

Apparent Molar Volume and Apparent Molar Expansibility of Lithium, Sodium, Potassium, and Tetramethylammonium Cyclohexylsulfamate in Aqueous Solution

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Summary. The apparent molar volume of lithium, sodium, potassium, and tetramethylammonium cyclohexylsulfamate was determined from the density data of their aqueous solutions at 293.15, 298.15, 303.15, 313.15, and 323.15 K. The apparent molar expansibility was calculated from the apparent molar volume at various temperatures. The limiting apparent molar volume and apparent molar expansibility were evaluated and divided into their ionic components. The partial molar ionic expansibilities were discussed in terms of the hydration of the ion in solution, as well as in terms of the hydration effects on the solute as a whole. From the partial molar expansibility of the solute at infinite dilution the partial molar expansibility of the hydration shell was deduced. The coefficients of thermal expansion of the investigated solutions at 298.15 K were calculated and are presented graphically. The density of the investigated solutions can be adequately represented by an equation derived by *Root*.

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

Introduction

The volumetric properties of an electrolyte in solution can provide useful information in elucidating the interactions which occur in aqueous solution between ions and the solvent. Of particular importance are the interactions of water with ions possessing non-polar groups because of the peculiar effects of such groups on the structure of water. Hydrophobic interactions of these groups play an important role in the characteristic reactions and on the stability of many biological systems in water. From a theoretical point of view, the most useful quantities are the limiting values of the apparent molar volume and the apparent molar expansibility, since these values depend only on the intrinsic size of the ion and on ion-solvent inter-

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actions. An accurate knowledge of the apparent molar expansibility of an electrolyte at low concentrations is of fundamental interest, *e.g.* in connection with the pressure-dependence of ionic equilibria in solution for many engineering processes. The variation of the apparent molar volume of electrolytes with temperature in aqueous solutions has been employed to study interactions in solution by many authors, *e.g.* Refs. [1–3]. They have shown that the limiting apparent molar volume and the limiting apparent molar expansibility of salts are additive within experimental uncertainties.

Cyclohexylsulfamic acid and its sodium and calcium salts are used as intense sweeteners [4]. According to the most widely accepted and relevant theory in the field of sweet-taste chemoreception, besides the role of the cation, sulfamate functions, and the role of the radical [5], the role of water must be crucial [6]. So, the interactions of sapid solutes with water may influence their accession to, and binding with, receptor sites, thus influencing their taste properties. Therefore it is important to study ion-solvent and solvent-solvent interactions in aqueous solution since water is the medium for all sweet taste chemoreception processes [6].

In order to investigate the nature of the solute-solvent interactions of some cyclohexylsulfamates in aqueous solution, the apparent molar volume as well as the apparent molar expansibility were determined. Namely, experimental studies of the volumetric properties of aqueous solutions of cyclohexylsulfamates are scarce [7–10]. In the literature there are few data on partial molar volumes of their alkali-metal, ammonium, and calcium salts reported at 298.15 K [9, 10].

Results and Discussions

The values of density, d ($\text{g} \cdot \text{cm}^{-3}$), measured at various temperatures as a function of molality, m ($\text{mol} \cdot \text{kg}^{-1}$), are given in Table 1. The apparent molar volume, V_{Φ} ($\text{cm}^3 \cdot \text{mol}^{-1}$), of a solute with molar mass, M_2 ($\text{g} \cdot \text{mol}^{-1}$), was calculated from solution density using Eq. (1) where $v = 1/d$ and $v_0 = 1/d_0$ are the specific volume of the solution and solvent, respectively, and d_0 is the density of pure water.

$$V_{\Phi} = \frac{10^3(v - v_0)}{m} + vM_2 \quad (1)$$

The uncertainty in the apparent molar volume, δV_{Φ} , due to uncertainties in the specific volume, δv , was evaluated from Eq. (2) since V_{Φ} is not seriously influenced by errors in molality [11].

$$(\delta V_{\Phi})^2 = \left[\left(\frac{10^3}{m} \right)^2 + M_2^2 \right] (\delta v)^2 \quad (2)$$

The dependence of V_{Φ} on molality at a definite temperature and for an electrolyte solution can be conventionally given by Eq. (3) [3] where V_{Φ}^0 represents the apparent molar volume of solute at infinite dilution, equal to the limiting partial molar volume of solute, \bar{V}_2^0 ($\text{cm}^3 \cdot \text{mol}^{-1}$), A_v is the *Debye-Hückel* limiting slope, and B_v is an empirical constant which depends on solute, solvent, and temperature.

$$V_{\Phi} = V_{\Phi}^0 + A_v(d_0m)^{1/2} + B_v m + \dots \quad (3)$$

Table 1. Density of aqueous solutions of lithium, sodium, potassium, and tetramethylammonium cyclohexylsulfamates from 293.15 to 323.15 K

$m/\text{mol} \cdot \text{kg}^{-1}$	$d/\text{g} \cdot \text{cm}^{-3}$ at T/K				
	293.15	298.15	303.15	313.15	323.15
LiCy					
0.00471	0.99852	0.99735	0.99594	0.99252	0.98831
0.07033	1.00258	1.00138	0.99992	0.99648	0.99222
0.14330	1.00702	1.00577	1.00420	1.00078	0.99642
0.21655	1.01136	1.01009	1.00845	1.00501	1.00056
0.29140	1.01579	1.01443	1.01290	1.00922	1.00471
0.36860	1.02023	1.01883	1.01723	1.01349	1.00889
0.44500	1.02448	1.02306	1.02143	1.01768	1.01303
0.52486	1.02897	1.02741	1.02571	1.02216	1.01723
0.60530	1.03337	1.03171	1.02996	1.02616	1.02138
0.68876	1.03774	1.03614	1.03434	1.03051	1.02542
NaCy					
0.00522	0.99862	0.99747	0.99607	0.99264	0.98844
0.07395	1.00401	1.00280	1.00135	0.99775	0.99354
0.14228	1.00921	1.00797	1.00645	1.00279	0.99852
0.21750	1.01486	1.01357	1.01199	1.00828	1.00379
0.28983	1.02017	1.01886	1.01714	1.01336	1.00878
0.36589	1.02566	1.02425	1.02258	1.01859	1.01403
0.44312	1.03118	1.02965	1.02781	1.02375	1.01908
0.52370	1.03671	1.03502	1.03332	1.02904	1.02433
0.60299	1.04203	1.04031	1.03852	1.03409	1.02936
0.68941	1.04773	1.04583	1.04407	1.03944	1.03465
KC ₆					
0.00284	0.99834	0.99728	0.99588	0.99246	0.98826
0.00564	0.99860	0.99751	0.99612	0.99269	0.98849
0.02061	0.99984	0.99875	0.99737	0.99391	0.98969
0.03055	1.00069	0.99957	0.99819	0.99471	0.99049
0.04836	1.00219	1.00106	0.99966	0.99610	0.99187
0.06247	1.00335	1.00221	1.00081	0.99729	0.99303
0.10159	1.00657	1.00544	1.00396	1.00042	0.99607
0.13722	1.00950	1.00832	1.00682	1.00325	0.99892
0.16571	1.01178	1.01062	1.00909	1.00539	1.00110
0.19807	1.01436	1.01314	1.01158	1.00786	1.00346
(CH ₃) ₄ N ₄ Cy					
0.00268	0.99831	0.99715	0.99573	0.99230	0.98812
0.02541	0.99920	0.99802	0.99660	0.99313	0.98895
0.04584	0.99998	0.99878	0.99735	0.99387	0.98966
0.06823	1.00084	0.99963	0.99818	0.99468	0.99047
0.09138	1.00172	1.00049	0.99903	0.99550	0.99124
0.11244	1.00253	1.00130	0.99981	0.99625	0.99200
0.13420	1.00334	1.00209	1.00061	0.99700	0.99272
0.15568	1.00416	1.00287	1.00137	0.99774	0.99346
0.17841	1.00499	1.00370	1.00218	0.99853	0.99418
0.20017	1.00585	1.00453	1.00298	0.99930	0.99496

Table 2. The limiting apparent molar volume, V_{Φ}^0 , and parameter B_v (in parenthesis) of lithium, sodium, potassium, and tetramethylammonium cyclohexylsulfamates and the limiting partial molar ionic volume, $\bar{V}_{\text{Cy}^-}^0$, of the cyclohexylsulfamate ion in aqueous solution from 293.15 to 323.15 K

Solute/Ion	V_{Φ}^0 or $\bar{V}_{\text{Cy}^-}^0/\text{cm}^3 \cdot \text{mol}^{-1}$ and B_v (Eq. (3)) at T/K				
	293.15	298.15	303.15	313.15	323.15
LiCy	122.13 ± 0.06 (−0.93 ± 0.11)	122.78 ± 0.06 (−0.77 ± 0.11)	123.58 ± 0.06 (−1.06 ± 0.11)	124.26 ± 0.06 (−1.08 ± 0.11)	125.57 ± 0.06 (−0.88 ± 0.11)
NaCy	121.69 ± 0.06 (0.23 ± 0.11)	122.05 ± 0.06 (1.32 ± 0.11)	123.31 ± 0.06 (0.29 ± 0.11)	124.55 ± 0.06 (1.17 ± 0.11)	126.12 ± 0.06 (0.37 ± 0.11)
KCy	132.38 ± 0.09	133.03 ± 0.14	134.03 ± 0.04	135.58 ± 0.14	136.67 ± 0.21
(CH ₃) ₄ NCy	213.54 ± 0.21 (−6.88 ± 1.30)	214.40 ± 0.21 (−6.32 ± 1.30)	215.34 ± 0.21 (−6.23 ± 1.31)	217.02 ± 0.21 (−5.31 ± 1.32)	218.65 ± 0.22 (−3.51 ± 1.33)
Cy [−]	123.5 ± 0.6	123.9 ± 0.7	124.8 ± 0.6	125.8 ± 0.7	126.8 ± 0.3

By combination of Eqs. (1) and (3) the values of V_{Φ}^0 and parameter B_v were calculated by a weighted least squares procedure for all the systems investigated except for aqueous solutions of potassium cyclohexylsulfamate where a single coefficient V_{Φ}^0 of Eq. (3) was sufficient to represent the density data adequately. The values of coefficient A_v at a particular temperature were taken from Refs. [12, 13]. The calculated values of V_{Φ}^0 are given in Table 2.

Considering the separation of the limiting apparent molar volume of an electrolyte into the individual values for the cation, \bar{V}_{cat}^0 , and anion, \bar{V}_{ani}^0 , the limiting partial molar ionic volume of the cyclohexylsulfamate ion was estimated according to Eq. (4).

$$\bar{V}_{\text{Cy}^-}^0 = \bar{V}_{\Phi}^0 - \bar{V}_{\text{cat}}^0 \quad (4)$$

The limiting partial molar ionic volumes of the corresponding cations at a particular temperature were taken from the compilation of *Millero* [14] as so-called conventional partial molar volumes of ions based on the assumption that $\bar{V}_{\text{H}^+}^0$ is zero. The \bar{V}_{cat}^0 values for temperatures other than 298.15 K were obtained by analytical interpolation to *Millero's* data [14]. The average value of $\bar{V}_{\text{Cy}^-}^0$ calculated for all salts investigated and at a definite temperature are compiled in Table 2.

On differentiation of Eq. (3) with respect to temperature at constant pressure, and taking into account that $(\partial V_{\Phi}/\partial T)_P = \phi_E$, *i.e.* the apparent molar expansibility of solution, Eq. (5) can be obtained.

$$\phi_E = \phi_E^0 + \left(\frac{\partial A_v d_0^{1/2}}{\partial T} \right)_P m^{1/2} + \dots \quad (5)$$

The limiting apparent molar expansibility of solute, ϕ_E^0 , was calculated from the linear dependence of V_{Φ}^0 on temperature, except for the potassium salt, where a polynomial of the second degree was used. The ϕ_E^0 values are given in Table 3. From this table can be seen that the limiting apparent expansibilities of lithium, sodium, potassium, and tetramethylammonium cyclohexylsulfamates increase with increasing ionic radius.

Table 3. Limiting apparent molar expansibility, ϕ_E^0 , hydration number, n_h , and partial molar expansibility of the hydration shell, \bar{E}_h^0 , of lithium, sodium, potassium, and tetramethylammonium cyclohexylsulfamates in aqueous solution at 298.15 K

Solute	ϕ_E^0 $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	n_h	\bar{E}_h^0 $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
LiCy	0.110 ± 0.008	12 ^a	0.014 ± 0.001
NaCy	0.151 ± 0.009	9 ^a	0.021 ± 0.001
KCy	0.174 ± 0.016	4 ^a	0.048 ± 0.004
$(\text{CH}_3)_4\text{NCy}$	0.171 ± 0.002	19 ^b	0.014 ± 0.001

^a Given in Ref. [19]; ^b given in Ref. [20]

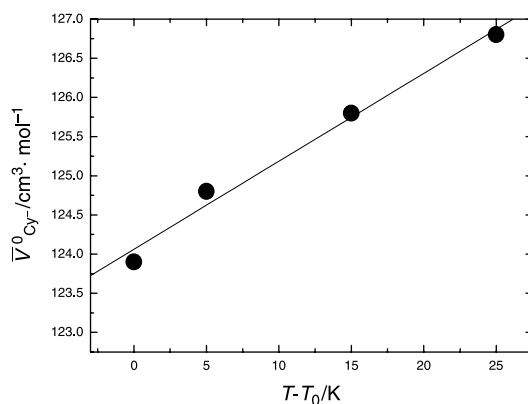


Fig. 1. Dependence of partial molar ionic volume of the cyclohexylsulfamate ion on temperature; $T_0 = 298.15 \text{ K}$

The derivative $(\partial A_v d_0^{1/2} / \partial T)_P$ was obtained from the corresponding data [12, 13] and amounts to $0.0174 \pm 0.0008 \text{ cm}^3 \cdot \text{kg}^{0.5} \cdot \text{mol}^{-1.5} \cdot \text{K}^{-1}$ at 298.15 K.

The limiting partial molar expansibility of the cyclohexylsulfamate ion, \bar{E}_{ion}^0 , was obtained from the linear dependence of $\bar{V}_{\text{Cy}^-}^0$ versus temperature (see Fig. 1). $\bar{E}_{\text{Cy}^-}^0$ amounts to $0.112 \pm 0.006 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. This value permits to calculate the limiting partial molar ionic expansibility of the lithium, sodium, potassium, and tetramethylammonium ions by dividing the ϕ_E^0 value of the salts into their ionic components (Eq. (6)) [2].

$$\phi_E^0 = \bar{E}_+^0 + \bar{E}_-^0 \quad (6)$$

The calculated values of \bar{E}_{ion}^0 are collected in Table 4. These values are within experimental uncertainties equal to those determined by *Millero* [2], except for the potassium and tetramethylammonium ions ($\bar{E}_{\text{ion}}^0 = 0.023 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for potassium and $\bar{E}_{\text{ion}}^0 = 0.033 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for tetramethylammonium ions) where the differences between these values and those of *Millero* are substantial. *Millero* and coworkers [2] examined the values of \bar{E}_{ion}^0 of a large number of ions in water at 298.15 K. For simple monovalent cations and anions they found that \bar{E}_{ion}^0

Table 4. Partial molar ionic expansibility, \bar{E}_{ion}^0 , crystal radius, r , and ratio of Z^2/r of lithium, sodium, potassium, tetramethylammonium, and cyclohexylsulfamate ions in aqueous solution at 298.15 K

Ion	$\frac{\bar{E}_{\text{ion}}^0}{\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}$	$\frac{r}{\text{Å}}$	$\frac{Z^2}{r}$
Li ⁺	−(0.002 ± 0.007)	0.60 ^a	1.67
Na ⁺	0.039 ± 0.009	0.95 ^a	1.05
K ⁺	0.062 ± 0.016	1.33 ^a	0.75
(CH ₃) ₄ N ⁺	0.059 ± 0.002	3.47 ^a	0.29
Cy [−]	0.112 ± 0.006	3.70 ^b	0.27

^a Taken from Ref. [2]; ^b taken from Ref. [9]

varies in size or radius in the inverse order noted by *Fajans* and *Johnson* [15] and that the ion–water interactions are different for cations and anions of similar size.

The partial molar ionic expansibility, \bar{E}_{ion}^0 , can be divided into individual components [2], as shown by Eq. (7) by describing the hydration of an ion in solution by the *Frank* and *Wen* model [16]. According to this model, the intrinsic expansibility, \bar{E}_{int}^0 , which is the volume change due to expansion of the ion, can be neglected for monovalent ions. On the other hand, this term in Eq. (7) is dictated mostly by the expansibility of covalent bonds for ions with hydrocarbon portion, and as a first approximation it can be neglected. The electrostriction expansibility, \bar{E}_{elect}^0 , which is the volume change due to changes in the electrostriction region, is negative and proportional to Z^2/r , where Z is the charge of the ion and r its crystal radius. The disordered expansibility, $\bar{E}_{\text{disord}}^0$, is due to changes in a disordered region. $\bar{E}_{\text{disord}}^0$ appears to be different for cations and anions of the same size owing to the different orientation of water molecules in the first electrostricted region. This term in Eq. (7) depends on the temperature and magnitude of the electrostriction region, *i.e.* on Z^2/r . Thus, for ions with a large electrostricted region (large Z^2/r), the disordered region is very small or even nonexistent. However, for ions with a small electrostriction region (small Z^2/r), this region is very important. So, $\bar{E}_{\text{disord}}^0$ accounts for the large and positive values for monovalent ions at room temperature and for the noticed differences between cation and anion in ϕ_E^0 . The caged expansibility, \bar{E}_{caged}^0 , is due to the changes in highly structured water around the hydrocarbon portion of an ion. This term in Eq. (7) is important for ions that have a hydrocarbon portion and is positive and also increases in magnitude with the size of the hydrocarbon portion of the ion.

$$E_{\text{ion}}^0 = \bar{E}_{\text{int}}^0 + \bar{E}_{\text{elect}}^0 + \bar{E}_{\text{disord}}^0 + \bar{E}_{\text{caged}}^0 \quad (7)$$

The \bar{E}_{ion}^0 values (Table 4) for the investigated ions, except for the lithium ion, are positive. With an assumption that the \bar{E}_{int}^0 term in Eq. (7) is zero, these ions greatly differ in electrostriction expansibility, \bar{E}_{elect}^0 , as can be seen from the ratio Z^2/r given in Table 4.

It was found that for the alkali metal ions \bar{E}_{ion}^0 linearly depends on the ratio of Z^2/r (see Fig. 2). The slope of this line according to *Noyes* [17] is equal to $-0.069 \pm 0.003 \text{ Å} \cdot \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and the intercept is equal to

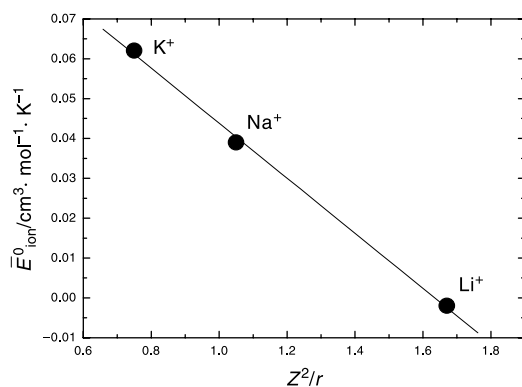


Fig. 2. Partial molar ionic expansibility of some monovalent ions as a function of Z^2/r

$0.113 \pm 0.003 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. The positive intercept indicates that there is a positive contribution to the ϕ_E^0 value of monovalent ions. The slope of the line in Fig. 2 is in the opposite order to the \bar{E}_{ion}^0 values of the divalent cations [2]. Thus the effect of temperature on the hydration of monovalent and divalent cations is different. The relatively large value of Z^2/r of the lithium ion is presumably responsible for the negative value of \bar{E}_{ion}^0 and consequently for the low or even nonexistent \bar{E}_{disord}^0 value. It seems that for other alkali metal ions \bar{E}_{elect}^0 is less important and that \bar{E}_{disord}^0 becomes gradually dominant. This term together with \bar{E}_{caged}^0 accounts for the positive values of \bar{E}_{ion}^0 of the other investigated ions. The \bar{E}_{caged}^0 and \bar{E}_{disord}^0 terms in Eq. (7) are responsible for the large and positive value of \bar{E}_{ion}^0 of the cyclohexylsulfamate ion and have less influence on \bar{E}_{ion}^0 of the tetramethylammonium ion. This term primarily depends on the relative proportions of the hydrophilic and hydrophobic parts of the ion. The \bar{E}_{ion}^0 value for cyclohexylsulfamate ion is higher than for simple monovalent ions [2] since their crystal radius is much higher. The experimental values of \bar{E}_{ion}^0 clearly indicate that solute–solvent interactions are important and dependent upon the structure of water.

To interpret the expansibility data in terms of hydration effects *Chalikian et al.* [18] proposed Eq. (8) in which n_h is the hydration number of the solute, \bar{E}_h^0 and \bar{E}_1^0 are the partial molar expansibilities of the hydration shell of the solute and of pure water.

$$\phi_E^0 = n_h \left(\bar{E}_h^0 - \bar{E}_1^0 \right) \quad (8)$$

In Eq. (8) they assumed that the temperature dependence of the hydration number and that of the intrinsic volume of the solute can be neglected. From the known hydration numbers for the investigated solutes [19, 20] and the partial molar expansibility of water ($\bar{E}_1^0 = 4.65 \times 10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) [21] we calculated the partial molar expansibility of the hydration shell. The values obtained are given in Table 3.

From the collected data it can be seen that \bar{E}_h^0 increases with increasing molecular weight of the alkali metal salts and is considerably low for tetramethylammonium cyclohexylsulfamate. Furthermore, the partial molar expansibility of water in the hydration shell is substantially higher than in the bulk water.

The coefficient of thermal expansion of the solution, α , as a function of concentration was calculated from Eq. (9) [11] where c is the concentration of solute in $\text{mol} \cdot \text{dm}^{-3}$ and α_0 is the coefficient of thermal expansion of pure water.

$$\alpha = \alpha_0 + \left[\frac{\phi_E^0 - \alpha_0 \phi_v^0}{1000} \right] c + \left[\frac{A_E - \alpha_0 A_v}{1000} \right] c^{3/2} \quad (9)$$

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 of definite temperature. Its value for a 1:1 electrolyte and at 298.15 K amounts to $1.723 \times 10^{-5} \text{ cm}^3 \cdot \text{dm}^{1.5} \cdot \text{mol}^{-1.5} \cdot \text{K}^{-1}$. The coefficient of the c term is characteristic for a given solute and amounts to 7.84×10^{-5} , 1.20×10^{-4} , 1.40×10^{-4} , and $1.16 \times 10^{-4} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for lithium, sodium, potassium, and tetramethylammonium cyclohexylsulfamates, respectively, at the same temperature. In calculation of the coefficient of thermal expansion of solution at 298.15 K we used the α_0 value determined by *Kell* [21], and for A_E a value of $0.01771 \pm 0.00008 \text{ cm}^3 \cdot \text{dm}^{1.5} \cdot \text{mol}^{-1.5} \cdot \text{K}^{-1}$ obtained from the data of Refs. [12, 13]. A value of $A_E = 0.017 \text{ cm}^3 \cdot \text{dm}^{1.5} \cdot \text{mol}^{-1.5} \cdot \text{K}^{-1}$ was used by *Perron et al.* [3]. The dependence of the coefficient of thermal expansion on the square root of concentration at 298.15 K for the investigated solutions is shown in Fig. 3.

Similar to Eq. (9), the density of solution as a function of the concentration of solute ($\text{mol} \cdot \text{dm}^{-3}$) and temperature can be given as Eq. (10) [22] where the term in $c^{3/2}$ is common to all strong electrolytes of the same valence type in a given solvent and temperature, while the coefficient of the c term is an additive property of the ions. The values of the coefficient of Eq. (10) are given in Table 5. The common term in $c^{3/2}$ was calculated from the data of Refs. [12, 13, 21], while the term in c was obtained from the data given in Table 2.

$$d = d_0 + \left[\frac{M_2 - d_0 \phi_v^0}{1000} \right] c - \left[\frac{A_v d_0}{1000} \right] c^{3/2} \quad (10)$$

Equation (10) describes the density data satisfactorily. Standard deviation values, s , were obtained from Eq. (11) where d_{exp} and d_{cal} are experimental density data

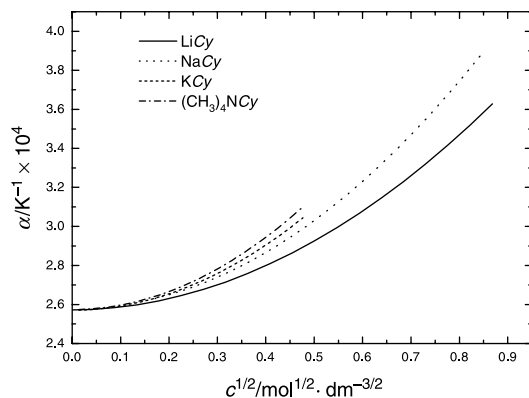


Fig. 3. Coefficient of thermal expansion of aqueous solutions of lithium, sodium, potassium, and tetramethylammonium cyclohexylsulfamate at 298.15 K

Table 5. Values of the coefficient of Eq. (10) for lithium, sodium, potassium, and tetramethylammonium cyclohexylsulfamates in aqueous solution

<i>T</i> /K	$\left[\frac{A_v d_0}{1000}\right] \times 10^3$	$\left[\frac{M_2 - d_0 V_\Phi^0}{1000}\right] \times 10^2$			
		LiCy	NaCy	KCy	(CH ₃) ₄ NCy
293.15	1.78	6.326	7.974	8.518	3.922
298.15	1.86	6.275	7.953	8.469	3.861
303.15	1.95	6.212	7.844	8.388	3.797
313.15	2.12	6.187	7.763	8.280	3.704
323.15	2.31	6.110	7.656	8.229	3.586

(Table 1) or calculated ones (Eq. (10)) and *n* is the number of experimental density data taken at all concentrations and temperatures for a given aqueous salt solution.

$$s = \left[\frac{(d_{\text{exp}} - d_{\text{cal}})^2}{n - 1} \right]^{1/2} \quad (11)$$

The calculated values of *s* amount to 8.9×10^{-5} , 1.0×10^{-4} , 5.4×10^{-5} , and $3.6 \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$ for lithium, sodium, potassium, and tetramethylammonium cyclohexylsulfamates, respectively.

Experimental

Materials

Lithium (LiCy), potassium (KC_y), and tetramethylammonium cyclohexylsulfamate ((CH₃)₄NC_y) were obtained by careful neutralization of cyclohexylsulfamic acid (purchased from Sigma) with the corresponding base (Fluka, or Merck in the case of potassium hydroxide), while sodium cyclohexylsulfamate (NaCy) was purchased from Sigma. The purity of the salts was checked after repeated recrystallizations from water (except that the tetramethylammonium salt was recrystallized from 2-propanol) 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 99.8% at least (tetramethylammonium salt) or better, *e.g.* 99.9% for the lithium (monohydrate), sodium, and potassium salts was determined. The salts were kept in a vacuum desiccator over P₂O₅.

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 $\pm 1 \times 10^{-5} \text{ g}$. 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 $\pm 0.01 \text{ K}$. The apparatus was calibrated with doubly distilled water [21] and dry air [23] at each investigated temperature at atmospheric pressure. The temperature in the measuring cell was regulated to better than $\pm 0.01 \text{ K}$, using an external bath circulator (Haake, DC3-B3, Karlsruhe, Germany). The uncertainty of the density measurements was $\pm 2 \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$.

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