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Hydrophobic hydration of the propionate ion

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The complex dielectric permittivity of aqueous potassium propionate, caesium propionate and caesium formate solutions was studied, and a conclusion on the the hydrophobic hydration of the propionate ion was drawn.

The hydrophobic hydration is connected with the stabilization of an H-bond net near non-polar groups of molecules or ions and with the ordering of the tetrahedral water structure.[1–5] Microwave dielectric spectroscopy is an informative method for studying hydrophobic hydration in both nonelectrolyte and electrolyte solutions. It gives information about changes in the molecular-kinetic mobility of water molecules under the influence of various dissolved ions. The hydrophobic hydration in tetraalkylammonium salt solutions was determined using this method.[2–4] While the hydrophobic hydration of cations was found,[1,5] the hydrophobic hydration of anions remains an open question. We studied the hydrophobic hydration of anions using the solutions of alkali metal propionates as an example.

The microwave dielectric permittivity ε' and losses ε'' in aqueous potassium and caesium propionate solutions were studied in concentration ranges of 0.52–6.65 and 0.52–8.58 m (mol per kg of water) at 288, 298 and 308 K and frequencies of 10.25, 12.17, 13, 16, 19.2, 22, 23.54 and 25 GHz. The values of ε' and ε'' in aqueous caesium formate solutions were measured at frequencies of 10.22, 16 and 23.5 GHz, concentrations of 1.67–4.69 m and temperatures of 283, 298 and 313 K. Thus, published dielectric data[6] were refined. The complex dielectric permittivity of aqueous solutions in the microwave range was measured by the thin dielectric rod in the wave-guide method.[7,8] The accuracy was 1.5–2% for ε' and 2–2.5% for ε''. The solutions were prepared from pure EtCOOK and EtCOOCs salts and distilled water. Caesium formate was obtained from caesium carbonate and 99% formic acid of chemically pure grade. The caesium concentration in solution was determined using sodium tetraphenilborate.[9] The specific conductivity (κ) of EtCOOK and EtCOOCs solutions was measured at a frequency of 1 kHz. The conductivities of HCOOCs solutions were taken from ref. 10.

The complex dielectric permittivity is[11]

$$\varepsilon^* = \varepsilon' - \mathrm{i}\varepsilon'', \tag{1}$$

where ε' is the high-frequency dielectric permittivity and ε'' denotes dielectric losses. Dipole losses were calculated by the equation $\varepsilon''_d = \varepsilon'' - \varepsilon''_i$, where ionic losses are $\varepsilon''_i = \kappa/\varepsilon_0\omega$,[11] ω is the circular frequency, ε_0 is the dielectric permittivity of vacuum.

The potassium and caesium ions weakly interact with water molecules and anions in aqueous solutions. Therefore, the ionic association was insignificant in the test solutions. No strong H-bonds were formed between water molecules and the polar groups of propionate anions. Therefore, the spectral contribution related to the associated forms of ions and molecules should be insignificant. They would be manifested at lower frequencies. Hence, the contributions that correspond to these processes are small or absent in the test frequency range. This allowed us to use the chosen range for studying changes in the molecular-kinetic state of water H-bonds in these systems.

The relaxation of water molecules in the test solutions is described by the Cole–Cole equation

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \mathrm{i}\tau\omega^{1-\alpha}}, \tag{2}$$

where ε_s is the low-frequency limit of the dispersion region (static dielectric constant), τ is the dielectric relaxation time, α is the parameter of relaxation time distribution, ε_∞ is the high-frequency limit for considered dispersion region. For water and aqueous solutions, $\varepsilon_\infty \approx 5$.[3,12,13] Static dielectric constant was determined from the Cole–Cole diagrams by extrapolation to zero frequency. The Cole–Cole diagrams of EtCOOCs solutions are shown in Figure 1. The dielectric relaxation time was found graphically using the function $f = [(\varepsilon_s - \varepsilon')^2 + (\varepsilon''_d)^2]/\ [(\varepsilon' - \varepsilon_\infty)^2 + (\varepsilon''_d)^2]$. The accuracy of τ is 5–7%. The functions $\ln\tau = f(1/T)$ are linear for the EtCOOK, EtCOOCs and HCOOCs solutions at the test temperatures. The theory of absolute speeds of reactions was used for calculating the enthalpy $\Delta H_\varepsilon^{++}$, free energy $\Delta G_\varepsilon^{++}$ and entropy $\Delta S_\varepsilon^{++}$. The calculated values of ε_s, τ, α, $\Delta H_\varepsilon^{++}$, $\Delta G_\varepsilon^{++}$ and $T\Delta S_\varepsilon^{++}$ are given in Tables 1 and 2.

Table 1 Dielectric properties of aqueous EtCOOK and EtCOOCs solutions.

mol per kg H_2O	288 K			298 K			308 K			$\Delta H_\varepsilon^{++}$/ kJ mol^{-1}	$\Delta G_\varepsilon^{++}$/ kJ mol^{-1}	$T\Delta S_\varepsilon^{++}$/ kJ mol^{-1}
	ε_s	τ/ps	α	ε_s	τ/ps	α	ε_s	τ/ps	α			
EtCOOK												
0	82.1	11.0	0.00	78.4	8.25	0.00	74.9	6.25	0.00	17.8	9.7	8.1
0.52	75.5	11.6	0.02	73.3	8.8	0.03	69.9	6.8	0.03	17.2	9.9	8.3
1.07	70.5	12.7	0.04	68.0	9.4	0.04	64.8	7.2	0.03	18.4	10.0	9.4
2.33	60.8	14.7	0.07	58.0	10.4	0.06	57.6	8.1	0.07	19.8	10.3	9.5
3.82	56.2	19.0	0.15	52.5	12.6	0.10	52.5	9.4	0.15	23.4	10.8	12.6
5.56	50.1	21.4	0.20	44.9	14.6	0.14	46.9	10.4	0.18	24.2	11.1	13.1
6.65	45.2	22.0	0.19	43.1	13.9	0.13	45.9	11.4	0.20	22.1	11.0	11.1
EtCOOCs												
0	82.1	11.0	0.00	78.4	8.3	0.00	74.9	6.5	0.00	17.8	9.7	8.1
0.53	76.4	11.7	0.01	73.6	8.8	0.00	69.6	6.8	0.00	17.8	9.9	7.9
1.1	72.0	12.6	0.03	68.3	9.2	0.01	65.4	7.2	0.01	18.5	10.0	8.5
2.41	65.5	15.5	0.08	62.5	11.2	0.06	59.5	8.3	0.06	20.7	10.5	10.2
3.87	59.1	18.7	0.12	54.7	12.6	0.13	54.5	9.6	0.11	22.5	10.8	11.7
5.91	54.6	25.4	0.20	51.0	16.5	0.16	47.5	10.9	0.14	28.8	11.4	17.4
8.58	46.6	27.7	0.22	43.8	18.4	0.22	43.0	12.5	0.16	26.9	11.7	15.2

Table 2 Dielectric properties of aqueous HCOOCs solutions.

mol per kg H_2O	283 K			298 K			313 K			$\Delta H_\varepsilon^{++}$/ kJ mol^{-1}	$\Delta G_\varepsilon^{++}$/ kJ mol^{-1}	$T\Delta S_\varepsilon^{++}$/ kJ mol^{-1}
	ε_s	τ/ps	α	ε_s	τ/ps	α	ε_s	τ/ps	α			
0	84.0	12.8	0.00	78.4	8.3	0.00	73.2	5.8	0.00	17.8	9.7	8.1
1.67	71.2	11.5	0.00	69.9	8.1	0.06	64.6	5.5	0.05	15.6	9.7	5.9
1.89	65.9	11.1	0.04	65.5	8.0	0.10	59.7	5.6	0.11	14.4	9.6	4.8
2.44	59.8	10.6	0.06	60.2	7.9	0.13	54.9	5.4	0.14	14.2	9.6	4.6
4.69	46.0	10.5	0.24	43.9	7.7	0.21	42.2	5.5	0.30	13.4	9.5	3.9

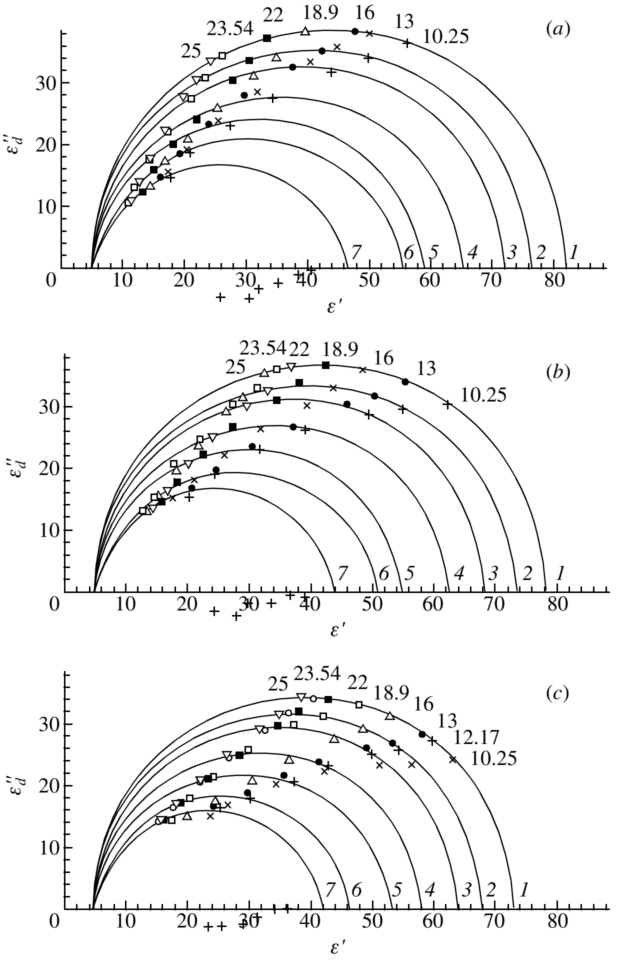

Figure 1 The Cole-Cole diagrams of aqueous EtCOOCs solutions. (*a*) 288, (*b*) 298 and (*c*) 308 K. Numbers above the diagrams indicate frequency in GHz. (*1*) water, (*2*) 0.52, (*3*) 1.1, (*4*) 2.41, (*5*) 3.87, (*6*) 5.91, (*7*) 8.58 mol per kg H_2O.

The values of ε_s decreased with concentration in all the test systems. This is typical of aqueous electrolyte solutions.[11,12] The values of α increased with salt concentration. In caesium formate solutions, α increased more strongly. The relaxation times of potassium and caesium propionate solutions increased with concentration (Figure 2). At high concentrations, the values of τ for caesium propionate were higher than those for potassium propionate. The relaxation times of caesium formate solutions decreased with concentration. The similar changes of τ were observed in potassium formate and other electrolyte solutions.[11–13] As can be seen in Figure 3, the values of $\Delta H_\varepsilon^{++}$ increase with concentration for potassium and caesium propionate solutions. At the same time, the values of $\Delta H_\varepsilon^{++}$ for caesium formate solutions decrease in comparison with pure water. The same behaviour of $\Delta H_\varepsilon^{++}$ was observed in potassium formate solutions.[6,13] Thus, the dielectric relaxation characteristics of formate and propionate solutions with the same cation change in a different manner in relation to pure water.

The decrease of τ and $\Delta H_\varepsilon^{++}$ for caesium formate solutions testifies to the breaking of an H-bond net, as well as in other cases.[12] The growth of τ and $\Delta H_\varepsilon^{++}$ in potassium and caesium propionate solutions indicates the structure-making influence of anions on the tetrahedral hydrogen bond net of water. Propionate and formate ions have identical polar groups but different non-polar parts. The presence of H-bonds between water molecules and formate ions results in the breaking of the tetrahedral H-bond net of water. Therefore, an increase of τ and $\Delta H_\varepsilon^{++}$ is determined by the influence of the non-polar part of the $EtCOO^-$ ion. Thus, the structure-making effect of $EtCOO^-$ ions on the hydrogen bond net of water is mainly associated with the hydrophobic hydration of these ions.

The similar influence of the same non-polar group on the structure of water was observed earlier in carbonic acid solutions.[14] The change of the sign of concentration changes of $\Delta H_\varepsilon^{++}$ occurs at the transition from formic acid to propionic acid. Similar changes were observed in the concentration dependences of τ and $\Delta H_\varepsilon^{++}$ for other solutions with hydrophilic and hydrophobic hydration. In Figures 2 and 3, the values of τ and $\Delta H_\varepsilon^{++}$ are plotted for aqueous electrolyte solutions with hydrophobic or hydrophilic hydration of ions. In the typical case of hydrophilic hydration,[12] $\tau^{s} < \tau^{H_2O}$ and $\Delta H_\varepsilon^{s} < \Delta H_\varepsilon^{H_2O}$. The changes of dielectric relaxation parameters for HCOOCs solutions are similar to changes of parameters for KCl solutions[12] (the typical case of the hydrophilic hydration of ions). The hydrophobic hydration of Bu_4N^+ ions is characteristic of aqueous Bu_4NCl solutions.[2,3] In this case, $\tau^{s} > \tau^{H_2O}$ and $\Delta H_\varepsilon^{s} > \Delta H_\varepsilon^{H_2O}$. Figures 2 and 3 show that changes in the relaxation characteristics are similar for Bu_4NCl and alkali metal propionate solutions. The hydrophobic hydration is less pronounced in caesium and potassium propionate solutions than in Bu_4NCl solutions. Weaker concentration changes in the dielectric relaxation time at elevated temperatures indicate the reduction of hydrophobic hydration with temperature.

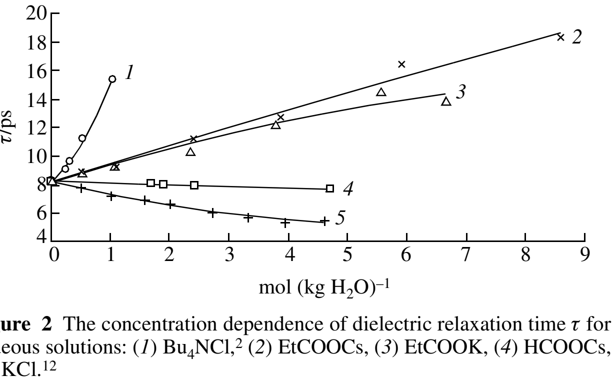

Figure 2 The concentration dependence of dielectric relaxation time τ for aqueous solutions: (*1*) Bu_4NCl,[2] (*2*) EtCOOCs, (*3*) EtCOOK, (*4*) HCOOCs, (*5*) KCl.[12]

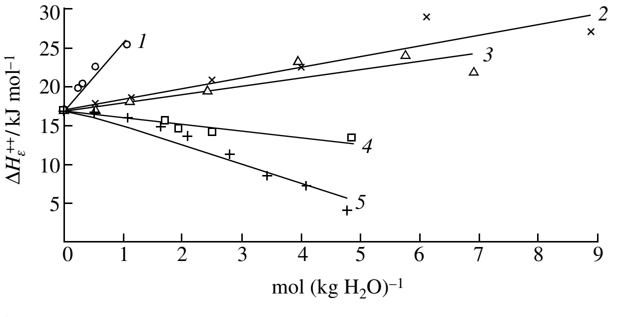

Figure 3 The concentration dependence of the activation enthalpy of dielectric relaxation $\Delta H_\varepsilon^{++}$ for aqueous solutions: (*1*) Bu_4NCl,[2] (*2*) EtCOOCs, (*3*) EtCOOK, (*4*) HCOOCs, (*5*) KCl.[12]

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