



Effect of temperature on the dilution enthalpies of carboxylic acids in aqueous solutions

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ABSTRACT

Dilution enthalpies of propionic, butyric, valeric and caproic acid in water were measured at 293.15, 298.15, 303.15 and 308.15 K using an LKB flow microcalorimeter. Experimental data were treated according to the McMillan–Mayer theory to obtain the homotactic enthalpic interaction coefficients. The value of the coefficients is positive and increases with chain length showing that hydrophobic interactions are enhanced. The obtained values of the interaction coefficients are interpreted in terms of solute–solvent and solute–solute interactions and are used as indicative of hydrophobic behavior of the carboxylic acids studied.

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1. Introduction

Thermodynamic properties of aqueous solutions of small model compounds are important as they provide information about the various contributions to the interaction between hydrated molecules and help understanding the behavior of more complex systems in aqueous solutions.

Among these solutes, aqueous solutions of carboxylic acids are important (i) for their industrial and practical applications in hydrothermal and biological systems, (ii) they are useful in the elucidation of the effect of hydrocarbon chain length on the interactions between non polar and polar groups and water and because their thermodynamic properties can be used as a valuable tool to model complex molecules using additivity principles and (iii) for the information they can give about their effect on water structure.

Carboxylic acids show a complex thermodynamic behavior in aqueous solution that is consequence of the possibility of inter- and intramolecular hydrogen bonding, hydrophobic interactions and a small degree of ionization [1–4]. Their behavior depends strongly on concentration and on acid chain length. As solute concentration decreases, hydrogen bond association diminishes and the acid water interactions become dominant [3,4]. For aliphatic acids in aqueous solution it has been established that dimerization constants increase with chain length [2,4].

Aqueous solutions of carboxylic acids have been studied mainly on small chain acids at 298.15 K. Very few data are reported in literature for acids of four, five or six carbon atoms at temperatures different from 298.15 K. In particular, the information about dilution enthalpies is very scarce [5–9]. In this work we report the dilution enthalpy ΔH_{dil} for aqueous solutions of propionic, butyric, valeric and caproic acid at 293.15, 298.15, 303.15 and 308.15 K. These enthalpies were used to determine the enthalpic pair interaction coefficients derived from the McMillan–Mayer theory and are discussed in terms of interactions of hydrated carboxylic acid molecules.

2. Experimental

The materials used in this work were propionic acid (Fluka 99.5% puriss), butyric acid (Fluka 99.5% puriss), valeric acid (Sigma 99% min), and caproic acid (Aldrich 99.5% min). Water was doubly distilled, degassed and treated according to literature [10]. All solutions were prepared by weight using a Mettler balance AT-261 dual range with a sensitivity of 10^{-5} g in the lower range.

Dilution heats were measured at 293.15, 298.15, 303.15 and 308.15 ± 0.01 K using an LKB Flow Microcalorimeter, model 10700-1 (Bromma/Sweden) in the mixing mode, following the procedure described in a previous paper [11]. The liquids were pumped using two peristaltic pumps and the flow rates were determined by weighing the masses of liquids passing through the pumps in a given time. The sensitivity of the microcalorimeter amounted to $100 \mu\text{V mW}^{-1}$. The calorimetric signal was registered

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by a Hewlett–Packard multimeter 34401A, which measures up to 1000 V with 6.5 digits resolution and accuracy in the order of 0.002%.

3. Results and discussion

Tables 1–4 show the experimental results for the dilution enthalpies of propionic, butyric, valeric and caproic acid in water at 293.15, 298.15, 303.15 and 308.15 K as well as the initial and final molalities m_i and m_f . In all cases the relative standard deviation is less than 1 J mol⁻¹. No corrections were done for ionization. The contribution of the ionized species was calculated taking into account the acid dissociation degree; it is negligible and smaller than the experimental uncertainty as shown by other authors [7].

Dilution enthalpies of carboxylic acids in water are exothermic. Fig. 1 shows the experimental behavior of dilution enthalpies of the four acids in aqueous solutions at 298.15 K.

Table 1
Dilution enthalpies of propionic acid in water.

m_i (mol kg ⁻¹)	m_f (mol kg ⁻¹)	ΔH_{dil} (J mol ⁻¹)			
		293.15 K	298.15 K	303.15 K	308.15 K
7.26160	3.11839	-1122.82	-1071.62	-1124.19	-1021.11
5.18840	2.36148	-1279.68	-1209.17	-1169.03	-1083.34
3.96510	1.87077	-1287.43	-1233.79	-1178.72	-1125.80
2.76140	1.35156	-946.38	-944.95	-943.50	-942.08
2.21430	1.10252	-749.18	-747.46	-745.78	-744.04
1.84350	0.92877	-625.61	-614.31	-602.70	-591.55
1.53280	0.78000	-523.83	-503.96	-483.55	-463.95
1.13560	0.58539	-371.75	-356.18	-340.19	-324.83
0.82160	0.42791	-243.53	-241.20	-238.94	-236.58
0.61480	0.32238	-203.61	-195.15	-186.92	-178.35
0.48160	0.25368	-180.91	-165.39	-150.28	-134.55

Table 2
Dilution enthalpies of butyric acid in water.

m_i (mol kg ⁻¹)	m_f (mol kg ⁻¹)	ΔH_{dil} (J mol ⁻¹)			
		293.15 K	298.15 K	303.15 K	308.15 K
5.63970	2.53386	-232.32	-219.48	-208.29	-194.62
5.28930	2.40040	-312.29	-283.74	-258.88	-228.49
4.89518	2.24704	-401.59	-358.54	-321.04	-275.21
4.67980	2.16173	-452.68	-402.55	-358.89	-305.53
3.98508	1.87908	-636.28	-567.46	-507.52	-434.26
3.61877	1.72526	-721.04	-654.7	-596.92	-526.3
2.63873	1.29646	-969.19	-927.07	-890.38	-845.54
2.51060	1.23845	-1007.83	-965.67	-928.95	-884.07
2.13665	1.06647	-1065.53	-1027.27	-993.95	-953.22
1.64497	0.83404	-927.92	-910.14	-894.66	-875.73
1.12450	0.57986	-672.51	-648.02	-626.69	-600.62
0.86413	0.44942	-503.65	-483.14	-465.28	-443.45

Table 3
Dilution enthalpies of valeric acid in water.

m_i (mol kg ⁻¹)	m_f (mol kg ⁻¹)	ΔH_{dil} (J mol ⁻¹)			
		293.15 K	298.15 K	303.15 K	308.15 K
0.19080	0.10149	-129.63	-126.22	-125.55	-120.77
0.17740	0.09440	-123.92	-120.66	-120.02	-115.45
0.17130	0.09118	-120.39	-117.23	-116.6	-112.17
0.16430	0.08747	-115.98	-112.93	-112.32	-108.05
0.15940	0.08488	-113.40	-110.42	-109.83	-105.66
0.15160	0.08074	-108.75	-105.89	-105.32	-101.32
0.14230	0.07581	-100.79	-98.14	-97.62	-93.91
0.13710	0.07306	-96.94	-94.39	-93.89	-90.32
0.12890	0.06871	-91.23	-88.83	-88.36	-85.00
0.12080	0.06441	-81.43	-79.29	-78.86	-75.87
0.11200	0.05973	-71.34	-69.46	-69.09	-66.46
0.10430	0.05564	-64.44	-62.75	-62.41	-60.04

Table 4
Dilution enthalpies of caproic acid in water.

m_i (mol kg ⁻¹)	m_f (mol kg ⁻¹)	ΔH_{dil} (J mol ⁻¹)			
		293.15 K	298.15 K	303.15 K	308.15 K
0.08200	0.04378	-137.66	-136.32	-135.34	-133.6
0.07800	0.04165	-135.54	-134.37	-133.41	-132.13
0.07490	0.04000	-133.71	-130.32	-131.03	-130.63
0.07120	0.03803	-130.82	-129.26	-128.35	-126.46
0.06940	0.03707	-128.08	-127.14	-126.09	-126.66
0.06450	0.03445	-127.29	-122.46	-123.48	-119.29
0.06210	0.03318	-125.47	-120.56	-120.73	-118.32
0.05860	0.03131	-120.81	-118.94	-118.54	-117.11

The dependence of the dilution enthalpies on concentration gives information about solute–solute interactions, while the dilution enthalpies at infinite dilution provide information about solute–solvent interactions. At constant temperature, enthalpies decrease in the dilute region, as the acid concentration increases. For each solute in the same concentration range, the dilution enthalpy has a slight dependence on temperature and becomes less exothermic as the temperature increases.

The limiting slopes at infinite dilution of the curves of dilution enthalpies plotted versus concentration have been related to hydrophobic hydration by several authors [12]. For the aqueous carboxylic acid solutions the limiting slopes are negative, indicating that the acids interact with water primarily through their alkyl groups. Table 5 shows the value of the limiting slopes at the selected temperatures. At all temperatures, the largest negative value is for caproic acid and becomes less negative as the number of methylene groups decrease. The slopes decrease as temperature increases. A minimum in the water-rich region is observed for propionic and butyric acid that reflects the complex behavior of the aqueous solutions of carboxylic acids and has not been reported in previous studies with acids [13]. The position of the minimum in the molality scale is lower for butyric acid.

The behavior of excess thermodynamic properties as function of molality has been used in solution theories to determine molecular interaction coefficients of binary systems giving information about solute–solute interactions between hydrated molecules. The McMillan–Mayer theory relates the osmotic properties of dilute solutions to interactions between solute molecules [14], allowing the separation of effects that result from molecular pair, triplet and higher order interactions. However, the contribution of three-body interactions is small compared to that of two-body interactions and higher order interactions are usually negligible [15–18].

The McMillan–Mayer theory and its application to aqueous solutions of nonelectrolytes [19–21] establish that the excess thermodynamic properties can be expressed as a function of molality using a virial expansion and that the coefficients obtained are related to the magnitude and sign of solute–solute interactions [4–8]. In this way, the dilution enthalpies are expressed as a virial expansion of solute molalities using Eq. (1), and the interaction coefficients are obtained fitting the experimental data by least

Table 5
Limiting slopes of the dilution heats of carboxylic acids at 293.15, 298.15, 303.15 and 308.15 K.

Acid	$\left(\frac{\partial \Delta H_{dil}}{\partial m_2}\right)$ (J mol ⁻¹)			
	293.15 K	298.15 K	303.15 K	308.15 K
Propionic	-679	-666	-651	-638
Butiric	-1156	-1131	-1110	-1084
Valeric	-1524	-1484	-1467	-1420
Caproic	-3753	-3682	-3673	-3641

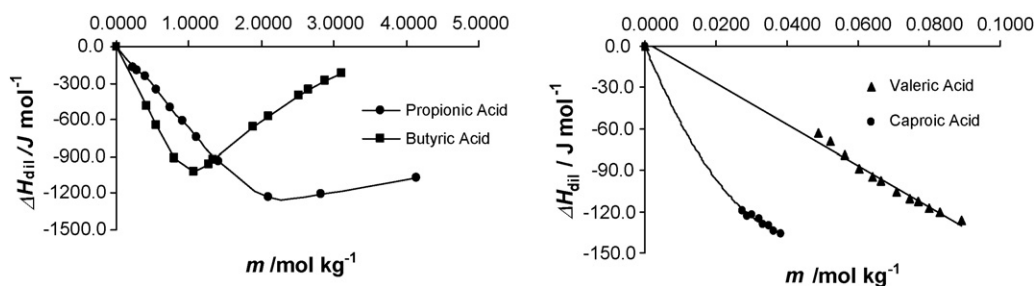


Fig. 1. Dilution enthalpies of organic acids at 298.15 K.

Table 6

Virial enthalpic coefficients h_{xx} and h_{xxx} of carboxylic acids in water.

T (K)	Acid	h_{xx} (J kg mol ⁻²)	h_{xxx} (J kg ² mol ⁻³)	Δm (mol kg ⁻¹) ^a
293.15	Propionic	736 ± 18	-20 ± 4	3.9651–0.25368
293.15	Butyric	1348 ± 54	-81 ± 25	1.64496–0.44942
293.15	Valeric	1577 ± 67	-320 ± 272	0.19080–0.05564
293.15	Caproic	6535 ± 118	-23,500 ± 1064	0.08200–0.03131
298.15	Propionic	733 ± 25; 661 ^b	-23 ± 5	3.9651–0.25368
298.15	Butyric	1262 ± 48; 1213 ^b	-55 ± 23	1.64496–0.44942
298.15	Valeric	1536 ± 66	-311 ± 265	0.19080–0.05564
298.15	Caproic	6161 ± 108	-20,766 ± 976	0.08200–0.03131
303.15	Propionic	730 ± 36	-26 ± 8	3.9651–0.25368
303.15	Butyric	1187 ± 43	-33 ± 20	1.64496–0.44942
303.15	Valeric	1528 ± 65	-309 ± 263	0.19080–0.05564
303.15	Caproic	6235 ± 80	21529 ± 728	0.08200–0.03131
308.15	Propionic	727 ± 47	-28 ± 10	3.9651–0.25368
308.15	Butyric	1095 ± 37	-5 ± 17	1.64496–0.44942
308.15	Valeric	1470 ± 61	-299 ± 253	0.19080–0.05564
308.15	Caproic	6029 ± 129	-20,087 ± 1169	0.08200–0.03131

^a Molality range.

^b Ref [7].

squares to a polynomial expression [11,13,22–24]:

$$\Delta H_{\text{dil}} = H^E(m_f) - H^E(m_i) = h_{xx}(m_f - m_i) + h_{xxx}(m_f^2 - m_i^2) + \dots \quad (1)$$

In this equation m_i and m_f represent the initial and final solute molalities, h_{xx} and h_{xxx} are the interaction coefficients that represent the contribution of solute–solute interactions between pairs and triplets of solvated solute molecules in a binary solution.

The concentration range used is wide for propionic and butyric acid while it is small for valeric and caproic acid due to solubility limitations. The experimental data were fitted using two parameters to obtain the best adjustment. For propionic and butyric acid the data corresponding to the dilute concentration region before the minimum were used to make the adjustment. Due to the large uncertainty in the higher order coefficients the analysis is restricted to the first pairwise coefficient h_{xx} .

The interaction coefficients obtained in this work at each temperature, the concentration range and literature data are presented in Table 6 when they are available.

The pair interaction coefficients describe the solute–solute interactions when two solute particles approach each other in dilute solutions. The pairwise associations of carboxylic acids involving the side-chains are significant and affected by the number and position of the CH₂ groups. The pair enthalpic interaction coefficients, h_{xx} , between acid molecules are positive for propionic, butyric, valeric and caproic acid in aqueous solutions at the temperatures considered. At each temperature the highest h_{xx} value is for caproic acid; the values become smaller as the number of methylene groups decrease.

The sign and magnitude of the enthalpic coefficient can be interpreted as the result of different contributions: (i) The polar–polar

interaction between carboxylic groups strongly hydrated with water that can participate in hydrogen-bonding interactions and have a negative contribution to h_{xx} . (ii) The endothermic effect due to partial dehydration of the solvation layers characterized by a positive contribution to h_{xx} . (iii) Hydrophobic interactions involving apolar chains characterized by a positive contribution to h_{xx} . According to this, the positive value of the coefficients obtained in this work can be attributed to dominant apolar group interactions mediated by water.

The increase of the positive values of the coefficients with increasing chain length shows the contribution of CH₂ groups to the enthalpic pairwise coefficients and reflects that hydrophobic interactions are enhanced.

The results demonstrate that caproic acid is the solute that presents the most hydrophobic behavior due to the combined effect of partial dehydration of solvation layers and apolar chain interaction. The value of the coefficient decreases as the accessible surface area decreases. The behavior is similar to that observed for other solutes with an alkyl chain [20,25] and reflects that net repulsion grows for the acids as the length of the alkyl chain increases.

According to the magnitude and sign of the pairwise enthalpic coefficients, the carboxylic acids studied can be arranged at each temperature in order of increasing hydrophobicity as follows:

propionic < butyric < valeric < caproic acid

The pairwise enthalpic coefficients decrease as temperature increases following the trend reported in literature for other solutes [26–28].

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