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Sodium Salts of Benzoic, *m*-Salicylic, and *p*-Salicylic Acid: A Conductivity Study of Diluted Aqueous Solutions

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Supporting Information

ABSTRACT: The electric conductivities of aqueous solutions of sodium salts of benzoic acid, *m*-salicylic acid, and *p*-salicylic acid were measured in the temperature range from $T = (278.15 \text{ to } 313.15)$ K and in the concentration range $c = (\approx 2 \cdot 10^{-4} \text{ to } \approx 5 \cdot 10^{-3})$ mol·dm^{-3}. The data were analyzed with Barthel's low-concentration chemical model yielding the limiting molar conductivity, Λ^{∞} (T), and the association constant, $K_A(T)$. Using the known data of the limiting conductivities of sodium ion the limiting conductivities of the anions were evaluated, and their hydrodynamic radii in water were estimated. From $\Lambda^{\infty}(T)$ the Eyring activation enthalpy of charge transport was determined and found to be higher than the corresponding value for viscous flow of water. Practically the total dissociation of the investigated salts in water is evident, and considerable differences in the anion mobilities are observed. They are discussed in terms of diffusivity and permeability of related acids at different carrier systems.

INTRODUCTION

Recently a conductivity study of some nonsteroidal anti-inflammatory drugs (NSAIDs) in water has been carried out,[1] among them also 2-hydroxybenzoic acid sodium salt (salicylic acid sodium salt, IUPAC name sodium salicylate) was investigated. It not only acts as a NSAID but also is used in medicine as an analgetic and antipyretic and induces apoptosis in cancer cells[2−4] and also necrosis.[5] It is also a potential replacement for aspirin for people sensitive to it. In our previous investigation it has been found that sodium salicylate in water acts as a "strong electrolyte"; thus it is completely dissociated, and no explicit hydration of the salicylate anion can be assumed.[1]

However, besides 2-hydroxybenzoic acid (known as salicylic acid), there are two more isomers of hydroxybenzoic acid: 3-hydroxybenzoic acid (*m*-salicylic acid) and 4-hydroxybenzoic acid (*p*-salicylic acid). As it is reported, they differ in solubility,[6−8] diffusivity,[6,7] apparent molar enthalpies of solutions in water, and in pK_a values.[9] Takagi et al.[10] studied the transport of salicylic acid and related compounds across the lipid bilayer. A distinctive difference in the transport of these compounds across the Caco-2 cell monolayer and in the permeability of rat intestinal membrane (in vivo) was observed. The difference in antioxidant activity of these compounds is reported by Simić et al.[11] The effect of salicylates and related compounds on ablastic response in rats infected with *Trypanosoma lewisi* was studied by Becker.[12] He found out that *m*-salicylic acid and *p*-salicylic acid solubilized in 3 % sodium bicarbonate do not produce the antiablastic effect as demonstrated by salicylic acid and its sodium salt.

Almost 100 years ago Jones[13] measured electric conductivity of *m*-salicylic acid, and this seems to be the only report on the conductivity of this compound. No similar study on *p*-salicylic acid and their sodium salts can be found in the literature.

Whereas the transport properties at different temperatures of benzoic acid have already been investigated,[14,15] the data on electric conductivity for its sodium salt only at 298.15 K are reported.[14,16] For this reason it was included in the present study.

In this work, electrical conductivity measurements of aqueous solutions of sodium salts of benzoic (NaBen), *m*-salicylic (NaSal-m), and *p*-salicylic acid (NaSal-p) at temperatures $T = (278.15 \text{ to } 313.15)$ K in the concentration range $c = (\approx 2 \cdot 10^{-4} \text{ to } \approx 5 \cdot 10^{-3})$ mol·dm^{-3} were carried out. Data analysis is done in the framework of the low concentration chemical model (lcCM) of Barthel et al.,[17] giving the information on the ion association and mobility of ions in aqueous solutions. A comparison to the reported data on sodium salicylate (NaSal) and benzoate anion (Ben$^-$) is made.

EXPERIMENTAL SECTION

Materials. Benzoic acid sodium salt (sodium benzoate, NaBen, p.a. Fluka, Germany ≥ 99.0 %, MW = 144.10 g·mol^{-1}), *m*-salicylic acid sodium salt (sodium *m*-salicylate, NaSal-m, TCI, Belgium, > 99.0 %, MW = 160.10 g·mol^{-1}), and *p*-salicylic acid sodium salt (sodium *p*-salicylate, NaSal-p, Fluka, Germany, > 99.0 %, MW = 160.10 g·mol^{-1}) were dried for 24 h at $T \approx 400$ K with a vacuum line ($p < 0.01$ Pa) and stored in a desiccator over P_2O_5 before use.

Stock solutions were prepared by mass from the pure compounds and demineralized distilled water. Demineralized water was distilled two times in a quartz bidestillation apparatus (Destamat Bi 18E, Heraeus). The final product with specific conductivity $<6 \cdot 10^{-7}$ S·cm^{-1} was distilled into a flask permitting storage under an atmosphere of nitrogen permitting storage and transfer of water into the measuring cell under an atmosphere of nitrogen.

Conductivity Measurement. The conductivities of the solutions were determined with the help of a three-electrode measuring cell, described elsewhere.[18] The cell was calibrated with dilute potassium chloride solutions[19] and immersed in the high precision thermostat described previously.[20] The temperature dependence

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Table 1. Densities, d, of Stock and Final Solutions in the Conductivity Cell of the Investigated Systems at 298.15 K

m	d
$\mathrm{mol \cdot kg^{-1}}$	$\mathrm{kg \cdot dm^{-3}}$
NaBen	
0	0.997048[22]
0.004950	0.99726
0.084663	1.00194
NaSal-m	
0	0.997048[22]
0.005007	0.99741
0.092015	1.00359
NaSal-p	
0	0.997048[22]
0.005464	0.99744
0.098716	1.00411

of the cell constant was taken into account.[19] The water bath can be set to each temperature using a temperature program with a reproducibility of 0.005 K. The temperature in the precision thermostat bath was additionally checked with calibrated Pt100 resistance thermometer (MPMI 1004/300 Merz) in connection with a Multimeter HP 3458 A. The resistance measurements of the solutions in the cell were performed using a precision LCR Meter Agilent 4284 A.

At the beginning of every measuring cycle, the cell was filled with a known mass of water (~660 g). After measurements of water conductivity at all temperatures of the temperature program, the stepwise concentration was carried out by successive additions of known masses of stock solution with a gastight syringe. After every addition, the temperature program was run by the computer, and all measured data (frequency dependent resistance, temperature) were stored and partially shown on display to track the measuring process. A home-developed software package was used for temperature control and acquisition of conductivity data. The measuring procedure, including corrections and extrapolation of the sample conductivity, κ, to infinite frequency, has been previously described.[20]

The densities, d, of the stock solutions and the final solutions in the conductivity cell, collected in Table 1, were determined by the method of Kratky et al.[21] using a Paar densimeter (DMA 60, DMA 601 HT) at 298.15 ± 0.01 K combined with a precision thermostat. A linear change of d with increasing salt content for diluted solutions was assumed, $d = d_0 + b \cdot m$, where d_0 is the density of water, listed in Table 2 together with other known properties.[22−25] From these data the density gradients b for all examined electrolytes were determined. As usually they are considered to be independent of temperature and are quoted in Table 3 together with molar conductivities, $\Lambda = \kappa/c$, of all investigated systems. Molar conductivities are given as a function of electrolyte molality, m, which relates to the corresponding (temperature-dependent) molar concentration, c, via $c = m \cdot d/(1{+}M_2 \cdot m)$, where M_2 is the molar mass of the solute and d is the density of solution. The estimated uncertainty of d is within 0.05 $\mathrm{kg \cdot m^{-3}}$. Considering the sources of error (calibration, measurements, impurities), the specific conductivities are estimated to be accurate within 0.3 %.

Table 2. Densities, d_0, Viscosities, η, Relative Permittivity, ε, of Pure Water, and Limiting Ionic Conductivity of Sodium Ion, $\lambda^0(\mathrm{Na^+})$, in Water at Temperatures from T = (278.15 to 313.15) K

T	d_0[22]	$10^3 \cdot \eta$[23]		$\lambda^0(\mathrm{Na^+})$[25]
K	$\mathrm{kg \cdot dm^{-3}}$	$\mathrm{Pa \cdot s}$	ε[24]	$\mathrm{S \cdot cm^2 \cdot mol^{-1}}$
278.15	0.999967	1.5192	85.897	30.30
283.15	0.999702	1.3069	83.945	34.88
288.15	0.999102	1.1382	82.039	39.72
293.15	0.998206	1.0020	80.176	44.81
298.15	0.997048	0.8903	78.358	50.15
303.15	0.995651	0.7975	76.581	55.72
308.15	0.994036	0.7195	74.846	61.53
313.15	0.992219	0.6531	73.151	67.55

DATA ANALYSIS

The present molar conductivities, $\Lambda(c)$ (Table 3, Figures 1 and 2) were analyzed in the framework of the low concentration chemical model (lcCM) of Barthel.[17] This approach uses the set of equations

$$\frac{\Lambda}{\alpha} = \Lambda^{\infty} - S\sqrt{\alpha c} + E\alpha c \ln(\alpha c) + J_1 \alpha c - J_2 (\alpha c)^{3/2} \tag{1}$$

$$K_{\mathrm{A}} = \frac{1-\alpha}{c\alpha^2 (y'_{\pm})^2}; \qquad y'_{\pm} = \exp\left(-\frac{\kappa q}{1+\kappa R}\right)$$

$$\kappa^2 = 16\pi N_{\mathrm{A}} q \alpha c; \qquad q = \frac{e_{\mathrm{o}}{}^2}{8\pi\varepsilon\varepsilon_{\mathrm{o}} kT} \tag{2a − d}$$

$$K_{\mathrm{A}} = 4\pi N_{\mathrm{A}} \int_a^R r^2 \exp\left[\frac{2q}{r} - \frac{W^*}{kT}\right] \mathrm{d}r \tag{3}$$

where Λ and Λ^{∞} are the molar conductivities at molarity c and in the infinite dilution, respectively, $(1 - \alpha)$ is the fraction of oppositely charged ions acting as ion pairs, and K_{A} is the equilibrium constant of the lcCM with upper association limit R; $y'_{\pm}$ is the corresponding activity coefficient of the free ions, $(y'_{\pm})^2 = y'_{+}y'_{-}$, κ is the Debye parameter, e is the proton charge, ε is the relative permittivity of the solvent, ε_{o} is the permittivity of vacuum and T the absolute temperature. The other symbols have their usual meaning. W^* is a step function for the potential of mean force between cation and anion due to non-Coulombic interactions.

The coefficients of eq 1 from ref 17 are given in the Supporting Information. The limiting slope S and the parameter E are calculable when the solvent data are available (Table 2). The coefficients J_1 and J_2 are functions of the distance parameter R, representing the distance to which oppositely charged ions can approach as freely moving particles in solution.

Analyses of the conductivity data of associated electrolytes are carried out by setting the coefficients S, E, and J_1 of eq 1 to their calculated values[17] and then usually using three-parameter fits to obtain the limiting values of molar conductivity Λ^{∞}, the association K_{A}, and the coefficient J_2 by nonlinear least-squares iterations. A three-parameter evaluation is reduced to a two-parameter procedure for very weak associating electrolytes,[17]

Table 3. Experimental Molar Conductivities, Λ, as a Function of Molality, *m*, of Investigated Systems, and Density Gradient, *b*, in Water

$10^3 \cdot m$	T/K							
$\text{mol} \cdot \text{kg}^{-1}$	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
$\Lambda/\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$								
NaBen, $b = 0.0581\ \text{kg}^2 \cdot \text{dm}^{-3} \cdot \text{mol}^{-1}$								
0.21356	48.277	55.838	63.843	72.326	81.199	90.431	100.015	109.830
0.46495	47.903	55.415	63.387	71.822	80.634	89.820	99.365	109.120
0.73344	47.650	55.139	63.078	71.494	80.269	89.399	98.811	108.521
0.9986	47.458	54.933	62.830	71.215	79.860	88.913	98.295	108.022
1.2993	47.298	54.737	62.534	70.887	79.579	88.600	98.015	107.804
1.5998	47.076	54.476	62.345	70.641	79.333	88.369	97.705	107.313
1.9961	46.903	54.275	62.111	70.368	79.014	88.007	97.328	107.068
2.4877	46.711	54.068	61.903	70.103	78.718	87.696	96.628	106.301
3.1073	46.489	53.802	61.641	69.781	78.112	87.059	96.249	105.913
3.8322	46.344	53.620	61.285	69.454	77.960	86.834	95.975	105.454
4.9503	46.036	53.199	60.844	68.955	77.422	86.228	95.390	104.828
NaSal-m, $b = 0.0711\ \text{kg}^2 \cdot \text{dm}^{-3} \cdot \text{mol}^{-1}$								
0.17887	47.016	54.357	62.128	70.352	78.909	87.810	97.022	106.474
0.41587	46.591	53.863	61.587	69.747	78.245	87.088	96.253	105.588
0.71151	46.319	53.536	61.186	69.278	77.728	86.526	95.622	104.891
1.0032	46.108	53.295	60.909	68.964	77.309	86.063	95.114	104.353
1.3218	45.911	53.062	60.600	68.616	76.983	85.695	94.704	103.959
1.6979	45.662	52.770	60.323	68.304	76.645	85.345	94.323	103.593
2.0881	45.472	52.563	60.079	68.028	76.319	84.980	93.951	103.114
2.6459	45.260	52.315	59.814	67.724	75.986	84.575	93.274	102.445
3.2880	45.045	52.062	59.505	67.375	75.416	83.986	92.860	101.965
4.1127	44.828	51.781	59.051	66.876	75.040	83.564	92.400	101.518
5.0073	44.573	51.401	58.731	66.503	74.618	83.074	91.838	100.868
NaSal-p, $b = 0.0716\ \text{kg}^2 \cdot \text{dm}^{-3} \cdot \text{mol}^{-1}$								
0.87665	44.627	51.594	58.990	66.794	74.949	83.451	92.128	101.150
1.20508	44.513	51.454	58.803	66.484	74.615	83.077	91.844	100.799
1.57164	44.361	51.219	58.546	66.288	74.388	82.833	91.577	100.485
1.9758	44.159	51.054	58.350	66.080	74.144	82.576	91.363	100.259
2.4535	44.014	50.872	58.149	65.838	73.875	82.248	90.917	99.638
3.0097	43.824	50.651	57.897	65.555	73.557	81.783	90.442	99.329
3.6956	43.638	50.436	57.652	65.177	73.143	81.460	90.090	98.922
4.5385	43.450	50.217	57.338	64.929	72.853	81.121	89.687	98.439
5.4643	43.322	49.928	57.066	64.617	72.510	80.729	89.265	97.984

where usually coefficient J_2 is also fixed. The input data for the calculation of the coefficients are the known solvent properties (Table 2) and the distance parameter R. The lower limit a of the association integral is the distance of closest approach of cation and anion (contact distance), $a = a_+ + a_-$.

Organic anions, such as carboxylates, sulfonates, and so forth, bear their negative charge of an oxygen atom on the surface of the ionic molecule. The "radius" of such ions may be taken to be the effective van der Waals radius of the carboxylate or sulfonate group.[17] Thus, we used the value $a_- = 0.162$ nm which was estimated for formic acid[17] assuming that the radicals in the anions of the investigated drugs do not change the interionic distance between the cation and the basic oxygen atom in their structure. The same assumption was applied also in our previous work with NaSal.[1] For Na^+ the value of $a_+ = 0.098$ nm[17] was used.

From extended investigations of electrolyte solutions in amphiprotic hydroxylic solvents (water, alcohols) it is known that the upper limit of association is given by an expression of the type $R = a + n \cdot s$, where s is the length of an oriented solvent molecule, n is an integer, $n = 0, 1, 2$, etc. Here, s is the length of an OH-group, d_{OH} and $s = d_{OH} = 0.28$ nm. In this study we fixed the distance parameter R at $R = 0.820$ nm, allowing thus three types of ion pairs in the solutions: contact ion pairs, solvent-shared, and solvent-separated ion pairs.

RESULTS AND DISCUSSION

Figure 1 shows the experimental data for molar conductivities, Λ, of the NaBen aqueous solutions given in Table 3 and the results of the lcCM calculations executed using eqs 1 to 3 at

298.15 K. For comparison, literature data at 298.15 K[14,16] are presented. Evidently, the data from Saxton and Meier[14] fit excellently to our experiment, whereas the values reported by Niazi and Khan[16] are shifted slightly to higher values. In the inset of Figure 1 the agreement between experimental conductivity data and fits for NaBen in the whole temperature range is presented. NaSal-m and NaSal-p show similar dependences.

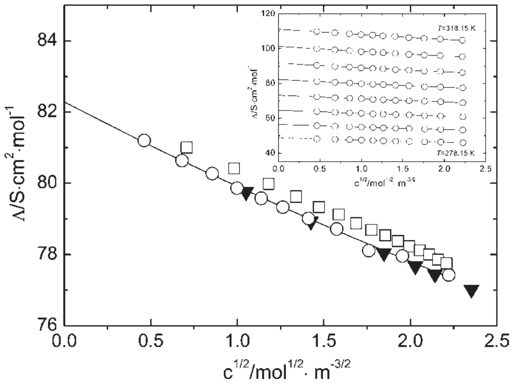

Figure 1. Molar conductivities, Λ, of aqueous NaBen solutions at T = 298.15 K; ○, this study, □, ref 16; ▼, ref 14. The full line represents the result from lcCM calculations using eqs 1 to 3. Inset: Λ of the same system from T = (278.15 to 318.15) K in steps of 5 K.

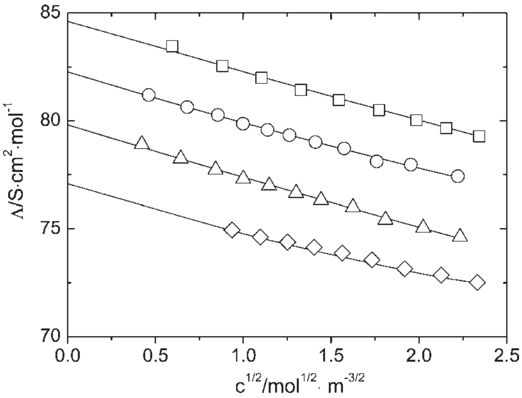

Figure 2. Molar conductivities of ○, NaBen; △, NaSal-m; and ◇, NaSal-p in water at 298.15 K. For comparison the data for □, NaSal from ref 1 are also shown. Full lines present the results from lcCM calculation, eqs 1 to 3.

In Figure 2 the conductivity data for NaBen, NaSal-m, and NaSal-p at 298.15 K are presented together with the literature data for NaSal[1] For NaSal-p solutions the experiment was performed in the same concentration range as for other salts, but for unknown reasons the experimental data can only be satisfactorily fitted over a narrow range of concentration.

Table 4 gives a comparison of the calculated lcCM data for all investigated salts. The limiting conductivities are dependent on the structure of the anions, as can be expected. The values of the association constants are very low, and all of the investigated salts could be regarded as completely dissociated in water solutions ("strong electrolytes"). The values of K_A for NaCl aqueous solutions obtained from precise conductance measurements by using the lcCM are in the range $0.6 < K_A/\text{mol}^{-1}\cdot\text{dm}^3 < 2.6$ in the temperature range T = (278.15 to 303.15 K).[26] Whereas the temperature coefficient dK_A/dT is usually positive for the alkali salt water solutions, no reliable evidence for the temperature dependence of the association process of aqueous solutions of the discussed drugs was found. The literature data for NaBen at 298.15 K[14,16] were re-evaluated by lcCM, and the obtained results are in good agreement with ours.

Combining the limiting conductivities Λ^∞ of Table 4 and the known limiting values of Na⁺, $\lambda^\infty(\text{Na}^+)$, given in Table 2

$$\lambda^\infty(T, \text{A}^-) = \Lambda^\infty(T, \text{NaA}) - \lambda^\infty(T, \text{Na}^+) \qquad (4)$$

yields the limiting anion conductivities $\lambda^\infty(\text{A}^-)$ and their temperature dependence; see Table 5.

For comparison $\lambda^\infty(\text{Ben}^-)$ as obtained from the literature data on $\Lambda^\infty(T)$ for benzoic acid in water[15] and $\lambda^\infty\,(T, \text{H}^+)$[25] are presented also. These data are in good agreement with λ^∞-(Ben⁻) obtained in this work, as well as with other literature data.[14−16]

From the Walden rule[17]

$$\lambda^\infty(T)\eta(T) = \frac{Fe|z|}{6\pi a_i^{(\eta)}} \qquad (5)$$

the solvent dependent ionic radii $a_i^{(\eta)}$ were estimated (F is the Faraday constant and z the ionic charge). In water, $a_i^{(\eta)}$ are usually called hydrodynamic radii, r_h. Values for the hydrodynamic radii of the anions of investigated salts are collected in

Table 4. Limiting Molar Conductivities, Λ^∞, and Association Constants, K_A, of the Investigated Salts in Water

T	Λ^∞	K_A	Λ^∞	K_A	Λ^∞	K_A	Λ^∞	K_A
/K	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$\text{mol}^{-1}\cdot\text{dm}^3$	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$\text{mol}^{-1}\cdot\text{dm}^3$	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$\text{mol}^{-1}\cdot\text{dm}^3$	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$\text{mol}^{-1}\cdot\text{dm}^3$
	NaBen		NaSal[c]		NaSal-m		NaSal-p	
278.15	48.84 ± 0.03	1.4 ± 0.3	50.44 ± 0.02	1.720 ± 0.09	47.51 ± 0.03	2.1 ± 0.3	45.87 ± 0.05	0.1 ± 0.4
283.15	56.53 ± 0.02	1.5 ± 0.2	58.30 ± 0.02	1.738 ± 0.08	54.94 ± 0.03	2.5 ± 0.2	53.06 ± 0.02	0.1 ± 0.2
288.15	64.66 ± 0.02	1.3 ± 0.2	66.63 ± 0.02	1.726 ± 0.08	62.82 ± 0.03	2.7 ± 0.2	60.67 ± 0.02	0.1 ± 0.2
293.15	73.28 ± 0.02	1.3 ± 0.1	75.42 ± 0.02	1.757 ± 0.08	71.14 ± 0.03	2.6 ± 0.2	68.68 ± 0.04	0.1 ± 0.2
298.15	82.27 ± 0.04	1.4 ± 0.2	84.61 ± 0.02	1.779 ± 0.08	79.81 ± 0.04	2.6 ± 0.2	77.08 ± 0.04	0.1 ± 0.2
	82.21 ± 0.01[a]	1.43 ± 0.03[a]						
	82.74 ± 0.02[b]	1.6 ± 0.1[b]						
303.15	91.63 ± 0.04	1.3 ± 0.2	94.22 ± 0.02	1.796 ± 0.08	88.84 ± 0.03	2.4 ± 0.2	85.83 ± 0.05	0.1 ± 0.2
308.15	101.32 ± 0.06	1.4 ± 0.3	104.19 ± 0.02	1.795 ± 0.07	98.17 ± 0.04	2.3 ± 0.2	94.86 ± 0.11	0.1 ± 0.4
313.15	111.21 ± 0.05	1.6 ± 0.2	114.32 ± 0.03	2.205 ± 0.08	107.61 ± 0.06	2.5 ± 0.3	103.97 ± 0.06	0.1 ± 0.2

[a] Re-evaluated data from ref 14 by lcCM. [b] Re-evaluated data from ref 16 by lcCM . [c] Data reported in ref 1.

Table 5. Limiting Conductance, λ^∞, of Anions of Investigated Salts In Water as a Function of Temperature. Literature Values for Salicylate Anion Are Included

T/K	λ^∞ (Ben$^-$)	λ^∞ (Sal$^-$)^a	λ^∞ (Sal-m$^-$)	λ^∞ (Sal-p$^-$)
278.15	18.54 18.88^b	20.14	17.20	15.57
283.15	21.65 21.84^b	23.42	20.06	18.18
288.15	24.94 25.34^b	26.91	23.10	20.95
293.15	28.47 28.89^b	30.61	26.33	23.87
298.15	32.12 31.87^b 32.06^c 32.59^d	34.46	29.66	26.93
303.15	35.91 35.91^b	38.50	33.12	30.11
308.15	39.79 40.69^b	42.66	36.64	33.33
313.15	43.66 45.00^b	46.77	40.06	36.42

[a] Reference 1. [b] Values are obtained from $\Lambda^\infty(T)$, reported for benzoic acid in ref 15. [c] Reference 14. [d] Reference 16.

Table 6. Hydrodynamic Radii, r_h, of the Investigated Salts in Water from Walden Rule as a Function of Temperature

	r_h/nm				
T/K	Na$^+$	Ben$^-$	Sal^{-a}	Sal-m$^-$	Sal-p$^-$
278.15	0.178	0.291	0.268	0.313	0.346
283.15	0.180	0.289	0.267	0.312	0.345
288.15	0.181	0.288	0.267	0.311	0.343
293.15	0.182	0.287	0.267	0.310	0.342
298.15	0.183	0.286	0.267	0.310	0.342
303.15	0.184	0.286	0.267	0.310	0.341
308.15	0.185	0.286	0.267	0.311	0.341
313.15	0.186	0.287	0.268	0.313	0.344

[a] Reference 1.

Table 6. It is well-known that a comparison of the values of the hydrodynamic radii and the crystal radii of cations show large differences for Na$^+$ ions. It is relatively small and has, therefore, an exceptionally high charge to radius ratio (charge density) and tends to orient the water molecules in its vicinity. Contrarily, its hydrated radius is much larger than similar ions, and the large solvation shell around the ion also causes its low mobility and low limiting conductivities, λ^∞, in solution. For the sodium ion the hydration number, h, obtained from transport process measurements, is reported in the literature as h (Na$^+$, 298.15 K) = 5.[17]

The obtained hydrodynamic radii, r_h, for the studied anions are ranked in order Sal$^-$ < Ben$^-$ < Sal-m$^-$ < Sal-p$^-$ (Table 6). The van der Waals radius, r_{vdw}, of the benzoate anion, calculated from the optimized geometries using the Winmostar program,[27] is rather close to the estimated hydrodynamic radius r_{vdw}(Ben$^-$) = 0.296 nm, whereas r_{vdw} for all salicylate isomers are the same, r_{vdw}(Sal$^-$) = 0.303 nm.

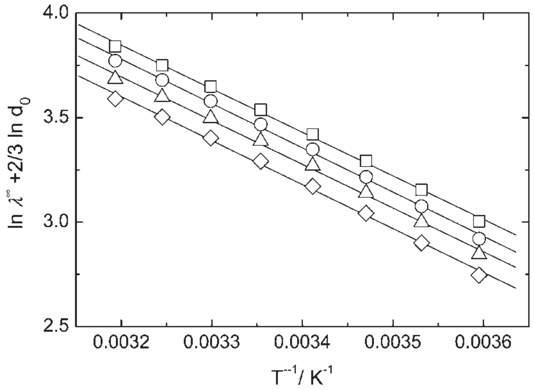

Figure 3. Plot of ln λ^∞ + (2/3)ln d_0 as a function of 1/T for ○, Ben$^-$; △, Sal-m$^-$; ◇, Sal-p$^-$; and □, Sal$^-$ (ref 1) in water. From the slope the Eyring enthalpy of activation of charge transport, $\Delta H_\lambda^{\neq}$, is obtained.

It should be noted that Walden's rule treats ion migration as the movement of a rigid sphere through a viscous continuum, and also the van der Waals radii were calculated by assuming spherical shapes. Therefore, values listed in Table 6 can be discussed only as the rough estimation of real dimensions of the investigated anions in water. Obviously, values of r_h and r_{vdw} for Sal-m$^-$ and Ben$^-$ are close together. It appears that no explicit hydration of these anions can be assumed. A larger difference between r_h and r_{vdw} for Sal-p$^-$ may lead to the assumption that here the hydration is more pronounced. It can be assumed that among the investigated anions Sal$^-$ possesses the weakest hydration shell resulting in the highest mobility. From Table 6 it is evident that r_h of studied anions are almost temperature-insensitive. This again may lead to the conclusion that hydration—which is more pronounced at lower temperatures—is not very expressed.

Despite the fact that the properties of acids often are not quite comparable to the properties of their salts, there are some data in the literature which can support the observed difference in the behavior of investigated anions. Apparent molar enthalpies of solutions follow the sequence salicylic < benzoic < m-salicylic < p-salicylic acid, whereas their enthalpies of fusion are ranked in a different order (benzoic < salicylic < p-salicylic < m-salicylic acid).[8] This observation indicates that these acids (and their anions thus) interact with water in a different way. Some distinctive differences were observed in the diffusivity and permeability studies. In the transport across the Caco-2 cell monolayer salicylic acid is the fastest, followed by benzoic, p-salicylic, and m-salicylic acid.[10] Different order was obtained in the investigation of the permeability of rat intestinal membrane in vivo, where the ability for transport is ordered in benzoic > salicylic > m-salicylic > p-salicylic acid.[10] In the study of phloem mobility of these acids, m-salicylic and p-salicylic acid show similar rather poor mobility, whereas the distinctive difference between salicylic and benzoic acid was observed in favor of the first.[28] All of these results indicate that the mobility of investigated acids exhibits high specificity with regard to the relative position of the carboxyl and hydroxyl groups.

Eyring's approach to the temperature dependence of the limiting conductivities leads to the relationship[29,30]

$$\left(\frac{\partial \ln[\lambda^\infty(T)d_0^{2/3}(T)]}{\partial T}\right)_p = \frac{\Delta H_\lambda^{\neq}}{RT^2} \qquad (6)$$

where $\Delta H_\lambda^{\neq}$ is the partial molar enthalpy associated with the ion movement (Eyring enthalpy of activation of charge transport).

When $\Delta H_{\lambda}^{\neq}$ is independent of temperature, the integral form of eq 6 is

$$\ln \lambda^{\infty} + \frac{2}{3}\ln d_0 = -\frac{\Delta H_{\lambda}^{\neq}}{RT} + B \qquad (7)$$

where B is the integration constant.

For $\Delta H_{\lambda}^{\neq}$ values of (17.6 ± 0.3, 17.4 ± 0.4 and 17.5 ± 0.4) $\text{kJ}\cdot\text{mol}^{-1}$ for Ben^-, Sal-m^-, and Sal-p^-, respectively, were obtained (Figure 3). Thus, all values are—in the range of the experiential error—practically identical. The reported molar ionic enthalpy of activation for Sal^- is 17.4 $\text{kJ}\cdot\text{mol}^{-1}$ and for Na^+ 16.5 $\text{kJ}\cdot\text{mol}^{-1}$.[1] All values are distinctly higher than the corresponding Eyring activation enthalpy for viscous flow for pure water, $\Delta H_{\eta}^{\neq} = 14.97 \pm 0.30\ \text{kJ}\cdot\text{mol}^{-1}$. This indicates that charge transport in these solutions requires ion desolvation and rearrangement of water molecules in the vicinity of the ion to some extent.

CONCLUSION

Molar conductivities, Λ, for dilute solutions of sodium salts of benzoic (NaBen), *m*-salicylic (NaSal-m), and *p*-salicylic acid (NaSal-p) in water were determined as a function of temperature. The experimental data were analyzed with Barthel's low chemical model yielding the association constant, K_A, and limiting values of molar conductivity, Λ^{∞}. As expected, the obtained K_A values show that ion association for these salts in water is negligible.

From known limiting ionic conductivity for sodium ion at all investigated temperatures, the limiting ionic conductivities of Ben^-, Sal-m^-, and Sal-p^- anions were determined. From the Walden rule the hydrodynamic radii of the anions were estimated and compared to the literature values of salicylate anion (Sal^-). They are ranked in the order $\text{Sal}^- < \text{Ben}^- <$ Sal-$\text{m}^- <$ Sal-p^-. Sal^- shows the highest mobility in water, and the same was found also for the transport of salicylic acid across the CaCo-2 cell monolayer[10] and in the phloem mobility study.[28]

From the derived limiting conductivities, $\Lambda^{\infty}(T)$, the Eyring enthalpy of activation of charge transport, $\Delta H_{\lambda}^{\neq}$, was determined. It was found that this quantity is similar for all investigated systems and is somewhat larger than Eyring's activation enthalpy of viscous flow, $\Delta H_{\eta}^{\neq}$, for water. This indicates that charge transport in these solutions requires ion desolvation and rearrangement of water molecules in the vicinity of the ion to some extent.

However, the mobility of investigated anions is strongly dependent on the relative position of the carboxyl and hydroxyl groups which obviously influences also the possible hydration of anions and observed differences in permeability and transport studies. In this context the present investigation can contribute to the enlightening of the mechanisms of monocarboxylic acid transport.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Coefficients of eq 1 from ref 17. This material is available free of charge via the Internet at http://pubs.acs.org.

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