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Viscosity of Aqueous Solutions of Tetramethyl-, Tetraethyl-, Tetra-n-propyl-, Tetra-n-butyl-, and Tetra-n-pentylammonium Cyclohexylsulfamates from 293.15 K to 323.15 K

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Dedicated to Professor Josef Barthel on the occasion of his 80th birthday

Abstract

The viscosities of aqueous solutions of tetramethyl-, tetraethyl-, tetra-n-propyl-, tetra-n-butyl-, and tetra-n-pentylammonium cyclohexylsulfamate were determined at 293.15, 298.15, 303.15, 313.15 and 323.15 K. The relative viscosity was analysed and interpreted in terms of the *Kaminsky* equation, $\eta_r = 1 + Ac^{1/2} + Bc + Dc^2$. The viscosity A-coefficient was calculated from *Falkenhagen-Dole* theory and its temperature coefficient estimated. The viscosity B-coefficients of the solutes are positive and relatively large, while their temperature coefficients are negative and decrease with increasing molecular weight of the solutes. The viscosity D-coefficient was discussed in terms of higher terms of the long-range *Coulombic* forces and hydrodynamic effects, as well as structural solute-solute interactions. The limiting thermodynamic functions of activation for viscous flow of solute, i. e. the *Gibbs* free energy, enthalpy and entropy, were evaluated using the theoretical approach given by *Feakins et al.* From the limiting partial molar functions of activation of the solute the contribution to the activation functions of solvent molecules were calculated using the corresponding limiting functions of activation for charge transport of solute ions.

Keywords: Viscosity data, viscosity A-, B- and D-coefficients, activation parameters, cyclohexylsulfamates, aqueous solutions

1. Introduction

The thermodynamic and transport properties of very dilute electrolyte solution are important in chemistry and biology. Studies of the viscosities of such solutions were among the earliest in the field of solution chemistry and have strongly influenced the development of our view of the solution process. The viscosity B-coefficient of the *Jones-Dole* equation[1] has been a subject of considerable interest and has been measured for a wide range of electrolytes in aqueous and non-aqueous solutions.[2] It is the quantity which defines the degree of water structuring around the ions. The viscosity B-coefficient is positive for all cosmotropic ions and negative for chaotropic ions. The B-coefficient though operationally useful, however, is simply an empirical parameter and provides no framework for interpretation. As was shown by *Feakins* et al.,[3,4] the viscosity B-coefficient can be related to the limiting partial molar volume of solute and solvent, as well to the limiting *Gibbs* free energy of activation for viscous flow of the pure solvent and solute. Furhermore, it was suggested that the activation *Gibbs* free energy for movement of the solute could be approximated by that for diffusion or conductance of the solute[5] or by that for viscous flow of the solvent.[4]

Some properties of tetra-n-alkylammonium cyclohexylsulfamates are now of considerable interest in different fields of electrolyte solution chemistry and as potential artificial sweeteners. The interactions of an ion with water molecules is highly specific, therefore a correlation can be expected for a group of closely related species such as R_4N^+-ions. Since no data are available in the literature on the viscosity of aqueous solutions of tetra-n-alkylammonium cyclohexylsulfamates, we investigated the solution properties of a series of tetra-n-alkylammonium cyclohexylsulfamates. Our previous papers reported the volumetric measurements of some tetra-n-alkylammonium cyclohexylsulfamates.[6,7] In this work we reported our study of viscosity of aqueous solutions of these compounds from 293.15 to 323.15 K over a sufficiently wide concentration range. Our prime interest was to determine the thermodynamic functions of activation of viscous flow of the solute and solvent and to provide a better understanding of the solute effect on the viscosity of solution.

2. Experimental

2. 1. Materials

All tetraalkylammonium salts investigated, i. e. tetramethyl- (Me_4NCy), tetraethyl- (Et_4NCy), tetra-n-propyl- (n-Pr_4NCy), tetra-n-butyl- (n-Bu_4NCy), and tetra-n-pentylammonium cyclohexylsulfamates (n-Pe_4NCy) were obtained by careful neutralization of cyclohexylsulfamic acid (purchased from Sigma) with the corresponding base (Fluka). The purity of the salts were checked after recrystallization from various organic solvents (Me_4NCy from 2-propanol, Et_4NCy from ethyl methyl ketone, n-Pr_4NCy from ethyl acetate, n-Bu_4NCy and n-Pe_4NCy from cyclohexane) by analysis of the elements C, H and N (Perkin Elmer, 2400 Series II CHNS/O Analyzer) and also by ion exchange of the cation of the salt by the hydrogen ion (DOWEX, Type 50 WX8); a purity of 99.7% at least (Et_4NCy) or better, e. g. 99.9% for n-Bu_4NCy was determined. The salts were kept in a vacuum desiccator over P_2O_5.

2. 2. Preparation of Solutions

The solutions investigated were prepared on a molal concentration scale by precise weighing, using a digital balance (Mettler Toledo, model AT201, Switzerland) accurate to within 1×10^{-5} g. Before use the solutions were degassed by ultrasound (ultrasonic bath, Bandelin Sonorex, type TK 52, Berlin, Germany).

2. 3. Viscosity Measurements

The viscosity of the investigated solutions was determined with an Ubbehlode viscometer (Schott Visco Clock CT 52 measuring system, equipped with a transparent thermostat and flow-through cooler CK 300). The absolute viscosity of solution, η (cP = 10^{-3} kgm^{-1} s^{-1}) was calculated by means of the equation[8]

$$\eta = C\,d\,t - \frac{E\,d}{t^2} \tag{1}$$

where d (kgm^{-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 $C = 3.17 \times 10^{-9}$ m^2 s^{-2} and $E = 3.4 \times 10^{-4}$ m^2 s were determined by a least squares fit to Eq. (1), using the density[9] and absolute viscosity of water,[10] and the flow times at the experimental temperatures. The bath temperature was maintained to ±0.02 °C. The accuracy of the measured viscosities of 3×10^{-7} kg m^{-1}s^{-1} was obtained by using the method of propagation of random errors where $\delta t = \pm 0.01$ s, $\delta d = \pm 0.02$ kg m^{-3}, $\delta C = 7 \times 10^{-13}$ m^2 s^{-2} and $\delta E = \pm 2 \times 10^{-5}$ m^2 s.

3. Results and Discussion

The values of viscosity, η (cP), of aqueous solutions of some tetra-n-alkylammonium cyclohexylsulfamates at various temperatures as a function of molality, m (mol kg^{-1}), are presented in Table 1. The relative viscosity, $\eta_r = \eta/\eta_0$, (where η_0 is the viscosity of pure water) of the investigated solutions was analysed by the *Kaminsky* relation[11]

$$\eta_r = 1 + Ac^{1/2} + Bc + Dc^2 \tag{2}$$

where c is the molarity (mol dm^{-3}) calculated from the known density of solution[6,12] as $c = md/(1 + mM_2 \times 10^{-3})$ where d is the density of solution, and M_2 the molecular weight of the solute. The A-coefficient is a measure of long-range ion-ion interactions (*Coulombic* 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 $Ac^{½}$ and Bc terms at higher concentration. The viscosity A-coefficient was calculated theoretically from the relation valid in the case of symmetrical electrolytes, where $z_+ = |z_-| = z$.[2]

$$A = \frac{A_*}{\eta_0(\varepsilon_0 T)^{1/2}} \cdot f\left(\lambda_+^0, \lambda_-^0\right) \tag{3}$$

and $f(\lambda_+^0, \lambda_-^0)$ takes the following form

$$f\left(\lambda_+^0, \lambda_-^0\right) = \left[\frac{\lambda^0}{4\left(2+\sqrt{2}\right)\lambda_+^0\lambda_-^0}\right]\left[1 - \frac{4\left(\lambda_+^0 - \lambda_-^0\right)^2}{\left(1+\sqrt{2}\right)^2\lambda_0^2}\right] \tag{4}$$

In Eqs. (3) and (4) $A_* = 111.3$ cP (cm^2 S mol^{-1}) K$^{1/2}$ (mol dm^{-3})$^{-1/2}$, ε_0 is the relative permittivity of water, T the absolute temperature, function $f\ (\lambda_+^0, \lambda_-^0)$ depends on the equivalent conductances at infinite dilution of the ions, λ_+^0 and λ_-^0 and $\lambda^0 = \lambda_+^0 + \lambda_-^0$. In calculation of the viscosity A-coefficient, the relative permittivity of water was taken from ref.,[13] while the equivalent conductances of tetra-n-alkylammonium ions were obtained as follows: the equivalent conductances of tetramethyl-, tetraethyl- and tetra-n-propylammonium ions were obtained by analytical interpolation of the primary data of *Robinson* and *Stokes*[14] and *Kay* and *Evans*,[15] while for the tetra-n-butyl-, and tetra-n-pentylammonium ions the primary data at higher temperatures were obtained from ref.[16] For the cyclohexylsulfamate ion the equivalent conductances were obtained as the average values taken from refs.[17,18] and at 338.15 K from ref.[19] The values of viscosity A-coefficients are given in Table 2. The values of viscosity B-, and

Table 1. Viscosity of aqueous solutions of tetramethyl- (Me$_4$NCy), tetraethyl- (Et$_4$NCy), tetra-n-propyl- (n-Pr$_4$NCy), tetra-n-butyl- (n-Bu$_4$NCy), and tetra-n-pentylammonium (n-Pe$_4$NCy) cyclohexylsulfamates at the indicated molalities and temperatures.

m	***η* (cP) at *T* (K)**				
(mol kg^{-1})	**293.15**	**298.15**	**303.15**	**313.15**	**323.15**
			Me$_4$NCy		
0.09138	1.0601	0.9408	0.8416	0.6876	0.5744
0.11244	1.0741	0.9527	0.8520	0.6956	0.5808
0.13420	1.0892	0.9656	0.8632	0.7044	0.5877
0.15568	1.1036	0.9780	0.8740	0.7125	0.5943
0.17841	1.1201	0.9922	0.8860	0.7218	0.6016
0.20017	1.1355	1.0051	0.8972	0.7303	0.6085
			Et$_4$NCy		
0.06843	1.0702	0.9489	0.8480	0.6917	0.5773
0.09139	1.0937	0.9688	0.8653	0.7051	0.5876
0.11415	1.1167	0.9886	0.8824	0.7182	0.5981
0.13647	1.1404	1.0085	0.8994	0.7312	0.6080
0.15981	1.1645	1.0289	0.9171	0.7444	0.6186
0.18429	1.1909	1.0512	0.9362	0.7588	0.6299
0.20785	1.2171	1.0732	0.9548	0.7729	0.6409
			n-Pr$_4$NCy		
0.02484	1.0367	0.9197	0.8223	0.5714	0.5614
0.04995	1.0725	0.9499	0.8481	0.6910	0.5763
0.07524	1.1091	0.9809	0.8748	0.7107	0.5916
0.10047	1.1468	1.0127	0.9018	0.7311	0.6071
0.12595	1.1854	1.0453	0.9295	0.7520	0.6231
0.15066	1.2238	1.0775	0.9573	0.7731	0.6388
0.17660	1.2656	1.1128	0.9866	0.7952	0.6560
0.19998	1.3032	1.1444	1.10139	0.8161	0.6714
			n-Bu$_4$NCy		
0.00984	1.0192	0.9051	0.8101	0.6624	0.5542
0.02418	1.0455	0.9269	0.8289	0.6769	0.5650
0.05076	1.0962	0.9694	0.8655	0.7034	0.5853
0.07495	1.1436	1.0094	0.8993	0.7282	0.6046
0.10106	1.1968	1.0536	0.9365	0.7554	0.6253
0.12504	1.2470	1.0952	0.9712	0.7805	0.6450
			n-Pe$_4$NCy		
0.01959	1.0429	0.9252	0.8276	0.6757	0.5642
0.02545	1.0556	0.9359	0.8367	0.6827	0.5695
0.03518	1.0772	0.9541	0.8521	0.6944	0.5783
0.04556	1.1007	0.9738	0.8688	0.7068	0.5881
0.05043	1.1119	0.9833	0.8767	0.7127	0.5924
0.05529	1.1234	0.9927	0.8847	0.7187	0.5973
0.06494	1.1461	1.0118	0.9008	0.7305	0.6064
0.07586	1.1729	1.0338	0.9193	0.7440	0.6168
0.08471	1.1945	1.0521	0.9346	0.7552	0.6255
0.10086	1.2357	1.0858	0.9630	0.7759	–

D-coefficients were obtained by a least-squares analysis of Eq. (2) in the form

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

and are given in Table 2. The relation (2) satisfactory reproduces the experimental values of solution viscosity, η. Standard deviation, *s*

$$s = \pm\left[\frac{\eta - \eta_{cal}}{n-2}\right]^{1/2} \qquad (6)$$

calculated for each compound at a definite temperature amounts to an average value of ±2.5 × 10^{-4} cP. In rel. (6), η_{cal} is the viscosity of solution calculated via rel. (2) and *n* is the number of experimental points.

From Table 2 it can be seen that the values of the *A*-coefficient are small and in the range of simple 1:1 electrolytes and that the $Ac^{½}$ term in rel. (2) appreciably affects the measured viscosities only at the lowest concentration. According to *Falkenhagen* and *Vernon*, the value of the viscosity *A*-coefficient ia always greater than zero.[20,21] The values of the viscosity *A*-coefficient at a definite temperature increase with increasing ionic radius of the tetra-n-alkylammonium ion, contrary to the alkali-metal cyclohexylsulfamates where the viscosity *A*-coefficient decreases with increasing ionic radius of alkali-metal ions.[22]

Furthermore, the viscosity *A*-coefficients of tetramethyl-, and tetraethylammonium cyclohexylsulfamate slightly increases with increasing temperature, that of tetra-n-propylammonium cyclohexylsulfamate is temperature independent, while the viscosity *A*-coefficients of tetra-n-butyl-, and tetra-n-pentylammonium cyclohexylsulfamates slightly decreases with temperature (see Table 2). The dependence of the viscosity *A*-coefficient on temperature was expressed by the function

$$Y = a_0 + a_1\left(T - T_0\right) + a_2\left(T - T_0\right)^2 \qquad (7)$$

where $Y = A$ and a_0, a_1 and a_2 are empirical constants depending on the solute, and T_0 = 298.15 K. The values of the empirical constants were evaluated by a least-squares procedure. The values of the temperature coefficient, $\partial A/\partial T = a_1$, at 298.15 K are given in Table 3. The temperature coefficient $\partial A/\partial T$ at 298.15 K almost linearly decreases with increasing ionic radius of the cation. On the other hand, the dependence of $\partial A/\partial T$ at the same temperature on the ionic radius of the alkali-metal cation in al-

Table 2. Values of viscosity *A*-, *B*- and *D*-coefficients (Eq. 2) of aqueous solutions of tetramethyl- (Me_4NCy), tetraethyl- (Et_4NCy), tetra-n-propyl- (n-Pr_4NCy), tetra-n-butyl- (n-Bu_4NCy), and tetra-n-pentylammonium (n-Pe_4NCy) cyclohexylsulfamates as a function of temperature

Salt	***T* (K)**	***A* × 10^3 ($L^{1/2}$ $mol^{-1/2}$)**	***B* (L mol^{-1})**	***D* (L^2 mol^{-2})**
Me_4NCy	293.15	3.309	0.594±0.002	0.490±0.016
	298.15	3.330	0.586±0.003	0.422±0.017
	303.15	3.356	0.579±0.002	0.363±0.013
	313.15	3.397	0.568±0.003	0.262±0.022
	323.15	3.430	0.535±0.002	0.275±0.011
Et_4NCy	293.15	3.914	0.959±0.003	0.610±0.020
	298.15	3.925	0.932±0.002	0.517±0.017
	303.15	3.947	0.904±0.001	0.470±0.010
	313.15	3.988	0.859±0.002	0.380±0.020
	323.15	4.026	0.801±0.002	0.380±0.020
n-Pr_4NCy	293.15	4.640	1.345±0.002	1.340±0.020
	298.15	4.640	1.284±0.001	1.240±0.010
	303.15	4.640	1.225±0.001	1.180±0.012
	313.15	4.640	1.116±0.001	1.180±0.010
	323.15	4.640	1.044±0.002	0.950±0.010
n-Bu_4NCy	293.15	5.102	1.705±0.015	2.940±0.020
	298.15	5.092	1.636±0.007	2.489±0.092
	303.15	5.088	1.587±0.009	2.098±0.118
	313.15	5.070	1.488±0.006	1.338±0.085
	323.15	5.047	1.344±0.003	1.448±0.043
n-Pe_4NCy	293.15	5.380	1.994±0.002	4.309±0.041
	298.15	5.367	1.920±0.002	3.652±0.032
	303.15	5.361	1.868±0.003	2.893±0.042
	313.15	5.331	1.760±0.002	2.040±0.036
	323.15	5.290	1.573±0.004	2.520±0.089

kali-metal cyclohexylsulfamates showed the reverse behaviour.[22] The behaviour of tetra-n-alkylammonium cyclohexylsulfamates can be attributed to hydrophobic hydration of the R_4N^+ ion, by decreasing influence of the R_4N^+ ion, and to the increasing effect of the alkyl group. Namely, the viscosity *A*-coefficient is based on the drag that the ion causes that retards to movement of the ion and indirectly diminishes the viscosity of solution. In aqueous system the hydrocarbon residues occupy a space which would otherwise be void and the volume contraction on this account is greater than the expansion of bulk water. Thus, the effect of the alkyl group of the R_4N^+ ion on water structure is pronounced and increases with the ionic radius of the R_4N^+ ion or with the number of CH_2 –group in alkyl residues. Regarding the temperature coefficient $\partial A/\partial T$ according to *Kaminsky*[11] it should be under all circumstances greater than zero which was not the case of n-Bu_4NCy and n-Pe_4NCy.

Values of the viscosity *B*-coefficients, given in Table 2, are positive and relatively large which is typical for salts with large hydrophobic ions such as the tetra-n-alkylammonium[23] and cyclohexylsulfamate ions.[7] The sign of the viscosity *B*-coefficient depends on the degree of solvent structuring introduced by the ions. A positive value of viscosity *B*-coefficient is associated with cosmotropic ions (structure makers), while a negative value is associated with chaotropic ions (structure breakers) according to their relative abilities to induce the structuring of water.[24] From this point of view, the viscosity *B*-coefficient, given in Table 2, belongs to the cosmotropic class of ions. Furthermore, the viscosity *B*-coefficient was found to be linearly related to the limiting partial molar volume, $\overline{V}_2^0$ of the tetra-n-alkylammonium cyclohexylsulfamates.[6,12]

The viscosity *B*-coefficients given in Table 2 decrease with increasing temperature for all the investigated compounds. The temperature dependence of the viscosity *B*-coefficient was expressed by rel. (7) in a linear form and the values of the empirical constants determinated by the least-squares procedure. The temperature coefficients $\partial B/\partial T = a_1$ at 298.15 K are given in Table 3. The temperature coefficients $\partial B/\partial T$ at 298.15, collected in Table 3, are negative and decrease with increasing molecular weight of the tetra-n-alkylammonium cyclohexylsulfamates. A large and negative temperature dependence of the viscosity *B*-coefficient was also observed by *Wen*[25] who studied the viscosity of aqueous solutions of n-Bu_4Br at 20 and 30 °C. It is interesting to note that temperature coefficients $\partial B/\partial T$, determined at the same temperature for the alkali-metal cyclohexylsulfamates, increase with increasing temperature.[22]

The viscosity *D*-coefficients, collected in Table 2, are positive and relatively large and increase at a definite temperature with increasing limiting partial molar volume of the solute, from tetra-n-propylammonium cyclohexylsulfamate onwards almost linearly. With increasing temperature the viscosity *D*-coefficient decreases. The temperature coefficient $\partial D/\partial T$ was obtained like $\partial B/\partial T$ using rel. (7) in a linear form. The temperature coefficients $\partial D/\partial T = a_1$ at 298.15 K are negative and relatively large and are given in Table 3. From this table it can be seen that their values decrease with increasing molecular weight of the solute.

As was shown by *Desnoyers* and *Perron*,[26] the Dc^2 term in Eq. (2) includes all solute-solvent and solute-solute interactions that are not accounted for by the $Ac^{½}$ and Bc terms at higher concentration. According to these authors, the main contribution to the viscosity *D*-coefficient should include the higher terms of the long-range *Coulombic* forces. Furthermore, the viscosity *D*-coefficient is also influenced by the higher terms of the hydrodynamic effect. These terms are the leading contribution to the Dc^2 term in Eq. (2). According to this approach, the viscosity *D*-coefficient should always be positive and given by[26]

$$D \cong 10.05 \times 10^{-6} \left(\overline{V}_2^0\right)^2 \tag{8}$$

The calculated values of viscosity *D*-coefficients, using rel. (8) are: 0.462 $(\text{mol L}^{-1})^{-2}$ for tetramethyl-, 0.747 $(\text{mol L}^{-1})^{-2}$ for tetraethyl-, 1.150 $(\text{mol L}^{-1})^{-2}$ for tetra-n-propyl-, 1.606 $(\text{mol L}^{-1})^{-2}$ for tetra-n-butyl-, and 2.152 $(\text{mol L}^{-1})^{-2}$ for tetra-n-pentylammonium cyclohexylsulfamate at 298.15 K. For tetramethyl- and tetraethylammonium cyclohexylsulfamates the calculated values are higher than the experimental ones, while for tetra-n-propyl-, tetra-n-butyl-, and tetra-n-pentylammonium cyclohexyl-

Table 3. Temperature coefficient of the viscosity *A*-, *B*- and *D*-coefficients of tetramethyl- (Me_4NCy), tetraethyl- (Et_4NCy), tetra-n-propyl- (n-Pr_4NCy), tetra-n-butyl- (n-Bu_4NCy) and tetra-n-pentylammonium (n-Pe_4NCy) cyclohexylsulfamates in aqueous solutions at 298.15 K.

Salt	$\frac{\partial A}{\partial T}\times 10^4$ $(\text{L}^{1/2}\text{ mol}^{-1/2}\text{ K}^{-1})$	$-\frac{\partial B}{\partial T}\times 10^3$ $(\text{L mol}^{-1}\text{ K}^{-1})$	$-\frac{\partial D}{\partial T}\times 10^2$ $(\text{L}^2\text{ mol}^{-2}\text{ K}^{-1})$
Me_4NCy	4.73±0.24	1.8±0.3	0.7±0.2
Et_4NCy	3.57±0.40	5.2±0.1	0.8±0.2
n-Pr_4NCy	0.0	10.1±0.6	1.1±0.2
n-Bu_4NCy	−(1.78±0.12)	11.6±0.5	5.2±1.2
n-Pe_4NCy	−(1.90±0.29)	13.5±1.0	6.3±2.3

sulfamates the calculated values are lower than the experimental ones. The relation (8) does not correctly predict the temperature dependence of the viscosity *D*-coefficient since the $\overline{V}_2^0$ values of tetra-n-alkylammonium cyclohexylsulfamates increase with temperature,[6,12] while the viscosity *D*-coefficient decreases with increasing temperature (see Table 2).

According to *Eyring*[27] the viscosity *B*-coefficient can be related to the thermodynamic functions of activation for viscous flow. In this model the molecules of solvent and ions of solute move one by-one from their equilibrium positions through their transition states in which intermolecular bonds are stretched to their equilibrium positions. *Feakins et al*, e. g.[3,4] have successfully applied the transition state theory to the viscosity of electrolyte or non-electrolyte solutions in aqueous or non-aqueous media. They showed that the viscosity *B*-coefficient can be given by

$$B=\left(\nu\overline{V}_1^0-\overline{V}_2^0\right)+\overline{V}_1^0\left(\frac{\Delta^{\#}\overline{G}_2^0-\nu\Delta^{\#}\overline{G}_1^0}{RT}\right) \qquad (9)$$

where $\nu = 2$ for a fully dissociated univalent electrolyte, $\overline{V}_1^0$ is the limiting partial molar volume of solvent, $\Delta^{\#}\overline{G}_2^0$ and $\Delta^{\#}\overline{G}_1^0$ are the limiting *Gibbs* free energy of activation for the viscous flow of solute and solvent, and *R* is the gas constant. The use of rel. (9) provides a framework for interpreting the effects of the solute on the solution viscosity since it is more rigorous than the direct consideration of the viscosity *B*-coefficient and its temperature coefficient. So, for example from rel. (9) it follows that a negative viscosity *B*-coefficient will result when $\nu\overline{V}_1^0 < \overline{V}_2^0$ and $\Delta^{\#}\overline{G}_2^0 < \nu\Delta^{\#}\overline{G}_1^0$.[4]

The limiting *Gibbs* free energy of activation for the viscous flow of solutes, calculated through rel. (9), was obtained from the viscosity *B*-coefficient (Table 2), the limiting partial molar volumes of tetra-n-alkylammonium cyclohexylsulfamates at the desired temperature determined previously,[7,12] and the *Gibbs* free energy of activation for viscous flow of water.[22] The values of $\Delta^{\#}\overline{G}_2^0$ as a function of temperature are given in Table 4. The uncertainties in $\Delta^{\#}\overline{G}_2^0$ were calculated from rel. (10)

$$\left(\delta\Delta^{\#}\overline{G}_2^0\right)^2=\left(\frac{RT}{\overline{V}_1^0}\right)^2\left[\left(\delta B\right)^2+\left(\delta\overline{V}_2^0\right)^2\right] \qquad (10)$$

in which only the uncertainties in the viscosity *B*-coefficient and the limiting partial molar volume of solute were taken into account. From Table 4 it can be seen that $\Delta^{\#}\overline{G}_2^0$ values for the investigated compounds are positive and decrease with increasing temperature except for tetramethylammonium cyclohexylsulfamate where a slight increase of $\Delta^{\#}\overline{G}_2^0$ occurs. The limiting *Gibbs* free energy of activation of viscous flow of tetra-n-alkylammonium cyclohexylsulfamates linearly increases with increasing molecular weight at all temperatures studied. The temperature dependence of the limiting partial molar *Gibbs* free energy for activation of viscous flow of solute can be explained by the electrostatic ordering of water molecules by the ion, a process which is not strongly dependent on temperature. On the contrary, breaking of water-water hydrogen bonds takes place with increasing temperature.[24]

Furthermore, the $\Delta^{\#}\overline{G}_2^0$ value contains contributions from two effects:[4] first, the activation energy of solvent molecules are affected by the interaction between the solute and the surrounding solvent molecules in the transition state, $\Delta^{\#}\overline{G}_2^0(1 \rightarrow 1')$, and second, the solute moves through its own transition state, $\Delta^{\#}\overline{G}_2^0(2 \rightarrow 2')$. According to this view, the limiting *Gibbs* free energy of solute can be given as the sum of the two effects

$$\Delta^{\#}\overline{G}_2^0=\Delta^{\#}\overline{G}_2^0\left(1\rightarrow 1'\right)+\Delta^{\#}\overline{G}_2^0\left(2\rightarrow 2'\right) \qquad (11)$$

It has been suggested that $\Delta^{\#}\overline{G}_2^0(2 \rightarrow 2')$ might be well approximated for small ions by the *Gibbs* free energy of activation for viscous flow of the solvent,[4] or by the activation energy for conductance, $\Delta^{\#}\overline{G}_{2(cd)}^0$.[5] Thus, from $\Delta^{\#}\overline{G}_2^0$ the value of $\Delta^{\#}\overline{G}_2^0(1 \rightarrow 1')$ can be calculated. For the investigated electrolytes the value of $\Delta^{\#}\overline{G}_2^0(2 \rightarrow 2')$ was approximated by the *Gibbs* free energy for conductance, $\Delta^{\#}\overline{G}_{2(cd)}^0$. The change of the *Gibbs* free energy for conductance, $\Delta^{\#}\overline{G}_{2(cd)}^0$, was obtained from the corresponding ionic *Gibbs* free energy for conductance, $\Delta^{\#}\overline{G}_{i(cd)}^0$ which was given by *Brummer* and *Hills*[28] as

$$\Delta^{\#}\overline{G}_{i(cd)}^0=-RT\ln\left(\frac{6\lambda_i^0 h}{ze_0FL^2}\right) \qquad (12)$$

where e_0 is the electronic charge, *F* the *Faraday* constant and *L* the distance between adjacent equilibrium positions in the liquid, i. e. the jump distance obtained from[29]

$$L=\left(\frac{V_1^0}{N_A}\right)^{1/3} \qquad (13)$$

The $\Delta^{\#}\overline{G}_{i(cd)}^0$ values of tetra-n-alkylammonium ions were calculated from the λ_i^0 values given in ref.[14] The ionic *Gibbs* free energy for the conductance of the cyclohexylsulfamate ion, $\Delta^{\#}\overline{G}_{i(cd)}^0 = 12.09$ kJ mol^{-1} was determined previously.[22] The values of $\Delta^{\#}\overline{G}_{2(cd)}^0$, i. e. the sum of ionic *Gibbs* free energy for the conductance of the tetraalkylammonium ion and cyclohexylsulfamate ion, are collected in Table 5; from these values it can be seen that they are in a relatively narrow range from 23.0 to 25.4 kJ mol^{-1}. So, $\Delta^{\#}\overline{G}_2^0(2 \rightarrow 2')$ contributes only from 0.1 to 0.2 parts of $\Delta^{\#}\overline{G}_2^0$. The $\Delta^{\#}\overline{G}_2^0(1 \rightarrow 1')$ values collected in Table 5 are positive and increase with increasing size of the R_4N^+ ions. The variations of $\Delta^{\#}\overline{G}_2^0$ (see Table 4) would seem to reflect differences in the effect of tetra-n-alkylammonium cyclohexylsulfamates on the activation *Gibbs* free energy for movement of water molecules. A positive value of $\Delta^{\#}\overline{G}_2^0(1 \rightarrow 1')$ can be explained by the fact that

Table 4. Limiting *Gibbs* free energy of activation for the viscous flow of tetramethyl- (Me_4NCy), tetraethyl- (Et_4NCy), tetra-n-propyl- (n-Pr_4NCy), tetra-n-butyl- (n-Bu_4NCy) and tetra-n-pentylammonium (n-Pe_4NCy) cyclohexylsulfamates from 293.15 K to 323.15 K.

Compound	$\Delta^{\#}\overline{G}_2^0$ **(kJ mol^{-1})**				
	293.15 K	**298.15 K**	**303.15 K**	**313.15 K**	**323.15 K**
Me_4NCy	122.83±0.31	123.18±0.34	123.74±0.27	124.97±0.45	126.53±0.24
Et_4NCy	179.95±0.41	178.65±0.28	177.08±0.14	175.14±0.29	170.90±0.30
n-Pr_4NCy	240.87±0.27	235.94±0.14	231.55±0.28	221.57±0.14	216.64±0.30
n-Bu_4NCy	297.70±2.03	292.66±0.96	290.08±1.25	284.06±0.86	270.48±0.43
n-Pe_4NCy	345.68±0.27	340.27±0.27	337.99±0.42	332.10±0.29	313.60±0.59

Table 5. Thermodynamic functions of activation for conductance, $\Delta^{\#}\overline{G}_{2(cd)}^0$, $\Delta^{\#}\overline{H}_{2(cd)}^0$ and $\Delta^{\#}\overline{S}_{2(cd)}^0$ of some tetra-n-alkylammonium cyclohexylsulfamates and the contributions of the solute to the activation free energy, $\Delta^{\#}\overline{G}_2^0(1\rightarrow1')$, enthalpy, $\Delta^{\#}\overline{H}_2^0(1\rightarrow1')$ and entropy, $\Delta^{\#}\overline{S}_2^0(1\rightarrow1')$ of solvent molecules in aqueous solutions at 298.15 K.

Solute	$\Delta^{\#}\overline{G}_{2(cd)}^0$ **(kJ mol^{-1})**	$\Delta^{\#}\overline{H}_{2(cd)}^0$ **(kJ mol^{-1})**	$\Delta^{\#}\overline{S}_{2(cd)}^0$ **(J mol^{-1} K^{-1})**	$\Delta^{\#}\overline{G}_2^0(1\rightarrow1')$ **(kJ mol^{-1})**	$\Delta^{\#}\overline{H}_2^0(1\rightarrow1')$ **(kJ mol^{-1})**	$\Delta^{\#}\overline{S}_2^0(1\rightarrow1')$ **(J mol^{-1} K^{-1})**
Me_4NCy	23.06	33.19±0.15	34	100.12±0.34	63.31±0.3	–124±7
Et_4NCy	23.86	33.51±0.24	32	154.80±0.28	231.99±0.4	258±24
n-Pr_4NCy	24.68	35.29±0.19	36	211.26±0.14	447.21±0.2	791±61
n-Bu_4NCy	25.14	35.73±0.16	36	267.52±0.96	511.57±1.0	818±93
n-Pe_4NCy	25.41	36.06±0.01	36	314.86±0.27	599.44±0.3	954±158

Table 6. Solute contributions to the limiting partial molar entropy $\Delta^{\#}\overline{S}_2^0$ and enthalpy $\Delta^{\#}\overline{H}_2^0$ to activation of viscous flow at 298.15 K.

Solute	$\Delta^{\#}\overline{S}_2^0$ **(J mol^{-1} K^{-1})**	$\Delta^{\#}\overline{H}_2^0$ **(kJ mol^{-1})**
Me_4NCy	–89±7	96.6±0.3
Et_4NCy	291±24	265.4±0.3
n-Pr_4NCy	827±61	482.5±0.1
n-Bu_4NCy	854±93	547.3±1.0
n-Pe_4NCy	990±158	635.4±0.3

transfer of a tetra-n-alkylammonium cyclohexylsulfamate from the ground-state solvent to the transition-state-solvent is not favoured.

The solute contribution to the limiting partial molar entropy of activation for viscous flow, $\Delta^{\#}\overline{S}_2^0$, can be calculated from the relation

$$\Delta^{\#}\overline{S}_2^0 = -\left(\frac{\partial\Delta^{\#}\overline{G}_2^0}{\partial T}\right)_P \tag{14}$$

The limiting entropy of activation for viscous flow was estimated from the dependence of $\Delta^{\#}\overline{G}_2^0$ on temperature. The dependence of $\Delta^{\#}\overline{G}_2^0$ on temperature was expressed for Me_4NCy by function (7), while for other salts only a linear form of rel. (7) was used. The values of constants a_1 in rel. (7) were calculated by the least squres procedure and $\Delta^{\#}\overline{S}_2^0 = -a_1$ at 298.15 K. Table 6 lists the contribution of tetra-n-alkylammonium cyclohexylsulfamates to the limiting partial molar entropy for viscous flow, $\Delta^{\#}\overline{S}_2^0$. From this table it can be seen that $\Delta^{\#}\overline{S}_2^0$ values increase with increasing molecular weight of the salt and are positive except for Me_4NCy.

The limiting partial molar enthalpies for activation of viscous flow, $\Delta^{\#}\overline{H}_2^0$, calculated from the *Gibbs-Helmholtz* relation

$$\Delta^{\#}\overline{G}_2^0 = \Delta^{\#}\overline{H}_2^0 - T\Delta^{\#}\overline{S}_2^0 \tag{15}$$

are given in Table 6. The $\Delta^{\#}\overline{H}_2^0$ values are positive and increase with increasing molecular weight of the solute. According to *Tamamushi* and *Isono*[30] the following conditions are characteristic of a hydrophobic ion-solvent interaction: $\Delta^{\#}\overline{G}_2^0 > \Delta^{\#}\overline{G}_1^0$, $\Delta^{\#}\overline{H}_2^0 > \Delta^{\#}\overline{H}_1^0$ and $\Delta^{\#}\overline{S}_2^0 > \Delta^{\#}\overline{S}_1^0$. For the investigated R_4NCy solutes these conditions are satisfied for all solutes except for Me_4NCy where $\Delta^{\#}\overline{S}_2^0 < \Delta^{\#}\overline{S}_1^0$. Me_4NCy behaves differently from the higher members of the R_4NCy series due to its solvation properties.[12]

The effect of the solute on the activation enthalpy and entropy of the solvent molecules, $\Delta^{\#}\overline{H}_2^0(1 \rightarrow 1')$ and $\Delta^{\#}\overline{S}_2^0(1 \rightarrow 1')$, can be estimated from the enthalpy $\Delta^{\#}\overline{H}_{i(cd)}^0$ and entropy $\Delta^{\#}\overline{S}_{i(cd)}^0$ of activation for conductance of the ions. From the limiting molar conductivity of the R_4N^+ ions, given in refs.,[14,15,16] the *Eyring's* enthalpy of activation of charge transport, i. e. the enthalpy change required for unit displacement of one mole of R_4N^+ ions, can be evaluated from[28]

$$\ln\lambda_i^0 + \frac{2}{3}\ln d_0 = -\frac{\Delta^{\#}\overline{H}_{i(cd)}^0}{RT} + C \tag{16}$$

where C is an integration constant and d_0 the density of pure water. The enthalpy of activation for conductance of the cyclohexylsulfamate ion, $\Delta^{\#}\bar{H}^{0}_{i(cd)}$ = 18.34 kJ mol^{-1}, was estimated previously.[22] In Table 5, $\Delta^{\#}\bar{H}^{0}_{(cd)}$ represents the sum of the ionic enthalpy for conductance of R_4N^+ ions, calculated via rel. (16) and the corresponding values of the cyclohexylsulfamate ion. From this table it follows that $\Delta^{\#}\bar{H}^{0}_{2(cd)}$ values are positive and slightly increase with increasing molecular weight of the tetra-n-alkylammonium cyclohexylsulfamates. The integration constant *C* of rel. (16) amounts to: 5.179±0.059 (Me_4N^+), 5.499±0.095 (Et_4N^+), 5.372±0.074 (n-Pr_4N^+), 5.356±0.063 (n-Bu_4N^+) and 5.377±0.034 (n-Pe_4N^+), respectively. The entropy of activation for conductance, $\Delta^{\#}\bar{S}^{0}_{2(cd)}$ of R_4NCy salts was obtained from the *Gibbs-Helmholtz* relation (15) and are given in Table 5. The calculated values of $\Delta^{\#}\bar{S}^{0}_{2(cd)}$ are low and almost independent of the molecular weight of the solute and their average value amounts to (34.8±2) J mol^{-1} K^{-1}.

Since the enthalpies and entropies of activation for conductance of R_4NCy salts are positive, therefore the effect of the solute on the activation enthalpy and entropy of the solvent molecules obtained from the analogous relation as (11), $\Delta^{\#}\bar{H}^{0}_{2}(1\rightarrow1')$ and $\Delta^{\#}\bar{S}^{0}_{2}(1\rightarrow1')$ is high (see Table 5). So, the positive and high values of $\Delta^{\#}\bar{H}^{0}_{2}$ and $\Delta^{\#}\bar{S}^{0}_{2}$ given in Table 6, primarily arise from the breaking of solvent-solvent bonds in the transition state. This is in accordance with the fact that very large ions with hydrophobic surfaces do not display peripheral hydration.[12] The hydrophobic surface of such ions literally repels the water molecules from its surface with the formation of a more ordered and rigid structure of water surrounding the ions.[23]

4. References

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Povzetek

Relativno viskoznost vodne raztopine nekaterih tetra-n-alkilamonijevih soli v temperaturnem intervalu od 293,15 do 323,15 K smo interpretirali s *Kaminsky*-jevo enačbo. Vrednosti koeficientov viskoznosti *A*, *B* in *D* smo razložili z naravo soli, velikostjo ionov, s strukturnimi interakcijami med topilom in topljencem ter dalekosežnimi interakcijami med ioni. Izračunali smo limitne termodinamske funkcije viskoznega toka topila in topljenca in določili njihove prispevke k transportnemu prenosu raztopine. Razliko med preiskovanimi solmi smo razložili kot posledico različne velikosti tetra-n-alkilamonijevega iona in vpliva hidrofobnih lastnosti alkilnih skupin v tetra-n-alkilamonijevem ionu.