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Apparent Molar Volume and Apparent Molar Expansibility of Rubidium, Cesium, and Ammonium Cyclohexylsulfamate in Aqueous Solution

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Summary. The apparent molar volume of rubidium, caesium, and ammonium cyclohexylsulfamate was determined from the density data of their aqueous solutions at 293.15, 298.15, 303.15, 313.15, 323.15, and 333.15 K. From the apparent molar volume, determined at various temperatures, the apparent molar expansibility was calculated. The limiting apparent molar volume and apparent molar expansibility were evaluated and apportioned into their ionic components. The limiting partial molar ionic volumes and expansibilities are discussed in terms of the various effects of the ion in solution on the structure of water. It was shown that the limiting partial molar ionic expansibilities of the alkali-metal cations increase with their ionic radii. The coefficients of thermal expansion of the investigated solutions at 298.15 K were calculated and are presented graphically together with some alkali-metal cyclohexylsulfamates and tetramethylammonium cyclohexylsulfamate. The densities of the investigated solutions can be adequately represented by an equation derived by *Redlich*.

Keywords. Density data; Expansibility; Cyclohexylsulfamates; Aqueous solution.

Introduction

This study is a continuation of the programme of measuring the apparent molar volume of aqueous salt solutions of cyclohexylsulfamic acid at various temperatures [1]. Interest in cyclohexylsulfamates arises from their ability to act as intense sweeteners [2]. In an aqueous solution of an artificial sweetener some degree of solute–solvent interaction occurs. The taste of such a substance can be interpreted by understanding the structure and properties of ions in aqueous solution. Recently, the effects of temperature, pH, and some monovalent and divalent cations on the intensity of sweetener ratings ranging widely in chemical structure have been evaluated [3]. The volumetric parameters of electrolyte solutions can provide information

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concerning the nature of entities from which the ion–solvent interactions can be inferred.

With this in mind, precision density measurements were made on dilute solutions of rubidium, caesium, and ammonium cyclohexylsulfamates in the temperature range from 293.15 to 333.15 K. The apparent molar volume and apparent molar expansibility were then calculated from the density data.

Results and Discussion

The values of density, d ($\mathrm{g \cdot cm^{-3}}$), measured at various temperatures as a function of molality, m ($\mathrm{mol \cdot kg^{-1}}$), are presented in Table 1. The apparent molar volume, V_Φ ($\mathrm{cm^3 \cdot mol^{-1}}$), of a solute with molar mass, M_2 ($\mathrm{g \cdot mol^{-1}}$), is defined by Eq. (1) where $v = 1/d$ and $v_o = 1/d_o$ are the specific volume ($\mathrm{cm^3 \cdot g^{-1}}$) of the solution and solvent, respectively, and d_o is the density of pure water.

$$V_\Phi = \frac{10^3(v - v_o)}{m} + vM_2 \tag{1}$$

In calculating the uncertainty in apparent molar volume, δV_Φ, only the uncertainty in specific volume was taken into account since V_Φ is not seriously influenced by errors in molality [1, 4]. The dependence of V_Φ on molality at a definite temperature was fitted with Eq. (2) [5] where V_Φ^o represents the apparent molar volume of solute at infinite dilution, equal to the limiting partial molar volume of solute, $\overline{V}_2^o$ ($\mathrm{cm^3 \cdot mol^{-1}}$), A_v ($\mathrm{cm^3 \cdot kg^{1/2} \cdot mol^{-3/2}}$) is the *Debye-Hückel* limiting law slope for apparent molar volume, and B_v and D_v are empirical constants which depend on solute, solvent, and temperature.

$$V_\Phi = V_\Phi^o + A_v m^{1/2} + B_v m + D_v m^{3/2} + \ldots \tag{2}$$

In calculation of V_Φ the value of coefficient A_v was taken from Ref. [6]. To represent the data adequately, only two experimentally determined coefficients, *i.e.* V_Φ^o and B_v were sufficient. The regression values of parameters V_Φ^o and B_v of Eq. (2) are given in Table 2. In Fig. 1 the dependence of V_Φ^o of alkali-metal cyclohexylsulfamate on a cube with the ionic radius of the cation at 298.15 K is shown. The values of V_Φ^o for lithium, sodium, and potassium cyclohexylsulfamate were taken from Ref. [1] and ionic radii from Ref. [7]. From Fig. 1 it can be seen that except for lithium cyclohexylsulfamate, the V_Φ^o values of other solutes gradually increase with the ionic radius of the cation. The value of V_Φ^o for lithium cyclohexylsulfamate seems to be anomalous. The relatively high value of its V_Φ^o is due to its coordination structure having a coordination number higher than the other alkali metal ions. As a consequence its hydrated structure expands the hydration shell which leads to an increase of its ionic volume [8].

The values of V_Φ^o and B_v obtained were tested by a *Redlich* equation (Eq. (3)) [9] where c is the concentration of salt ($\mathrm{mol \cdot dm^{-3}}$), calculated from $c = md/(1 + mM_2 \times 10^{-3})$; the factor 1000 appears when densities are given in $\mathrm{g \cdot cm^{-3}}$.

$$d = d_o + \frac{(M_2 - V_\Phi^o d_o)}{1000}c - \left(\frac{A_v d_o^{1/2}}{1000}\right)c^{3/2} - \left(\frac{B_v}{1000}\right)c^2 \tag{3}$$

The densities calculated, using Eq. (3) are within an average value of $2.45 \times 10^{-5}\ \mathrm{g \cdot cm^{-3}}$ equal to the experimental values given in Table 1. The apparent

Table 1. Density of aqueous solutions of rubidium (Rb*Cy*), caesium (Cs*Cy*), and ammonium cyclohexylsulfamate (NH_4*Cy*) from 293.15 to 323.15 K

$m/\mathrm{mol \cdot kg^{-1}}$	$d/\mathrm{g \cdot cm^{-3}}$ at T/K					
	293.15	298.15	303.15	313.15	323.15	333.15
			Rb*Cy*			
0.0060	0.99897	0.99780	0.99640	0.99296	0.98877	0.98393
0.0262	1.00152	1.00033	0.99891	0.99543	0.99121	0.98635
0.0555	1.00517	1.00396	1.00251	0.99899	0.99473	0.98983
0.0816	1.00842	1.00718	1.00571	1.00214	0.99785	0.99291
0.1021	1.01093	1.00966	1.00817	1.00457	1.00025	0.99528
0.1324	1.01462	1.01333	1.01181	1.00817	1.00381	0.99880
0.1516	1.01692	1.01562	1.01409	1.01042	1.00603	1.00101
0.1695	1.01908	1.01775	1.01621	1.01251	1.00810	1.00305
0.2040	1.02317	1.02182	1.02025	1.01651	1.01205	1.00697
0.2341	1.02683	1.02545	1.02385	1.02005	1.01555	1.01043
0.2778	1.03183	1.03040	1.02877	1.02490	1.02035	1.01518
0.3278	1.03758	1.03611	1.03442	1.03048	1.02586	1.02063
			Cs*Cy*			
0.0046	0.99898	0.99781	0.99640	0.99297	0.98878	0.98394
0.0215	1.00179	1.00061	0.99918	0.99571	0.99150	0.98663
0.0493	1.00636	1.00514	1.00370	1.00017	0.99592	0.99101
0.0726	1.01013	1.00890	1.00743	1.00387	0.99958	0.99464
0.1030	1.01505	1.01379	1.01229	1.00868	1.00435	0.99937
0.1339	1.01998	1.01869	1.01717	1.01351	1.00913	1.00410
0.1524	1.02291	1.02161	1.02007	1.01639	1.01198	1.00693
0.1737	1.02627	1.02494	1.02339	1.01967	1.01523	1.01014
0.2075	1.03155	1.03019	1.02861	1.02483	1.02034	1.01521
0.2396	1.03653	1.03514	1.03352	1.02969	1.02515	1.01998
0.2813	1.04288	1.04145	1.03980	1.03590	1.03130	1.02606
0.3262	1.04970	1.04823	1.04653	1.04256	1.03789	1.03260
0.5552	1.08286	1.08117	1.07927	1.07492	1.06991	1.06431
			NH_4*Cy*			
0.0252	0.99954	0.99838	0.99698	0.99354	0.98935	0.98448
0.0481	1.00082	0.99963	0.99821	0.99473	0.99051	0.98564
0.0787	1.00245	1.00124	0.99980	0.99630	0.99206	0.98716
0.1095	1.00409	1.00286	1.00140	0.99786	0.99359	0.98868
0.1207	1.00467	1.00344	1.00198	0.99843	0.99416	0.98923
0.1556	1.00651	1.00525	1.00377	1.00019	0.99588	0.99093
0.1757	1.00758	1.00630	1.00480	1.00119	0.99686	0.99190
0.1969	1.00867	1.00738	1.00587	1.00224	0.99790	0.99292
0.2298	1.01033	1.00902	1.00749	1.00383	0.99946	0.99446
0.2550	1.01161	1.01028	1.00874	1.00506	1.00066	0.99564
0.3199	1.01488	1.01351	1.01193	1.00818	1.00373	0.99867
0.3732	1.01746	1.01605	1.01443	1.01062	1.00613	1.00103
0.4293	1.02017	1.01873	1.01708	1.01321	1.00867	1.00352
0.5014	1.02357	1.02208	1.02039	1.01644	1.01184	1.00665
0.5825	1.02732	1.02578	1.02403	1.02000	1.01533	1.01008
0.6270	1.02935	1.02777	1.02601	1.02193	1.01722	1.01193

Table 2. Limiting apparent molar volume, V^o_Φ, and deviation constant B_v (in parentheses) of rubidium, caesium, and ammonium cyclohexylsulfamates and limiting partial molar ionic volume, $\overline{V}^o_{Cy^-}$, of the cyclohexylsulfamate ion in aqueous solution at the indicated temperatures

Solute/Ion	V^o_Φ or $\overline{V}^o_{Cy^-}/\mathrm{cm^3 \cdot mol^{-1}}$ ($B_v/\mathrm{cm^3 \cdot kg \cdot mol^{-2}}$) at T/K					
	293.15	298.15	303.15	313.15	323.15	333.15
Rb*Cy*	136.65 ± 0.17	137.64 ± 0.17	138.64 ± 0.17	140.17 ± 0.17	141.54 ± 0.18	142.91 ± 0.18
	(1.47 ± 0.65)	(1.30 ± 0.68)	(1.23 ± 0.68)	(0.89 ± 0.68)	(0.83 ± 0.72)	(0.24 ± 0.70)
Cs*Cy*	144.57 ± 0.08	145.50 ± 0.08	146.38 ± 0.07	147.97 ± 0.07	149.36 ± 0.07	150.67 ± 0.07
	(0.69 ± 0.19)	(0.62 ± 0.19)	(0.53 ± 0.17)	(0.39 ± 0.16)	(0.31 ± 0.17)	(0.13 ± 0.18)
NH_4*Cy*	141.14 ± 0.05	141.88 ± 0.04	142.53 ± 0.07	143.76 ± 0.041	144.92 ± 0.031	146.03 ± 0.04
	(0.32 ± 0.10)	(0.30 ± 0.08)	(0.25 ± 0.07)	(0.18 ± 0.07)	(0.24 ± 0.07)	(0.35 ± 0.08)
Cy^-	123.2 ± 0.4	123.8 ± 0.4	124.4 ± 0.5	125.5 ± 0.6	126.6 ± 0.6	127.8 ± 0.9

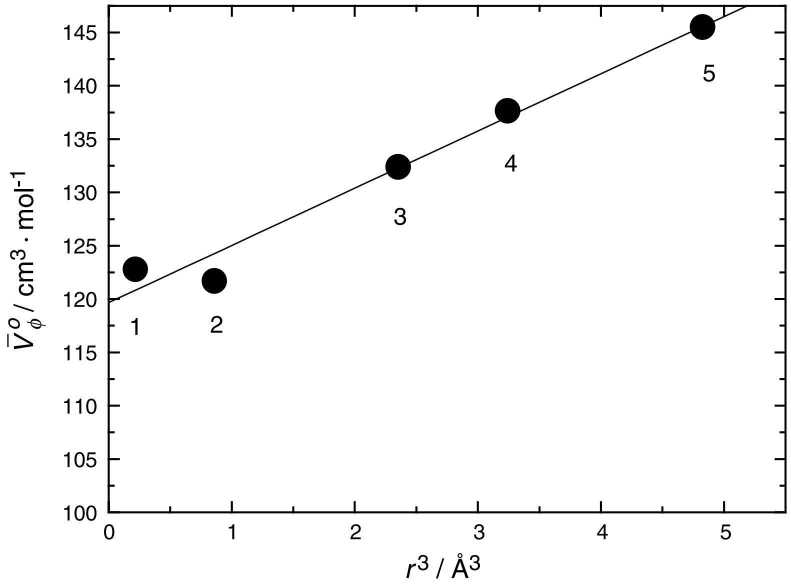

Fig. 1. Dependence of the limiting apparent molar volume of lithium (1) [1], sodium (2) [1], potassium (3) [1], rubidium (4), and caesium (5) cyclohexylsulfamate in aqueous solution on r^3 at 298.15 K

molar volume of ammonium cyclohexylsulfamate, determined earlier at 298.15 K is close to the value given in Table 2 (141.40 $\mathrm{cm^3 \cdot mol^{-1}}$) [10]. Recently, a value of 142.0 $\mathrm{cm^3 \cdot mol^{-1}}$ was determined by *Birch et al.* [11] for ammonium cyclohexylsulfamate and 138.0 $\mathrm{cm^3 \cdot mol^{-1}}$ for rubidium cyclohexylsulfamate at a concentration 6.38% (w/w) and at 293.15 K. Considering Eq. (2) and using the corresponding parameters from Table 2, the calculated values are 142.06 $\mathrm{cm^3 \cdot mol^{-1}}$ for ammonium and 137.92 $\mathrm{cm^3 \cdot mol^{-1}}$ for the rubidium salt, which are in good agreement with the corresponding values given by *Birch et al.*

From Table 2 it can be seen that the deviation constant B_v is positive for the rubidium and caesium salts with a negative value of $\partial B_v/\partial T$, while for the ammonium salt the deviation constant B_v is positive with a negative value of $\partial B_v/\partial T$ at 298.15 K. As was shown by *Millero* [12] the magnitude and sign of the deviation constant B_v is a function of the size, charge, temperature, and the solvent used and is a direct measure of the ion–ion interactions that cause the deviations. So, the main contribution for the deviations from the limiting law in moderately concentrated solutions are associated with long-range *Coulombic* interactions, primary hydration of ions and ion-pairing. From the ionic association constant $K_A = 2$–3 for the investigated systems [13, 14], except for Cs*Cy* where $K_A = 5$–6, it follows that alkali-metal salts of cyclohexylsulfamic acid could be regarded as completely dissociated in aqueous solutions. Furthermore, no evidence for the temperature dependence of the association process of alkali-metal cyclohexylsulfamates was found. Cation–anion ion-pairing can be minimized, except for Cs*Cy*, as a possible cause for the observed deviations. As far as the primary hydration of ions is concerned, the cyclohexylsulfamate ion is very weakly hydrated due to its hydrophobicity [10], whereas the hydration of cations depends on their charge densities. The observed deviation could be ascribed to the extended terms in *Debye-Hückel* theory which includes the closest distance of ions. As far as the alkali-metal cyclohexylsulfamates are concerned, the deviation constant B_v roughly increases with the size of the cation, except for the caesium ion where B_v (caesium ion) $< B_v$ (rubidium ion), or with the limiting apparent molar volume [1].

Considering the separation of the limiting apparent molar volume of an electrolyte into the individual values for the cation, $\overline{V}^{o}_{cat}$ and anion, $\overline{V}^{o}_{ani}$ [12], the limiting partal molar ionic volume of the cyclohexylsulfamate ion, $\overline{V}^{o}_{Cy^-}$, at a definite temperature was obtained as Eq. (4) where for the limiting partial molar ionic volume of the individual cations the literature values were used [12, 15].

$$\overline{V}^{o}_{Cy^-} = \overline{V}^{o}_{\Phi} - \overline{V}^{o}_{cat} \tag{4}$$

The so-called conventional partial molar ionic volumes based on the assumption that $\overline{V}^{o}_{H^+}$ is zero were employed. The $\overline{V}^{o}_{cat}$ values for temperatures other than 298.15 K were obtained by analytical interpolation to *Millero*'s data, except for the ammonium ion where the value of $\overline{V}^{o}_{NH_4^+}$ at different temperatures was obtained from the limiting apparent molar volumes of ammonium chloride [14] and $\overline{V}^{o}_{Cl^-}$ values [12]. The average values of $\overline{V}^{o}_{Cy^-}$ for all salts investigated at a definite temperature are compiled in Table 2. The calculated values of $\overline{V}^{o}_{Cy^-}$ are within experimental error equal to those obtained previously [1].

Applying the multilayer hydration model for ion–water interactions the partial molar volume of an ion at infinite dilution, $\overline{V}^{o}_{ion}$, can be attributed to various parts of partial molar ionic volumes [15], *i.e.* to the intrinsic partial molar ionic volume, $\overline{V}^{o}_{int}$ (usually evaluated from the crystal volume, $\overline{V}^{o}_{cryst}$), to the electrostriction partial molar ionic volume, $\overline{V}^{o}_{elect}$, to the disordered or void space partial molar ionic volume, $\overline{V}^{o}_{disord}$, and to the caged or structured partial molar ionic volume, $\overline{V}^{o}_{caged}$. From the crystal molar volume of the cyclohexylsulfamate ion determined by the X-ray structural data ($\overline{V}^{o}_{cryst} = 127.65\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ [10]) the difference $\overline{V}^{o}_{ion} - \overline{V}^{o}_{cryst}$ amounts to $-4.45\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ at 293.15 K and this difference decreases linearly with increasing temperature until at 333.15 K $\overline{V}^{o}_{ion} = \overline{V}^{o}_{int}$. The difference can be attributed to the electrostriction, $\overline{V}^{o}_{elect}$, disordered, $\overline{V}^{o}_{disord}$, and $\overline{V}^{o}_{caged}$ partial molar ionic volumes.

The relative contribution of $\overline{V}^{o}_{elect}$ to $\overline{V}^{o}_{ion}$ depends upon the charge and radius of the ion. When $\overline{V}^{o}_{ion} - \overline{V}^{o}_{cryst}$ is negative, the $\overline{V}^{o}_{elect}$ region is greater than $\overline{V}^{o}_{disord}$, and the ion can be classified as a structure-making or positive-hydration ion. In the past

Padova [16, 17] estimated the average theoretical electrostriction per mol of water and found it to be $-2.1\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ at 298.15 K. The partial molar ionic electrostriction volume, $\overline{V}^o_{elect}$, was calculated from the *Drude-Nernst* equation (Eq. (5)) [18] which is suitable for sufficiently large ions and where $B = 4.175\,\mathrm{cm}^3 \cdot \mathrm{\AA} \cdot \mathrm{mol}^{-1}$ at 298.15 K [15], Z is the valency of the ion, and r is the crystallographic radius ($r = 3.70\,\mathrm{\AA}$, [10]).

$$\overline{V}^o_{elect} = -\frac{BZ^2}{r} \tag{5}$$

Applying Eq. (5) $\overline{V}^o_{elect}$ amounts to $-1.1\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$.

The large cyclohexylsulfamate ion causes structural effects which are different from those of simple monovalent ions. For such ions the difference $\overline{V}^o_{ion} - \overline{V}^o_{cryst}$ is negative and one must consider another component of $\overline{V}^o_{ion}$, the so-called structural partial molar ionic volume. Water molecules at the surface of this ion are not strongly influenced by the ionic charge which is distributed along the three oxygen atoms and the hydrocarbon portion of the molecule as can be seen in Fig. 2 [10]. The water–water interactions next to the hydrophobic part of the ion appear to have a higher degree of hydrogen bonding or structure, leading to a decrease of the volume. $\overline{V}^o_{elect}$ and $\overline{V}^o_{caged}$ appear to be negative. It is difficult to separate the two effects only on a volume basis. One might conclude that $\overline{V}^o_{caged}$ becomes less important as the temperature is increased, while $\overline{V}^o_{elect}$ for anions decreases with increasing temperature [15].

The cyclohexylsulfamate ion is also interesting from another point of view. Its ionic viscosity B_{ion} coefficient of *Jones-Dole* equation is positive, $B_{ion} = 0.341 \pm 0.004\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ at 298.15 K, then increases with temperature and reaches a maximum value at 309 K [19]. *Nightingale* [20] has suggested that the values of $B_{ion} > 0$

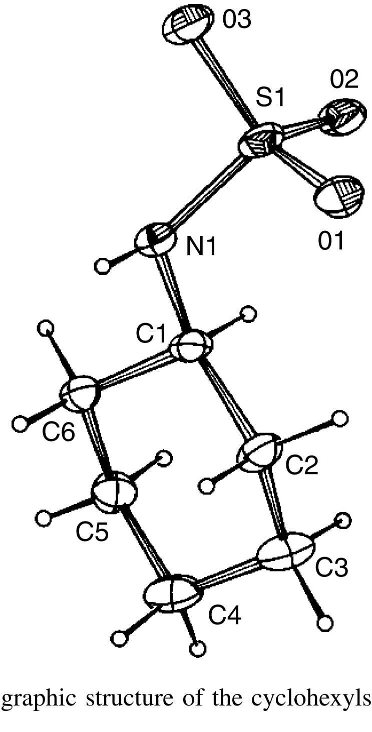

Fig. 2. Crystallographic structure of the cyclohexylsulfamate ion [10]

and $dB_{ion}/dT > 0$ are characteristic of anomalous structure-making ions. According to this view when there being less water structure to begin with, these structure-making ions produce more structure and have positive dB_{ion}/dT values up to 309 K. After this temperature $B_{ion} > 0$ and $dB_{ion}/dT < 0$, cyclohexylsulfamate ion can be classified as large structure-making ion with ''aperipheral hydration'', *i.e.* the ion is unhydrated.

The apparent molar expansibility, ϕ_E, can be obtained by differentiation of Eq. (2) with respect to temperature at constant pressure (Eq. (6)), taking into account that $(\partial V_\Phi/\partial T)_P = \phi_E$.

$$\phi_E = \phi_E^o + \left(\frac{\partial A_v}{\partial T}\right)_P m^{1/2} + \left(\frac{\partial B_v}{\partial T}\right) m + \ldots \tag{6}$$

The limiting apparent molar expansibility of the solute, ϕ_E^o, was calculated from the temperature dependence of V_Φ^o given by Eq. (7) where a_o, a_1, and a_2 are empirical constants depending on solute and solvent, and $T_o = 298.15$ K.

$$V_\Phi^o = a_o + a_1(T - T_o) + a_2(T - T_o)^2 \tag{7}$$

The values of the constants of Eq. (7) are given in Table 3 together with the standard error of the estimate. From Eq. (7) it follows that ϕ_E^o is a linear function of temperature and that $\phi_E^o = a_1$ at 298.15 K. From Table 3 it can be seen that the limiting apparent expansibilities of rubidium and caesium cyclohexylsulfamates are within experimental error equal at 298.15 K. The limiting apparent molar expansibilities of alkali-metal cylohexylsulfamates [1] increase with increasing radius of the cation, with the exception of the caesium ion.

The limiting partial molar ionic expansibility of the cyclohexylsulfamate ion, $\overline{E}_{ion}^o$, was obtained from the linear dependence of $\overline{V}_{Cy^-}^o$ on temperature given in Table 2 and the data from Ref. [1]. The calculated value of $\overline{E}_{Cy^-}^o$ (given in Table 4)

Table 3. Values of constants a_i of Eq. (7) and standard error of the estimate, s

Solute	$\frac{a_o}{\mathrm{cm^3 \cdot mol^{-1}}}$	$\frac{a_1}{\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-1}}}$	$\frac{-a_2 \times 10^4}{\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-2}}}$	s
Rb*Cy*	137.61 ± 0.025	0.1810 ± 0.0039	8.66 ± 1.2	0.046
Cs*Cy*	145.49 ± 0.015	0.1774 ± 0.0023	8.56 ± 0.71	0.027
NH_4*Cy*	141.85 ± 0.016	0.1346 ± 0.0024	4.45 ± 0.76	0.029

Table 4. Partial molar ionic expansibility, $\overline{E}_{ion}^o$, crystal radius, r, and ratio of Z^2/r of rubidium, caesium, ammonium, and cyclohexylsulfamate ions in aqueous solution at 298.15 K

Ion	$\frac{\overline{E}_{ion}^o}{\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-1}}}$	$\frac{r}{\text{Å}}$	$\frac{Z^2}{r}$
Rb^+	0.074 ± 0.006	1.48[a]	0.68
Cs^+	0.062 ± 0.005	1.69[a]	0.59
NH_4^+	0.020 ± 0.005	1.48[a]	0.68
Cy^-	0.115 ± 0.004	3.70[b]	0.27

[a] Taken from Ref. [7]; [b] taken from Ref. [10]

amounts to $0.115 \pm 0.004\,\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-1}}$ which within experimental error is equal to the value given previously [1]. The $\overline{E}^o_{Cy^-}$ value permits us to calculate the limiting partial molar expansibility of the investigated cations by dividing the ϕ^o_E value of the salts into their ionic components (Eq. (8)) [21].

$$\phi^o_E = \overline{E}^o_+ + \overline{E}^o_- \tag{8}$$

The values of $\overline{E}^o_{ion}$ obtained are positive and given in Table 4. The $\overline{E}^o_{ion}$ values for the rubidium, caesium, and ammonium ions are substantially greater than those given in Ref. [21], which are 0.016 for rubidium, 0.012 for caesium, and $-0.028\,\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-1}}$ for the ammonium ion, with relatively high experimental uncertainties of 0.009–$0.03\,\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-1}}$. In Fig. 3 $\overline{E}^o_{ion}$ is plotted against Z^2/r, where Z is the charge of the ion and r the crystal radius [7]. According to *Noyes* [22] the slope of this line is equal to $-0.067 \pm 0.009\,\mathrm{\AA \cdot cm^3 \cdot mol^{-1} \cdot K^{-1}}$ and the intercept to $0.111 \pm 0.009\,\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-1}}$. Both values are within experimental error equal to those given previously for the lithium, sodium, and potassium ions [1]. The positive intercept indicates that there is a positive contribution to the $\overline{E}^o_{ion}$ value of monovalent ions.

The partial molar limiting ionic expansibility, $\overline{E}^o_{ion}$ can be divided into individual components [21]. According to this model, the intrinsic expansibility, $\overline{E}^o_{int}$, can be neglected for monoatomic and monovalent ions. The investigated cations do not greatly differ in electrostriction expansibility. This component of partial molar limiting ionic expansibility describes the volume change due to changes in the electrostriction region which are proportional to Z^2/r. From Table 4 it can be seen that the ratio Z^2/r is equal for the ammonium and rubidium ions, while for caesium it is somewhat smaller. The disordered expansibility, $\overline{E}^o_{disord}$, depends on the temperature and magnitude of the electrostriction region, *i.e.* on Z^2/r. For ions with a small electrostricted region (small Z^2/r), this region is very important.

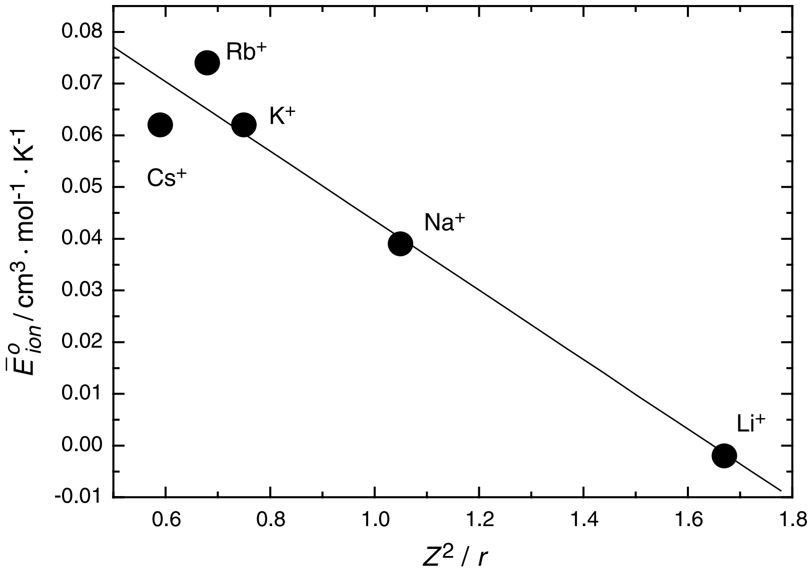

Fig. 3. Partial molar ionic expansibility of alkali-metal ions as a function of Z^2/r at 298.15 K

Furthermore, $\overline{E}^{o}_{disord}$ accounts for the large and positive values of monovalent ions at room temperature. As was shown previously [21] for alkali-metal ions, except for lithium, $\overline{E}^{o}_{elect}$ is less important and the $\overline{E}^{o}_{disord}$ term becomes gradually dominant as can be seen from Fig. 3. The relatively low value of $\overline{E}^{o}_{ion}$ of the ammonium ion is apparently due to its low expansibility of water in the hydration shell which has an expansibility similar to water. On the other hand, the larger tetramethylammonium ion with $r = 3.47$ Å [21], $\overline{E}^{o}_{ion} = 0.059 \pm 0.002\,\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-1}}$ [1], and low Z^2/r has an expansibility of water in the hydration shell quite different from that of water. Its expansibility is close to the expansibility of the caesium ion. The $\overline{E}^{o}_{caged}$ and $\overline{E}^{o}_{disord}$ terms in $\overline{E}^{o}_{ion}$ are responsible for the large and positive value of $\overline{E}^{o}_{ion}$ of the cyclohexylsulfamate ion. These terms primarly depend on the relative proportions of the hydrophilic and hydrophobic surface of the ion. Besides the hydrophobic nature of the cyclohexylsulfamate ion, the possible conformational structure of the cyclohexyl radical may play an additional role on the structure of water. The $\overline{E}^{o}_{ion}$ value of the cyclohexylsulfamate ion is higher than for simple monovalent ions [21] since their crystal radius is much greater.

The apparent molar expansibility of the investigated solutions can be obtained from Eq. (6). The derivative $(\partial A_v/\partial T)_P = A_E$ was calculated from the A_v data [6]. The derivatives $(\partial B_v/\partial T)_P$ at 298.15 K are −0.016 for lithium, 0.0046 for sodium, 0.0 for potassium [1], −0.028 for rubidium, and $-0.0134\,\mathrm{cm^3 \cdot kg \cdot mol^{-2} \cdot K^{-1}}$ for caesium cyclohexylsulfamate, respectively. In Fig. 4 the apparent molar expansibility of the alkali-metal cyclohexylsulfamates at 298.15 K is plotted against $m^{1/2}$. From Fig. 4 it can be seen that the ϕ_E values for potassium, rubidium, and caesium cyclohexylsulfamates are close together at low molality; *e.g.* at $m = 0.20\,\mathrm{mol \cdot kg^{-1}}$ their ϕ_E values are 0.181, 0.183, and $0.182\,\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-1}}$.

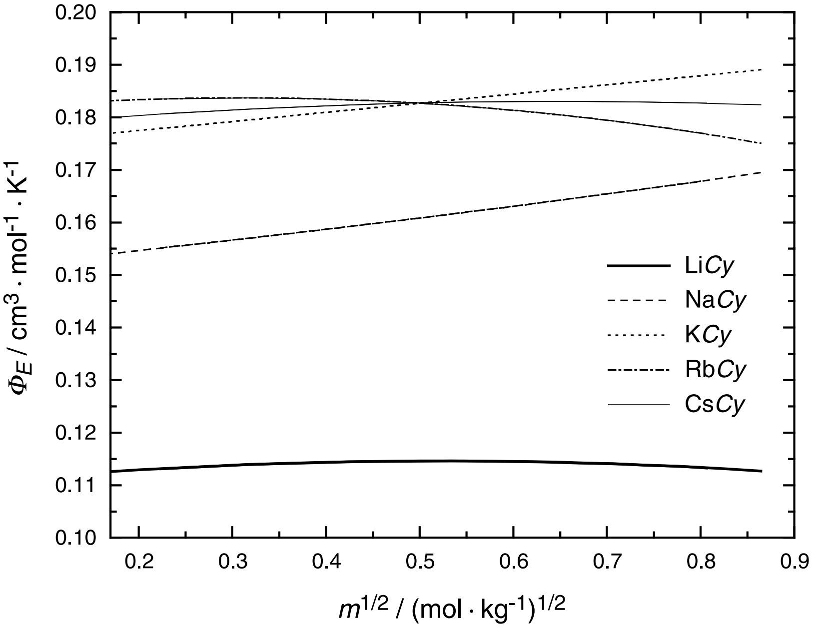

Fig. 4. Dependence of the apparent molar expansibility of alkali-metal cyclohexylsulfamates in aqueous solution on $m^{1/2}$ at 298.15 K

The coefficient of thermal expansion of solution, α (K^{-1}), as a function of concentration was calculated from Eq. (9) [4] where α_o (K^{-1}) is the coefficient of thermal expansion of pure water.

$$\alpha = \alpha_o + \left[\frac{\phi_E^o - \alpha_o \phi_v^o}{1000}\right] c + \left[\frac{A_E - \alpha_o A_v}{1000}\right] c^{3/2} - \frac{B_v \alpha_o}{1000} c^2 \tag{9}$$

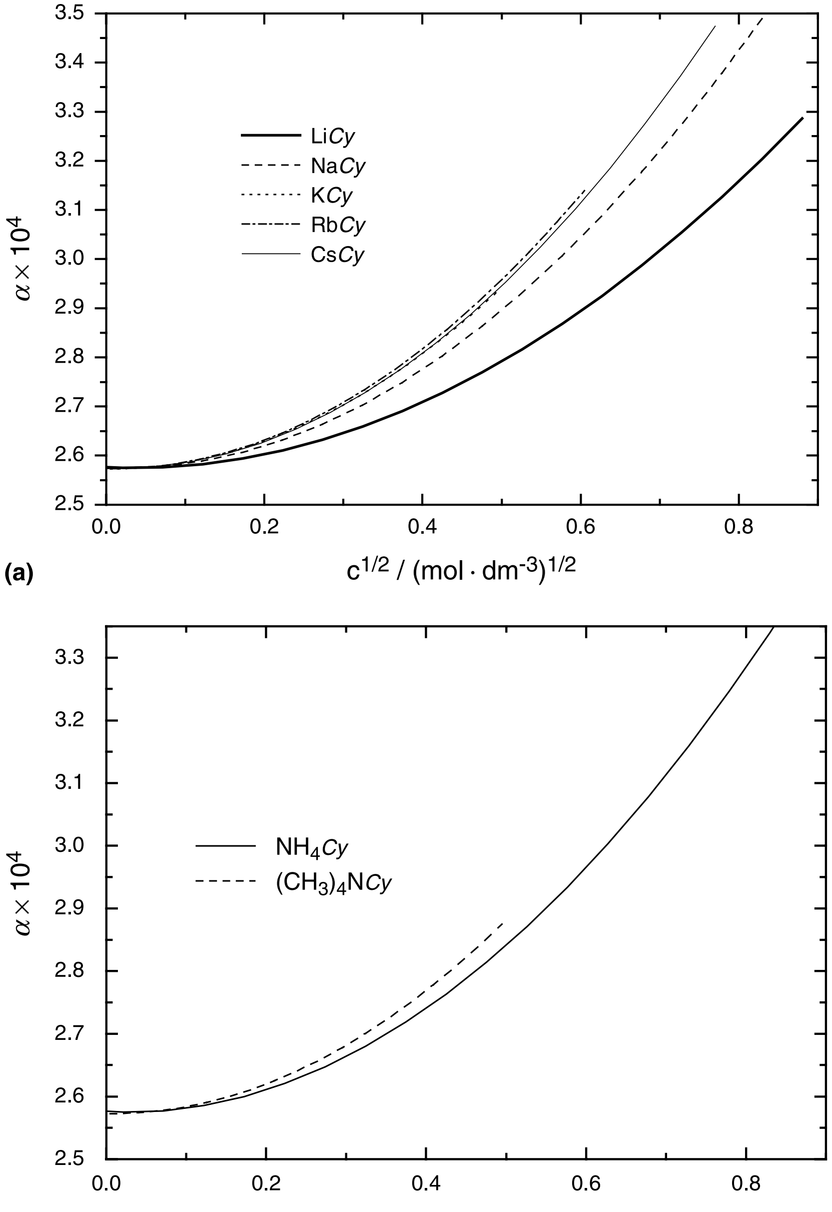

Fig. 5. Coefficient of thermal expansion of aqueous solutions of (a) lithium, sodium, potassium, rubidium, and caesium cyclohexylsulfamate and (b) ammonium and tetramethylammonium cyclohexylsulfamate at 298.15 K

According to the *Debye-Hückel* theory, the coefficient of the $c^{3/2}$ term is common to all strong electrolytes of the same valence type in a given solvent at definite temperature. On the other hand, the coefficient of the c term is a characteristic of a given solute and amounts to 1.456×10^{-4}, 1.400×10^{-4}, and $9.81\times10^{-5}\,\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-1}}$ for rubidium, caesium, and ammonium cyclohexylsulfamate, respectively, at 298.15 K. In calculation of the value of α of a solution at 298.15 K we used the α_o value determined by *Kell* [23], and for A_E a value of $0.01771 \pm 0.00008\,\mathrm{cm^3 \cdot dm^{1.5} \cdot mol^{-1.5} \cdot K^{-1}}$ [1]. The dependence of the coefficient of thermal expansion on the square root of concentration at 298.15 K for the investigated solutions, together with some solutions of alkali-metal cyclohexylsulfamates and tetramethylammonium cyclohexylsulfamate determined earlier, are shown in Fig. 5. From Fig. 5(a) it can be seen that at a definite concentration of solute α increases with increasing radius of the cation from lithium to rubidium, with the exception of caesium, where α is within experimental uncertainties equal to the value for potassium. The behaviour of α of tetramethylammonium and ammonium cyclohexylsulfamates given in Fig. 5(b) can be explained by their effect on the structure of water.

Experimental

Materials

Rubidium (Rb*Cy*), caesium (Cs*Cy*), and ammonium cyclohexylsulfamate (NH_4*Cy*) were obtained by careful neutralization of cyclohexylsulfamic acid (purchased from Sigma) with the corresponding base (Fluka). The purity of the salts was checked after repeated recrystallizations 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 the salts with the hydrogen ion (DOWEX, Type 50 WX8); a purity of 99.9% was determined. The salts were kept in a vacuum desiccator over P_2O_5.

The investigated solutions were prepared on a molal concentration scale by precise weighing, using a digital balance (Mettler Toledo, model AT201, Switzerland) accurate to within $\pm1\times10^{-5}$ g. Before use the solutions were degassed by ultrasound (ultrasonic bath, Bandelin Sonorex, type TK 52, Berlin, Germany).

Density Measurements

The density, d, of aqueous solutions of cyclohexylsulfamates was measured by a vibrating-tube density meter (Anton Paar, model DMA 60, Graz, Austria) equipped with a measuring cell (Anton Paar, type 602) and a digital thermometer (Anton Paar, DT 100-20) with a precision of ±0.01 K. The apparatus was calibrated with doubly distilled water [23] and dry air [24] at each investigated temperature at atmospheric pressure. The temperature in the measuring cell was regulated to better than ±0.01 K, using an external bath circulator (Haake, DC3-B3, Karlsruhe, Germany). The accuracy of the density measurements was $\pm2\times10^{-5}\,\mathrm{g \cdot cm^{-3}}$.

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