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The enthalpy of solution of sodium, potassium and caesium chlorides in propionic acid–water mixtures at 298.15 K

Stefania Taniewska-Osińska and Mariola Tkaczyk *

Department of Physical Chemistry, University of Łódź, ul. Pomorska 18, 91-416 Łódź (Poland)

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Abstract

The enthalpies of solution of NaCl, KCl and CsCl in mixtures of water with propionic acid at 298.15 K were measured. The enthalpic pair interaction coefficients h_{xy} (salt–propionic acid) and the group shares for the interactions of NaCl and KCl with carboxylic group were calculated.

INTRODUCTION

The dissociation of simple organic acids in aqueous solutions has been studied by many authors [1–5]. Using various measuring methods, such as viscosity [6–8], electromotive force [9, 10], electrical conductivity [11], spectroscopy [12, 13] and calorimetry [14, 15], the effects of these acids on water structure, and their dissociation constants, and the dimerization constants of the acids in aqueous solutions, have been determined. Studies on two-component systems (a simple organic acid + organic co-solvent [8, 16]) and three-component systems (acid + water + organic solvent [17]) have also been reported. However, the literature reports no data concerning aqueous solutions of simple organic acids containing an electrolyte.

In order to determine the behaviour of a 1:1 electrolyte in propionic acid–water systems, we have measured the heats of solution of NaCl, KCl and CsCl in aqueous solutions of this acid at 298.15 K.

EXPERIMENTAL

The measurements of the enthalpy of solution of NaCl, KCl and CsCl in propionic acid–water mixtures were performed in an "isoperibol" calorimeter. The temperature inside the calorimeter was determined using three

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* Corresponding author.

thermistors working in a Wheatstone bridge system. The temperature sensitivity was approx. 5×10^{-5} K. The temperature in the thermostat was stable to 1×10^{-3} K. The experimental precision was 0.5%. The propionic acid (Aldrich-Chemie, 99%) was dried using 4A molecular sieves. Finally, the acid was fractionally distilled (boiling point, 141°C). Tri-distilled water was used. Sodium chloride (Merck, p.a.), potassium chloride (P.O.Ch., Poland; p.a.) and caesium chloride (L.R., BDH) were dried in vacuo for several days at 378 K. The water–organic mixtures were prepared by weight.

The propionic acid–water system

The numerous attempts to determine the effect of propionic acid molecules on the structure of water have not yet provided an explicit picture of interaction taking place in this mixture. Kovaleva [6] has measured the density and viscosity of aqueous propionic acid solutions at 25°C. The density versus mixed solvent composition shows a maximum corresponding to about 22 mol.% acid content in the mixture. The highest viscosity is shown by a solution containing 39.6 mol.% of the acid. This maximum shifts with lowering temperature towards systems with higher water contents, which, according to Kovaleva [6], is brought about by a decrease in the degree of dissociation.

The viscosity of aqueous solutions of carboxylic acids has also been studied by Miyajima et al. [7]. Based on the sign of the B_{st} coefficient (B_{st} is the contribution of solute to the structure of water) and that of the temperature relationship dB/dT (B is a coefficient in the Jones–Dole equation), they determined the effect of propionic acid on the structure of water. In the authors' opinion, the positive sign of B_{st} and the negative sign of dB/dT point to the "structure-making effect" of propionic acid on the structure of water. This influence is associated with the hydrophobic hydration of the alkyl chain and is increased with its length. A weaker destructive effect of the carboxylic group of the acid on the structure of water is compensated for by the "structure-making effect" associated with the presence of hydrophobic groups.

A converse opinion to that of Miyajima et al. has been reported by Subha and Brahmaji Rao [8], who used their densitometric and viscosimetric results to conclude that specific polar–polar interactions dominate in the propionic acid–water system. Using Raman spectroscopy, Tanaka et al. [13] have determined the dimerization constants (K_D, the monomer–dimer equilibrium constant) for an acid content ranging from 0.03 to 0.03 molar fraction in water. The increasing K_D with alkyl chain length and the decreasing K_D with increasing acid concentration in the system were attributed by the authors to the presence of hydrophobic interactions with differentiated forces. The view that hydrophobic interactions play an important part in the

TABLE 1

Enthalpies of solution of NaCl in water–propionic acid mixtures at 298.15 K

$m \times 10^3$ (mol kg^{-1})	ΔH_s (kJ mol^{-1})	$m \times 10^3$ (mol kg^{-1})	ΔH_s (kJ mol^{-1})
$x = 0.0$ [a]		$x = 0.01$	
4.99	4.003	4.45	4.049
11.08	4.042	8.03	4.074
20.60	4.093	10.50	4.071
32.39	4.141	16.34	4.095
		25.57	4.114
$x = 0.05$		26.55	4.110
3.54	4.331	36.07	4.133
5.57	4.367		
8.02	4.365	$x = 0.08$	
12.68	4.397	4.29	4.045
12.99	4.416	10.93	4.050
17.50	4.423	19.99	4.056
23.03	4.465	31.68	4.060
37.28	4.526		
		$x = 0.20$	
$x = 0.10$		2.89	1.370
3.45	3.802	7.89	1.533
4.08	3.812	10.54	1.593
7.86	3.841	14.10	1.672
9.79	3.865	16.68	1.718
13.52	3.884	21.48	1.803
16.65	3.912	23.29	1.828
20.06	3.928	30.09	1.924
24.11	3.954		
		$x = 0.30$	
$x = 0.25$		4.40	−0.636
5.20	0.306	6.72	−0.489
11.13	0.485	9.15	−0.490
22.32	0.781	14.76	−0.289
34.20	1.012	15.29	−0.352
		22.75	0.293
$x = 0.40$		22.99	0.297
4.39	−2.288	33.02	0.310
5.58	−2.165		
9.29	−2.068	$x = 0.50$	
13.76	−1.867	2.19	−3.792
15.86	−1.819	3.31	−3.523
22.69	−1.584	5.10	−3.457
34.62	−1.255	8.19	−3.187
		9.12	−2.931
		11.92	−2.916
		15.81	−2.473

[a] x is the mole fraction of propionic acid in mixed solvent.

TABLE 2

Enthalpies of solution of KCl in water–propionic acid mixtures at 298.15 K

$m \times 10^3$ (mol kg^{-1})	ΔH_s (kJ mol^{-1})	$m \times 10^3$ (mol kg^{-1})	ΔH_s (kJ mol^{-1})
$x = 0.0$[a]		$x = 0.01$	
1.65	17.38	1.37	17.18
1.86	17.39	4.04	17.23
3.82	17.38	7.20	17.26
4.23	17.38	11.31	17.31
6.83	17.40	14.18	17.34
12.00	17.41	16.25	17.37
$x = 0.03$		$x = 0.05$	
4.21	16.71	1.71	15.94
7.44	16.72	4.15	15.99
14.97	16.73	8.57	16.06
19.94	16.74	10.76	16.07
24.95	16.74	15.29	16.14
25.12	16.75	16.05	16.14
$x = 0.08$		$x = 0.10$	
1.17	14.78	1.45	14.05
3.81	14.87	3.51	14.07
7.89	14.95	6.36	14.10
11.50	15.03	9.72	14.12
14.02	15.09	13.21	14.16
15.41	15.13	14.80	14.17
$x = 0.20$		$x = 0.25$	
1.32	9.860	2.06	8.491
4.58	9.924	5.89	8.550
7.38	9.980	7.15	8.569
10.22	10.04	9.85	8.585
12.40	10.09	12.11	8.616
16.21	10.17	14.24	8.635
$x = 0.30$		$x = 0.40$	
1.96	6.446	2.08	3.403
4.22	6.546	5.21	3.740
7.78	6.686	9.06	4.048
11.93	6.809	13.79	4.351
$x = 0.50$			
2.16	1.889		
4.33	2.163		
5.51	2.354		
7.83	2.563		
8.93	2.684		
12.80	3.006		
12.98	3.039		

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[a] x is the mole fraction of propionic acid in mixed solvent.

TABLE 3

Enthalpies of solution of CsCl in water–propionic acid mixtures at 298.15 K

$m \times 10^3$ (mol kg^{-1})	ΔH_s (kJ mol^{-1})	$m \times 10^3$ (mol kg^{-1})	ΔH_s (kJ mol^{-1})
x[a] = 0.0		$x = 0.01$	
3.53	17.50	1.94	17.19
7.47	17.49	3.25	17.18
9.05	17.48	5.09	17.18
11.81	17.48	6.63	17.17
17.75	17.47	9.78	17.16
20.36	17.46	11.78	17.16
34.35	17.44	15.98	17.15
48.64	17.42	18.25	17.14
$x = 0.05$		$x = 0.10$	
1.69	15.44	1.19	12.62
1.76	15.44	1.76	12.69
4.01	15.46	2.89	12.72
4.16	15.46	3.69	12.76
6.56	15.48	5.89	12.84
7.90	15.48	6.89	12.91
12.09	15.51	11.42	13.02
15.45	15.51	14.39	13.12
$x = 0.20$		$x = 0.30$	
1.57	8.353	1.28	4.335
2.12	8.388	2.12	4.476
3.92	8.416	3.50	4.559
4.34	8.424	5.24	4.707
6.65	8.473	6.77	4.791
6.94	8.481	9.25	4.943
13.51	8.590	11.54	5.055
15.42	8.625	17.84	5.381
$x = 0.40$		$x = 0.50$	
1.77	1.339	2.78	0.352
3.46	1.621	3.48	0.458
3.97	1.710	5.94	0.540
8.09	1.924	8.60	0.731
8.58	1.985	12.84	0.894
14.66	2.273	16.31	1.036
15.67	2.307	20.30	1.149
23.99	2.632	25.19	1.305

[a] x is the mole fraction of propionic acid in mixed solvent.

dimerization of propionic acid in an aqueous solution has been confirmed by Schrier et al. [18] and Suzuki et al. [11]. Based on their conductometric results, Suzuki et al. have studied the dissociation constant of acid dimers (from formic acid to *n*-butyric acid) versus pressure, and also the variations in molar volume (ΔV_D) during dimerization. The shorter the hydrophobic acid chain length, i.e. the weaker its hydrophobic properties, the sharper the ΔV_D volume drop.

The electrolyte–propionic acid–water system

Measurements of the heats of solution of NaCl, KCl and CsCl in propionic acid–water mixtures were carried out at a temperature of 298.15 K. The enthalpy of solution of sodium chloride was determined within the salt concentration range 0.003–0.03 mol kg^{-1} and those of potassium chloride and caesium chloride over the range 0.002–0.02 mol kg^{-1}, using mixed solvent compositions from 0 to 50 mol.% of propionic acid. The range of mixed solvent compositions was restricted due to too slow a dissolution of the salts in organic-component-rich mixtures (yielding a considerable increase in the experimental error).

The values obtained for the integral molar solution enthalpies of the electrolytes (Tables 1–3) were extrapolated to an infinite dilution. The use of the extrapolation method of Criss and Coble was excluded owing to the lack of the dependence of the electric permittivity on temperature for propionic acid–water systems. Thus, the graphical extrapolation $\Delta H_s = f(\sqrt{m})$ to $m = 0$ was used. Values of the standard enthalpy of solution are given in Table 4. The plot of the standard enthalpy of solution

TABLE 4

Molal enthalpy of solution $\Delta H_s^\ominus$ at infinite dilution in aqueous mixtures of propionic acid (kJ mol^{-1}) at 298.15 K

x [a]	$\Delta H_s^\ominus$(NaCl)	$\Delta H_s^\ominus$(KCl)	$\Delta H_s^\ominus$(CsCl)
0.0	3.860	17.30	17.38
0.01	3.982	17.16	17.13
0.03	–	16.71	–
0.05	4.086	15.92	15.40
0.08	4.028	14.76	–
0.10	3.647	14.04	12.37
0.20	0.980	9.839	8.177
0.25	−0.427	8.397	–
0.30	−1.323	6.040	3.771
0.40	−3.182	2.435	0.670
0.50	−4.991	0.624	−0.352

[a] x is the mole fraction of propionic acid.

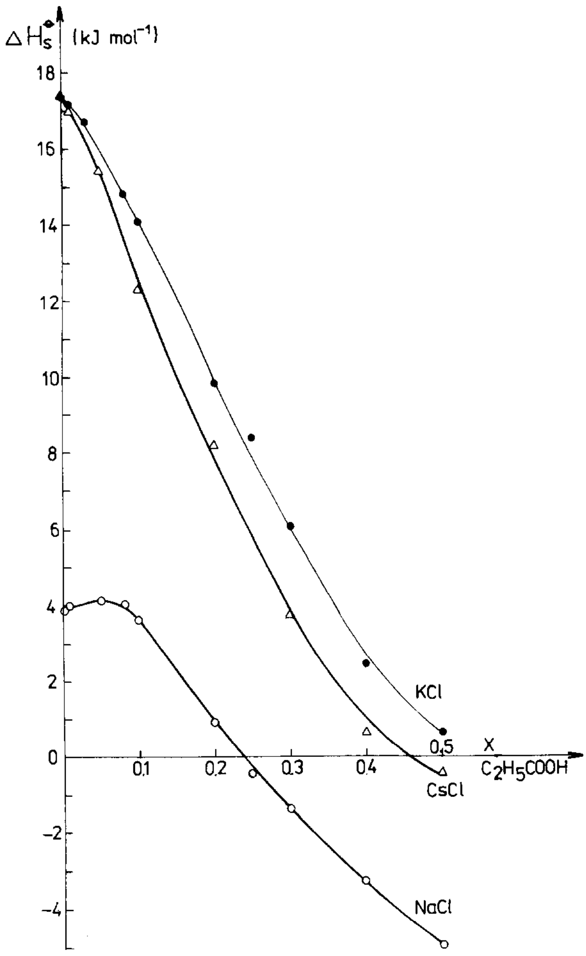

Fig. 1. Standard enthalpy of solution of NaCl, KCl and CsCl in the propionic acid–water mixtures as a function of solvent composition at 298.15 K.

of electrolyte versus the mixed solvent composition (Fig. 1) shows a different character for NaCl compared with the remaining salts (KCl and CsCl). The NaCl curve shows a slight extremum at 5 mol.% propionic acid in the system, while the functions $\Delta H_s^\ominus = f(\text{mol.\%})$ for potassium and caesium chlorides are monotonic with similar slopes, but different from that obtained for NaCl.

The dissolution of electrolyte in binary solvent is accompanied by three effects

(a) destruction of the solvent structure (an endothermic effect, which increases with increasing salt cation radius),

(b) destruction of the salt crystal lattice (exothermic effects in the order NaCl > KCl > CsCl),

(c) formation of a sheath of solvent molecules around the ion.

The thermal effect observed during salt dissolution is a result of these three contributions.

Enthalpic pair interaction coefficients

The enthalpic pair interaction coefficients (h_{xy}) are often used to analyse the interactions in two- and three-component systems. They are a measure of the thermal effect, i.e. the enthalpy of interaction, during the mutual approach of two molecules in the solution. The values of the molar enthalpies of solution $\Delta H_s^\ominus$ of electrolytes in aqueous solutions of propionic acid with infinitesimal concentrations were used to determine the enthalpic pair interaction coefficients h_{xy} in water (electrolyte–propionic acid). The procedure used has been described previously [19]. The following values were obtained.

$h_{xy}[(Na^+ + Cl^-)\text{–propionic acid}] = +127\ J\ kg\ mol^{-2}$

$h_{xy}[(K^+ + Cl^-)\text{–propionic acid}] = -153\ J\ kg\ mol^{-2}$

$h_{xy}[(Cs^+ + Cl^-)\text{–propionic acid}] = -189\ J\ kg\ mol^{-2}$

The positive value of h_{xy} for the NaCl–propionic acid interaction shows that the thermal effects associated with dehydration of both the salt and the non-electrolyte are predominant in this system. This conclusion is confirmed by the values of the hydration enthalpy which is most exothermic for the sodium ion and least for the caesium ion. It has been found [20] that positive values of h_{xy} coefficients are characteristic of systems in which maxima of the electrolyte transfer enthalpy from water to the mixed solvent occur for water-rich mixtures (alcohols, THF, cellosolves, HMPT, 2-butanone, 1,2-dimethoxyethane). This regularity is also met by the system under investigation. The negative values of h_{xy} for the KCl–propionic acid and CsCl–propionic acid interactions may point to the predominance of a salt–non-electrolyte interaction. This is probably associated with the weaker hydration (lower exothermic effects) of the larger potassium and caesium ions.

The enthalpic pair interaction coefficients can be expressed as a sum of group shares

$$h_{xy} = \sum^{j} n_j^Y h_{E-j}$$

where n_j^Y is the number of j groups in a non-electolyte molecule Y, and h_{E-j} is the group coefficient for the interaction of group j with the ions of the salt. Using our data [20], $h_{xy}[(Na^+ + Cl^-)\text{–}CH_2] = 266\ J\ kg\ mol^{-2}$ and those of Davis et al. [21], $h_{xy}[(K^+ + Cl^-)\text{–}CH_2] = 263\ J\ kg\ mol^{-2}$, along with the suggestion of Savage and Wood [22] that the presence of a single $-CH_3$ group corresponds to $1.5CH_2$, we have calculated the group shares for the interactions of NaCl and KCl with the carboxylic group. The obtained values are $h_{xy}[(Na^+ + Cl^-)\text{–}COOH] = -538\ J\ kg\ mol^{-2}$ and $h_{xy}[(K^+ + Cl^-)\text{–}COOH] = -810\ J\ kg\ mol^{-2}$.

The negative values of these coefficients suggest that the interactions of solvated ions with the solvated carboxylic group are dominated by attraction forces (ion–dipole). It is impossible to calculate the energetic effect of the direct interaction of the salt with the carboxylic group from the h_{xy} coefficients because the calculated group shares also include the thermal effect of dehydration of the species. The enthalpy effects associated with partial dehydration of the salt in the vicinity of a strongly polar group differentiate the values of h_{xy}(salt–COOH). In the face of the more exothermic enthalpy of hydration for NaCl, the observed trend of changes in the coefficients h_{xy} seems to be reasonable.

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