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Apparent Molar Volume and Surface Tension of Dilute Aqueous Solutions of Carboxylic Acids

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ABSTRACT: Density and surface tension of dilute aqueous solutions of propanoic, butanoic, pentanoic, and hexanoic acids have been measured at temperatures of (293.15, 298.15, 303.15, and 308.15) K. From experimental data apparent molar volumes and excess molar volumes were determined as a function of composition at each temperature. The limiting values of the partial volumes at infinite dilution of the acids in aqueous solution were determined at each temperature and the results were used to evaluate group contributions of the methylene and carboxylic groups. The surface tension measurements were used to evaluate the limiting experimental slopes of surface tension with respect to mole fraction. The influence of temperature on the behavior of volumetric and surface properties is discussed in terms of solute hydration and the balance between hydrophobic and hydrophilic interactions between the acids and water.

INTRODUCTION

Physicochemical properties of aqueous solutions of organic compounds are of considerable interest in the study of hydrophobic and hydrophilic interactions between these solutes and water and their effect on water structure. In particular, volumetric and surface properties of aqueous solutions of carboxylic acids are important for their theoretical and practical applications. Their study gives important information about the nature of interactions between nonpolar and polar groups with water and their effect on water structure.

In the case of carboxylic acids the information available in literature is limited and eventhough the effect of temperature has been used to obtain information about solute hydration, most studies have been done with small chain acids at 298.15 K.[1−13]

As a continuation of earlier work on the thermodynamic properties of organic solutes in aqueous solution, in the present paper, the apparent molar volumes, the excess volumes and surface tensions of propanoic, butanoic, pentanoic, and hexanoic acids in water are reported as a function of composition at temperatures of (293.15, 298.15, 303.15, and 308.15) K.

EXPERIMENTAL SECTION

Water was doubly distilled and deionized according to literature and degassed before use and the resulting product showed a conductivity less than 2 $\mu S \cdot m^{-1}$.[14,15] The solutes used in this work were propanoic acid (Fluka puriss, $w = 0.995$), butanoic acid (Fluka puriss, $w = 0.995$), pentanoic acid (Sigma, $w > 0.99$), and hexanoic acid (Adrich, $w \geq 0.995$). All of the chemicals were used without further purification since their mass fraction purity according to the certificate of analysis is higher than 0.99. All solutions were prepared by weight using a Mettler balance AT-261 dual range with readability of $1 \cdot 10^{-5}$ g and reproducibility better than 1×10^{-5} g in the lower range. In the case of solutions of pentanoic and hexanoic acid, the concentration range is defined by the acid solubility, which is very low at the temperatures considered.[11] The estimated uncertainty in mole fraction is less than $1 \cdot 10^{-5}$ g.

Densities of pure solutes and the aqueous solutions were measured using a vibrating U-tube densimeter Anton Paar DMA 5000 with temperature control better than 0.01 K and uncertainty of $\pm 5 \cdot 10^{-6}$ $g \cdot cm^{-3}$. The densimeter was calibrated with double distilled and deionized water at each temperature, density values are the average of three independent measurements and they were reproducible to within $\pm 1 \cdot 10^{-5}$ $g \cdot cm^{-3}$.

Surface tension measurements were done with a LAUDA TVT-2 drop volume tensiometer based on the principle of the pending drop volume, with temperature control better than 0.1 K. The volume of the syringe used for the measurements was 1.0 cm^3 and the inner radius of the capillary was 1.08 mm. Reported values are the average of 18 to 24 measurements and the uncertainty in the surface tension measurements is $\pm 10^{-2}$ $mN \cdot m^{-1}$.

RESULTS

Experimental data for density ρ and surface tension obtained in this work for the pure liquids obtained in this work are presented in Table 1[6,10,11,13,14,16−19] together with values from the literature. As can be seen, there is good agreement with published values.

Excess molar volumes V^E of the binary systems were calculated from density measurements at each temperature according to the following equation:

$$V^{E} = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right) \quad (1)$$

where M_1 and M_2 are the molar masses and ρ_1 and ρ_2 are the densities of the pure compounds of the pure components (1) water and (2) solute, x_1 and x_2 are the corresponding mole fractions and ρ is the solution density.

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Table 1. Density and Surface Tension of Pure Propanoic, Butanoic, Pentanoic, and Hexanoic Acids from T = 293.15 to 308.15 K

	ρ /g·cm^{-3}					σ/mN·m^{-1}						
acid	293.15 K	298.15 K		303.15 K	308.15 K	293.15 K		298.15 K		303.15 K		308.15 K
propanoic	0.993421 0.99336[16] 0.9934[14]	0.988213 0.9872[13]	0.98833[6] 0.9880[14]	0.982884 0.98260[11]	0.977491 0.97743[10] 0.97758[10]	26.68 26.66[17] 26.69[19]	26.70[14] 26.60[18]	26.19 26.17[17]	26.15[6] 26.06[18]	25.69 25.68[17] 25.70[19]	25.71[14] 25.75[18]	25.20 25.18[17]
butanoic	0.957608 0.9582[14]	0.952769 0.9532[14] 0.95317[6]		0.947942	0.942908	26.71 26.74[18]	26.74[14] 26.51[19]	26.21 26.19[6] 26.16[18]		25.61 25.57[14] 25.54[18]		25.07 24.99[18]
pentanoic	0.938288 0.9390[14]	0.933903 0.9345[14] 0.9340[13]		0.929387	0.924731	27.23 27.40[18]		26.63		26.06 26.35[14] 26.24[19]		25.56
hexanoic	0.925383 0.9272[14]	0.921201 0.9230[14] 0.9180[13]		0.917022 0.91832[14]	0.912602	27.98 28.05[14] 28 × 10[18]		27.51 27.55[14] 27.49[18]		27.14		26.72

Table 2. Density, Excess Molar Volume, and Apparent Molar Volume for Aqueous Solutions of Propanoic Acid from T = (293.15 to 308.15) K

	T/K = 293.15			T/K = 298.15		
x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}
0.40007	1.023224	−1.13073	74.80	1.018882	−1.13830	74.80
0.37008	1.024092	−1.11113	74.91	1.019954	−1.12197	74.91
0.33298	1.024969	−1.07610	75.08	1.020738	−1.07781	75.06
0.30426	1.025417	−1.03887	75.23	1.021279	−1.03923	75.20
0.27550	1.026192	−1.01057	75.43	1.021743	−0.99641	75.37
0.24852	1.026514	−0.96956	75.64	1.022214	−0.95602	75.57
0.23182	1.026542	−0.93868	75.79	1.022482	−0.92964	75.71
0.19472	1.025779	−0.84725	76.14	1.022210	−0.84532	76.06
0.17102	1.025100	−0.78537	76.43	1.021280	−0.77204	76.30
0.12803	1.020753	−0.60243	76.85	1.017923	−0.60454	76.75
0.10191	1.017459	−0.48569	77.15	1.014230	−0.47207	76.92
0.08690	1.014630	−0.40182	77.21	1.011949	−0.39687	77.02
0.05436	1.008586	−0.23654	77.37	1.006508	−0.23565	77.19
0.03268	1.004502	−0.13647	77.49	1.002954	−0.13980	77.39
0.01457	1.000943	−0.05713	77.50	0.999590	−0.05848	77.21
0.00000	0.998180			0.99701		

	T/K = 303.15			T/K = 308.15		
x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}
0.40007	1.014200	−1.11306	74.82	1.009369	−1.12480	74.86
0.37008	1.015501	−1.10338	74.93	1.010292	−1.09609	74.94
0.33298	1.016649	−1.06902	75.08	1.011571	−1.06129	75.08
0.30426	1.017047	−1.02257	75.20	1.012517	−1.03024	75.20
0.27550	1.017722	−0.98373	75.36	1.013104	−0.98236	75.34
0.24852	1.018124	−0.93825	75.53	1.013784	−0.94072	75.52
0.23182	1.018394	−0.91013	75.67	1.014033	−0.90879	75.63
0.19472	1.018257	−0.82539	75.99	1.01409	−0.82228	75.93
0.17102	1.017580	−0.75585	76.22	1.013888	−0.76050	76.17
0.12803	1.014772	−0.59553	76.65	1.011703	−0.60489	76.60
0.10191	1.011410	−0.46602	76.82	1.008859	−0.48015	76.80
0.08690	1.009329	−0.39237	76.91	1.006911	−0.40482	76.89
0.05436	1.004630	−0.23994	77.15	1.002082	−0.23944	76.99
0.03268	1.001283	−0.14301	77.36	0.998859	−0.13839	77.05
0.01457	0.998064	−0.05991	77.00	0.996207	−0.06364	77.37
0.00000	0.99561	0.00000		0.99400	0.00000	

Table 3. Density, Excess Molar Volume, and Apparent Molar Volume for Aqueous Solutions of Butanoic Acid from $T = (293.15$ to $308.15)$ K

	T/K = 293.15			T/K = 298.15		
x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}
0.17672	0.997159	−0.61893	88.07	0.993560	−0.61113	87.97
0.14429	0.998822	−0.54880	88.23	0.995314	−0.53720	88.08
0.13404	0.999591	−0.53175	88.32	0.996110	−0.51894	88.16
0.11715	1.000267	−0.48577	88.44	0.996947	−0.47366	88.26
0.09948	1.001124	−0.43937	88.64	0.997910	−0.42614	88.41
0.09004	1.001614	−0.41458	88.78	0.998480	−0.40115	88.53
0.08723	1.002343	−0.42110	88.94	0.999134	−0.40517	88.66
0.06959	1.002830	−0.36223	89.28	0.999900	−0.34861	88.96
0.05825	1.003608	−0.33393	89.74	1.000768	−0.31950	89.36
0.04995	1.004133	−0.31135	90.19	1.001392	−0.29694	89.77
0.04522	1.004299	−0.29555	90.48	1.001656	−0.28199	90.03
0.03727	1.004491	−0.26679	91.09	1.001942	−0.25290	90.56
0.03346	1.004382	−0.24888	91.38	1.001932	−0.23593	90.82
0.02141	1.003379	−0.17999	92.43	1.001030	−0.16539	91.58
0.01655	1.002547	−0.14454	92.83	1.000290	−0.13015	91.78
0.00000	0.99818	0.00000		0.99701	0.00000	

	T/K = 303.15			T/K = 308.15		
x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}
0.17672	0.989960	−0.60638	87.91	0.986448	−0.60820	87.89
0.14429	0.991798	−0.52883	87.98	0.988322	−0.52516	87.91
0.13404	0.992633	−0.50941	88.04	0.989313	−0.50822	87.98
0.11715	0.993629	−0.46495	88.12	0.990416	−0.46287	88.04
0.09948	0.994696	−0.41641	88.24	0.991514	−0.41108	88.12
0.09004	0.995238	−0.38858	88.32	0.991962	−0.37883	88.15
0.08723	0.995793	−0.38962	88.42	0.992853	−0.38766	88.31
0.06959	0.996960	−0.33845	88.72	0.994109	−0.33414	88.56
0.05825	0.997922	−0.30859	89.06	0.995178	−0.30387	88.88
0.04995	0.998638	−0.28611	89.43	0.995991	−0.28126	89.22
0.04522	0.999009	−0.27206	89.69	0.996460	−0.26805	89.48
0.03727	0.999384	−0.24269	90.15	0.996930	−0.23854	89.91
0.03346	0.999466	−0.22668	90.40	0.997108	−0.22323	90.16
0.02141	0.998673	−0.15457	90.92	0.996413	−0.14953	90.53
0.01655	0.998026	−0.11975	90.99	0.995860	−0.11486	90.54
0	0.99561	0.00000		0.994	0.00000	

Table 4. Density, Excess Molar Volume, and Apparent Molar Volume for Aqueous Solutions of Pentanoic Acid from $T = (293.15$ to $308.15)$ K

	T/K = 293.15			T/K = 298.15		
x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}
0.00350	0.998691	−0.03192	104.76	0.997431	−0.03170	104.43
0.00305	0.998634	−0.02797	104.82	0.997402	−0.02808	104.58
0.00289	0.998615	−0.02659	104.85	0.997369	−0.02638	104.51
0.00271	0.998581	−0.02479	104.81	0.997347	−0.02473	104.52
0.00250	0.998560	−0.02302	104.89	0.997327	−0.02289	104.57
0.00228	0.998539	−0.02125	104.98	0.997307	−0.02106	104.63
0.00222	0.998517	−0.02044	104.89	0.997296	−0.02038	104.59
0.00205	0.998497	−0.01901	104.93	0.997286	−0.01910	104.70

Table 4. Continued

	T/K = 293.15			T/K = 298.15		
x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}
0.00195	0.998490	−0.01821	105.02	0.997276	−0.01821	104.74
0.00180	0.998466	−0.01683	105.01	0.997253	−0.01679	104.71
0.00148	0.998428	−0.01407	105.17	0.997229	−0.01415	104.95
0.00143	0.998418	−0.01356	105.16	0.997215	−0.01354	104.87
0.00106	0.998358	−0.01008	105.19	0.997177	−0.01031	105.13
0.00060	0.998307	−0.00619	105.96	0.997135	−0.00641	106.03
0.00043	0.998279	−0.00457	106.32	0.997117	−0.00489	106.79
0.00015	0.998240	−0.00204	109.48	0.997075	−0.00219	110.23

	T/K = 303.15			T/K = 308.15		
x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}
0.00350	0.995935	−0.02944	104.10	0.994225	−0.03074	103.76
0.00305	0.995907	−0.02592	104.18	0.994211	−0.02707	103.85
0.00289	0.995889	−0.02451	104.17	0.994194	−0.02554	103.81
0.00271	0.995877	−0.02307	104.21	0.994191	−0.02410	103.88
0.00250	0.995860	−0.02132	104.24	0.994177	−0.02222	103.89
0.00228	0.995843	−0.01957	104.27	0.994163	−0.02033	103.90
0.00222	0.995827	−0.01884	104.20	0.994155	−0.01970	103.87
0.00205	0.995828	−0.01776	104.35	0.994137	−0.01812	103.81
0.00195	0.995824	−0.01699	104.42	0.994154	−0.01764	104.03
0.00180	0.995809	−0.01573	104.43	0.994127	−0.01603	103.88
0.00148	0.995788	−0.01320	104.60	0.994120	−0.01348	104.07
0.00143	0.995774	−0.01260	104.51	0.994117	−0.01303	104.09
0.00106	0.995773	−0.01010	105.21	0.994102	−0.00994	104.35
0.00060	0.995720	−0.00605	105.74	0.994089	−0.00622	105.29
0.00043	0.995682	−0.00420	105.47	0.994069	−0.00453	105.52
0.00015	0.995668	−0.00205	109.54	0.994066	−0.00233	110.71

Table 5. Density, Excess Molar Volume, and Apparent Molar Volume for Aqueous Solutions of Hexanoic Acid from T = (293.15 to 308.15) K

	T/K = 293.15			T/K = 298.15		
x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}
0.00148	0.998273	−0.03192	104.76	0.997071	−0.03170	104.43
0.00139	0.998269	−0.02797	104.82	0.997068	−0.02808	104.58
0.00132	0.998268	−0.02659	104.85	0.997067	−0.02638	104.51
0.00122	0.998266	−0.02479	104.81	0.997062	−0.02473	104.52
0.00109	0.998258	−0.02302	104.89	0.997063	−0.02289	104.57
0.00104	0.998251	−0.02125	104.98	0.997059	−0.02106	104.63
0.00093	0.998252	−0.02044	104.89	0.997059	−0.02038	104.59
0.00086	0.998244	−0.01901	104.93	0.997058	−0.01910	104.70
0.00077	0.998246	−0.01821	105.02	0.997056	−0.01821	104.74
0.00069	0.998244	−0.01683	105.01	0.997053	−0.01679	104.71
0.00063	0.998245	−0.01407	105.17	0.997056	−0.01415	104.95
0.00057	0.998240	−0.01356	105.16	0.997053	−0.01354	104.87
0.00046	0.998234	−0.01008	105.19	0.997052	−0.01031	105.13
0.00036	0.998225	−0.00619	105.96	0.997050	−0.00641	106.03
0.00032	0.998226	−0.00457	106.32	0.997049	−0.00489	106.79
0.00019	0.998217	−0.00204	109.48	0.997045	−0.00219	110.23

	T/K = 303.15			T/K = 308.15		
x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}
0.00350	0.99594	−0.02944	104.10	0.99423	−0.03074	103.76
0.00305	0.99591	−0.02592	104.18	0.99421	−0.02707	103.85

Table 5. Continued

	T/K = 303.15			T/K = 308.15		
x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ϕ_V/cm^3·mol^{-1}
0.00289	0.99589	−0.02451	104.17	0.99419	−0.02554	103.81
0.00271	0.99588	−0.02307	104.21	0.99419	−0.02410	103.88
0.00250	0.99586	−0.02132	104.24	0.99418	−0.02222	103.89
0.00228	0.99584	−0.01957	104.27	0.99416	−0.02033	103.90
0.00222	0.99583	−0.01884	104.20	0.99416	−0.01970	103.87
0.00205	0.99583	−0.01776	104.35	0.99414	−0.01812	103.81
0.00195	0.99582	−0.01699	104.42	0.99415	−0.01764	104.03
0.00180	0.99581	−0.01573	104.43	0.99413	−0.01603	103.88
0.00148	0.99579	−0.01320	104.60	0.99412	−0.01348	104.07
0.00143	0.99577	−0.01260	104.51	0.99412	−0.01303	104.09
0.00106	0.99577	−0.01010	105.21	0.99410	−0.00994	104.35
0.00060	0.99572	−0.00605	105.74	0.99409	−0.00622	105.29
0.00043	0.99568	−0.00420	105.47	0.99407	−0.00453	105.52
0.00015	0.99567	−0.00205	109.54	0.99407	−0.00233	110.71

Table 6. Coefficients of the Equation $y = ax^3 + bx^2 + cx + d$ for the Molar Apparent Volume vs Concentration for Aqueous Solutions of Propanoic, Butanoic, Pentanoic, and Hexanoic Acids

T/K	a/cm^3·kg^3·mol^{-4}	b/cm^3·kg^2·mol^{-3}	c/cm^3·kg·mol^{-2}	d/cm^3·mol^{-1}
		Propanoic Acid		
273.15	−142.09	112.86	−20.53	70.87
298.15	−124.56	98.83	−17.41	71.13
303.15	−105.04	83.39	−13.76	71.31
308.15	−129.78	99.83	−16.66	71.85
		Butanoic Acid		
273.15	1773.30	−776.07	122.19	81.20
298.15	1059.30	−524.90	93.46	82.87
303.15	552.60	−349.06	73.43	84.20
308.15	282.09	−258.15	63.42	85.09
		Pentanoic Acid		
273.15	0.00	0.00	168.69	98.97
298.15	0.00	0.00	199.79	99.43
303.15	0.00	0.00	211.54	100.05
308.15	0.00	0.00	122.56	101.01
		Hexanoic Acid		
273.15	0.00	0.00	774.03	114.00
298.15	0.00	0.00	637.40	114.73
303.15	0.00	0.00	1167.20	114.80
308.15	0.00	0.00	801.41	116.03

The apparent molar volumes ϕ_V were calculated from the equation

$$\phi_V = \frac{M_2}{\rho} + \left(\frac{1000(\rho_1 - \rho)}{m\rho\rho_1}\right) \qquad (2)$$

where m is the molality of the solute in the aqueous solution.

Tables 2−5 show the values for densities, excess volumes and apparent molar volumes of propanoic, butanoic, pentanoic, and hexanoic acids in aqueous solution as a function of acid mole fraction at (283.15, 288.15, 293.15, 298.15, and 303.15) K. The uncertainty in the determination of φ_V has been estimated to be of the order of (0.01 and 0.0005) cm^3·mol^{-1} for V^E. The estimated uncertainty was obtained from uncertainty equation obtained by propagation in the usual way.

Taking into account that the reported dissociation constants of the carboxylic acids considered in this study are very small and that the constants decrease with temperature, the small correction due to the contribution of the ionized species lies within the experimental uncertainty and the amount of dissociated acid can be considered negligible. Thus it is assumed that the acids can be treated as non electrolytes and no corrections are made for dissociation of carboxylic acids. This approach has been adopted by other authors such as Vong (1997), Estrada-Baltazar (2003), and Granados (2006). Apelblat studies the behavior of aqueous solutions of formic, acetic and propionic acid and states that in the concentration range investigated, which for propionic acid is $x_2 = 0.0053-0.9740$, the volume changes caused by ionization of carboxylic acids are too small to be considered in the analysis of excess volume. In later works with D,L-pyroglutamic and nicotinic acid (2005) and glutaric acid (2007), Apelblat assumes that considering that as concentration increases the degrees of dissociation are very small. The apparent molar volume at infinite dilution can be determined by linear extrapolation of the behavior the apparent molar volume as a function of molality.

Table 7. Partial Molar Volumes at Infinite Dilution for Aqueous Solutions of Propanoic, Butanoic, Pentanoic, and Hexanoic Acids from T = (293.15 to 308.15) K

	$\overline{V}_2^0$/cm^3·mol^{-1}			
T/K	propanoic acid	butanoic acid	pentanoic acid	hexanoic acid
293.15	70.87	82.90	98.99	114.00
298.15	71.13	83.02	99.43	114.71
	67.8[25] 67.9[6,8]	84.7[6] 84.6[8] 84.12[34]	100.5[8]	116.0[8]
303.15	71.31	85.52	100.05	114.84
308.13	71.85	86.31	101.01	116.14

No corrections were made for dissociation of carboxylic acids because reported dissociation constants are very small to have appreciable ionization and the small correction due to the contribution of the ionized species lies within the experimental uncertainties.[12] Besides the constants decrease with temperature so that the amount of dissociated acid can be considered negligible, thus it can be assumed that they can be treated as non electrolytes.[4,5,13,20−29]

The excess molar volumes reflect the nature of solute−solvent and solute−solute interactions. Their sign and magnitude have been interpreted as the result of three contributions:[30−32] (i) expansion due to hydrophobic interactions involving apolar chains that promote partial dehydration of the solvation layers, (ii) a small contraction effect due to free volume differences between unlike

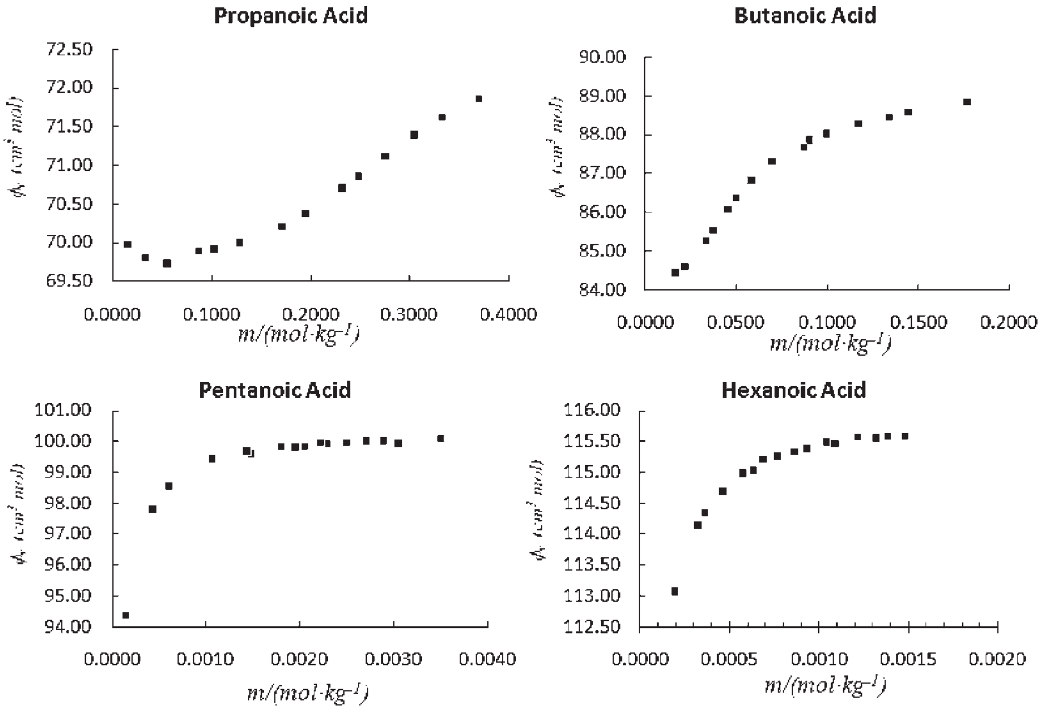

Figure 1. Partial molar volumes for propanoic, butanoic, pentanoic, and hexanoic acids at 298.15 K.

water and acid molecules, and (iii) contraction due to strong polar—polar interaction between carboxylic groups hydrated with water that can participate in hydrogen-bonding interactions.

The excess molar volumes are negative and their magnitude increases with concentration, According to this, the negative excess molar volumes obtained for the aqueous solutions of carboxylic acids can be attributed to dominant hydrogen bond interactions between acids and water.[4,13,33]

Apparent molar volumes of carboxylic acids show an important concentration dependence, In the dilute region, apparent molar volumes of propanoic acid decrease as mole fraction increases and a minimum is observed in the water-rich region at all the temperatures considered in this work. For butanoic, pentanoic and hexanoic acids apparent molar volumes increase as mole fraction increases, The dependence of the apparent molar volume on concentration at each temperature was fitted by least-squares to a polynomial equation to obtain by extrapolation the apparent molar volumes at infinite dilution which are equal to the limiting partial molar volumes $\overline{V}_2^0 = \overline{V}_2^0(\text{COOH}) + n\overline{V}_2^0(\text{CH}_2)$. The corresponding values of the parameters for the polynomic equations are reported in Table 6. The values of the limiting molar partial volume are showed in Table 7 together with literature values zwhen they are available, The differences observed in the limiting molar volumes of propanoic and butanoic acid can be attributed to the differences in the concentration range used in extrapolation and the resulting differences in least-squares fitting of experimental data and the behavior of the acids studied at high dilution.

The acids studied have a particular behavior that is shown in the Figure 1. The propanoic acid in a high dilute region has a change in the slope sign of the molar partial volume vs concentration that results in a minimum. This behavior is typical for mixed solutes, like alcohols and polyols.[27−29,32] The value for this minimum is lower for propanol than butanol and for the higher alcohols the minimum is not observed. For the organic acids, a similar behavior is found. The minimum is only observed for the propanoic acid and for the butanoic acid a large change in the slope is showed. For the pentanoic and hexanoic acids a minimum is not observed. The uncertainty for the molar partial volume is high for very dilute solutions of pentanoic and hexanoic acids due the increase in the uncertainty of the molality.

Several studies have established that the thermodynamic properties of organic compounds in water can be expressed in terms of the properties of the constituent groups in the molecule and different methods to calculate group contributions have been developed. The simpler approaches assume that that each methylene group interacts with the solvent independently of the other methylene groups and its contribution is independent of the polar or polar groups present. This simple model used to predict thermodynamic properties is based on the dependence of the property on the number of methylene groups and is frequently used specially with small organic molecules.[21] It assumes that the number of carbon atoms is approximately equivalent to the number of methylene groups and thus the partial molar volume at infinite dilution can be represented by eq 3. In order to analyze the effect of the length chain on the molar partial volume, this approach was used in this work.

$$\overline{V}_2^0 = \overline{V}_2^0(\text{COOH}) + n\overline{V}_2^0(\text{CH}_2) \tag{3}$$

To determine the volumetric contributions of the methylene and the carboxylic groups, the molar partial volumes at infinite dilution were correlated as function of the number of carbon atoms. The linear behavior obtained at all of the temperatures shows that the volumetric contribution of methylene groups is additive, The volumetric contribution of methylene and carboxylic groups do not

Table 8. Surface Tension for Aqueous Solutions of Propanoic Acid from $T = (293.15 \text{ to } 308.15)$ K

	$\sigma/\text{mN}\cdot\text{m}^{-1}$			
x_2	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15
0.18229	33.08	32.51	31.99	31.48
0.17102	33.15	32.76	32.14	31.35
0.14940	33.54	32.97	32.43	31.89
0.12803	34.18	33.65	32.78	31.97
0.10947	34.56	34.04	33.62	33.04
0.08690	35.30	34.71	34.12	33.53
0.07470	35.77	35.18	34.33	33.87
0.06602	36.43	35.73	34.82	33.91
0.05436	38.51	37.77	36.81	36.37
0.04550	40.07	39.50	38.89	38.28
0.03268	42.34	41.92	41.52	41.08
0.02075	46.78	46.22	45.47	44.82
0.01457	50.17	49.33	49.11	48.66
0.00861	53.61	52.32	51.87	51.24
0.00000	72.58	71.81	71.04	70.23

Table 9. Surface Tension for Aqueous Solutions of Butanoic Acid from $T = (293.15 \text{ to } 308.15)$ K

	$\sigma/\text{mN}\cdot\text{m}^{-1}$			
x_2	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15
0.17672	28.14	28.01	27.78	27.51
0.14284	28.27	28.09	27.81	27.53
0.13404	28.29	28.12	27.86	27.6
0.11469	28.46	28.2	27.84	27.59
0.09948	28.48	28.25	27.91	27.66
0.08723	28.49	28.25	27.94	27.73
0.05825	28.51	28.32	28.02	27.79
0.04522	28.62	28.46	28.22	28.06
0.03346	29.11	28.85	28.55	28.42
0.01655	34.22	33.96	33.62	33.29
0.01432	36.18	35.57	34.88	34.22
0.01274	38.14	37.14	36.14	35.14
0.00998	40.1	39.94	39.78	39.62
0.00903	42.06	41.18	40.83	40.42
0.00655	44.82	44.39	42.76	42.13
0.00475	50.98	50.45	50.22	49.39
0.00000	72.58	71.81	71.04	70.23

show a clear dependence on temperature in the range considered in this work. The average value for the contribution for the CH_2 group is 15.02 $\text{cm}^3\cdot\text{mol}^{-1}$ and for the COOH group is 24.72 $\text{cm}^3\cdot\text{mol}^{-1}$. Cabani[22] established a contribution of 20.34 $\text{cm}^3\cdot\text{mol}^{-1}$ for the carboxylic group and 15.80 for the methylene group, whereas Hoiland[8] reports a value of 25.9 $\text{cm}^3\cdot\text{mol}^{-1}$ assuming that the methylene contribution is 16.0 $\text{cm}^3\cdot\text{mol}^{-1}$. In previous works it was found that the methylene contribution depends of the nature of the polar group attached to the chain and this could explain the differences between the reported values.[24,25,34−39]

The limiting partial molar volumes for the acids show a slight increase with temperature and the behavior can be represented fitting the data to a second order polynomial equation. The influence of temperature shows a similar trend that the behavior found by Cibulka and Hnedkovsky,[40] who use the volumetric contributions to estimate the partial molar volumes at infinite dilution in water for various solutes at different temperatures.

Table 10. Surface Tension for Aqueous Solutions of Pentanoic Acid from $T = (293.15 \text{ to } 308.15)$ K

	$\sigma/\text{mN}\cdot\text{m}^{-1}$			
x_2	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15
0.00349	36.32	35.62	35.44	35.19
0.00326	37.25	36.48	35.63	35.75
0.00299	38.42	37.70	37.43	37.14
0.00283	38.97	38.07	37.43	36.72
0.00259	39.97	39.26	39.07	38.81
0.00219	41.68	41.11	40.87	40.73
0.00196	42.91	42.61	41.62	41.85
0.00173	44.52	44.11	43.91	43.66
0.00150	45.82	45.23	44.66	44.08
0.00121	48.03	47.42	46.71	46.12
0.00099	50.53	50.13	49.73	49.32
0.00083	52.56	52.37	52.04	51.83
0.00056	56.21	56.03	55.54	55.14
0.00048	57.47	57.26	56.96	56.72
0.00016	63.91	64.74	63.43	62.70
0	72.58	71.81	71.04	70.23

Table 11. Surface Tension for Aqueous Solutions of Hexanoic Acid from $T = 293.15$ to 308.15 K

	$\sigma/\text{mN}\cdot\text{m}^{-1}$			
x_2	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15
0.00115	33.55	32.94	32.57	32.11
0.00110	33.79	33.17	32.82	32.46
0.00091	35.66	35.23	35.04	34.96
0.00084	36.64	36.28	36.21	36.07
0.00077	37.72	37.36	37.36	37.20
0.00069	39.19	39.02	38.98	38.89
0.00062	40.57	40.60	40.57	40.45
0.00051	42.83	42.62	42.44	42.60
0.00046	44.03	43.54	43.22	43.67
0.00037	46.55	46.17	45.98	46.29
0.00032	48.25	47.98	47.93	48.06
0.00023	52.29	51.80	51.81	51.94
0.00016	56.60	56.02	56.09	56.02
0.00008	63.26	62.69	62.67	62.16
0	72.58	71.81	71.04	70.23

Tables 8−11 show the dependence of surface tension of acids with molar fraction at (283.15, 288.15, 293.15, 298.15, 303.15, and 308.15) K. The surface tensions of the pure components obtained in this work behave well according to literature data.[17,33] As expected, the change in surface tension with concentration is nonlinear. In all cases the surface tension shows a rapid decrease as concentration increases which is the typical behavior observed for aqueous solutions of surface-active solutes.

The negative slope of the surface tension curves becomes more pronounced as hydrocarbon chain length increases, reflecting the increasing hydrophobic character of the solute.

The determination of the surface activity requires the activity coefficients of the acids, which are not available in literature. However, the limiting slope of surface tension with concentration has been related with the hydrophobic or hydrophilic behavior of the solutes.[41] In this study, the limiting slopes are negative for the acids considered in this study, indicating that in all cases the surface excess is positive and is higher as the chain length increases.

The surface tension of the aqueous solutions of the carboxylic acids decrease with temperature. For the propanoic and butanoic acids, this variation is linear; for the pentanoic and hexanoic acid, it has a second order dependence with temperature.

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