Methanesulfonic and Trichloroacetic Acids: Densities of Aqueous Solutions at 20°, 25°, and 35°C

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Density data are obtained for aqueous solutions of methanesulfonic and trichloroacetic acids at 20°, 25°, and 35°C through the whole concentration range. Apparent molal volumes at infinite dilution for the acids are calculated. Polynomials in molality and molarity are fitted to the density data.

Anhydrous trichloroacetic acid, CCl_3COOH, of purity 99.9% was obtained from Anachemia Ltd. Methanesulfonic acid, CH_3SO_3H ("White Label"), from Eastman Kodak was used. Methanesulfonic acid solutions were tested for sulfate impurity according to Clarke and Woodward (*3*); no sulfate contaminant was found. The purity of the acid was 99.7% by acid-base titration (*15*). Both acids were used without further purification. Aqueous solutions were prepared by weight dilution.

The densities of the acid solutions were measured by a digital density meter, Model DMA 10, manufactured by Anton Paar K.G., calibrated with dry air and distilled water of densities given in refs. *10* and *19*. The temperature was controlled to within ±0.01°C of that desired by a Gebruder Haake (Model FS) constant temperature circulator. The reproducibility of the measurements was about 5×10^{-5} g/ml.

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Results

The complete experimental density results for acids at the three temperatures with attendant m, C, and φ_v values are given in Tables I and II (deposited with the ACS Microfilm Depository Service). Molality values for trichloroacetic acid are from 0.019 to 61.72m, whereas for methanesulfonic acid they range from 0.044 to 75.5m at 20°C, to 226m at 25°C, and to 62.5m at 35°C. Molarity (C) values were calculated from the obtained density data, and apparent molal volumes were calculated according to Relations 1 and 2 given in refs. *12* and *13*.

$$\varphi_v = \frac{1000(d_0 - d)}{mdd_0} + \frac{M_2}{d} \quad (1)$$

$$\varphi_v = \frac{1000(d_0 - d)}{Cd_0} + \frac{M_2}{d_0} \quad (2)$$

Empirical polynomial forms 3 and 4 have been used to represent the

$$d = d_0 + \sum_i^k A_i m^i \quad (3)$$

$$d = d_0 + \sum_j^p B_j C^j \quad (4)$$

density-concentration relations for each system at each temperature. Such forms have previously (*7, 9, 14, 16*) been used and are useful for direct interpolation. Optimum fits using Equations 3 and 4 were obtained by increasing the

Table III. Results for Density Data Fitted to Equations 3 and 4[a]

°C	Upper limit of concn	A_1/A_6	A_2/A_7	A_3/A_8	A_4/A_9	A_5/A_{10}	SD[b]
		B_1/B_6	B_2/B_7	B_3/B_8	B_4/B_9	B_5/B_{10}	
				Trichloroacetic acid			
20	19m	0.816083−1[c]	−0.878876−2	0.538661−3	0.166602−5	−0.142807−5	
		−0.171263−7	0.270495−8	0.114446−9	−0.21431−11	−0.18460−12	4.61−4
	6.8M	0.815633−1	−0.174973−2	−0.596867−3	0.155939−3	−0.103589−4	2.69−4
25	61m	0.692641−1	−0.464437−2	0.168781−3	−0.296333−5	0.193406−7	5.60−3
	8.8M	0.814275−1	−0.223502−2	−0.564586−3	0.223926−3	−0.288845−4	
		0.151590−5	−0.233946−7				2.67−4
35	25m	0.787561−1	−0.836158−2	0.587829−3	−0.216890−4	0.311088−6	1.00−3
	7.3M	0.818709−1	−0.444132−2	0.523103−3	−0.261436−4		2.65−4
				Methanesulfonic acid			
20	16m	0.402399−1	−0.245352−2	0.967892−4	−0.169755−5		4.29−4
	9.2M	0.402939−1	−0.166123−3	−0.679064−4	0.427100−5		3.72−4
25	7m	0.414498−1	−0.381283−2	0.440691−3	−0.273328−4		4.83−4
	14M	0.404131−1	−0.610730−3	0.381672−4	−0.223173−6		7.48−4
35	39m	0.404801−1	−0.263248−2	0.128680−3	−0.434730−5	0.943242−7	
		−0.117384−8	0.63113−11				2.32−3
	11M	0.424175−1	−0.125871−2	0.100538−3	−0.430299−5		1.84−3

[a] d_0 values are those of Kell (*10*): d_0(20°C) = 0.99823; d_0(25°C) = 0.99707; d_0(35°C) = 0.99406. [b] SD = standard deviation. [c] 0.816083−5 = 0.816083×10^{-5}.

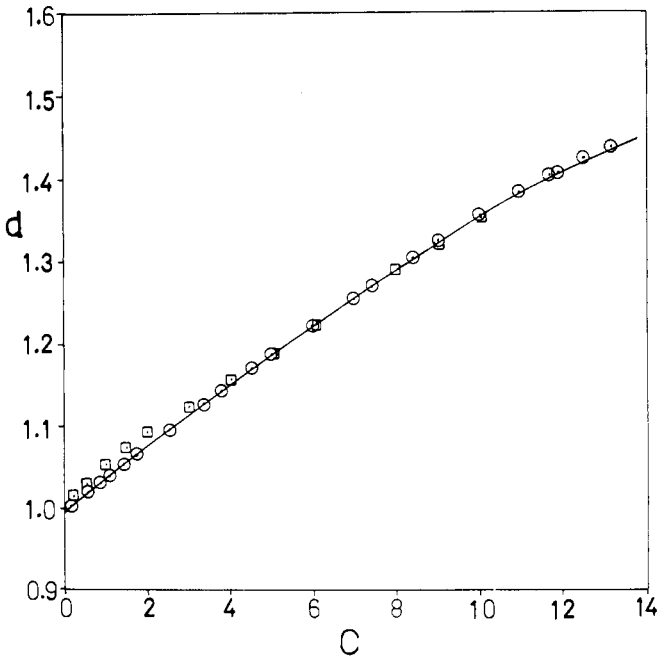

Figure 1. Density vs. molarity for aqueous methanesulfonic acid solutions at 25°C

□ Refs. *1, 4*
⊙ Present work
— Equation 4

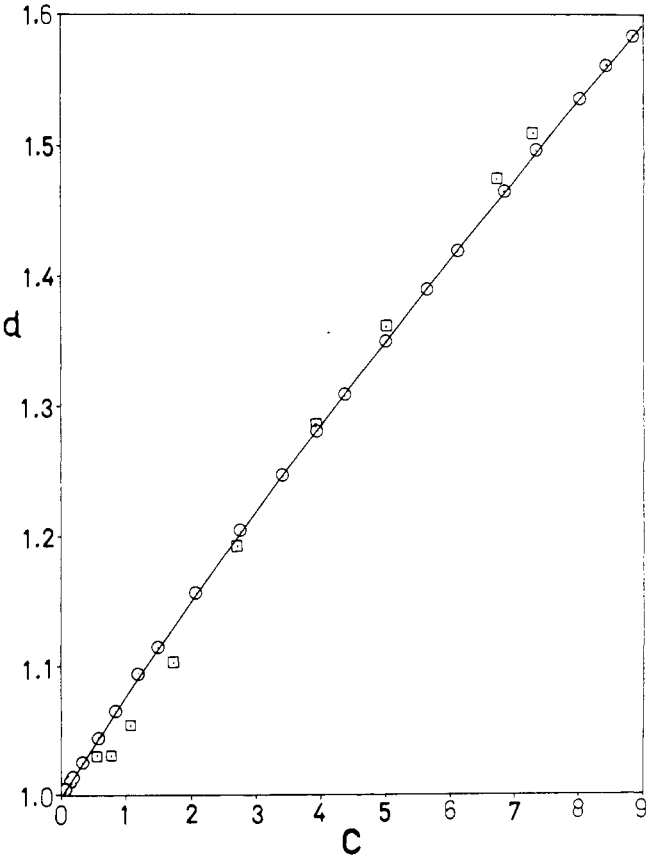

Figure 3. Density vs. molarity for aqueous solutions of trichloroacetic acid at 25°C

□ Ref. 1
⊙ Present work
— Equation 4

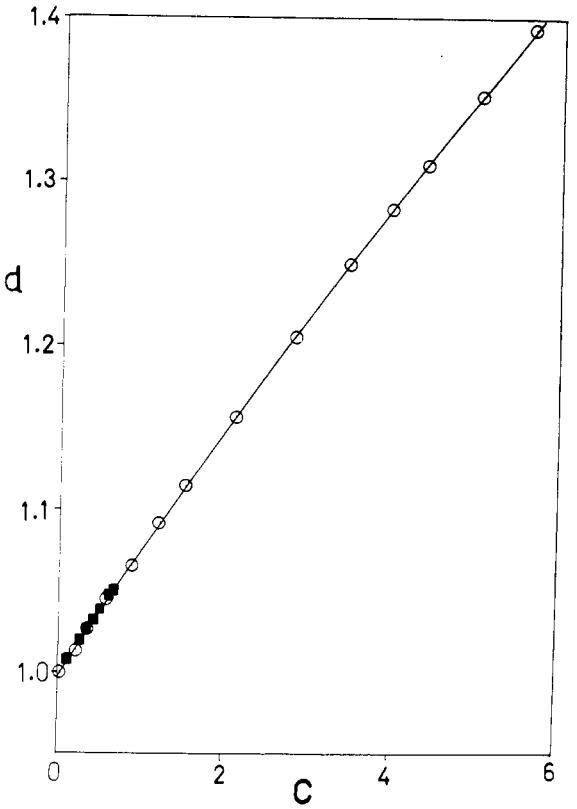

Figure 2. Density vs. molarity for aqueous trichloroacetic acid solutions at 20°C

■ Ref. *19*
⊙ Present work
— Equation 4

Table IV. Results Fitted to Equation 5 for Apparent Molal Volumes

°C	$\varphi_v°$	S_v*	SD
	Trichloroacetic acid		
20	79.5	2.74	0.85
25	80.6	2.41	0.19
35	81.7	3.35	0.39
	Methanesulfonic acid		
20	50.6	8.94	0.23
25	51.4	5.85	0.13
35	52.9	4.76	0.17

values of k and p until minimum standard deviations of regression were attained. These values were usually less than 10. Least-squares values of A_i and B_j for each system are listed in Table III.

Comparison with Previous Results

Densities of aqueous methanesulfonic acid solutions at 25°C have been determined by Bascombe and Bell (*1*). The density data of Covington and Thompson (*4*) and Covington and Lilley (*5*) are also derived (*6*) from the same source. Figure 1 shows good agreement with the present results except for the region 0.2–2.5*M*.

Densities of aqueous trichloroacetic acid solutions at 20°C up to 0.6*M* are given in ref. *19*. Present values are in good

Table V. Comparison of First Coefficients of Equations 3 and 4 with Calculated Values

Solute	M_2	°C	$A_1 \times 10$	$A^a \times 10$	$B_1 \times 10$	$B^b \times 10$
CCl_3COOH	163.4	20	0.816083	0.838820	0.815633	0.840304
		25	0.692641	0.827929	0.814275	0.830357
		35	0.787561	0.816477	0.818709	0.821353
CH_3SO_3H	96.11	20	0.402399	0.455088	0.402939	0.455894
		25	0.414498	0.447291	0.404131	0.448603
		35	0.404801	0.431965	0.424175	0.434545
Acetone[c]	58.08	25	−0.059957[d]	−0.086985	−0.086677[d]	−0.087240
H_3BO_3[e]	61.83	25	0.224312[d]	0.226593	0.224968[d]	0.227257
Sucrose[f]	342.3	25	1.30864[d]	1.31044	1.31490[d]	1.31429

[a] $A = (M_2 d_0 - \varphi_v^\circ d_0^2)/1000$. [b] $B = (M_2 - \varphi_v^\circ d_0)/1000$. [c] Ref. 2. [d] Ref. 17. [e] Ref. 18. [f] Ref. 8.

agreement, as shown in Figure 2. Bascombe and Bell (*1*) have also determined densities at 25°C. Figure 3 shows again some discrepancy between 0.2 and 2.5*M*.

Discussion

Masson's relation (*11*), Equation 5, has been used to obtain values

$$\varphi_v = \varphi_v^\circ + S_v^* \sqrt{C} \qquad (5)$$

of φ_v° and S_v^* by a linear least-squares method in the dilute region (up to ca. 0.3*M*). The results are given in Table IV.

From Equation 1,

$$\varphi_v = \frac{1000}{md} - \frac{1000}{md_0} + \frac{M_2}{d}$$

whence

$$d = \frac{\frac{1000}{m} + M_2}{\varphi_v + \frac{1000}{md_0}} = \frac{d_0 + \frac{md_0M_2}{1000}}{1 + \frac{md_0\varphi_v}{1000}}$$

expanding the binomial term in the denominator (since $-1 < md_0\varphi_v/1000 < 1$) gives

$$d = \left(d_0 + \frac{md_0M_2}{1000}\right)\left[1 - \frac{md_0\varphi_v}{1000} + \left(\frac{md_0\varphi_v}{1000}\right)^2 - \ldots\right]$$

whence

$$d = d_0 + \left(\frac{M_2d_0 - d_0^2\varphi_v}{1000}\right)m + \left(\frac{d_0^3\varphi_v^2 - M_2d_0^2\varphi_v}{10^6}\right)m^2 + \ldots \qquad (6)$$

Equations 3 and 4 are thus seen to be not entirely empirical. Table V compares the values of the first coefficients A_1, B_1 in Equations 3 and 4 with those calculated from Equation 6 in the case of molality and from ref. *13* in the case of molarity. The values of φ_v° in Table IV were used to obtain the calculated values of $(M_2d_0 - \varphi_v^\circ d_0^2)/1000$ in Equation 6 and of $(M_2 - \varphi_v^\circ d_0)/1000$ in ref. *13*. Data for some additional aqueous systems are also included in Table V. Empirical and theoretical coefficients are approximately equal.

Nomenclature

A_i = ith coefficient for the density vs. molality fit
B_j = jth coefficient for the density vs. molarity fit
C = concentration in mol/l. (molarity)
d = density of solution in g/ml
d_0 = density of pure water at a given temperature
m = concentration in mol/kg H_2O (molality)
M = symbol for molarity
M_2 = molecular weight of the solute
SD = standard deviation of regression
S_v^* = experimental slope in Masson's equation
φ_v = apparent molal volume in ml/mol
φ_v° = apparent molal volume at infinite dilution

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Supplementary Material Available. Tables I and II will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JCED-75-432.