

# Volumetric Properties of Some Aliphatic Mono- and Dicarboxylic Acids in Water at 298.15 K

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**Abstract** The apparent molar volumes,  $V_\phi$ , of two series of homologous aliphatic carboxylic acids,  $\text{H}(\text{CH}_2)_n\text{COOH}$  [ $n = 0-5$ ] and  $(\text{CH}_2)_n(\text{COOH})_2$  [ $n = 0-5$ ], were determined in dilute aqueous solutions by density measurements at  $T = 298.15$  K. Densities were measured using a vibrating-tube densimeter (DMA 5000, Anton Paar, Austria) at  $T = 298.15$  K. These results were used to calculate the apparent molar volumes of each solute over the concentration range  $0.0050 \leq m/(\text{mol}\cdot\text{kg}^{-1}) \leq 0.3000$ . Values of the apparent molar volumes of undissociated acids  $V_{\phi(u)}^0$  were also calculated. The variation of  $V_{\phi(u)}^0$  was determined as a function of the aliphatic chain length of the studied carboxylic acids.

**Keywords** Carboxylic acid · Apparent molar volume · Water

## 1 Introduction

In this paper, we report results on the effect of increasing the size of the hydrophobic side chain of homologous aliphatic mono- and dicarboxylic acids on the physicochemical properties of these electrolytes in aqueous solutions, which is part of a wider study [1–4]. Knowledge of the thermodynamic properties of aqueous solutions of acids and bases and their reactions provides many useful insights with theoretical and practical applications. The carboxylic acids are used in the production of polyester polyols, polyamides, ester plasticizers, in the synthesis of pharmaceuticals, and have applications as corrosion inhibitors, surfactants and metal finishing compounds.

Volumetric studies of carboxylic acids provide great help in characterizing the structure and properties of their solutions, which are important in understanding the nature of action of these bioactive molecules and their interactions in the human body. A review of the literature

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shows that only a few authors have attempted to determine values of the apparent molar volumes of carboxylic acids in water [5–15].

Therefore, the purpose of the present study is to determine the density, apparent molar volume, and apparent molar volume at infinite dilution, and the limiting partial molar volume of carboxylic acids of the types  $\text{H}(\text{CH}_2)_n\text{COOH}$  [ $n = 0\text{--}5$ ] and  $(\text{CH}_2)_n(\text{COOH})_2$  [ $n = 0\text{--}5$ ] in water at  $T = 298.15$  K.

## 2 Experimental

### 2.1 Materials

The sources of chemicals and methods of purification were described in our previous papers [1–4]. Water was passed through an ion exchanger and then distilled. The specific conductivity of this purified water was less than  $0.8 \times 10^{-6} \Omega^{-1}\cdot\text{cm}^{-1}$ .

### 2.2 Apparatus and Procedures

The densities of solutions were measured using a vibrating-tube digital densimeter (Model DMA 5000, Anton Paar, Austria) with a precision of  $\pm 1 \times 10^{-6} \text{ g}\cdot\text{cm}^{-3}$  and an accuracy of  $\pm 5 \times 10^{-6} \text{ g}\cdot\text{cm}^{-3}$ . The temperature of the water around the densimeter cell was controlled to  $\pm 0.001$  K. The densimeter was calibrated periodically with dry air and pure water.

The solutions were prepared by adding weighed amounts of the concentrated stock solutions into a cell containing a known amount of pure water. All of the solutions were prepared by mass using an analytical balance (Sartorius RC 210D) with an uncertainty of  $\pm 1 \times 10^{-5}$  g.

## 3 Results and Discussion

The densities ( $\rho$ ) of solutions of the studied carboxylic acids at  $T = 298.15$  K are given as a function of concentration in Table 1. From the measured densities the apparent molar volumes ( $V_\phi$ ), were calculated by using the following equation:

$$V_\phi = \left[ \frac{1000(\rho_0 - \rho)}{m\rho_0\rho} \right] + \frac{M_w}{\rho} \quad (1)$$

where  $V_\phi$  is the apparent molar volume,  $m$  is the molality,  $M_w$  is the molecular weight of the carboxylic acid, and  $\rho_0$  and  $\rho$  are the densities of water and of the solution, respectively. The values of  $V_\phi$  as a function of concentration of electrolyte are summarized in Tables 1a and 1b.

The dependence  $V_\phi$  as the function of the concentration for strong electrolytes can be described by the Redlich-Rosenfeld equation [16, 17]:

$$V_\phi = V_\phi^0 + S_v\sqrt{c} + b_v c \quad (2)$$

where:  $V_\phi^0$  is the limiting apparent molar volume,  $S_v$  is the theoretical limiting slope,  $b_v$  is an empirical constant determined from experimental results, and  $c$  is the molar concentration. The value of  $S_v$  for aqueous solutions of 1:1 and 2:1 type electrolytes at 298.15 K are equal, respectively, to 1.868 and  $9.706 \text{ cm}^3\cdot\text{dm}^{3/2}\cdot\text{mol}^{-3/2}$  [16, 17].

**Table 1a** Apparent molar volumes ( $V_\phi$ ), molarity ( $c$ ), molality ( $m$ ), and degree of dissociation  $\beta$  of solutions of aliphatic monocarboxylic acids in water at 298.15 K

$c$ (mol·dm <sup>-3</sup> )	$m$ (mol·kg <sup>-1</sup> )	$\rho$ (g·cm <sup>-3</sup> )	$V_\phi$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$\beta$
Formic acid				
0	0	0.997043	–	–
0.04001	0.04018	0.997443	36.13	0.069265
0.05934	0.05965	0.997626	36.31	0.057574
0.07897	0.07943	0.997815	36.36	0.050337
0.09912	0.09977	0.998011	36.37	0.045230
0.11912	0.11999	0.998202	36.40	0.041478
0.13871	0.13983	0.998392	36.41	0.038606
0.15870	0.16010	0.998586	36.41	0.036233
0.17791	0.17960	0.998773	36.41	0.034334
0.19774	0.19976	0.998964	36.42	0.032666
0.21773	0.22012	0.999156	36.43	0.031217
0.23719	0.23996	0.999344	36.43	0.029984
0.25697	0.26016	0.999534	36.44	0.028874
0.27623	0.27986	0.999720	36.44	0.027907
0.29592	0.30003	0.999908	36.45	0.027017
Acetic acid				
0	0	0.997043	–	–
0.03980	0.04001	0.997377	51.81	0.021468
0.05943	0.05980	0.997524	52.11	0.017664
0.07906	0.07962	0.997678	52.17	0.015375
0.09902	0.09983	0.997834	52.22	0.013780
0.11871	0.11980	0.997990	52.23	0.012617
0.13861	0.14004	0.998146	52.25	0.011701
0.15818	0.15998	0.998298	52.27	0.010974
0.17771	0.17990	0.998448	52.30	0.010371
0.19750	0.20015	0.998598	52.33	0.009852
0.21659	0.21972	0.998744	52.35	0.009421
0.23635	0.24001	0.998897	52.36	0.009030
0.25562	0.25984	0.999046	52.37	0.008693
0.27513	0.27996	0.999204	52.35	0.008388
0.29452	0.29999	0.999350	52.37	0.008116
Propionic acid				
0	0	0.997043	–	–
0.01960	0.01969	0.997183	67.13	0.026508
0.03861	0.03883	0.997301	67.60	0.019051
0.05960	0.06002	0.997430	67.78	0.015417
0.07863	0.07928	0.997549	67.84	0.013469
0.09916	0.10013	0.997679	67.86	0.012028
0.11867	0.11999	0.997802	67.88	0.011020
0.13815	0.13987	0.997925	67.89	0.010233
0.15772	0.15989	0.998048	67.91	0.009594
0.17740	0.18009	0.998172	67.91	0.009060
0.19695	0.20021	0.998295	67.92	0.008611
0.21632	0.22020	0.998417	67.93	0.008227
0.23803	0.24266	0.998554	67.93	0.007853

**Table 1a** (Continued)

$c$ (mol·dm <sup>-3</sup> )	$m$ (mol·kg <sup>-1</sup> )	$\rho$ (g·cm <sup>-3</sup> )	$V_\phi$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$\beta$
0.25480	0.26006	0.998660	67.93	0.007597
0.27383	0.27985	0.998780	67.94	0.007336
0.29315	0.30000	0.998901	67.94	0.007097
Butyric acid				
0	0	0.997043	–	–
0.02007	0.02016	0.997139	83.58	0.027770
0.03996	0.04022	0.997211	84.16	0.019860
0.05961	0.06009	0.997282	84.36	0.016344
0.07975	0.08054	0.997360	84.39	0.014183
0.09938	0.10052	0.997434	84.43	0.012742
0.11867	0.12024	0.997503	84.48	0.011688
0.13674	0.13876	0.997568	84.52	0.010909
0.15732	0.15992	0.997649	84.51	0.010189
0.17659	0.17981	0.997721	84.52	0.009632
0.19737	0.20132	0.997801	84.52	0.009125
0.21605	0.22073	0.997873	84.52	0.008733
0.23475	0.24022	0.997937	84.55	0.008388
0.25384	0.26018	0.998010	84.55	0.008075
0.27263	0.27990	0.998079	84.56	0.007800
0.29155	0.29981	0.998151	84.56	0.007550
Valeric acid				
0	0	0.997043	–	–
0.00958	0.00962	0.997068	99.81	0.038048
0.02009	0.02019	0.997091	100.03	0.026554
0.03875	0.03901	0.997127	100.25	0.019280
0.05948	0.06001	0.997169	100.30	0.015654
0.07909	0.07996	0.997208	100.34	0.013615
0.09857	0.09985	0.997246	100.37	0.012230
0.11831	0.12008	0.997284	100.39	0.011190
0.13770	0.14004	0.997318	100.43	0.010392
0.15682	0.15979	0.997358	100.42	0.009755
0.17636	0.18006	0.997397	100.42	0.009213
0.19555	0.20004	0.997433	100.43	0.008761
Caproic acid				
0	0	0.997043	–	–
0.01666	0.01674	0.997061	115.41	0.027743
0.03330	0.03352	0.997073	115.59	0.019793
0.04980	0.05023	0.997084	115.67	0.016264
0.06634	0.06705	0.997095	115.71	0.014140
0.08249	0.08353	0.997105	115.74	0.012714
0.11704	0.11899	0.997127	115.78	0.010720
0.13867	0.14135	0.997140	115.80	0.009869
0.15595	0.15928	0.997150	115.81	0.009320
0.17646	0.18067	0.997163	115.82	0.008776
0.19500	0.20009	0.997175	115.82	0.008359

**Table 1b** Apparent molar volumes ( $V_\phi$ ), molarity ( $c$ ), molality ( $m$ ), and fractions ( $\beta_1$ ,  $\beta_2$ ) of solutions of aliphatic dicarboxylic acids in water, at 298.15 K

$c$ (mol·dm <sup>-3</sup> )	$m$ (mol·kg <sup>-1</sup> )	$\rho$ (g·cm <sup>-3</sup> )	$V_\phi$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$\beta_1$	$\beta_2$
Oxalic acid					
0	0	0.997043	–	–	–
0.05957	0.05992	0.999610	47.08	0.656714	0.001886
0.07941	0.07994	1.000434	47.47	0.614268	0.001518
0.09898	0.09975	1.001251	47.66	0.581477	0.001288
0.11899	0.12003	1.002095	47.72	0.554155	0.001124
0.13875	0.14009	1.002926	47.78	0.531559	0.001004
0.15782	0.15950	1.003726	47.83	0.512800	0.000914
0.17794	0.18000	1.004567	47.89	0.495534	0.000837
0.19752	0.19999	1.005384	47.95	0.480701	0.000776
0.21687	0.21980	1.006189	48.00	0.467581	0.000726
0.23499	0.23838	1.006946	48.03	0.456455	0.000685
0.25588	0.25984	1.007816	48.08	0.444791	0.000644
0.27549	0.28002	1.008633	48.11	0.434806	0.000611
0.29467	0.29980	1.009433	48.13	0.425811	0.000582
Malonic acid					
0	0	0.997043	–	–	–
0.04062	0.04085	0.998583	66.34	0.183795	0.000072
0.05955	0.05996	0.999298	66.39	0.155864	0.000051
0.07936	0.08001	1.000048	66.39	0.137529	0.000039
0.09895	0.09990	1.000790	66.39	0.124836	0.000032
0.11862	0.11992	1.001534	66.40	0.115252	0.000028
0.13818	0.13988	1.002274	66.40	0.107732	0.000024
0.15753	0.15967	1.003001	66.44	0.101657	0.000021
0.17750	0.18015	1.003758	66.43	0.096412	0.000019
0.19687	0.20007	1.004489	66.44	0.092075	0.000018
0.21632	0.22013	1.005226	66.43	0.088297	0.000016
0.23565	0.24011	1.005954	66.44	0.084996	0.000015
0.25483	0.25998	1.006687	66.41	0.082085	0.000014
0.27387	0.27977	1.007416	66.38	0.079491	0.000013
0.29327	0.29997	1.008161	66.35	0.077102	0.000013
Succinic acid					
0	0	0.997043	–	–	–
0.03959	0.03984	0.998460	82.54	0.097455	0.000077
0.05948	0.05995	0.999171	82.55	0.080841	0.000052
0.07932	0.08008	0.999877	82.60	0.070783	0.000040
0.09893	0.10004	1.000575	82.63	0.063908	0.000033
0.11856	0.12009	1.001272	82.66	0.058768	0.000028
0.13815	0.14016	1.001968	82.68	0.054746	0.000024
0.15727	0.15981	1.002646	82.70	0.051551	0.000022
0.17688	0.18004	1.003343	82.71	0.048815	0.000019
0.19628	0.20010	1.004031	82.73	0.046514	0.000018
0.21554	0.22010	1.004714	82.74	0.044536	0.000016
0.23463	0.23998	1.005393	82.74	0.042815	0.000015

**Table 1b** (Continued)

$c$ (mol·dm <sup>-3</sup> )	$m$ (mol·kg <sup>-1</sup> )	$\rho$ (g·cm <sup>-3</sup> )	$V_\phi$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$\beta_1$	$\beta_2$
0.25383	0.26004	1.006076	82.74	0.041280	0.000014
0.27292	0.28004	1.006754	82.75	0.039915	0.000013
0.29258	0.30072	1.007454	82.75	0.038646	0.000012
Glutaric acid					
0	0	0.997043	–	–	–
0.03932	0.03959	0.998375	98.53	0.034677	0.000113
0.05905	0.05957	0.999036	98.65	0.028529	0.000077
0.07893	0.07978	0.999702	98.71	0.024817	0.000058
0.09846	0.09972	1.000352	98.80	0.022315	0.000047
0.11824	0.11999	1.001014	98.82	0.020435	0.000040
0.13745	0.13975	1.001662	98.80	0.019009	0.000034
0.15696	0.15990	1.002310	98.85	0.017834	0.000030
0.17602	0.17966	1.002948	98.86	0.016879	0.000027
0.19558	0.20003	1.003599	98.89	0.016045	0.000025
0.21497	0.22028	1.004250	98.88	0.015334	0.000023
0.23393	0.24016	1.004877	98.92	0.014724	0.000021
0.25295	0.26020	1.005509	98.94	0.014181	0.000019
0.27163	0.27994	1.006135	98.93	0.013705	0.000018
0.29034	0.29980	1.006760	98.94	0.013274	0.000017
Adipic acid					
0	0	0.997043	–	–	–
0.02011	0.02021	0.997666	115.49	0.043184	0.000214
0.03967	0.03997	0.998272	115.51	0.031173	0.000112
0.05942	0.06002	0.998879	115.59	0.025665	0.000076
0.07910	0.08013	0.999483	115.66	0.022357	0.000058
0.09881	0.10028	1.000086	115.70	0.020090	0.000047
0.11795	0.11998	1.000666	115.78	0.018447	0.000040
0.13739	0.14009	1.001259	115.81	0.017140	0.000034
0.15669	0.16013	1.001849	115.83	0.016089	0.000030
0.17548	0.17975	1.002420	115.86	0.015235	0.000027
0.18411	0.18879	1.002680	115.88	0.014887	0.000026
Pimelic acid					
0	0	0.997043	–	–	–
0.02994	0.03014	0.997915	131.42	0.032812	0.000144
0.04949	0.04996	0.998482	131.49	0.025759	0.000089
0.06910	0.06994	0.999047	131.55	0.021929	0.000065
0.08963	0.09097	0.999637	131.61	0.019342	0.000050
0.09845	0.10004	0.999890	131.64	0.018486	0.000046
0.11788	0.12009	1.000450	131.65	0.016948	0.000039
0.12756	0.13013	1.000727	131.68	0.016314	0.000036
0.14689	0.15024	1.001283	131.70	0.015241	0.000032
0.16581	0.17002	1.001823	131.73	0.014376	0.000028
0.17539	0.18009	1.002095	131.76	0.013991	0.000027
0.18469	0.18988	1.002361	131.76	0.013647	0.000025
0.19440	0.20013	1.002640	131.77	0.013314	0.000024

In the case of weak electrolytes such as mono and dicarboxylic acids, Eq. 2 must be modified. For the studied monocarboxylic acids (HA) Eq. 2 adopts the following form:

$$V_\phi = \beta V_{HA(i)} + (1 - \beta) V_{HA(u)} \tag{3}$$

where:  $V_{HA(i)}$  is the apparent molar volume of the acid in its dissociated form, and  $V_{HA(u)}$  is the apparent molar volume of the acid in the undissociated form.

$$V_{HA(i)} = V_{HA(i)}^0 + S_v \sqrt{\beta c} + b_{vi} \beta c \tag{4}$$

$$V_{HA(u)} = V_{HA(u)}^0 + b_{vu} (1 - \beta) c \tag{5}$$

The values of  $\beta$  can be calculated by optimization using:

$$K_A = \frac{1}{K_D} = \frac{1 - \beta}{\beta^2 c y_{\pm}^2}, \quad \ln y_{\pm} = \frac{-A_{DH} \sqrt{\beta c}}{1 + R_y B_{DH} \sqrt{\beta c}}$$

where  $y_{\pm}$  is the molarity-based activity coefficient,  $A_{DH}$  and  $B_{DH}$  are coefficients defined by the Debye-Hückel limiting law; for water at 298.15 K,  $A_{DH} = 1.1727 \text{ mol}^{-1/2} \cdot \text{dm}^{3/2}$  and  $B_{DH} = 0.3286 \times 10^8 \text{ mol}^{-1/2} \cdot \text{dm}^{3/2} \cdot \text{cm}^{-1}$ . The values of  $R_y$  were assumed to be equal to  $q = 3.58 \times 10^{-8} \text{ cm}$  (the Bjerrum distance). The  $\beta$  coefficients can be determined from values of the association constants  $K_A$  reported in the literature [18]. Calculated values of  $\beta$  are collected in Table 1a.

Equation 3, after taking into consideration Eqs. 4 and 5, assumes the following form:

$$V_\phi = \beta (V_{HA(i)}^0 + S_{v(i)} \sqrt{\beta c} + b_{v(i)} \beta c) + (1 - \beta) \{V_{HA(u)}^0 + b_{v(u)} (1 - \beta) c\} \tag{6a}$$

A similar approach was applied by King [5] for the analysis of the apparent molar volumes of monocarboxylic acids. However, King transformed Eq. 6 into the following form:

$$V_\phi - \beta \Delta V^0 - \beta S_{v(i)} \sqrt{\beta c} = V_{HA(u)}^0 + b_{v(i)} \beta^2 c + b_{v(u)} (1 - \beta)^2 c \tag{6b}$$

where

$$\Delta V^0 = V_{HA(i)}^0 - V_{HA(u)}^0$$

King [5] assumed that component terms  $\beta \Delta V^0$ ,  $\beta S_{v(i)} \sqrt{\beta c}$  and  $b_{v(i)} \beta^2 c$  are small enough to treat the left side of the Eq. 6b as being linearly dependent on  $(1 - \beta)^2 c$ . On the basis of this assumption, he estimated values of  $V_{HA(u)}^0$  and  $b_{v(u)}$  for formic, acetic and butyric acids. A similar method was applied by Høiland [6] for estimation of  $V_{H_2A(u)}^0$  and  $b_{v(u)}$  for dicarboxylic acids  $(\text{CH}_2)_n(\text{COOH})_2$  with  $n = 0-5$ .

A different procedure proposed by King [5] has been applied in this work. Assuming that:  $S_{v(i)} = 1.868$  [16, 17]:

$$V_{HA(i)} = V_{NaA(i)}^0 + (V_{H^+}^0 - V_{Na^+}^0) \\ V_{H^+}^0 - V_{Na^+}^0 = 1.2 \text{ cm}^3 \cdot \text{mol}^{-1} \tag{6}$$

Then Eq. 6a assumes the following form:

$$V_\phi = \beta V_{HA(i)}^0 + 1.868 \beta \sqrt{\beta c} + b_{v(i)} \beta^2 c + (1 - \beta) V_{HA(u)}^0 + b_{v(u)} (1 - \beta)^2 c \tag{7}$$

Values of  $V_{\text{NaA}}^0$  were reported in our previous work [19] whereas  $V_{\text{HA}(u)}^0$ ,  $b_{vu}$  and  $b_{v(i)}$  of Eq. 7 are unknowns.

The dependences of the separate terms of Eq. 7 on the concentration are shown for formic ( $n = 0$ ) and caproic ( $n = 5$ ) acids in Figs. 1a and 1b, and the numerical values of these terms are presented in Tables 3a and 3b. The  $\beta^2 cb_{v(i)}$  term was omitted since its value is smaller than the experimental error.

As shown at Fig. 1 and Table 3, the values of the apparent molar volumes of the acids are practically affected only by the  $\beta V_{\text{HA}(i)}^0$  and  $(1 - \beta)V_{\text{HA}(u)}^0$  terms. The impact of  $(1 - \beta)^2 cb_{v(u)}$  is definitely smaller. In the case of the higher monocarboxylic acids for which the values of  $\beta$  are smaller, this conclusion is more certain.

The values  $V_{\text{HA}(u)}^0$  and  $b_{v(u)}$  were obtained using a nonlinear least-squares method and they are reported in Table 2. The  $V_{\phi(u)}^0$  results given in Table 2 for monocarboxylic acids correlate well with results reported by King [5] and Hamman [8]. Only for formic acid, and to a lesser degree for acetic acid, is this correlation worse. Values for valeric ( $n = 4$ ) and caproic ( $n = 5$ ) acids have been determined for the first time.

The dependence of  $V_{\phi}^0 = f(n)$  is shown in Fig. 2. This plot is linear with a slope equal to 15.88 for  $n = 0-5$ . For  $n = 0$  there is no alkyl group in the studied molecule and there is only one  $-\text{CH}_3$  group for  $n = 1$ . Therefore, on the basis of the observed dependence  $V_{\phi}^0 = f(n)$  for  $n = 2-5$ , we estimate that the value of the partial molar volume of the  $-\text{CH}_2-$  group is  $16.01 \text{ cm}^3 \cdot \text{mol}^{-1}$ . This value is very close to that estimated by other authors [20–22],  $V_{\text{CH}_2}^0 = 15.9-16.0 \text{ cm}^3 \cdot \text{mol}^{-1}$ , and by us [19] ( $V_{\text{CH}_2}^0 = 15.6 \text{ cm}^3 \cdot \text{mol}^{-1}$ ) from studies on the apparent molar volumes of sodium salts of the monocarboxylic acids.

Equation 2 for dicarboxylic acids can be rewritten the following form:

$$V_{\phi} = \beta_1 V_{\text{H}_2\text{A}(i1)} + \beta_2 V_{\text{H}_2\text{A}(i2)} + (1 - \beta_1 - \beta_2) V_{\text{H}_2\text{A}(u)} \quad (8)$$

where:  $\beta_1$  is the fraction of dissociated acid occurring in the form  $\text{H}^+ + \text{HA}^-$ ,  $\beta_2$  is the fraction of dissociated electrolyte occurring in the form  $2\text{H}^+ + \text{A}^{2-}$ , and  $1 - \beta_1 - \beta_2$  is the fraction of the electrolyte in its undissociated form.

Values of  $\beta_1$  and  $\beta_2$  can be determined by optimization methods from the equation:

$$K_{\text{A1}} = \frac{1}{K_{\text{D1}}} = \frac{1 - \beta_1 - \beta_2}{\beta_1(\beta_1 + 2\beta_2)c y_{\pm}^2} \quad (9)$$

$$K_{\text{A2}} = \frac{1}{K_{\text{D2}}} = \frac{\beta_1}{\beta_2(\beta_1 + 2\beta_2)c y_{\text{A}^{2-}}} \quad (10)$$

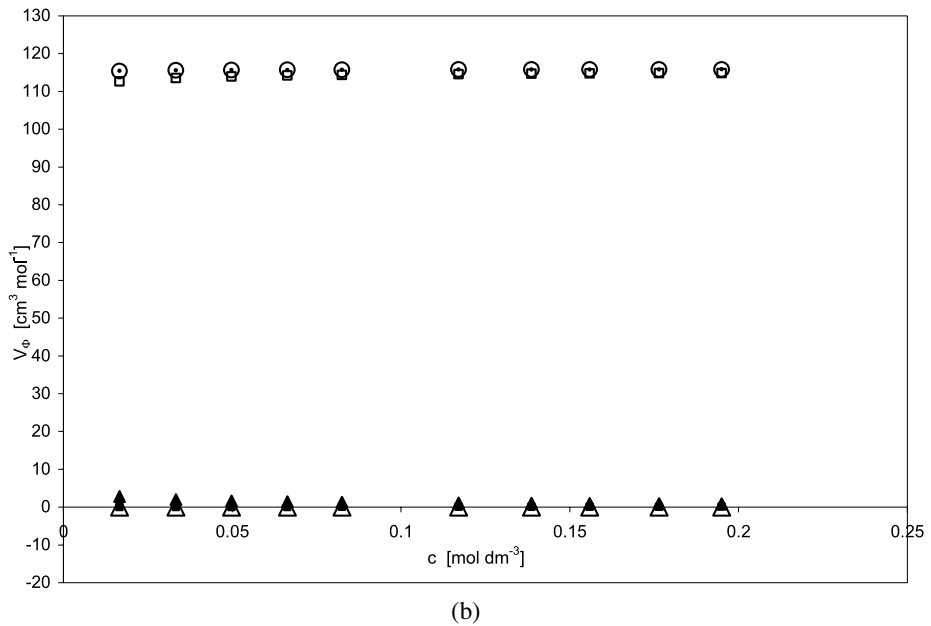
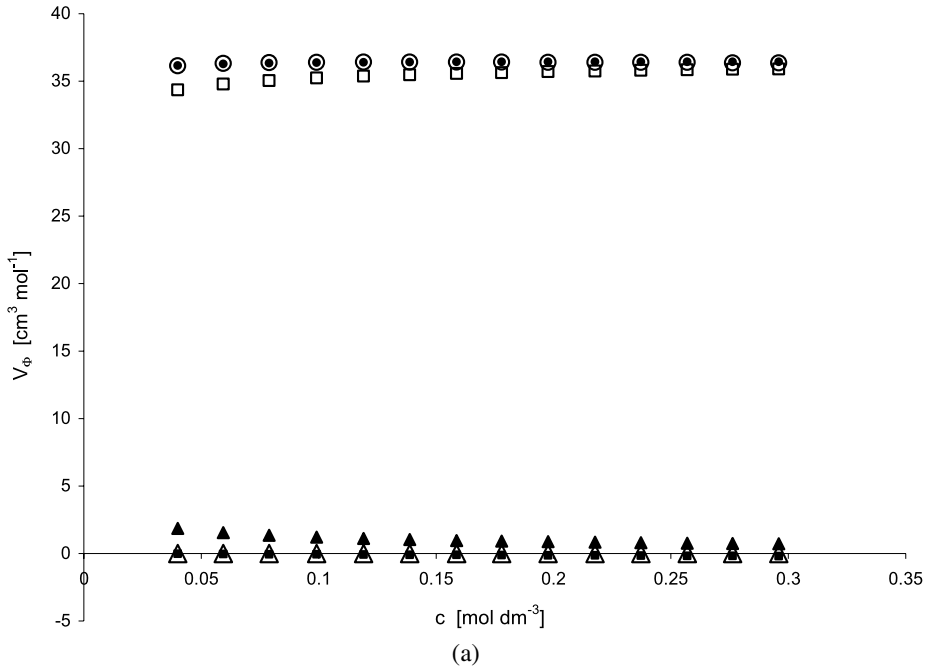
$$\ln y_{\pm} = \frac{-A_{\text{DH}}\sqrt{I}}{1 + R_y B_{\text{DH}}\sqrt{I}} \quad (11)$$

$$\ln y_{\text{A}^{2-}} = \frac{-4A_{\text{DH}}\sqrt{I}}{1 + R_y B_{\text{DH}}\sqrt{I}} \quad (12)$$

The symbols  $K_{\text{D}}$  and  $K_{\text{A}}$  indicate, respectively, dissociation and association equilibrium constants.

As in the case of monocarboxylic acids we assumed that  $R_y = q$ , and dissociation constants were taken from Ref. [18].





**Fig. 1** The experimental (○) and calculated (●) values of  $V_\phi$  and the values of component terms of Eq. 7: (□)  $(1 - \beta)V_{HA(u)}^0$ ; (▲)  $\beta V_{HA(i)}^0$ ; (■)  $(1 - \beta)^2 cb_{v(u)}$ ; (△)  $\beta S_{v(i)} \sqrt{\beta c}$  for formic acid (a), for caproic acid (b)

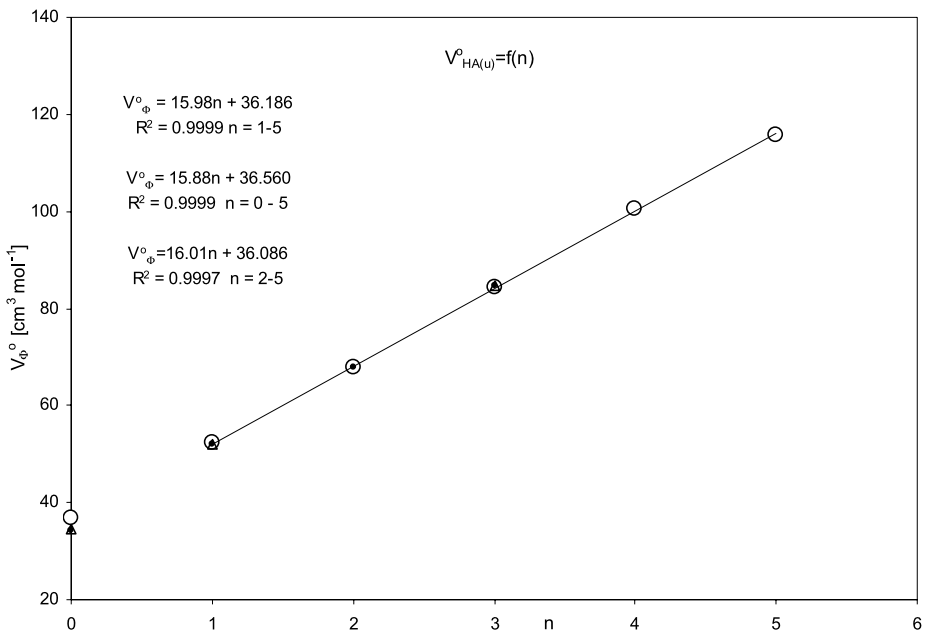
**Table 2** Values of  $V_{\phi}^0$  at  $T = 298.15$  K for the studied carboxylic acids in the undissociated form

H(CH <sub>2</sub> ) <sub>n</sub> COOH			HOOC(CH <sub>2</sub> ) <sub>n</sub> COOH		
<i>n</i>	$V_{\phi}^0$	$V_{\phi}^0$ lit.	<i>n</i>	$V_{\phi}^0$	$V_{\phi}^0$ lit.
0	36.90	34.1 [8]; 34.69 [5]	0	53.36	49.12 [6]; 49.43 [9]
1	52.22	52.0 [8]; 51.93 [5]	1	68.11	67.22 [6]; 66.82 [9]
2	67.82	67.9 [8]	2	83.64	82.94 [6]; 82.44 [9]
3	84.38	84.7 [8]; 84.61 [5]	3	98.99	99.14 [6]; 98.98 [9]
4	100.44	–	4	115.87	115.66 [6]; 115.15 [9]
5	115.83	–	5	131.81	131.93 [6]

**Table 3** The experimental and calculated values of  $V_{\phi}$  and the values of chosen component terms of Eq. 7:  $(1 - \beta)V_{\text{HA}(u)}^0$ ,  $\beta V_{\text{HA}(i)}^0$ ,  $(1 - \beta)^2 cb_{v(u)}$ , and  $\beta S_{v(i)} \sqrt{\beta c}$ 

<i>c</i> (mol·dm <sup>-3</sup> )	$V_{\phi}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V_{\phi}$ , calculated (cm <sup>3</sup> ·mol <sup>-1</sup> )	$(1 - \beta)V_{\text{HA}(u)}^0$	$\beta V_{\text{HA}(i)}^0$	$(1 - \beta)^2 cb_{v(u)}$
(a) Formic acid					
0.04001	36.13	36.16	34.35	1.85	-0.02
0.05934	36.31	36.27	34.78	1.54	-0.04
0.07897	36.36	36.33	35.05	1.35	-0.05
0.09912	36.37	36.37	35.24	1.21	-0.06
0.11912	36.40	36.40	35.37	1.11	-0.08
0.13871	36.41	36.41	35.48	1.03	-0.09
0.15870	36.41	36.43	35.57	0.97	-0.10
0.17791	36.41	36.43	35.64	0.92	-0.12
0.19774	36.42	36.44	35.70	0.87	-0.13
0.21773	36.43	36.44	35.75	0.84	-0.14
0.23719	36.43	36.44	35.80	0.80	-0.16
0.25697	36.44	36.44	35.84	0.77	-0.17
0.27623	36.44	36.43	35.87	0.75	-0.18
0.29592	36.45	36.43	35.91	0.72	-0.20
(b) Caproic acid					
0.01666	115.41	115.46	112.62	2.83	0.01
0.03330	115.59	115.58	113.54	2.02	0.02
0.04980	115.67	115.64	113.95	1.66	0.03
0.06634	115.71	115.68	114.20	1.44	0.04
0.08249	115.74	115.71	114.36	1.30	0.05
0.11704	115.78	115.76	114.60	1.09	0.07
0.13867	115.80	115.79	114.69	1.01	0.09
0.15595	115.81	115.81	114.76	0.95	0.10
0.17646	115.82	115.83	114.82	0.90	0.11
0.19500	115.82	115.84	114.87	0.85	0.12

The values of term  $\beta S_{v(i)} \sqrt{\beta c}$  are smaller than 0.01



**Fig. 2** The dependence of the limiting partial volume of undissociated acids ( $V_{\phi}^0_{(HA,u)}$ ) on the number of carbon atoms ( $n$ ) in the molecules of monocarboxylic acids  $H(CH_2)_nCOOH$ : (○) experimental values; (●) literature [8]; (△) literature [5]

Values of  $\beta_1$  and  $\beta_2$  are reported in Table 1b. The molar volumes  $V_{H_2A(i1)}$ ,  $V_{H_2A(i2)}$ , and  $V_{H_2A(u)}$  can be expressed by the following equations:

$$V_{H_2A(i1)} = V_{H_2A(i1)}^0 + S_{vH_2A(i1)}\sqrt{\beta_1 c} + b_{v(i1)}\beta_1 c \tag{13}$$

$$V_{H_2A(i2)} = V_{H_2A(i2)}^0 + S_{vH_2A(i2)}\sqrt{\beta_2 c} + b_{v(i2)}\beta_2 c \tag{14}$$

$$V_{H_2A(i1)} = V_{H_2A(u)}^0 + b_{v(u)}(1 - \beta_1 - \beta_2) \tag{15}$$

Therefore, Eq. 7 can be rewritten in the following form:

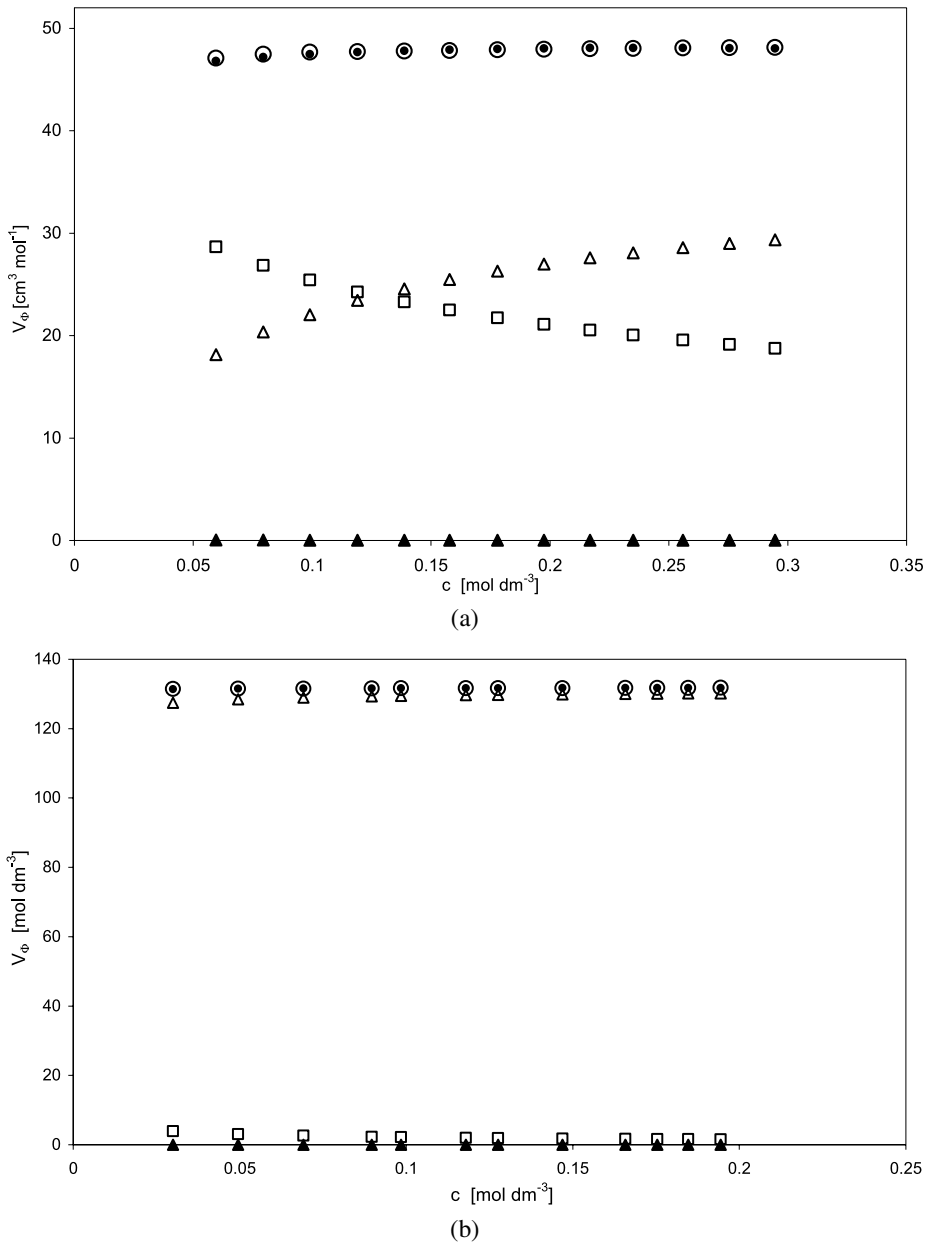
$$V_{\phi} = \beta_1(V_{H_2A(i)}^0 + 1.868\sqrt{\beta_1 c} + b_{v(i1)}\beta_1 c) + \beta_2(V_{H_2A(i2)}^0 + 9.706\sqrt{\beta_2 c} + b_{v(i2)}\beta_2 c)\beta_1(V_{H_2A(u)}^0 + b_{v(u)}(1 - \beta_1 - \beta_2)) \tag{16}$$

Values of  $V_{H_2A(i1)}^0$  were calculated using the following equation:

$$V_{H_2A(i1)}^0 = V_{NaHA}^0 + (V_{H^+}^0 - V_{Na^+}^0)$$

Value of  $V_{NaHA}^0$ , obtained from studies of the apparent molar volumes of monosodium salts of dicarboxylic acids were used these calculations [23]. The value of  $V_{H_2A(i2)}^0$  was calculated similarly:

$$V_{H_2A(i2)}^0 = V_{Na_2A}^0 + 2(V_{H^+}^0 - V_{Na^+}^0)$$



**Fig. 3** The experimental (○) and calculated values (●) of  $V_\phi$  and the values of terms of Eq. 7: (□)  $\beta_1 V_{H_2A(i1)}^0$ ; (▲)  $\beta_2 V_{H_2A(i2)}^0$ ; (△)  $(1 - \beta_1 - \beta_2) V_{H_2A(u)}^0$  for oxalic acid (a), for pimelic acid (b)

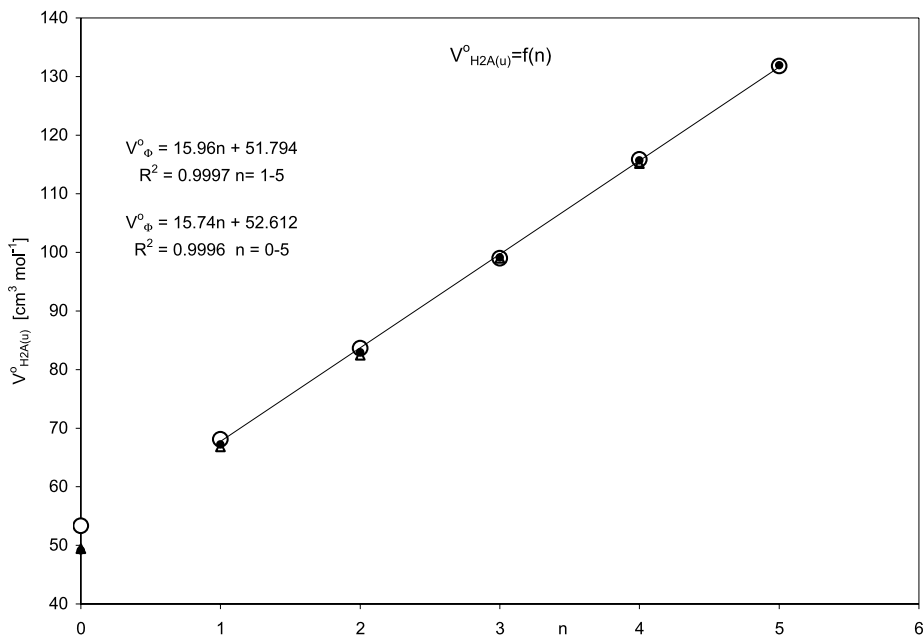
using the values of  $V_{Na_2HA}^0$  reported in our earlier work [19]. The values of component terms:  $\beta_1 V_{H_2A(i1)}^0$ ,  $\beta_2 V_{H_2A(i2)}^0$  as well as values of  $\beta_1 1.868\sqrt{\beta_1 c}$ , and  $\beta_2 9.706\sqrt{\beta_2 c}$  are known. Values of  $b_{v(i1)}$ ,  $b_{v(i2)}$ ,  $b_{v(u)}$  and  $V_{H_2A(u)}^0$  remain unknowns in Eq. 16.

**Table 4** The experimental and calculated values  $V_\phi$  and the values of chosen components of Eq. 7:  $\beta_1 V_{\text{H}_2\text{A}(i1)}^0$ ,  $\beta_2 V_{\text{H}_2\text{A}(i2)}^0$ , and  $(1 - \beta_1 - \beta_2) V_{\text{H}_2\text{A}(u)}^0$ 

$c$ (mol·dm <sup>-3</sup> )	$V_\phi$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V_\phi$ , calculated (cm <sup>3</sup> ·mol <sup>-1</sup> )	$(1 - \beta_1 - \beta_2) V_{\text{H}_2\text{A}(u)}^0$	$\beta_1 V_{\text{H}_2\text{A}(i1)}^0$	$\beta_2 V_{\text{H}_2\text{A}(i2)}^0$
(a) Oxalic acid					
0.05957	47.08	46.80	18.13	28.67	0.049
0.07941	47.47	47.19	20.35	26.84	0.040
0.09898	47.66	47.46	22.04	25.44	0.034
0.11899	47.72	47.66	23.43	24.26	0.030
0.13875	47.78	47.81	24.55	23.29	0.026
0.15782	47.83	47.91	25.47	22.48	0.024
0.17794	47.89	47.99	26.29	21.74	0.022
0.19752	47.95	48.04	26.99	21.10	0.020
0.21687	48.00	48.06	27.58	20.54	0.019
0.23499	48.03	48.08	28.08	20.06	0.018
0.25588	48.08	48.07	28.58	19.56	0.017
0.27549	48.11	48.06	29.00	19.13	0.016
0.29467	48.13	48.03	29.36	18.74	0.015
(b) Pimelic acid					
0.02994	131.42	131.39	127.48	3.89	0.015
0.04949	131.49	131.50	128.43	3.06	0.009
0.06910	131.55	131.56	128.95	2.60	0.007
0.08963	131.61	131.61	129.31	2.30	0.005
0.09845	131.64	131.63	129.43	2.19	0.005
0.11788	131.65	131.67	129.65	2.01	0.004
0.12756	131.68	131.68	129.74	1.94	0.004
0.14689	131.70	131.71	129.90	1.81	0.003
0.16581	131.73	131.73	130.03	1.71	0.003
0.17539	131.76	131.75	130.08	1.66	0.003
0.18469	131.76	131.76	130.14	1.62	0.003
0.19440	131.77	131.77	130.19	1.58	0.002

The component terms of Eq. 16 linked with  $b_{v(i1)}$ ,  $b_{v(i2)}$  as  $\beta_1^2 b_{v(i1)} c$  and  $\beta_2^2 b_{v(i2)} c$ , are in general neglected since they are small in comparison to the values of  $V_\phi$ . An exception occurs in the case of oxalic acid where the  $\beta_1^2 b_{v(i1)} c$  term of the equation has values within 0.03–0.04. Therefore, values  $b_{v(i1)}$  accepted for oxalic acid have been set equal to the analogous values for HCOO–COONa [23]. This approximation seems to be better than the assumption that  $b_{v(i1)} = 0$ .

Figures 3a and 3b show the concentration dependences of the individual terms of Eq. 16. As is seen at Fig. 3a and Table 4a for oxalic acid, values of  $\beta_1 V_{\text{H}_2\text{A}(i1)}^0$  are comparable with the term representing the undissociated portion of the acid  $(1 - \beta_1 - \beta_2) V_{\text{H}_2\text{A}(u)}^0$  over the studied concentration range. For pimelic acid (Fig. 3b and Table 4b), the contribution of the  $\beta_1 V_{\text{H}_2\text{A}(i1)}^0$  term to  $V_\phi$  is small. It results of course from the fact that oxalic acid is more



**Fig. 4** The dependence of the limiting partial volume of undissociated acids ( $V_{H_2A(u)}^0$ ) as a function of the number of carbon atoms ( $n$ ) in the molecules of dicarboxylic acids  $HOOC(CH_2)_nCOOH$ : (○) experimental values; (●) literature [6]; (△) literature [9]

dissociated. Values for the  $\beta_2 V_{H_2A(i2)}^0$  term for the studied acids are comparable to or much less than the errors of  $V_{\phi}$  (oxalic acid).

While choosing the method for determining the value of  $V_{H_2A(u)}^0$  for dicarboxylic acids  $(CH_2)_n(COOH)_2$ , it is necessary to take into account the distinct increase of the value of  $\beta_1$  (and thereby the contribution of the component term  $\beta_1 V_{H_2A(i1)}^0$ ) when  $n = 0$  (and for  $n = 1, 2$ ). Values of  $V_{H_2A(u)}^0$  determined by the nonlinear least-squares method are reported in Table 2.

It is observed that for carboxylic acids with  $n = 3-5$ , consistency among the results of Høiland [6], Sipkes [9], and our results are good, for  $n = 2$  it is slightly worse, whereas for  $n = 0$  (oxalic acid) the divergence reaches approximately  $4 \text{ cm}^3 \cdot \text{mol}^{-1}$ . Høiland omitted the second dissociation step in Eq. 16 as quantitatively inessential and, after examining the King's method, he presented Eq. 16 in the alternative form:

$$V_{\phi}'' = V_{\phi} - \beta_1(\Delta V_1) - \beta_1 1.868\sqrt{\beta_1 c} = V_{H_2A(u)}^0 + (1 + \beta_1)^2 b_{v(u)} c \quad (17)$$

where:

$$\Delta V_1 = V_{H_2A(i1)}^0 - V_{H_2A(u)}^0$$

According to Høiland [6], the left side of the Eq. 17 differs slightly from  $V_{\phi}$ . Høiland evaluated these differences as being small ( $0.1-0.5 \text{ cm}^3 \cdot \text{mol}^{-1}$ ) for dissociation constants ranging from  $10^{-4}$  to  $10^{-5}$ . However, for oxalic acid such differences cannot be neglected.

It is also worth mentioning that according to Høiland, values of  $V_{\phi(u)}^0$  and  $\Delta V_i$  could be burdened with a large error. After taking into account the value  $\Delta V_1 = -6.7 \text{ cm}^3 \cdot \text{mol}^{-1}$  estimated by Høiland and values  $\beta_1$  for this acid included in Table 1, it is clear that differences

between values of  $V_{\phi}'' - V_{\phi}$  must be considerably greater since only the  $\beta_1 \Delta V_1$  term reaches a value of a few  $\text{cm}^3 \cdot \text{mol}^{-1}$ . The same concern also applies to the acids  $(\text{CH}_2)_n(\text{COOH})_2$  with  $n = 1$  and  $n = 2$ , although to a smaller degree. The above mentioned comments may be useful for explaining the differences between values of  $V_{\text{H}_2\text{A}(u)}^0$  estimated in the present work and Høiland's results.

Similar comments apply to the consistency with Sijpkens [9] data. Sijpkens treated  $\Delta V_1$  as the chosen parameter in Eq. 17 and obtained its value using least-squares analysis. However, values  $\Delta V_1$  that he determined differ considerably from the results reported by Høiland. Such differences are particularly noticeable for acids ( $n > 0$ ) for which the approximations used by Høiland are very justified.

The dependence of  $V_{\phi, \text{H}_2\text{A}(u)}^0$  on the number of carbon atoms ( $n$ ) in the hydrocarbon chain for  $n = 1$ –5 is shown in Fig. 4. It is linear indicating that the molar volume of the  $-\text{CH}_2-$  group is approximately equal to  $15.96 \text{ cm}^3 \cdot \text{mol}^{-1}$ . This value is very close to the value obtained in the present work for monocarboxylic acids.

Knowledge of the value  $\text{H}_2\text{A}_{(i1)}$  [23] is necessary for a detailed analysis of the apparent molar volumes of a dicarboxylic acid. This value can be determined from results of studies of monosodium salts ( $\text{NaHA}$ ) of dicarboxylic acids after taking into account all equilibria occurring in the solutions. This will be a subject of our future studies.

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