial sweeteners are observed.

The viscosity coefficient  $B_\eta$  of electrolytes is an approximately additive property of the respective ionic components

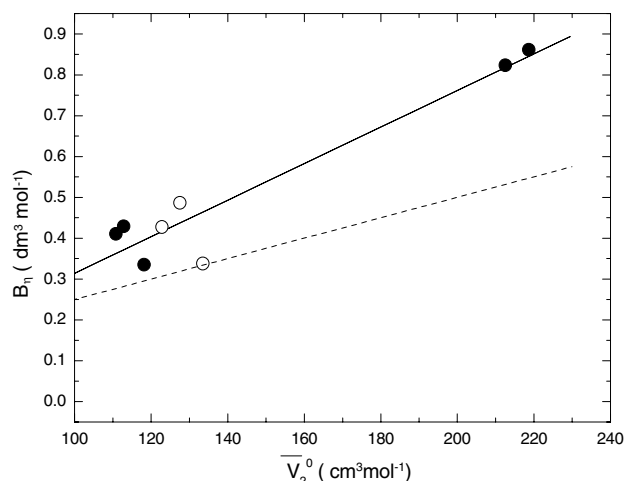


Fig. 3. Dependence of  $B_\eta$  on  $\bar{V}_2^0$  for some sweeteners in water at 25.0 °C (● – Mathlouthi et al., 1993, Tables 2 & 3, ○ – investigated alkali cyclohexylsulfamates, --- Einstein law).

$$B_\eta = B_+ + B_- \quad (9)$$

On the basis of literature values of the contributions from cations (Millero, 1972) the contribution from the cyclohexylsulfamate anion was calculated for the salts investigated (Table 4) and its average value,  $\bar{B}_{\text{Cy}^-} = (0.341 \pm 0.004) \text{ dm}^3 \text{ mol}^{-1}$  was found to be close to the value obtained for cyclohexylsulfamic acid,  $B_i = B_{\text{H}^+} + B_{\text{Cy}^-} = (0.343 \pm 0.004) \text{ dm}^3 \text{ mol}^{-1}$ , assuming that  $B_{\text{H}^+} = 0.0 \text{ dm}^3 \text{ mol}^{-1}$ .

While the coefficients  $B_\eta$  are operationally useful, greater insight into viscous flow is achieved using the thermodynamic activation parameters of viscous flow.

Thus the partial Gibbs free energy for activation of viscous flow of an electrolyte solute at infinite dilution,  $\Delta\bar{G}_2^{0\#}$  is given by (Feakins, Waghorne, & Lawrence, 1986):

$$B_\eta = \left( \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} \right) + \left( \frac{\bar{V}_1^0}{1000} \right) \left( \frac{\Delta\bar{G}_2^{0\#} - \Delta\bar{G}_1^{0\#}}{RT} \right) \quad (10)$$

where  $\Delta\bar{G}_1^{0\#}$  is the Gibbs energy of activation per mole for the pure solvent,  $R$  is the gas constant,  $T$  is the absolute temperature and  $\bar{V}_1^0 (= V_1^0)$  is the partial molar volume of the solvent as  $c \rightarrow 0$ . It is interesting that the first term in Eq. (10) for aqueous solutions of alkali cyclohexylsulfamates is a negative contribution to the viscosity coefficient  $B_\eta$  and it reduces the value of  $B_\eta$  from 22% to 34% along the series of alkali salts (Table 5). The second term is uniformly positive since  $\Delta\bar{G}_2^{0\#} > \Delta\bar{G}_1^{0\#}$ , where for  $\Delta\bar{G}_1^{0\#}$  a value of  $9163.85 \text{ J mol}^{-1}$  was used (Feakins, Freemantle, & Lawrence, 1974); this phenomenon suggests that ion–solvent bonds are stronger than solvent–solvent bonds in the transition state and tend to decrease from  $\text{Li}^+$  to  $\text{K}^+$ . Moreover, in the same series,  $\Delta\bar{G}_2^{0\#}$ , like  $B_\eta$ , was found to decrease linearly with increase in the molecular weight of the cation.

Information on the hydration of solutes can be obtained by a procedure given by Linow and Philipp (1984). The hydration number,  $n_h$ , i.e., the number of moles of bonded water molecules in the inner hydration sphere per mole of solute, was evaluated from the change of solution viscosity with solute concentration:

$$\frac{\eta_{\text{sp}}}{c} = 2.5\bar{V}_\eta + \bar{V}_\eta n_{\text{sp}} \quad (11)$$

Table 3

Limiting partial molar volume of the solute, viscosity coefficients  $B_\eta$ ,  $B_{\text{size}}$  and  $B_{\text{solv}}$  for the investigated cyclohexylsulfamates and for some other sweeteners at 25.0 °C

| Solute                    | $\bar{V}_2^0$ (cm <sup>3</sup> mol <sup>-1</sup> ) | $B_\eta$ (dm <sup>3</sup> mol <sup>-1</sup> ) | $B_{\text{solv}}$ (dm <sup>3</sup> mol <sup>-1</sup> ) | $\frac{B_{\text{size}}}{B}$ | $\frac{B_{\text{size}}}{B}$ |
|---------------------------|--|---|--|-----------------------------|-----------------------------|
| LiCy                      | 127.52 <sup>a</sup>                                | 0.486   | 0.167  | 0.344                       | 0.656                       |
| NaCy                      | 122.81 <sup>a</sup>                                | 0.427   | 0.120  | 0.281                       | 0.719                       |
| KCy                       | 133.50 <sup>a</sup>                                | 0.338   | 0.004  | 0.093                       | 0.987                       |
| Aspartame <sup>b</sup>    | 218.67   | 0.861   | 0.315  | 0.365                       | 0.634                       |
| Saccharin-Na <sup>b</sup> | 118.19   | 0.335   | 0.040  | 0.119                       | 0.880                       |
| Glucose <sup>b</sup>      | 112.80   | 0.429   | 0.148  | 0.345                       | 0.655                       |
| Fructose <sup>b</sup>     | 110.80   | 0.410   | 0.133  | 0.324                       | 0.675                       |
| Sucrose <sup>b</sup>      | 212.56   | 0.823   | 0.292  | 0.354                       | 0.645                       |

<sup>a</sup> Rudan-Tasic and Klofutar (2004).

<sup>b</sup> Mathlouthi et al. (1993), Tables 2 and 3.

Table 4

Viscosity ionic coefficients of some alkali cyclohexylsulfamates at 25.0 °C

| Solute | $B_\eta$ (dm <sup>3</sup> mol <sup>-1</sup> ) | $B_+^a$ (dm <sup>3</sup> mol <sup>-1</sup> ) | $B_-$ (dm <sup>3</sup> mol <sup>-1</sup> ) |
|--------|---|--|--|
| LiCy   | $0.486 \pm 0.014$                             | 0.149  | 0.337                                      |
| NaCy   | $0.427 \pm 0.013$                             | 0.086  | 0.341                                      |
| KCy    | $0.338 \pm 0.013$                             | -0.007                                       | 0.345                                      |

<sup>a</sup> Millero (1972).

Table 5

Contributions of the terms of Eq. (10) to the viscosity coefficient  $B_\eta$  for some cyclohexylsulfamates at 25.0 °C

| Solute | $\left(\frac{\bar{V}_1^0 - \bar{V}_2^0}{1000}\right)$ (dm <sup>3</sup> mol <sup>-1</sup> ) | $\left(\frac{\bar{V}_1^0}{1000}\right)\left(\frac{-\bar{G}_2^{0\#} - \Delta G_1^{0\#}}{RT}\right)$ (dm <sup>3</sup> mol <sup>-1</sup> ) | $(\Delta \bar{G}_2^{0\#} - \Delta \bar{G}_1^{0\#})$ (J mol <sup>-1</sup> ) | $\Delta \bar{G}_2^{0\#}$ (J mol <sup>-1</sup> ) |
|--------|--|---|--|---|
| LiCy   | -0.109   | 0.595   | 81,695   | 90,859  |
| NaCy   | -0.105   | 0.532   | 72,954   | 82,118  |
| KCy    | -0.115   | 0.453   | 62,210   | 71,374  |

where  $\bar{V}_\eta$  is the volume of hydrated solute and can be obtained as the slope of the plot of  $\eta_{sp}/c = \eta_{red}$  vs.  $\eta_{sp}$ . Then the hydration number is given by

$$n_h = \frac{\bar{V}_\eta - \bar{V}_2^0}{V_1^0} \quad (12)$$

As an example, in Fig. 4 the dependence of  $\eta_{red}$  on  $\eta_{sp}$  for the sodium salt of cyclohexylsulfamic acid is given, from which it can be seen that Eq. (11) satisfactorily represents the experimental results. The calculated values of hydration numbers for the investigated alkali salts are given in Table 6.

The hydration of the cyclohexylsulfamate ion was deduced from Einstein's equation (Dasgupta, Das, & Hazra, 1989)

$$B_\pm = 2.5 \frac{4\pi R_\pm^3 N}{3 \cdot 1000} \quad (13)$$

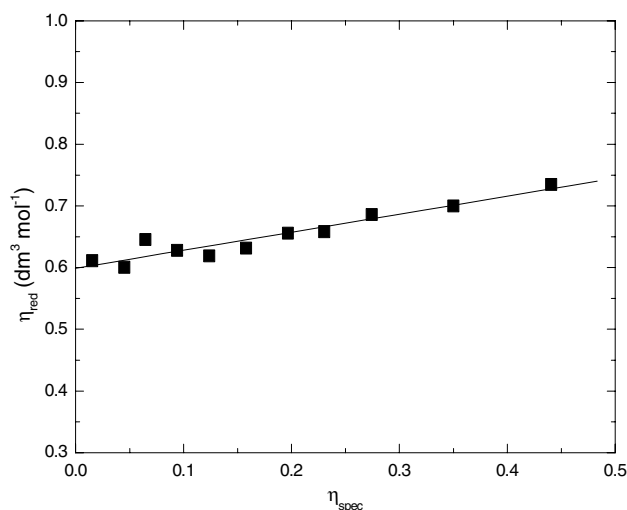


Fig. 4. The dependence of reduced viscosity on specific viscosity of sodium cyclohexylsulfamate at 25 °C.

Table 6

Molar volumes of some hydrated alkali cyclohexylsulfamates, hydration numbers, limiting ionic conductances and Gibbs energies of hydration of the cations at 25.0 °C

| Solute | $\bar{V}_\eta$ (dm <sup>3</sup> mol <sup>-1</sup> ) | $n_h$ | $\lambda_\pm^{0,a}$ (S cm <sup>2</sup> mol <sup>-1</sup> ) | $-\Delta G_{\pm(h)}^a$ (kJ mol <sup>-1</sup> ) |
|--------|---|-------|--|--|
| LiCy   | 0.338 ± 0.025                                       | 12    | 38.68  | 479  |
| NaCy   | 0.292 ± 0.031                                       | 9     | 50.10  | 375  |
| KCy    | 0.209 ± 0.066                                       | 4     | 73.50  | 307  |

<sup>a</sup> Robinson and Stokes (2002).

where  $R_\pm$  is the radius of the ion, assumed to be a rigid sphere moving in a continuum and 2.5 is the shape factor for a sphere. The number of water molecules bound to the ion in the primary sphere of hydration,  $n_{\pm(h)}$ , can be calculated from (Feakins & Lawrence, 1966):

$$B_\pm = \frac{2.5}{1000} (V_i + n_{\pm(h)} V_1^0) \quad (14)$$

where the bare ion molar volume,  $V_i$ , is related to the crystallographic radius of the ion. For the cyclohexylsulfamate ion with a value of  $V_{Cy^-} = 127.65$  cm<sup>3</sup> mol<sup>-1</sup>, the hydration number  $n_{Cy^-(h)}$  determined on the basis of Eq. (14) was found to be 0.48 which is very close to the value obtained on the basis of volumetric measurements (i.e., 0.54, Rudan-Tasic & Klofutar, 2004).

There is no clear relationship observed between the transport and volumetric properties of the systems studied. The results shown in Table 3 suggest that the viscosity coefficient  $B_\eta$  accounts for the hydrodynamic solvation of the solutes, whereas the apparent molar volume reflects the static arrangement of the solute molecule within the structure of water. Therefore, a comparison of the two volumes for the same solute shows a great difference even though both parameters reflect the volume of solvent associated with one mole of the solute. Thus, the value of  $B_\eta$  is about three to four times as high as the apparent molar volume for KCy to LiCy and the same is true for each of the sugars presented in Table 3.

There is also no direct relation found between the transport properties of the alkali cyclohexylsulfamates and the published sweetness values. However, data on the relative sweetness, RS, are not available and are known only for the sodium and potassium salts (39.8 and 40.2, respectively, Spillane et al., 1996). So, we may speak only of a trend, i.e., an increase in the relative sweetness in the order of decreasing value of the thermodynamic parameter of activation for viscous flow,

$\Delta\bar{G}_2^{0\#}$  (Table 5). Namely, weaker solute–solvent interactions (i.e., lower  $\Delta\bar{G}_2^{0\#}$ ) mean higher mobility of water molecules around the sweetener molecule, which seems to be essential in increasing the sweetness. Similarly, the relatively high sweetness of D-fructose (RS = 1.2,  $\Delta\bar{G}_2^{0\#} = 79.2 \text{ kJ mol}^{-1}$ ) compared to other natural sugars, e.g., D-glucose (RS = 0.7,  $\Delta\bar{G}_2^{0\#} = 79.5 \text{ kJ mol}^{-1}$ ) or D-galactose (RS = 0.4,  $\Delta\bar{G}_2^{0\#} = 84.4 \text{ kJ mol}^{-1}$ ) may be due to the higher mobility of water around it; the relative sweetness data were taken from Mathlouthi and Suvre (1988) and the  $\Delta\bar{G}_2^{0\#}$  values from Klofutar, Paljk, and Kač (1989). When water mobility is increased in the region of sweet receptors in the taste epithelium, the  $\text{Na}^+/\text{K}^+$  transport across the membrane of the taste cells is supposed to be facilitated, leading to a high value of the membrane potential and this could enhance the intensity of the sweetness (Mathlouthi, 1984). In fact, alkali cyclohexylsulfamates belong to the ionic type of sweeteners with a light bitter aftertaste (Rudan-Tasic & Klofutar, 2004), confirming that sweetness may, therefore, be thought of as a sensation involving a complicated interplay of structural and solution properties, i.e., a variety of interactions in solutions of sweeteners. An understanding of this interplay may lead to a better understanding of sweet taste chemoreception.

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