

## Viscosity of Aqueous Solutions of Lithium, Sodium, Potassium, Rubidium and Caesium Cyclohexylsulfamates from 293.15 to 323.15 K

Jaka Horvat · Marija Bešter-Rogač · Cveto Klofutar · Darja Rudan-Tasic

Received: 18 January 2008 / Accepted: 22 April 2008 / Published online: 19 July 2008  
© Springer Science+Business Media, LLC 2008

**Abstract** The viscosities of aqueous solutions of lithium, sodium, potassium, rubidium and caesium cyclohexylsulfamates were measured at 293.15, 298.15, 303.15, 313.15 and 323.15 K. The relative viscosity data were analyzed and interpreted in terms of the Kaminsky equation,  $\eta_r = 1 + Ac^{1/2} + Bc + Dc^2$ . The viscosity *A*-coefficient was calculated from the Falkenhagen-Dole theory. The viscosity *B*-coefficients are positive and relatively large. Their temperature coefficient  $\partial B/\partial T$  is negative or near zero for lithium and sodium salts whereas for potassium, rubidium and caesium salts it is positive. The viscosity *D*-coefficient is positive. This was explained by the size of the ions, structural solute–solute interactions, hydrodynamic effect, and by higher terms of the long-range Debye–Hückel type of forces. From the viscosity *B*-coefficients the thermodynamic functions of activation of viscous flow were calculated. The limiting partial molar Gibbs energy of activation of viscous flow of the solute was divided into contributions due to solvent molecules and the solute in the transition state. The activation energy of the solvent molecules was calculated using the limiting Gibbs energy of activation for the conductance of the solute ions. The activation energy of the solvent molecules was then discussed in terms of the nature of the alkali-metal ions and their influence on the structure of water. The limiting activation entropy and enthalpy of the solute for activation of viscous flow were interpreted by ion–solvent bond formation or breaking in the transition state of the solvent. The hydration numbers of the investigated electrolytes were calculated from the specific viscosity of the solutions.

**Keywords** Viscosity data · Alkali-metal cyclohexylsulfamates · Kaminsky *A*-, *B*- and *D*-coefficients · Aqueous solution · Hydration · Activation parameters

---

J. Horvat · C. Klofutar · D. Rudan-Tasic (✉)  
Department of Food Technology, Biotechnical Faculty, University of Ljubljana, SI-1000, Ljubljana, Slovenia  
e-mail: [darja.rudan.tasic@bf.uni-lj.si](mailto:darja.rudan.tasic@bf.uni-lj.si)

M. Bešter-Rogač  
Faculty of Chemistry and Chemical Technology, University of Ljubljana, SI-1000, Ljubljana, Slovenia

## 1 Introduction

Sodium and calcium salts of cyclohexylsulfamic acid are intense sweeteners widely used in the food industry and pharmaceuticals [1]. The mechanism of the process of sweet taste chemoreception supposes that in the first step the hydrated ion reaches the region of sweet receptors in the taste epithelium. This process depends on the volumetric and transport properties, as well as on the structure of ionic sweeteners [2]. In such a process the hydration of ionic solutes and their effect on the structure of the solvent are of crucial importance. The viscosity of an ionic solution of an artificial sweetener can provide some useful information concerning the nature of the ionic species moving in the aqueous solution.

The viscosity of aqueous electrolyte solutions is of fundamental importance for an understanding of the various processes occurring in chemical technology and in food processing. It was observed very early that the viscosity of solutions of an electrolyte may differ significantly from those of the pure solvent. Jones and Dole [3] showed that the viscosity of dilute solutions varied simply with the solute concentration. The viscosity  $B$ -coefficient has been the subject of considerable interest and has been measured for a wide range of electrolytes in aqueous and non-aqueous solvents, e.g., [4]. In the transition-state treatment of the relative viscosity of an electrolyte Feakins et al. [5, 6] showed how the viscosity  $B$ -coefficient is related to the solute's contribution to the molar Gibbs energy of activation for viscous flow. According to this simple model the molecules of solvent and ions of the solute move one by one from their equilibrium positions through transition states in which the intermolecular bonds are stretched from their equilibrium positions. Thereby, the effect of the ions of the solute on the viscosity of the solution is determined by both their intrinsic rate of motion and their effect on the rate of flow of surrounding solvent molecules. Thus, the contribution of the ions of solute to the activation Gibbs energy for viscous flow is the sum of two terms. It has been suggested that the Gibbs energy for the movement of solute in viscous flow could be approximated by that for diffusion or conductance of the solute ions [7], or by that for viscous flow of the solvent [6] to obtain the Gibbs energy of activation of solvent molecules due to the movement of solute.

In this work we extended our previous viscosity measurements of some alkali-metal cyclohexylsulfamates [8] from 293.15 up to 323.15 K over a sufficiently wide concentration range in order to determine their viscosity  $A$ -,  $B$ -, and  $D$ -coefficients. Our prime interest was the temperature dependence of the viscosity  $B$ -coefficient in connection with thermodynamic functions of activation of viscous flow of the solute and solvent.

## 2 Experimental

### 2.1 Materials

Lithium (LiCy), potassium (KCy), rubidium (RbCy) and caesium cyclohexylsulfamate (CsCy) were obtained by careful neutralization of cyclohexylsulfamic acid (purchased from Sigma) with the corresponding base (Fluka, or Merck in the case of potassium hydroxide), whereas sodium cyclohexylsulfamate (NaCy) was purchased from Sigma. The purity of the salts was checked after repeated recrystallization from water by analysis of the elements C, H and N (Perkin Elmer, 2400 Series II CHNS/O Analyzer) and also by ion exchange of the cations of salts with the hydrogen ion (DOWEX, Type 50 WX8); a purity of 99.9% for all the salts was determined. The salts were kept in a vacuum desiccator over  $P_2O_5$ . Solutions were prepared on the molal concentration scale by precise weighing, using a digital balance

(Mettler Toledo, model AT201, Switzerland) accurate to within  $\pm 1 \times 10^{-5}$  g. Before use the solutions were degassed by ultrasound (ultrasonic bath, Bandelin Sonorex, type TK 52, Berlin, Germany).

## 2.2 Viscosity Measurements

The viscosity of the investigated solutions was determined with an Ubbelohde viscometer (Schott Visco Clock CT 52 measuring system, equipped with a transparent thermostat and flow-through cooler CK 300). The absolute viscosity of a solution,  $\eta$  ( $\text{cP} = 10^{-3} \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$ ) was calculated by means of the equation [9]

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

where  $d$  ( $\text{kg}\cdot\text{m}^{-3}$ ) is the density of solution,  $t$  (s) is the flow time and  $C$  and  $E$  are constants characteristic of the viscometer. The viscometer was calibrated with water. The values of  $C = (3.1694 \times 10^{-9} \pm 7 \times 10^{-13}) \text{ m}^2\cdot\text{s}^{-2}$  and  $E = (3.4 \times 10^{-4} \pm 2 \times 10^{-5}) \text{ m}^2\cdot\text{s}$  were determined by a least-squares fit by Eq. 1, using the absolute viscosity and density data of water [10], and the flow times at the experimental temperatures. The bath temperature was maintained to  $\pm 0.02^\circ\text{C}$ . The accuracy of the measured viscosities of  $3 \times 10^{-7} \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$  was obtained by using the method of propagation of random errors where  $\delta t = \pm 0.01$  s,  $\delta d = \pm 0.02 \text{ kg}\cdot\text{m}^{-3}$ , while  $\delta C$  and  $\delta E$  are mentioned above.

## 3 Results and Discussion

### 3.1 Viscosity $A$ -, $B$ - and $D$ -Coefficients

The values of viscosity,  $\eta$  (cP), measured at various temperatures as a function of the temperature-independent molality,  $m$  ( $\text{mol}\cdot\text{kg}^{-1}$ ), are presented in Table 1. The relative viscosity,  $\eta_r = \eta/\eta_0$  (where  $\eta_0$  is the viscosity of pure water) of the investigated systems was analyzed by the Kaminsky relation [11]

$$\eta_r = 1 + Ac^{1/2} + Bc + Dc^2 \quad (2)$$

which is valid for more concentrated electrolyte solutions. In Eq. 2  $c$  is the electrolyte molarity ( $\text{mol}\cdot\text{dm}^{-3}$ ) calculated from the relation  $c = md/(1 + mM_2 \times 10^{-3})$  where  $d$  is the density of solution [12, 13], and  $M_2$  the molecular weight of the solute in  $\text{g}\cdot\text{mol}^{-1}$ . The  $A$ -coefficient depends on the interionic forces, the  $B$ -coefficient takes into account the ion–solvent interaction and the  $D$ -coefficient includes all solute–solvent and solute–solute structural interactions that are not accounted for by the  $Ac^{1/2}$  and  $Bc$  terms at high concentration.

The  $A$ -coefficient is a measure of the long-range ion–ion interaction (Coulombic forces) and can be evaluated theoretically. It is based on the drag that the ion atmosphere causes that retards the movement of the ion and indirectly diminishes the viscosity of the solution [14]. The  $A$ -coefficient was calculated from the relation valid in the case of symmetrical electrolytes, where  $z_+ = |z_-| = z$  [4, 14]

$$A = \frac{A_*}{\eta_0(\epsilon_0 T)^{1/2}} \cdot f(\lambda_+^0, \lambda_-^0) \quad (3)$$

**Table 1** Viscosity,  $\eta$ , of aqueous solutions of lithium, sodium, potassium, rubidium and caesium cyclohexylsulfamate in the temperature range from 293.15 to 333.15 K<sup>a</sup>

<i>m</i>	$\eta$ at <i>T</i>				
	293.15	298.15	303.15	313.15	323.15
LiCy					
0.11281	1.0779	0.9560	0.8547	0.6978	0.5823
0.13651	1.0950	0.9707	0.8675	0.7075	0.5898
0.16366	1.1146	0.9874	0.8819	0.7186	0.5985
0.18807	1.1326	1.0024	0.8949	0.7288	0.6067
0.21205	1.1507	1.0180	0.9081	0.7390	0.6147
0.23001	1.1636	1.0288	0.9174	0.7458	0.6202
0.27277	1.1974	1.0577	0.9409	0.7652	0.6355
NaCy					
0.04352	1.0276	0.9131	0.8176	0.6686	0.5593
0.07330	1.0455	0.9289	0.8313	0.6797	0.5680
0.09407	1.0579	0.9398	0.8413	0.6875	0.5741
0.12494	1.0782	0.9564	0.8553	0.6983	0.5829
0.15396	1.0959	0.9730	0.8697	0.7094	0.5918
0.16954	1.1072	0.9813	0.8768	0.7149	0.5961
0.19439	1.1236	0.9953	0.8890	0.7243	0.6036
0.22971	1.1467	1.0152	0.9061	0.7375	0.6142
0.28621	1.1842	1.0472	0.9337	0.7588	0.6312
0.33222	1.2165	1.0747	0.9581	0.7774	0.6458
KCy					
0.03975	1.0208	0.9071	0.8126	0.6648	0.5565
0.06083	1.0312	0.9163	0.8204	0.6714	0.5615
0.08070	1.0406	0.9245	0.8278	0.6773	0.5663
0.09737	1.0492	0.9318	0.8343	0.6823	0.5703
0.11602	1.0584	0.9397	0.8412	0.6878	0.5748
0.14070	1.0719	0.9515	0.8514	0.6957	0.5809
0.16515	1.0846	0.9626	0.8611	0.7032	0.5873
0.17885	1.0914	0.9683	0.8660	0.7073	0.5902
0.19528	1.1008	0.9765	0.8730	0.7127	0.5948
0.20880	1.1074	0.9820	0.8778	0.7164	0.5977
RbCy					
0.05056	1.0243	0.9105	0.8157	0.6675	0.5585
0.07540	1.0359	0.9203	0.8243	0.6747	0.5640
0.10193	1.0485	0.9315	0.8343	0.6824	0.5704
0.12811	1.0609	0.9419	0.8431	0.6896	0.5762
0.15151	1.0718	0.9516	0.8516	0.6960	0.5814
0.17738	1.0839	0.9620	0.8608	0.7034	0.5874
0.20158	1.0957	0.9723	0.8696	0.7104	0.5931
0.22600	1.1079	0.9828	0.8789	0.7177	0.5992
0.25383	1.1226	0.9953	0.8887	0.7252	0.6057

**Table 1** (Continued)

<i>m</i>	$\eta$ at <i>T</i>				
	293.15	298.15	303.15	313.15	323.15
	CsCy				
0.05013	1.0243	0.9100	0.8151	0.6672	0.5584
0.07574	1.0357	0.9199	0.8242	0.6742	0.5642
0.10085	1.0471	0.9302	0.8329	0.6815	0.5696
0.12534	1.0585	0.9399	0.8415	0.6879	0.5753
0.15204	1.0706	0.9510	0.8512	0.6959	0.5813
0.17652	1.0820	0.9605	0.8595	0.7025	0.5866
0.20116	1.0933	0.9704	0.8685	0.7097	0.5921
0.22637	1.1051	0.9807	0.8771	0.7163	0.5977

<sup>a</sup>Units: *m*, mol·kg<sup>-1</sup>;  $\eta$ , cP; *T*, K

and

$$f(\lambda_+^{\circ}, \lambda_-^{\circ}) = \left[ \frac{\lambda^{\circ}}{4(2 + \sqrt{2})\lambda_+^{\circ}\lambda_-^{\circ}} \right] \left[ 1 - \frac{4(\lambda_+^{\circ} - \lambda_-^{\circ})^2}{(1 + \sqrt{2})^2\lambda_+^{\circ}\lambda_-^{\circ}} \right] \quad (4)$$

In Eqs. 3 and 4,  $A_* = 111.3 \text{ cP} \cdot (\text{cm}^2 \cdot \text{S} \cdot \text{mol}^{-1}) \cdot \text{K}^{1/2} \cdot (\text{mol} \cdot \text{dm}^{-3})^{-1/2}$ ,  $\epsilon_0$  is the relative permittivity of water,  $T$  the absolute temperature, and the function  $f(\lambda_+^{\circ}, \lambda_-^{\circ})$  depends on the equivalent conductances at infinite dilution of the ions,  $\lambda_+^{\circ}$  and  $\lambda_-^{\circ}$  and  $\lambda^{\circ} = \lambda_+^{\circ} + \lambda_-^{\circ}$ . In the calculation of constant  $A$ , the relative permittivity of water was taken from ref. [15], whereas the equivalent conductances of alkali ions were obtained from ref. [16] and that of the cyclohexylsulfamate ion as the average values taken from refs. [17, 18] and at 338.15 K from [19], not including results for ammonium cyclohexylsulfamate [17]. The values of the viscosity  $A$ -coefficients are given in Table 2. The values of viscosity  $B$ - and  $D$ -coefficients were determined by a least-squares analysis of Eq. 2 in the form

$$\frac{\eta_r - 1 - Ac^{1/2}}{c} = B + Dc \quad (5)$$

and are given in Table 2.

From the data collected in Table 2, it may be seen that the values of the viscosity  $A$ -coefficient are small and in the range of those for simple 1:1 electrolytes [20], and that the  $Ac^{1/2}$  term in Eq. 2 appreciably affects the measured viscosity only for the data at the lowest concentration. The values of the viscosity  $A$ -coefficient at a definite temperature decrease with increasing size of the alkali cyclohexylsulfamate. Furthermore, the viscosity  $A$ -coefficient slightly increases with increasing temperature (see Table 2) in accordance with theory [21, 22]. The dependence of the viscosity  $A$ -coefficient on temperature was calculated from the relation

$$A = a_0 + a_1(T - T_0) + a_2(T - T_0)^2 \quad (6)$$

where  $a_0$ ,  $a_1$  and  $a_2$  are empirical constants depending on the solute, and  $T_0 = 298.15 \text{ K}$ . The values of the empirical constants were evaluated by a least-squares procedure. Only in the case of lithium and potassium cyclohexylsulfamates was the last term in Eq. 6 needed, whereas for the other compounds a linear relation was used. The values of the temperature

**Table 2** Values of viscosity  $A$ -,  $B$ - and  $D$ -coefficients of aqueous solutions of lithium (LiCy), sodium (NaCy), potassium (KCy), rubidium (RbCy) and caesium (CsCy) cyclohexylsulfamate as a function of temperature<sup>a</sup>

Salt	$T$	$A \times 10^3$	$B$	$D$
LiCy	293.15	3.588	$0.629 \pm 0.001$	$0.395 \pm 0.007$
	298.15	3.590	$0.619 \pm 0.003$	$0.330 \pm 0.014$
	303.15	3.601	$0.615 \pm 0.003$	$0.249 \pm 0.015$
	313.15	3.619	$0.591 \pm 0.004$	$0.222 \pm 0.020$
	323.15	3.640	$0.554 \pm 0.003$	$0.226 \pm 0.018$
NaCy	293.15	3.106	$0.567 \pm 0.002$	$0.323 \pm 0.014$
	298.15	3.119	$0.570 \pm 0.001$	$0.240 \pm 0.006$
	303.15	3.141	$0.566 \pm 0.002$	$0.189 \pm 0.009$
	313.15	3.176	$0.551 \pm 0.002$	$0.138 \pm 0.012$
	323.15	3.207	$0.517 \pm 0.001$	$0.164 \pm 0.007$
KCy	293.15	2.493	$0.454 \pm 0.001$	$0.306 \pm 0.011$
	298.15	2.522	$0.459 \pm 0.002$	$0.224 \pm 0.018$
	303.15	2.556	$0.464 \pm 0.003$	$0.154 \pm 0.019$
	313.15	2.618	$0.459 \pm 0.002$	$0.106 \pm 0.015$
	323.15	2.675	$0.435 \pm 0.002$	$0.125 \pm 0.014$
RbCy	293.15	2.415	$0.428 \pm 0.003$	$0.236 \pm 0.016$
	298.15	2.444	$0.434 \pm 0.002$	$0.170 \pm 0.010$
	303.15	2.479	$0.444 \pm 0.002$	$0.082 \pm 0.014$
	313.15	2.543	$0.448 \pm 0.003$	0.000
	323.15	2.607	$0.415 \pm 0.002$	$0.097 \pm 0.015$
CsCy	293.15	2.422	$0.432 \pm 0.001$	$0.157 \pm 0.007$
	298.15	2.454	$0.428 \pm 0.002$	$0.153 \pm 0.013$
	303.15	2.490	$0.437 \pm 0.001$	$0.082 \pm 0.008$
	313.15	2.557	$0.441 \pm 0.004$	0.000
	323.15	2.619	$0.422 \pm 0.002$	0.000

<sup>a</sup>Units:  $T$  (K);  $A$  (mol·dm<sup>-3</sup>)<sup>-1/2</sup>;  $B$  (mol·dm<sup>-3</sup>)<sup>-1</sup>;  $D$  (mol·dm<sup>-3</sup>)<sup>-2</sup>

coefficient,  $\partial A/\partial T = a_1$ , at 298.15 K are given in Table 3. From the collected data it is seen that the temperature coefficient  $\partial A/\partial T$  gradually increases with increasing size of the alkali-metal ions from lithium to caesium.

The values of the viscosity  $B$ -coefficients, given in Table 2, are positive and relatively large, which is typical of salts with large hydrophobic ions such as the cyclohexylsulfamate ion [12]. At a definite temperature the viscosity  $B$ -coefficients decrease with increasing molecular weight of the salt. The temperature dependence of the viscosity  $B$ -coefficient was expressed by Eq. 6 and the values of the empirical constants were determined by a least-squares procedure. The temperature coefficient,  $\partial B/\partial T = a_1$  at 298.15 K, is negative for the lithium salt, zero for the sodium salt, and positive for the potassium, rubidium and caesium salts (see Table 3). The sign of the viscosity  $B$ -coefficient and its temperature coefficient depends on the degree of solvent structuring induced by the ions. A positive value of the temperature coefficient  $\partial B/\partial T$  at 298.15 K is associated with chaotropic ions (structure-

**Table 3** Temperature coefficients of viscosity,  $\partial A/\partial T$ ,  $\partial B/\partial T$  and  $\partial D/\partial T$ , of aqueous solutions of lithium, sodium, potassium, rubidium and caesium cyclohexylsulfamate at the temperature 298.15 K<sup>a</sup>

Salt	$\frac{\partial A}{\partial T} \times 10^6$	$\frac{\partial B}{\partial T} \times 10^4$	$-\frac{\partial D}{\partial T} \times 10^2$
LiCy	1.36 ± 0.26	-(13.2 ± 3.0)	(1.29 ± 0.2)
NaCy	3.44 ± 0.11	0.0	(1.32 ± 0.04)
KCy	6.40 ± 0.21	(10.9 ± 1.6)	(1.45 ± 0.7)
RbCy	6.44 ± 0.06	(21.3 ± 5.9)	(1.77 ± 0.3)
CsCy	6.61 ± 0.09	(9.9 ± 7)	(0.95 ± 0.3)

<sup>a</sup>Units:  $\partial A/\partial T$  (mol·dm<sup>-3</sup>)<sup>-1/2</sup>·K<sup>-1</sup>;  $\partial B/\partial T$  (mol·dm<sup>-3</sup>)<sup>-1</sup>·K<sup>-1</sup>;  $\partial D/\partial T$  (mol·dm<sup>-3</sup>)<sup>-2</sup>·K<sup>-1</sup>

breaking ions), whereas a negative value is associated with cosmotropic ions (structure-making ions) [20, 23]. According to this view, the ions of the lithium and sodium salts are structure-making ions whereas ions of the potassium, caesium and rubidium salts are structure-breaking ions.

Recently, a comprehensive model for calculating the viscosity *B*- and *D*-coefficients of electrolyte solutions has been developed, e.g., [24]. The model includes a long-range electrostatic interaction term, contributions of individual ions, and a contribution from specific interactions between ions or neutral species. On the basis of such a model, even the viscosity of multicomponent systems can be predicted accurately.

As in the case of the viscosity *B*-coefficient, no model exists for a quantitative description of the *D*-coefficient. The viscosity *D*-coefficients given in Table 2 are positive and relatively large and at a definite temperature almost linearly depend on the radius of the cation. With increasing temperature the viscosity *D*-coefficient initially decreases to a minimum value that depends on the nature of the cation, and then slightly increases. In Table 3 the temperature coefficients of the viscosity *D*-coefficients of the investigated solutions calculated by Eq. 6 are given using a least-squares procedure at 298.15 K. The temperature coefficient,  $\partial D/\partial T = a_1$ , is negative and relatively large.

According to Desnoyers and Perron [25], the  $Dc^2$  term in Eq. 2 includes all solute–solvent and solute–solute interactions that are not accounted for by the  $Ac^{1/2}$  and  $Bc$  terms at high concentration. The main contributions to this coefficient should include higher terms of the long-range Coulombic forces. The viscosity *D*-coefficient is also influenced by higher terms of the hydrodynamic effect, which are the leading contribution to the  $Dc^2$  term in Eq. 2. According to this approach, the viscosity *D*-coefficient should always be positive as given by [25]

$$D \cong 10.05 \times 10^{-6} (\bar{V}_2^0)^2 \quad (7)$$

where  $\bar{V}_2^0$  is the limiting partial molar volume of the solute [12, 13]. Values of the viscosity *D*-coefficient, using Eq. 7, are 0.152 (mol·dm<sup>-3</sup>)<sup>-2</sup> for lithium, 0.150 (mol·dm<sup>-3</sup>)<sup>-2</sup> for sodium, 0.178 (mol·dm<sup>-3</sup>)<sup>-2</sup> for potassium, 0.190 (mol·dm<sup>-3</sup>)<sup>-2</sup> for rubidium and 0.215 (mol·dm<sup>-3</sup>)<sup>-2</sup> for caesium cyclohexylsulfamate at 298.15 K. For lithium, sodium and potassium cyclohexylsulfamates the calculated values are lower than the experimental values, whereas for rubidium and caesium cyclohexylsulfamates the values of the calculated *D*-coefficients are overestimated. Thus, Eq. 7 based solely on the hydrodynamic effect cannot predict the viscosity *D*-coefficients, nor even their sequence.

### 3.2 Thermodynamic Functions of Activation of Viscous Flow of the Solvent and Solute

The viscosity  $B$ -coefficient can be related to the thermodynamic functions of activation for viscous flow proposed by Eyring [26]. The transition state theory has been successfully developed to treat viscosities of electrolyte or non-electrolyte solutions in aqueous or non-aqueous media by Feakins et al., e.g., [6, 27]. They showed that the viscosity  $B$ -coefficient of an electrolyte solution can be given by

$$B = (\nu \bar{V}_1^\circ - \bar{V}_2^\circ) + \bar{V}_1^\circ \left( \frac{\Delta^\# \bar{G}_2^\circ - \nu \Delta^\# \bar{G}_1^\circ}{RT} \right) \quad (8)$$

where the coefficient  $\nu = 2$  for a fully dissociated univalent electrolyte,  $\bar{V}_1^\circ$  and  $\bar{V}_2^\circ$  are the limiting partial molar volumes of the solvent and solute,  $\Delta^\# \bar{G}_2^\circ$  and  $\Delta^\# \bar{G}_1^\circ$  are the limiting Gibbs energy of activation for viscous flow of the solute and solvent, and  $R$  is the gas constant. The Gibbs energy of activation for viscous flow of the pure solvent can be obtained from [26]

$$\eta_1^\circ = \left( \frac{h N_A}{\bar{V}_1^\circ} \right) \exp \left( \frac{\Delta^\# \bar{G}_1^\circ}{RT} \right) \quad (9)$$

where  $h$  is Planck's constant and  $N_A$  is Avogadro's number.

The solute contributions to the molar entropy,  $\Delta^\# \bar{S}_2^\circ$ , and the enthalpy,  $\Delta^\# \bar{H}_2^\circ$ , of activation for viscous flow, can be calculated from the temperature variation of the Gibbs energy, using the following relations:

$$\Delta^\# \bar{S}_2^\circ = - \left( \frac{\partial \Delta^\# \bar{G}_2^\circ}{\partial T} \right) \quad (10)$$

and

$$\Delta^\# \bar{G}_2^\circ = \Delta^\# \bar{H}_2^\circ - T \Delta^\# \bar{S}_2^\circ. \quad (11)$$

The use of relations 8, 10 and 11 provides a framework for interpreting the effects of the solute on the solution viscosity which is more rigorous than direct consideration of the viscosity  $B$ -coefficient and its temperature coefficient. Thus, for example from relation 8 it follows that a negative viscosity  $B$ -coefficient will result for the systems where  $\nu \bar{V}_1^\circ < \bar{V}_2^\circ$  and  $\Delta^\# \bar{G}_2^\circ < \nu \Delta^\# \bar{G}_1^\circ$  [6].

In the calculation of the limiting Gibbs energy of activation for viscous flow of the investigated salts through Eq. 8, we used the limiting partial molar volumes of alkali metal cyclohexylsulfamates at the desired temperatures given previously [12, 13], and for the Gibbs energy of activation for viscous flow of water (see Eq. 9), the density and viscosity data of pure water at the desired temperature given in ref. [10]. Thermodynamic functions of activation for viscous flow of pure water, calculated using the relations 9, 10 and 11, are given in Table 4. For all investigated solutes the values of  $\Delta^\# \bar{G}_2^\circ$  are positive and initially increase slightly with temperature to a maximum value that depends on the size of the cation. The temperature dependence of  $\Delta^\# \bar{G}_2^\circ$  can be expressed by a similar function as for the temperature dependence of the viscosity  $A$ -coefficient, i.e., by Eq. 6. The values of the empirical constants,  $a_i$ , calculated by a least-squares procedure, are compiled in Table 5. The limiting partial molar entropy of activation for viscous flow of the salts was calculated considering Eq. 10 in the form

$$\Delta^\# \bar{S}_2^\circ = -[a_1 + 2a_2(T - T_0)] \quad (12)$$



**Table 4** Thermodynamic functions of activation for viscous flow of pure water  $\Delta^\# \bar{G}_1^\circ$ ,  $\Delta^\# \bar{S}_1^\circ$  and  $\Delta^\# \bar{H}_1^\circ$  in the temperature range from 293.15 to 323.15 K<sup>a</sup>

<i>T</i>	$\Delta^\# \bar{G}_1^\circ$	$\Delta^\# \bar{S}_1^\circ$	$\Delta^\# \bar{H}_1^\circ$
293.15	9.295	26.8	17.164
298.15	9.164	25.1	16.644
303.15	9.043	23.3	16.116
313.15	8.829	19.8	15.036
323.15	8.647	16.3	13.918

<sup>a</sup>Units: *T*, K;  $\Delta^\# \bar{G}_1^\circ$ , kJ·mol<sup>-1</sup>;  $\Delta^\# \bar{S}_1^\circ$ , J·mol<sup>-1</sup>·K<sup>-1</sup>;  $\Delta^\# \bar{H}_1^\circ$ , kJ·mol<sup>-1</sup>

**Table 5** Values of empirical constants *a*<sub>0</sub>, *a*<sub>1</sub> and *a*<sub>2</sub> for calculation of  $\Delta^\# \bar{G}_2^\circ$  (Eq. 6),  $\Delta^\# \bar{S}_2^\circ$  (Eq. 13) and  $\Delta^\# \bar{H}_2^\circ$  (Eq. 14) for aqueous solutions of alkali-metal cyclohexylsulfamates in the temperature range from 293.15 to 323.15 K<sup>a</sup>

Electrolyte	<i>a</i> <sub>0</sub>	<i>a</i> <sub>1</sub>	− <i>a</i> <sub>2</sub>
LiCy	115580 ± 219	88 ± 43	9 ± 2
NaCy	108260 ± 76	250 ± 15	12 ± 1
KCy	94858 ± 49	363 ± 29	12 ± 1
RbCy	92428 ± 457	505 ± 89	17 ± 4
CsCy	92923 ± 512	345 ± 99	8 ± 5

<sup>a</sup>Units: *a*<sub>0</sub>, J·mol<sup>-1</sup>; *a*<sub>1</sub>, J·mol<sup>-1</sup>·K<sup>-1</sup>; *a*<sub>2</sub>, J·mol<sup>-1</sup>·K<sup>-2</sup>

**Table 6** Contributions of the solute to the activation of viscous flow at 298.15 K: partial molar Gibbs energy,  $\Delta^\# \bar{G}_2^\circ$ , entropy,  $\Delta^\# \bar{S}_2^\circ$ , enthalpy,  $\Delta^\# \bar{H}_2^\circ$ , Gibbs energy for activation of conductance,  $\Delta^\# \bar{G}_{2(\text{cd})}^\circ$ , and the contribution of the solute to the Gibbs energy of activation of molecules of solvent,  $\Delta^\# \bar{G}_2^\circ(1 \rightarrow 1')$ <sup>a</sup>

Compound	$\Delta^\# \bar{G}_2^\circ$	− $\Delta^\# \bar{S}_2^\circ$	$\Delta^\# \bar{H}_2^\circ$	$\Delta^\# \bar{G}_{2(\text{cd})}^\circ$	$\Delta^\# \bar{G}_2^\circ(1 \rightarrow 1')$
LiCy	115.13	88	89.29	23.44	91.69
NaCy	108.31	250	33.65	22.79	85.52
KCy	94.59	363	−13.77	21.84	72.75
RbCy	91.79	505	−58.77	21.70	70.09
CsCy	92.05	345	−10.78	21.72	70.33

<sup>a</sup>Units:  $\Delta^\# \bar{G}_2^\circ$ ,  $\Delta^\# \bar{H}_2^\circ$ ,  $\Delta^\# \bar{G}_{2(\text{cd})}^\circ$ ,  $\Delta^\# \bar{G}_2^\circ(1 \rightarrow 1')$ , kJ·mol<sup>-1</sup>;  $\Delta^\# \bar{S}_2^\circ$ , J·mol<sup>-1</sup>·K<sup>-1</sup>

and the limiting partial molar enthalpy of activation for the viscous flow of solutes, considering Eqs. 11 and 12 as

$$\Delta^\# \bar{H}_2^\circ = a_0 - a_1 T_0 + a_2 (T_0^2 - T^2). \tag{13}$$

Table 6 presents the standard limiting thermodynamic functions of activation for viscous flow of the investigated alkali-metal cyclohexylsulfamates at *T* = 298.15 K. From Table 6 it may be seen that  $\Delta^\# \bar{G}_2^\circ$  values are positive and decrease with increasing cation size, whereas  $\Delta^\# \bar{G}_2^\circ$  values for rubidium and caesium cyclohexylsulfamates are approximately equal. Sim-

ilar behavior was observed by Waghorne [28] in studying aqueous solutions of alkali-metal chlorides, though their  $\Delta^\# \bar{G}_2^0$  values are considerably lower than those given in Table 6.

According to Feakins et al. [6] the  $\Delta^\# \bar{G}_2^0$  value contains contributions from two effects: first, the activation energy of solvent molecules which are affected by the interaction between the solute and the surrounding solvent molecules in the transition state,  $\Delta^\# \bar{G}_2^0(1 \rightarrow 1')$ ; second, the solute moves through its own transition state,  $\Delta^\# \bar{G}_2^0(2 \rightarrow 2')$ . Thus, the limiting Gibbs energy contribution of the solute is given as the sum of the two mentioned effects

$$\Delta^\# \bar{G}_2^0 = \Delta^\# \bar{G}_2^0(1 \rightarrow 1') + \Delta^\# \bar{G}_2^0(2 \rightarrow 2'). \quad (14)$$

Feakins et al. [6] have suggested that  $\Delta^\# \bar{G}_2^0(2 \rightarrow 2')$  might be well approximated for small ions by the Gibbs energy of activation for viscous flow of the solvent, or by the activation energy for conductance,  $\Delta^\# \bar{G}_{2(\text{cd})}^0$ . So, from the measured  $\Delta^\# \bar{G}_2^0$  the  $\Delta^\# \bar{G}_2^0(1 \rightarrow 1')$  value can be calculated.

For the investigated electrolytes the value of  $\Delta^\# \bar{G}_2^0(2 \rightarrow 2')$  was approximated by the Gibbs energy for conductance,  $\Delta^\# \bar{G}_{2(\text{cd})}^0$ . The change of the Gibbs energy for ionic conductance,  $\Delta^\# \bar{G}_{i(\text{cd})}^0$ , accompanying unit displacement of one mole of ions was calculated from the relation given by Brummer and Hills [29] in the form

$$\Delta^\# \bar{G}_{i(\text{cd})}^0 = -RT \ln \left( \frac{6\lambda_i^0 h}{ze_0 F L^2} \right) \quad (15)$$

where  $e_0$  is the electronic charge,  $F$  is the Faraday constant and  $L$  is the distance between adjacent equilibrium positions in the liquid, i.e., the jump distance obtained from [30]

$$L = \left( \frac{V_1^0}{N_A} \right)^{1/3}. \quad (16)$$

The  $\Delta^\# \bar{G}_{i(\text{cd})}^0$  values of alkali-metal ions were calculated from the  $\lambda_i^0$  values given in ref. [16]. These values of  $\Delta^\# \bar{G}_{i(\text{cd})}^0$  are close to the value of water,  $\Delta^\# \bar{G}_1^0 = 9.163 \text{ kJ}\cdot\text{mol}^{-1}$  at 298.15 K. The average value of  $\Delta^\# \bar{G}_{i(\text{cd})}^0$  for the alkali-metal ions is  $(10.21 \pm 0.70) \text{ kJ}\cdot\text{mol}^{-1}$ . The ionic Gibbs energy for the conductance of cyclohexylsulfamate ions is  $\Delta^\# \bar{G}_{i(\text{cd})}^0 = 12.09 \text{ kJ}\cdot\text{mol}^{-1}$ . Thus, for  $\Delta^\# \bar{G}_{2(\text{cd})}^0$  we used the sum of the ionic Gibbs energy for the conductance of alkali-metal ions and the corresponding value of the cyclohexylsulfamate ion. The values of  $\Delta^\# \bar{G}_{2(\text{cd})}^0$  are collected in Table 6. From this table it can be seen that the  $\Delta^\# \bar{G}_{2(\text{cd})}^0$  values lie in a relative narrow range from 21.72 to 23.44  $\text{kJ}\cdot\text{mol}^{-1}$ . Thus,  $\Delta^\# \bar{G}_2^0(2 \rightarrow 2')$  contributes only about one fifth of its value to  $\Delta^\# \bar{G}_2^0$ .

The  $\Delta^\# \bar{G}_2^0(1 \rightarrow 1')$  values collected in Table 6 are positive and decrease with increasing cation size of the alkali-metal ions, being approximately equal for rubidium and caesium cyclohexylsulfamates. Thus, the variations of  $\Delta^\# \bar{G}_2^0$  (given in Table 6) would seem to reflect differences in the effect of alkali-metal cyclohexylsulfamates on the activation Gibbs energy for movement of the solvent molecules, i.e., on  $\Delta^\# \bar{G}_2^0(1 \rightarrow 1')$ . According to Feakins et al. [6] the positive value of  $\Delta^\# \bar{G}_2^0(1 \rightarrow 1')$  can be explained by the fact that transfer of alkali-metal cyclohexylsulfamates from the ground-state solvent to the transition-state solvent is not favored.

Table 6 lists the contribution of alkali-metal cyclohexylsulfamates to the limiting activation entropy,  $\Delta^\# \bar{S}_2^0$ , and to the limiting activation enthalpy for viscous flow,  $\Delta^\# \bar{H}_2^0$ . From Table 6 it can be seen that  $\Delta^\# \bar{S}_2^0$  values are negative, like  $\Delta^\# \bar{H}_2^0$  values for higher cyclohexylsulfamates. Similar trends were also observed by Feakins et al. [5] for aqueous solutions of

alkali-metal chlorides. Since the enthalpies and entropies of activation for diffusion or conductance of the ions are positive [5], the effects of the solute on the activation enthalpy and entropy of the solvent molecules,  $\Delta^\# \bar{H}_2^\circ(1 \rightarrow 1')$  and  $\Delta^\# \bar{S}_2^\circ(1 \rightarrow 1')$ , are low or even negative. In the case of lithium and sodium cyclohexylsulfamates, the positive contribution to the  $\Delta^\# \bar{H}_2^\circ$  value arises from the breaking of ion–solvent bonds in the transition state and the negative values of  $\Delta^\# \bar{S}_2^\circ$  and  $\Delta^\# \bar{H}_2^\circ$  for higher cyclohexylsulfamates are a consequence of ion–solvent bond formation in the transition state. Thus, the ion–solvent bond-making effect is responsible for the negative values of  $\Delta^\# \bar{S}_2^\circ$  and  $\Delta^\# \bar{H}_2^\circ$ . The ion–solvent bond-making mechanism is more pronounced for weakly coordinating ions in a highly structured solvent such as water.

### 3.3 Hydration Numbers of Alkali-Metal Cyclohexylsulfamates

The hydration numbers of the investigated electrolytes can be obtained from the change of the solution viscosity with solute concentration. Starting from a rather simple geometric model based on Einstein's viscosity law [31, 32], and from a fictive splitting of the process of hydration into two consecutive processes where in the first step some molecules of water are bound to the solute without any change of the specific volume of the solute and the solvent, and in the second step where hydrated species bind the additional solvent or lose some of the bound solvent from the first step, without change of the volume of the hydrated species, Linow and Philipp [33] have shown that the hydration number can be calculated from the volume of the hydrated species,  $\bar{V}_\eta^\circ$

$$\frac{\eta_{sp}}{c} = 2.5 \bar{V}_\eta^\circ + \bar{V}_\eta^\circ \eta_{sp} \quad (17)$$

where  $\eta_{sp} = \eta_r - 1$  is the specific viscosity of the solution. The hydration number is given by

$$n_h = \frac{\bar{V}_\eta^\circ - \bar{V}_2^\circ}{V_1^\circ} \quad (18)$$

where  $V_1^\circ$  is the molar volume of the solvent. The values of the hydration numbers of the alkali-metal cyclohexylsulfamates are given in Table 7. From these results it can be seen that the hydration numbers at a definite temperature decrease with increasing ionic radius of the alkali-metal cation and, that for a specific alkali-metal cyclohexylsulfamate, strongly depend on temperature. The explanation of the hydration numbers, given in Table 7, can

**Table 7** Hydration numbers,  $n_h$ , of alkali-metal cyclohexylsulfamates in the temperature range from 293.15 to 323.15 K<sup>a</sup>

Electrolyte	<i>T</i>				
	293.15	298.15	303.15	313.15	323.15
LiCy	19.3 ± 0.8	15.8 ± 0.9	9.0 ± 1.0	7.0 ± 1.4	10.3 ± 1.5
NaCy	17.0 ± 1.2	11.0 ± 0.6	7.0 ± 1.0	3.0 ± 1.2	5.7 ± 0.6
KCy	20.3 ± 1.3	12.6 ± 2.0	5.3 ± 2.3	0.0	2.4 ± 1.9
RbCy	15.4 ± 1.4	8.5 ± 1.1	0.0	0.0	0.0
CsCy	6.7 ± 0.9	6.2 ± 1.3	0.0	0.0	0.0

<sup>a</sup>Units: *T*, K

be visualized in terms of the structure of possible hydration shells around the ions. The structure of the first solvation shell of simple ions was obtained from Nielson et al. [34]. Their results clearly show that the first solvation shells of the alkali-metal cations larger than lithium ion are unsaturated in water and that the extent of unsaturation increases with the size of the cation [28]. Furthermore, these studies also show that the extent of perturbation of the water structure is limited primarily to the range of the first hydration shell [34]. The hydration numbers given by Lee and Rasaiah [35] are substantially higher than those determined by Nielson et al. [34] and are for the second hydration shell. They amount to:  $\text{Li}^+$  (16.1),  $\text{Na}^+$  (17.5),  $\text{K}^+$  (21.2),  $\text{Rb}^+$  (21.0) and  $\text{Cs}^+$  (21.3) at 298.15 K. Concerning the cyclohexylsulfamate anion, it was found previously [8, 17] that this ion is practically un-hydrated. Therefore, we ascribe the hydration numbers, given in Table 7, solely to the alkali-metal cations. Therefore, the hydration numbers given in Table 7 can be explained by the existence of more than one hydration shell around the ion. Thus, the relatively high Gibbs energy of activation of viscous flow of solute (see Table 6) is a consequence of the strong interaction of ions of the solute with water molecules which also affect the movement of water molecules beyond their solvation shells.

#### 4 Conclusions

The alkali-metal cyclohexylsulfamates are relatively strong 1:1 electrolytes in aqueous solutions. Their relative viscosity can be represented by the Kaminsky relation. The viscosity  $A$ -coefficient and its temperature coefficient,  $\partial A/\partial T$ , are small and gradually increase with increasing size of the alkali-metal ion. The values of viscosity  $B$ -coefficient are positive and relatively large which is typical of salts with large hydrophobic ions. They decrease with increasing molecular weight of the salt. The temperature coefficient,  $\partial B/\partial T$ , which depends on structuring of solvent molecules around ions, is negative for the lithium salt, near zero for the sodium salt (structure-breaking ions) and positive for the potassium, rubidium and caesium salts (structure-making ions). The viscosity  $D$ -coefficient is large and its temperature coefficient is negative and surprisingly large. The values of the limiting Gibbs energy of activation of viscous flow of the solute are positive and at a definite temperature linearly depend on the reciprocal value of the cation crystal radius. From the contributions which result from the interaction between the solute ions and water molecules in the transition state,  $\Delta^\# \bar{G}_2^\circ(1 \rightarrow 1')$ , and from that of the movement of solute ions through their own transition states,  $\Delta^\# \bar{G}_2^\circ(2 \rightarrow 2')$ , it was found that transfer of alkali-metal cyclohexylsulfamates from the ground-state solvent to the transition state-solvent is not favored. This effect is dominant for the investigated systems, whereas  $\Delta^\# \bar{G}_2^\circ(2 \rightarrow 2')$  contributes only about one fifth of its value to  $\Delta^\# \bar{G}_2^\circ$ . The sign of the limiting activation entropy,  $\Delta^\# \bar{S}_2^\circ$ , and limiting activation enthalpy,  $\Delta^\# \bar{H}_2^\circ$ , of the solute shows that in the case of lithium and sodium salts the breaking of ion–solvent bonds occurs in the transition state, whereas in the case of potassium, rubidium and caesium salts, ion–solvent bond formation take place. The relatively high limiting Gibbs energy of activation of the solute can be explained by the strong interaction of ions of the solute with water molecules, as was indeed observed for high hydration numbers.

#### References

1. O'Brien-Nabors, L., Gelardi, R.C.: Alternative sweeteners: an overview. In: Alternative Sweeteners, 2nd edn. Marcel Dekker, New York (1991)

2. Mathlouthi, M., Bressan, C., Portmann, M.O., Serghat, S.: Role of water. In: Mathlouthi, M., Kanters, J.A., Birch, G.G. (eds.) *Sweet Taste Chemoreception*, pp. 141–172. Elsevier, London & New York (1993)
3. Jones, G., Dole, M.: The viscosity of aqueous solutions of strong electrolytes with special reference to barium chloride. *J. Am. Chem. Soc.* **51**, 2950–2964 (1929)
4. Jenkins, H.D.B., Marcus, Y.: Viscosity B-coefficients of ions in solution. *Chem. Rev.* **95**, 2695–2724 (1995)
5. Feakins, D., Waghorne, W.E., Lawrence, K.G.: The viscosity and structure of solutions. A new theory of the Jones-Dole B-coefficient and the related activation parameters – application to aqueous-solutions. *J. Chem. Soc. Faraday Trans.* **82**(1), 563–568 (1986)
6. Feakins, D., Bates, F.M., Waghorne, W.E., Lawrence, K.G.: Relative viscosities and quasi-thermodynamics of solutions of tert-butyl alcohol in the methanol-water system – a different view of the alkyl water interaction. *J. Chem. Soc. Faraday Trans.* **89**, 3381–3388 (1993)
7. Feakins, D., Canning, F.M., Mullally, J.J., Waghorne, W.E.: The thermodynamics of solutions. *Pure Appl. Chem.* **61**, 133–142 (1989)
8. Rudan-Tasic, D., Klofutar, C., Horvat, J.: Viscosity of aqueous solutions of some alkali cyclohexylsulfamates at 25.0 °C. *Food Chem.* **86**, 161–167 (2004)
9. Cannon, M.R., Manning, R.E., Bell, J.D.: Viscosity measurement. The kinetic energy correction and a new viscometer. *Anal. Chem.* **32**, 355–358 (1960)
10. Riddick, J.A., Bunger, W.B., Sakano, T.K.: *Organic Solvents, Physical Properties and Methods of Purification*, 4th edn. Wiley, New York (1986)
11. Kaminsky, M.: The concentration and temperature dependence of the viscosity of aqueous solutions of strong electrolytes. III. KCl, K<sub>2</sub>SO<sub>4</sub>, MgCl<sub>2</sub>, BeSO<sub>4</sub>, and MgSO<sub>4</sub> solutions. *Z. Phys. Chem.* **12**, 206–231 (1957)
12. Klofutar, C., Horvat, J., Rudan-Tasic, D.: Apparent molar volume and apparent molar expansibility of rubidium, caesium, and ammonium cyclohexylsulfamate in aqueous solution. *Monatsh. Chem.* **137**, 1151–1162 (2006)
13. Klofutar, C., Rudan-Tasic, D.: Apparent molar volume and apparent molar expansibility of lithium, sodium, potassium, and tetramethylammonium cyclohexylsulfamate in aqueous solution. *Monatsh. Chem.* **136**, 1727–1736 (2005)
14. Falkenhagen, H., Dole, M.: Viscosity of electrolyte solutions and its significance to the Debye theory. *Physik. Z.* **30**, 611–622 (1929)
15. Archer, D.G., Wang, P.M.: The dielectric-constant of water and Debye-Hückel limiting law slopes. *J. Phys. Chem. Ref. Data* **19**, 371–411 (1990)
16. Harned, R.S., Owen, B.B.: *The Physical Chemistry of Electrolytic Solutions*, 3rd edn. Reinhold, New York (1958)
17. Rudan-Tasič, D., Župec, T., Klofutar, C., Bešter-Rogač, M.: A conductometric study of aqueous solutions of some cyclohexylsulfamates. *J. Solution Chem.* **34**, 631–644 (2005)
18. Rudan-Tasič, D., Klofutar, C., Bešter-Rogač, M.: The electric conductivities of aqueous solutions of rubidium and cesium cyclohexylsulfamates, potassium acesulfame and sodium saccharin. *Acta Chim. Slov.* **53**, 324–330 (2006)
19. Klofutar, C., Luci, M., Abramović, H.: The thermodynamics of dissociation of cyclohexylsulfamic acid in aqueous solution. *Physiol. Chem. Phys. Med. NMR* **31**, 1–8 (1999)
20. Out, D.J.P., Los, J.M.: Viscosity of aqueous-solutions of univalent electrolytes from 5 to 95 °C. *J. Solution Chem.* **9**, 19–35 (1980)
21. Falkenhagen, H.: Bemerkung zur inneren Reibung starker Electrolyte in sehr verdünnte Lösungen. *Physik. Z.* **32**, 365–369 (1931)
22. Falkenhagen, H.: The quantitative limiting law for the viscosity of strong binary electrolytes. *Physik. Z.* **32**, 745–764 (1931)
23. Kaminsky, M.: Investigation of the interaction between ion and solvent by measurement of viscosity. *Z. Naturforsch.* **12a**, 424–433 (1957)
24. Lencka, M.M., Anderko, A., Sanders, S.J., Young, R.D.: Modeling viscosity of multicomponent electrolyte solutions. *Int. J. Thermophys.* **19**, 367–378 (1998)
25. Desnoyers, J.E., Perron, G.: The viscosity of aqueous solutions of alkali and tetraalkylammonium halides at 25 °C. *J. Solution Chem.* **1**, 199–212 (1972)
26. Glasstone, S., Laidler, K.J., Eyring, H.: *The Theory of Rate Processes*. McGraw-Hill, New York (1941)
27. Feakins, D., Freemantle, D.J., Lawrence, K.G.: Transition-state treatment of relative viscosity of electrolyte solutions – applications to aqueous, non-aqueous and methanol+water systems. *J. Chem. Soc. Faraday Trans.* **70**, 795–806 (1974)
28. Waghorne, W.E.: Viscosities of electrolyte solutions. *Phil. Trans. R. Soc. London Ser. A* **359**, 1529–1543 (2001)

29. Brummer, S.B., Hills, G.J.: Kinetics of ionic conductance. Part 1 – Energies of activation and the constant volume principle. *J. Chem. Soc. Faraday Trans. 5*, 1816–1822 (1961)
30. Hickey, K., Waghorne, W.E., Sacco, A.: Comparison of the activation free energies for viscous flow and for diffusion in dilute solutions, derivation of the expression for the effect of the solute on the activation free energy of diffusion of the solvent, and application to solutions of N,N-dimethylformamide in water, methanol, and acetonitrile. *J. Phys. Chem. A* **105**, 1093–1096 (2001)
31. Einstein, A.: A new determination of molecular dimensions. *Ann. Physik* **19**, 289–306 (1911)
32. Einstein, A.: Berichtigung zu meiner Arbeit, eine neue Bestimmung der molekul Dimensionen. *Ann. Physik* **34**, 591–592 (1911)
33. Linow, K.J.; Philipp, B.: The concentration dependency of viscosity – a new method for the discovery of solutes. *Z. Phys. Chem.* **265**, 321–329 (1984)
34. Neilson, G.W., Mason, P.E., Ramos, S., Sullivan, D.: Neutron and X-ray scattering studies of hydration in aqueous solutions. *Phil. Trans. R. Soc. Lond. Ser. A* **359**, 1575–1591 (2001)
35. Lee, S.H., Rasaiah, J.C.: Molecular dynamics simulation of ion mobility. 2. Alkali metal and halide ions using the SPC/E model for water at 25 °C. *J. Phys. Chem.* **100**, 1420–1425 (1996)