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Volumetric properties of aqueous solutions of malonic acid

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ABSTRACT

Densities of aqueous solutions of malonic acid in the (0.01–1.0) mole·kg^{-1} concentration range were measured at 5 K intervals, from 278.15 K to 343.15 K. These densities served to determine the apparent molar volumes. Changes of densities with temperature permitted evaluation of the cubic expansion coefficients and the derivatives of isobaric heat capacities with respect to pressure which are interrelated with the second derivatives of volume with respect to temperature. Thermal dependence of volumetric properties of aqueous solutions of malonic acid is examined in terms of changes in the structure of water.

1. Introduction

Malonic acid (propanedioic acid) is the second acid, after oxalic acid, in the series of important aliphatic dicarboxylic acids. The acid is produced in a large quantities being one of constituents or intermediates in fabrication of many different materials. Malonic acid is precursor in fatty acid biosynthesis, condenses with urea to form barbituric acid, and it is used in synthesis of cinnamic acid. Malonic acid is useful in preparation of fragrances, polyamides, adhesives, lubricants, polyesters and biodegradable thermoplastics. Its role is vital in coating, flavour and fragrances, pharmaceutical and food industries (in the control of acidity in drags and foods).

Similarly to other dicarboxylic acids and their neutral and acidic salts, the volumetric properties of malonic acid aqueous solutions have been investigated a number times [1–4], but only at one temperature, at 298.15 K. In these investigations, measured densities as a function of concentration, have been primarily used to determine the molar volume of malonate anions at infinite dilution. Due to the two-step dissociation of the acid, this is a rather complex experimental and computational problem. The main difficulty arises from fact that quantities derived from malonic acid, acidic malonates and neutral malonates solutions should be consistent. A number of molecular models were proposed to solve this problem and they are discussed in a detail by Bald and his co-workers [5–10] and by others [11–13]. Since in the present investigation, the main emphasis is directed to volumetric properties as a function of temperature, the changes associated with concentration are not explicitly considered. It should be mentioned that there is consistency between results coming from different investigations, but also observed is a rather large scattering of the apparent molar volumes in dilute solutions of malonic acid (Fig. 1). This requires an additional re-examination of the molar volume values when more accurate densities in dilute solutions will be available in the future. This can be carried out only if the verification of measured densities will be performed by using different experimental techniques than by oscillation tube densimeters. Evidently, these considerations are less important for concentrated solutions of malonic acid, and when derived thermodynamic quantities are analysed as a function of temperature.

In this investigation, continuing our previous determinations of volumetric properties in systems with important organic acids [14–17] (for electrical conductivity of malonic acid see [18,19]), a number of aqueous solutions of malonic acid are considered. Using determined densities, the apparent molar volumes, the cubic expansion coefficients, the second derivatives of volume with respect to temperature (they are interrelated with changes of heat capacities with respect to pressure p) were evaluated as a function of concentration m (from 0.01 mol·kg^{-1} to 1.0 mol·kg^{-1}) and temperature T (from 278.15 K to 343.15 K). The thermal dependence of derived thermodynamic quantities is discussed in terms of changes in the structure of water when malonic acid is dissolved in it.

2. Experimental

Malonic acid $HOOCCH_2COOH$, (mass fraction >0.990) was from Riedel-de Haen and was used without further purification.

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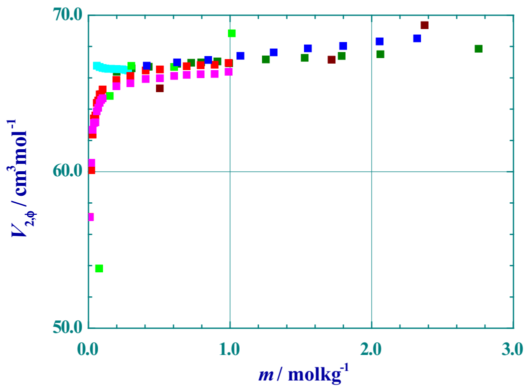

Fig. 1. The apparent molar volume of malonic acid as a function of concentration at constant temperature *T*. *T* = 293.15 K, 🟩 – [1]; 🟦 – [4]; 🟪 – this work; *T* = 298.15 K, 🟩 – [2]; 🟫 – [3]; 🟦 – [8]; 🟥 – this work.

Degassed solutions (malonic acid + double distilled water) were prepared by weight, and introduced into a Mettler-Toledo DA 310M densimeter. Calibration of the densimeter, and the applied procedures were similar to these described in our previous investigations. The thermal control and stability is estimated to be better than ±0.01 K. The accuracy of our density measurements is about ±0.00002 g·cm^{-3} and is discussed in a detail in [20]. Considering the effect of impurities, and the nature of density determinations in oscillation tube densimeters, the values of uncertainties reported in Table 1 should be regarded only as approximate values.

3. Results and discussion

Determined densities $d(m,T)$ of aqueous solutions of malonic acid at given molality m, within the T = (278.15–343.15) K temperature range. are presented in Table 1. As has been shown by the first author, with a sufficient accuracy, it is possible to correlate densities with the following two adjustable parameter equation [21]

$$d(T;\mathrm{w}) = \frac{d_{\mathrm{H_2O}}(T)}{1 - d_{\mathrm{H_2O}}(T)[\mathrm{Aw} + \mathrm{Bw}^2]} \qquad (1)$$

where w is the mass fraction of dissolved reagent and A and B are the temperature independent parameters. In the case of malonic acid, considering all available literature references for density (334 experimental densities in the 278.15 K to 334.15 K tempera-

Table 1
Densities of aqueous solutions of malonic acid as a function of concentration and temperature.

m/m^0	$d(m,T)$/g·cm^{-3}						
Θ	5	10	15	20	25	30	35
0.00000	0.99999	0.99973	0.99913	0.99823	0.99705	0.99568	0.99406
0.01001	1.00048	1.00021	0.99961	0.99870	0.99752	0.99614	0.99451
0.02001	1.00091	1.00062	1.00003	0.99910	0.99793	0.99653	0.99489
0.03000	1.00131	1.00100	1.00040	0.99947	0.99830	0.99690	0.99523
0.03962	1.00173	1.00140	1.00079	0.99985	0.99866	0.99728	0.99560
0.04998	1.00216	1.00183	1.00121	1.00027	0.99907	0.99766	0.99600
0.05936	1.00253	1.00219	1.00157	1.00061	0.99940	0.99799	0.99633
0.06926	1.00293	1.00258	1.00195	1.00099	0.99978	0.99837	0.99669
0.07949	1.00334	1.00298	1.00234	1.00137	1.00015	0.99872	0.99706
0.08906	1.00373	1.00336	1.00271	1.00173	1.00052	0.99908	0.99740
0.09935	1.00411	1.00373	1.00307	1.00212	1.00089	0.99945	0.99774
0.1984	1.00806	1.00760	1.00687	1.00580	1.00455	1.00305	1.00128
0.2977	1.01196	1.01140	1.01060	1.00946	1.00815	1.00660	1.00477
0.4040	1.01600	1.01536	1.01447	1.01326	1.01188	1.01027	1.00839
0.5055	1.01985	1.01912	1.01815	1.01689	1.01545	1.01379	1.01184
0.6055	1.02351	1.02271	1.02167	1.02035	1.01885	1.01714	1.01515
0.6936	1.02673	1.02586	1.02477	1.02339	1.02185	1.02008	1.01807
0.7926	1.03029	1.02935	1.02819	1.02676	1.02516	1.02335	1.02129
0.8910	1.03382	1.03280	1.03158	1.03010	1.02844	1.02658	1.02447
0.9895	1.03716	1.03610	1.03482	1.03327	1.03158	1.02966	1.02751
Θ	40	45	50	55	60	65	70
0.00000	0.99224	0.99024	0.98807	0.98573	0.98324	0.98059	0.97781
0.01001	0.99267	0.99067	0.98848	0.98612	0.98363	0.98099	0.97822
0.02001	0.99303	0.99104	0.98885	0.98650	0.98401	0.98137	0.97859
0.03000	0.99337	0.99139	0.98919	0.98683	0.98434	0.98169	0.97890
0.03962	0.99374	0.99175	0.98954	0.98717	0.98468	0.98203	0.97924
0.04998	0.99412	0.99209	0.98992	0.98755	0.98505	0.98241	0.97960
0.05936	0.99445	0.99244	0.99024	0.98786	0.98536	0.98272	0.97992
0.06926	0.99480	0.99280	0.99058	0.98821	0.98569	0.98300	0.98022
0.07949	0.99516	0.99316	0.99094	0.98856	0.98605	0.98339	0.98058
0.08906	0.99551	0.99349	0.99126	0.98889	0.98637	0.98368	0.98090
0.09935	0.99586	0.99383	0.99163	0.98926	0.98672	0.98402	0.98118
0.1984	0.99932	0.99727	0.99500	0.99258	0.99002	0.98731	0.98449
0.2977	1.00276	1.00066	0.99836	0.99589	0.99331	0.99055	0.98771
0.4040	1.00640	1.00417	1.00182	0.99932	0.99678	0.99395	0.99105
0.5055	1.00990	1.00757	1.00517	1.00263	0.99991	0.99716	0.99429
0.6055	1.01317	1.01078	1.00836	1.00578	1.00310	1.00024	0.99739
0.6936	1.01602	1.01361	1.01115	1.00854	1.00581	1.00293	1.00021
0.7926	1.01925	1.01673	1.01423	1.01164	1.00899	1.00600	1.00297
0.8910	1.02241	1.01967	1.01735	1.01468	1.01189	1.00894	1.00593
0.9895	1.02539	1.02280	1.02022	1.01749	1.01463	1.01116	1.00849

m^0 = 1 mol·kg^{-1}; Θ = T/K – 273.15; P = 101.3 kPa.
Uncertainties U are: U(d) = 0.00002 g·cm^{-3}; U(T) = 0.01 K; U(m) = 0.0005 mol·kg^{-1}.