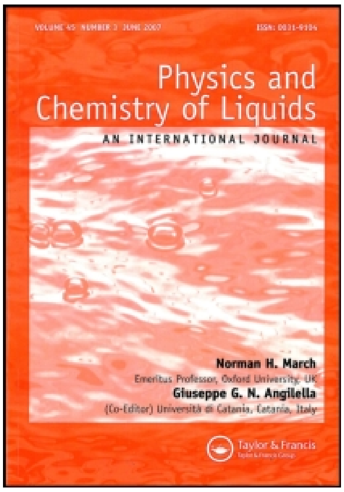

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Partial Molar Properties and Sound Velocities in Aqueous Methanol Solutions of Homologous Dicarboxylic Acids

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PARTIAL MOLAR PROPERTIES AND SOUND VELOCITIES IN AQUEOUS METHANOL SOLUTIONS OF HOMOLOGOUS DICARBOXYLIC ACIDS

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The parital molar volumes of oxalic, malonic, succinic, glutaric and adipic acids have been determined in water + methanol (5, 10, 20, 30 and 40 wt %) mixtures from density measurements in varying ranges of concentration at four different temperatures ranging from 288.15 to 318.15 K. The density data have been analysed by means of Masson equation. The apparent molar isentropic compressibilities of these acids have been determined in these water + methanol mixtures from sound velocity measurements in varying ranges of concentration at 298.15 K. The solvation numbers of the acids have been determined in these solvents. The results are discussed in terms of solute-solvent interactions.

Keywords: Ultrasonic velocity; homologous dicarboxylic acids; aqueous methanol solutions

INTRODUCTION

In an earlier work [1, 2] we reported the effect of increase of chain length upon the change in apparent molar volume, expansibility, apparent molar isentropic compressibility of the homologous dicarboxylic acids in water and water + acetone mixtures. In this work we report data of five homologous dicarboxylic acids [viz $(CH_2)_X$ $(COOH)_2$ where $X = 0$, 1, 2, 3 and 4] in water + methanol (5, 10, 20, 30 and 40 wt%) systems from density and ultrasonic velocity measurements.

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*Corresponding author.

The results have been discussed in terms of solute-solvent interactions. The limiting apparent molar isentropic compressibilities ($K^o_{s,\phi}$) and solvation numbers (S^o_n) of these acids have been determined and the effect of the hydrophobic chain length (—CH$_2$— groups) on these parameters has been discussed in different water + methanol mixtures.

EXPERIMENTAL

Oxalic (BDH, AnalaR), malonic (E MERCK, GR), succinic (BDH, AnalaR), glutaric (Fluka AG) and adipic (SRL, Pure) acids were of the same samples as used earlier [1]. These acids were kept in a vacuum desiccator over anhydrous calcium chloride until required. Methanol (BDH, AnalaR) was further purified by the method available in the literature [3]. Conductivity water (Sp. cond. $\approx 10^{-6}$ s cm^{-1}) was used for preparing water + methanol (5, 10, 20, 30 and 40 wt%) mixtures. The methanol content in the mixed solvent was accurate to within $\pm 0.01\%$. The solutions of these acids in water + methanol mixtures were prepared by weight and conversion of molality to molarity was done by using standard expression [4]. The densities were determined pycnometrically (uncertainty $\pm 1 \times 10^{-4}$ g ml^{-1}). The density measurements were made in a waterbath whose temperature was controlled to $\pm$ 0.05 K. Experiments were repeated at least 5 times for each solution and average was taken as final density value. Sound velocities of these acid solutions were measured using a multifrequency ultrasonic interferometer (M-84 Mittal Enterprises, New Delhi) at a frequency of 3 MHz after keeping for 2h in a water thermostat maintained at 298.15 ± 0.05 K. The uncertainty in sound velocity was within ± 0.5 m s^{-1}.

RESULTS AND DISCUSSION

The apparent molar volume ϕ_v of the acids was calculated by the relation [5]

$$\phi_v = 1000(cd_o)^{-1}(d_o - d) + M_2 d_o^{-1} \tag{1}$$

The ϕ_v data were fitted to Masson equation [5]

$$\phi_v = \phi_v^o + S_v c^{1/2} \tag{2}$$

The values of ϕ_v^o and S_v are given in Table I for the studied acids in different solvents at the four different temperatures.

The apparent molar expansibility ϕ_E of the acids was calculated using Equation (3)

$$\phi_E = \alpha_o \phi_v + (\alpha - \alpha_o)\frac{1000}{c} \tag{3}$$

α_o and α are the co-efficients of thermal expansion of solvent and solution, respectively.

The sound velocities, U of solutions of the dicarboxylic acids in water + methanol mixtures at different concentrations were fitted to an equation of the form [2]

$$U = U_o + Ac + Bc^{3/2} + Cc^2 \tag{4}$$

over the concentration range studied for the acid solutions, where U_o is the sound velocity in pure solvent, A, B and C are constants. Typical plots of $U - U^o/c$ vs $c^{1/2}$ are shown in Figure 1. U is related to density, d of the solution and isentropic compressibility, K_s by the relation [6]

$$U = (K_s d)^{-1/2} \tag{5}$$

The value of K_s obtained for solutions at different concentrations were fitted to an equation of the form

$$K_s = K_s^o + A'c + B'c^{3/2} + C'c^2 \tag{6}$$

where A', B' and C' are constants. The typical plots of $K_s - K_s^o/c$ vs $c^{1/2}$ are shown in Figure 2. The apparent isentropic molar compressibility, $K_{s,\phi}$ of the acid solutions in different concentrations was computed using Equation (7)

$$K_{s,\phi} = K_{s,\phi}^o + A''c^{1/2} + B''c \tag{7}$$

TABLE I Values of ϕ_v^o(ml mol^{-1}) and S_v (ml$^{3/2}$ mol$^{-3/2}$) for homologous oxalic acids in water + methanol (5, 10, 20, 30 and 40 wt%) mixtures at different temperatures

Acid	ϕ_v^o	S_v	ϕ_v^o	S_v	ϕ_v^o	S_v	ϕ_v^o	S_v	ϕ_v^o	S_v
288.15 K										
	*(5%, 0.9906)		(10%, 0.9827)		(20%, 0.9678)		(30%, 0.9528)		(40%, 0.9363)	
Oxalic	33.0(4)	17.1(7)	30.7(4)	17.3(7)	28.1(4)	18.1(7)	25.3(3)	18.8(7)	22.2(3)	19.7(8)
Malonic	44.1(4)	16.7(7)	41.9(4)	17.1(7)	39.4(4)	17.8(7)	36.7(4)	18.6(7)	33.8(4)	19.5(7)
Succinic	55.2(4)	16.5(7)	53.1(4)	16.8(7)	50.7(4)	17.6(7)	48.1(4)	18.3(7)	45.4(4)	19.1(7)
Glutaric	66.4(4)	16.2(6)	64.3(4)	16.5(7)	62.1(4)	17.2(7)	59.6(4)	17.9(7)	56.9(4)	18.9(7)
Adipic	77.5(4)	15.9(6)	75.5(4)	16.3(7)	73.4(4)	16.7(7)	71.0(4)	17.6(7)	68.5(4)	18.4(7)
298.15 K										
	*(5%, 0.9882)		(10%, 0.9802)		(20%, 0.9651)		(30%, 0.9497)		(40%, 0.9328)	
Oxalic	33.9(4)	17.1(7)	31.7(4)	17.5(8)	29.0(3)	18.3(8)	26.2(3)	19.1(8)	23.2(3)	19.9(8)
Malonic	45.1(4)	16.8(7)	42.9(4)	17.2(8)	40.6(4)	17.3(8)	37.7(4)	18.7(7)	34.8(4)	19.7(8)
Succinic	56.2(5)	16.5(6)	54.0(5)	17.0(7)	51.7(4)	17.7(8)	49.2(4)	18.4(7)	46.5(4)	19.0(7)
Glutaric	67.4(5)	16.0(6)	65.3(5)	16.5(7)	63.0(4)	17.1(8)	60.6(4)	18.2(7)	58.0(5)	19.1(7)
Adipic	78.5(5)	16.0(6)	76.6(5)	15.6(7)	74.4(5)	16.9(8)	72.1(5)	17.8(7)	69.6(4)	18.8(7)

	308.15 K									
	*(5%, 0.9849)		(10%, 0.9765)		(20%, 0.9610)		(30%, 0.9453)		(40%, 0.9278)	
Oxalic	34.9(4)	17.3(7)	32.7(4)	17.6(8)	30.0(4)	18.3(8)	27.2(3)	19.2(8)	24.1(3)	20.1(9)
Malonic	46.1(4)	17.0(7)	43.8(4)	17.5(8)	41.3(4)	18.2(8)	38.7(4)	18.9(8)	35.7(4)	19.9(8)
Succinic	57.3(5)	16.7(7)	55.1(5)	16.9(7)	52.7(5)	17.8(7)	50.2(4)	18.6(8)	47.3(4)	19.5(8)
Glutaric	68.4(5)	16.4(7)	66.3(5)	16.8(7)	64.1(5)	17.2(7)	61.6(5)	18.5(8)	59.1(4)	19.1(7)
Adipic	79.6(5)	16.2(6)	77.6(5)	16.5(7)	75.5(6)	17.1(7)	73.2(5)	17.9(7)	70.7(5)	18.7(8)
	318.15 K									
	*(5%, 0.9808)		(10%, 0.9720)		(20%, 0.9561)		(30%, 0.9399)		(40%, 0.9218)	
Oxalic	35.9(4)	17.4(7)	33.6(4)	17.9(8)	31.0(4)	18.6(8)	28.1(3)	19.5(8)	24.2(3)	20.5(8)
Malonic	47.0(4)	17.2(7)	44.8(4)	17.6(7)	42.4(4)	18.3(8)	39.7(4)	19.1(8)	36.6(3)	20.2(8)
Succinic	58.2(4)	16.9(7)	56.1(5)	17.3(7)	53.7(5)	18.1(7)	51.2(4)	18.9(7)	48.3(4)	18.9(8)
Glutaric	69,4(5)	16.7(6)	67.4(5)	17.0(6)	65.2(5)	17.8(7)	62.7(5)	18.5(7)	60.1(4)	18.8(8)
Adipic	80.7(5)	16.3(6)	78.7(5)	16.5(6)	76.5(5)	17.4(7)	74.2(5)	18.3(7)	71.7(5)	18.7(7)

*Values here are wt% methanol and d^o in g ml^{-1}. The figures in parentheses in ϕ_v^o and S_v are the standard deviations in the order of 10^{-2}.

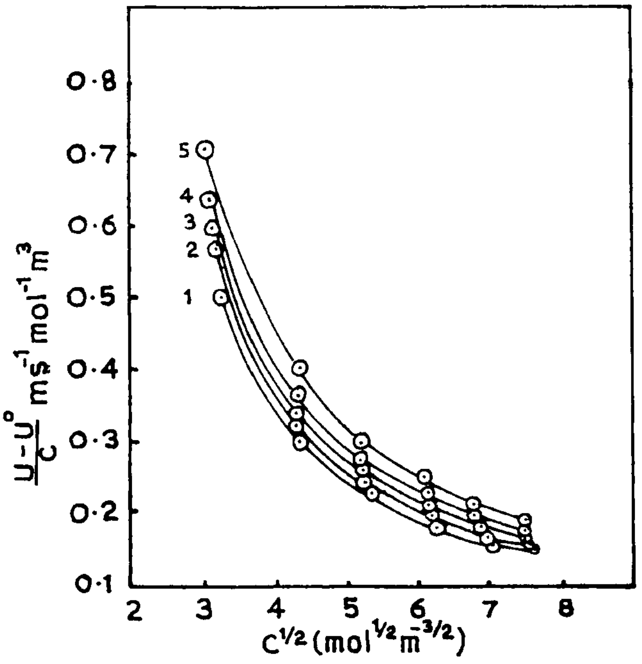

FIGURE 1 Plot of $(U-U^o)/c$ vs $c^{1/2}$ (1-oxalic acid in *w/w* methanol = 5%, 2-malonic acid in *w/w* methanol = 10%, 3- succinic acid in *w/w* methanol = 20%, 4-glutaric acid in *w/w* methanol = 30% and 5-adipic acid in *w/w* methanol = 40%).

The values of constants of Equations (4), (6) and (7) are given in Table IV. Typical plots of $K_{s,\phi}$ vs $c^{1/2}$ are shown in Figure 3. The variation of $K_{s,\phi}^o$ with hydrophobic chain length (—CH$_2$— group) is shown in Figure 4.

The solvation number, S_n of a solute is related to K_s by Equation (8)

$$S_n = n_1 n_2^{-1}[1 - VK_s(n_1 V_1^o K_s^o)^{-1}] \tag{8}$$

where V is the volume of the solution containing n_2 moles of the solute, V_1^o is the molar volume of the solvent and n_1 is the number of moles of the solvent. The variation of solvation number with molar concentration of the acid leads to the limiting solvation number, S_n^o which was also obtained from the relationship [7]

$$\lim_{c \to o} K_{s,\phi} = -S_n^o V_1^o K_s^o \tag{9}$$

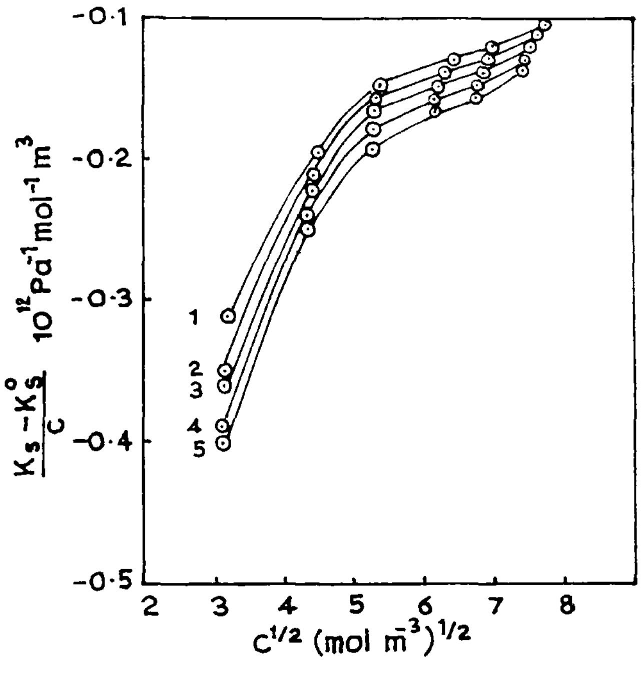

FIGURE 2 Plot of $(K_s - K_s^o)/c$ vs $c^{1/2}$ (1-oxalic acid in w/w methanol = 5%, 2-malonic acid in w/w methanol = 10%, 3-succinic acid in w/w methanol = 20%, 4-adipic acid in w/w methanol = 30% and 5-glutaric acid in w/w methanol = 40%).

The values of S_n^o along with $K_{s,\phi}^o$ are given in Table IV. The variation of S_n^o with hydrophobic chain length (—CH$_2$—) and with methanol content are shown in Figures 5 and 6, respectively.

It has been found from the conductance measurements that the degree of dissociation of oxalic, malonic, succinic, glutaric and adipic acids in various methanol mixtures lies in the range of 0.9301 – 0.7605, 0.7685 – 0.5190, 0.6118 – 0.3801, 0.5525 – 0.3115 and 0.5240 – 0.2903 respectively in 5 wt% methanol over the range of concentration 0.001 to 0.005 *M* and in the range of 0.7632 – 0.5201, 0.7452 – 0.4896, 0.5745 – 0.3302, 0.3823 – 0.2001, 0.3440 – 0.1734 in 40 wt% methanol-water mixture over the same range of concentration studied at the experimental temperatures. The values of degree of dissociation undoubtedly indicate that the acids ionise to a considerable extent in various water-methanol mixtures. However, the extent of ionisation of

TABLE II Values of ϕ_E^o(ml mol^{-1}) and S_E(ml$^{3/2}$ mol$^{-3/2}$) for homologous acids in water + methanol (5, 10, 20, 30 and 40 wt%) mixtures at different temperatures

Acid	$\phi_E^o \times 10^2$	$-S_E \times 10^2$	$\phi_E^o \times 10^2$	$-S_E \times 10^2$	$\phi_E^o \times 10^2$	$-S_E \times 10^2$	$\phi_E^o \times 10^2$	$-S_E \times 10^2$	$\phi_E^o \times 10^2$	$-S_E \times 10^2$
					288.15 K					
	*(5%, 3.334)		(10 %, 3,648)		(20 %, 4.055)		(30 %, 4.533)		(40 %, 5.168)	
Oxalic	10.2(7)	2.8(4)	10.4(7)	2.8(4)	11.8(7)	2.8(4)	13.3(7)	2.7(4)	14.4(7)	2.7(4)
Malonic	10.3(7)	2.8(4)	10.6(7)	2.8(4)	12.1(7)	2.8(4)	13.6(7)	2.7(4)	14.7(7)	2.7(4)
Succinic	10.5(7)	2.8(4)	10.8(7)	2.8(4)	12.3(7)	2.7(4)	13.9(7)	2.7(4)	15.1(7)	2.6(4)
Glutaric	10.7(7)	2.8(4)	11.0(7)	2.8(4)	12.6(7)	2.7(4)	14.2(7)	2.7(4)	15.5(8)	2.6(4)
Adipic	10.8(7)	2.8(4)	11.2(7)	2.8(4)	12.8(7)	2.7(4)	14.5(7)	2.7(4)	15.9(8)	2.6(4)
					298.15 K					
	*(5%, 3.342)		(10%, 3.657)		(20%, 4.067)		(30%, 4.548)		(40%, 5.188)	
Oxalic	10.2(6)	2.8(4)	10.5(6)	2.8(4)	11.9(7)	2.8(4)	13.4(8)	2.7(4)	14.6(6)	2.7(4)
Malonic	10.4(7)	2.7(4)	10.7(7)	2.8(4)	12.2(7)	2.8(4)	13.7(8)	2.7(4)	14.8(8)	2.7(4)
Succinic	10.5(7)	2.7(4)	10.9(7)	2.8(4)	12.4(7)	2.8(4)	14.0(8)	2.7(4)	15.2(8)	2.6(4)
Glutaric	10.7(7)	2.7(4)	11.1(7)	2.7(4)	12.7(8)	2.7(4)	14.3(8)	2.7(4)	15.6(8)	2.6(4)
Adipic	10.9(7)	2.7(4)	11.3(7)	2.8(4)	12.9(8)	2.7(4)	14.6(8)	2.7(4)	16.0(8)	2.6(4)

					308.15 K					
	*(5%, 3.354)		(10%, 3.671)		(20%, 4.084)		(30%, 4.569)		(40%, 5.215)	
Oxalic	10.3(6)	2.8(4)	10.6(6)	2.8(4)	12.0(7)	2.8(4)	13.5(8)	2.8(4)	14.6(8)	2.7(4)
Malonic	10.5(7)	2.8(4)	10.8(7)	2.8(4)	12.3(7)	2.8(4)	13.8(8)	2.7(4)	15.0(8)	2.7(4)
Succinic	10.6(7)	2.8(4)	11.0(7)	2.8(4)	12.5(7)	2.8(4)	14.1(8)	2.7(4)	15.4(8)	2.6(4)
Glutaric	10.8(7)	2.8(4)	11.2(7)	2.9(4)	12.8(7)	2.8(4)	14.4(8)	2.7(4)	15.7(8)	2.6(4)
Adipic	11.0(7)	2.8(4)	11.4(7)	2.8(4)	13.0(8)	2.8(4)	14.7(8)	2.7(4)	16.1(8)	2.6(4)
					318.15 K					
	(5%, 3.368)		(10%, 3.688)		(20%, 4.105)		(30%, 4.595)		(40%, 5.249)	
Oxalic	10.3(6)	2.8(4)	10.7(6)	2.8(4)	12.1(7)	2.8(4)	13.6(8)	2.8(4)	14.7(8)	2.7(4)
Malonic	10.5(4)	2.8(4)	10.9(7)	2.8(4)	12.4(7)	2.8(4)	13.9(8)	2.8(4)	15.1(8)	2.7(4)
Succinic	10.7(7)	2.8(4)	11.1(7)	2.8(4)	12.6(7)	2.8(4)	14.2(8)	2.7(4)	15.5(0)	2.6(4)
Glutaric	10.9(7)	2.8(4)	11.3(7)	2.8(4)	12.9(8)	2.8(4)	14.6(8)	2.8(4)	15.9(8)	2.6(4)
Adipic	11.0(7)	2.8(4)	11.5(7)	2.9(4)	13.1(8)	2.7(4)	14.9(8)	2.8(4)	16.3(8)	2.6(4)

*Values here are wt %.$10^4\alpha''$. The figures in parentheses in ϕ_E^o and S_E are the standard deviations in the order of 10^{-4}.

TABLE III Values of constants a and b of Equation (10) and a' and b' of Equation (11) for homologous dicarboxylic acids in water + methanol mixtures

Acid	a	$b\times 10^2$	$a'\times 10^2$	$b'\times 10^5$	a	$b\times 10^2$	$a'\times 10^2$	$b'\times 10^5$
		(5 wt% methanol)				(10 wt% methanol)		
Oxalic	5.3(4)	9.6(3)	8.4(5)	6.2(2)	3.6(2)	9.4(2)	8.3(5)	7.4(3)
Malonic	16.0(5)	9.8(3)	8.4(5)	6.8(2)	13.8(4)	9.7(2)	8.5(5)	7.5(3)
Succinic	26.2(5)	10.1(3)	8.5(5)	7.0(3)	24.1(5)	10.1(3)	8.6(5)	7.8(3)
Glutaric	36.7(6)	10.3(3)	8.6(5)	7.1(3)	34.6(6)	10.3(3)	8.7(5)	8.0(3)
Adipic	46.8(7)	10.6(4)	8.7(5)	7.2(3)	45.2(7)	10.5(3)	8.8(5)	8.4(3)
		(20 wt% methanol)				(30 wt% methanol)		
Oxalic	1.0(1)	9.4(3)	9.4(5)	9.0(3)	−1.4(1)	9.3(3)	10.3(3)	10.3(4)
Malonic	12.1(5)	9.5(3)	9.5(3)	9.1(3)	8.8(4)	9.7(3)	10.4(3)	11.1(3)
Succinic	21.6(5)	10.0(3)	9.6(5)	9.3(3)	19.3(5)	10.0(3)	10.7(3)	10.9(2)
Glutaric	32.1(6)	10.4(3)	9.9(5)	9.5(3)	29.8(5)	10.3(3)	10.8(3)	11.7(3)
Adipic	42.6(6)	10.7(3)	10.0(5)	9.7(3)	40.4(5)	10.6(3)	11.1(4)	11.6(3)
		(40 wt% methanol)						
Oxalic	−3.6(1)	9.0(3)	10.8(5)	12.2(4)				
Malonic	6.7(3)	9.4(3)	11.1(5)	12.7(4)				
Succinic	17.5(4)	9.7(3)	11.3(5)	13.1(4)				
Glutaric	26.0(5)	10.7(3)	11.7(5)	13.3(4)				
Adipic	37.5(6)	10.8(3)	11.9(5)	13.9(4)				

The figures in parentheses in a, b, a' and b' are the standared deviations in the order of 10^{-1}, 10^{-3}, 10^{-3} and 10^{-6} respectively.

the acids decreases as the methanol content in the mixed solvent increases.

The positive and large values of S_v for all the acids in all solvents at the experimental temperatures indicate the presence of strong ion – ion interaction. The ϕ_v^o are also positive and large for the studied acids in all solvents at the four temperatures indicating the presence of strong solute (ion) – solvent interactions. It was found that ϕ_v^o increased with increase of temperatures. The temperature dependence of ϕ_v^o for the acids in various solvents may be represented as

$$\phi_v^o = a + bT \tag{10}$$

over the temperature range 288.15 to 318.15 K, where a and b are the constants given in Table III. Since increase of ϕ_v^o with increase in temperature is attributed to increase in solvation, the solvation decreases with increasing methanol content indicating that the cavity occupation of crystal lattice by water molecules is more in pure water [1] than in water + methanol mixtures. The results suggest that the

TABLE IV The constants A, B and C of Equation (4), A′, B′ and C′ of Equation (6), A″, B″ and $K^o_{s,o}$(m^3 mol^{-1} pa^{-1}) of Equation (7) and limiting solvation number S^o_n of homologous oxalic acids in water + methanol mixtures at 298.15K

Acid	$A\times 10^2$	$B\times 10^2$	$C\times 10^2$	$A'\times 10^{14}$	$B'\times 10^{14}$	$C'\times 10^{14}$	$A''\times 10^{11}$	$B''\times 10^{11}$	$K^o_{s,o}\times 10^{11}$	S^o_n
(w/w = 5%, U_o = 1521.4 ms^{-1}, $K^o_s \times 10^{11}$ = 43.72 Pa^{-1})										
Oxalic	121.3(2)	−29.1(4)	2.02(4)	− 71.6(1)	16.6(3)	−1.15(2)	16.7(2)	−1.15(2)	− 70.4(8)	50.1
Malonic	140.5(2)	−34.1(5)	2.37(4)	− 82.8(1)	19.5(4)	−1.35(2)	19.5(3)	−1.35(2)	− 80.8(9)	56.8
Succinic	159.7(2)	−39.1(5)	2.72(5)	− 93.9(1)	22.3(4)	−1.55(2)	22.3(4)	−1.55(2)	− 91.5(9)	64.3
Glutaric	178.8(3)	−44.1(6)	3.07(5)	−105.1(2)	25.3(4)	−1.76(2)	25.1(4)	−1.75(2)	−101.7(9)	71.0
Adipic	198.9(3)	−49.4(6)	3.45(6)	−116.5(3)	28.2(4)	−1.97(2)	28.4(5)	−1.98(3)	−113.5(9)	77.9
(w/w = 10%, U_o = 1531.5 ms^{-1}, $K^o_s \times 10^{11}$ = 43.49 Pa^{-1})										
Oxalic	118.8(2)	−28.4(3)	1.96(4)	−69.7(1)	16.1(3)	−1.11(2)	16.9(3)	−1.18(2)	−17.2(7)	48.0
Malonic	138.3(2)	−33.5(4)	2.32(4)	−81.2(1)	19.1(4)	−1.32(2)	19.0(3)	−1.32(2)	−79.2(8)	55.0
Succinic	157.7(2)	−38.6(4)	2.67(4)	−91.9(1)	21.8(4)	−1.51(2)	21.8(3)	−1.51(2)	−89.5(9)	61.7
Glutaric	177.1(2)	−43.6(4)	3.02(5)	−102.9(2)	24.6(4)	−1.71(2)	25.6(4)	−1.81(3)	−100.9(9)	68.5
Adipic	203.2(3)	−50.9(5)	3.56(5)	−113.8(2)	27.5(4)	−1.90(2)	29.1(4)	−2.05(3)	−112.8(9)	75.3
(w/w = 20%, U_o = 1551.6 ms^{-1}, $K^o_s \times 10^{11}$ = 43.04 Pa^{-1})										
Oxalic	106.8(2)	−25.4(3)	1.77(4)	−61.9(1)	14.1(3)	−0.98(2)	14.2(3)	−0.98(2)	−60.6(6)	41.0
Malonic	126.5(2)	−30.6(3)	2.13(4)	−72.7(1)	16.9(3)	−1.18(2)	16.9(3)	−1.17(2)	−70.9(7)	47.3
Succinic	146.2(2)	−35.7(4)	2.50(4)	−83.6(1)	19.7(4)	−1.38(2)	19.7(3)	−1.37(2)	−81.3(8)	52.7
Glutaric	165.8(2)	−40.9(4)	2.86(5)	−94.7(2)	22.7(4)	−1.98(2)	22.7(3)	−1.58(3)	−91.9(9)	60.3
Adipic	185.5(2)	−46.2(4)	3.23(5)	−105.5(2)	25.5(4)	−1.78(2)	25.5(4)	−1.77(3)	−102.3(9)	66.8

TABLE IV (Continued)

(w/w = 30%, U_o = 1647.4 ms^{-1}, $K_s^o \times 10^{11}$ = 38.80 Pa^{-1})										
Oxalic	97.4(1)	−23.1(3)	1.62(4)	−48.2(1)	10.8(3)	−0.75(1)	10.9(3)	−0.76(2)	−47.2(4)	33.8
Malonic	117.1(2)	−28.3(3)	1.99(4)	−57.9(1)	13.4(3)	−0.94(1)	13.4(3)	−0.93(2)	−56.4(6)	39.7
Succinic	137.1(2)	−33.7(3)	2.36(4)	−67.9(1)	16.1(3)	−1.14(1)	16.1(3)	−1.14(2)	−65.9(7)	45.3
Glutaric	157.1(2)	−38.9(3)	2.74(4)	−76.6(1)	18.2(3)	−1.28(2)	18.3(3)	−1.28(2)	−74.2(7)	51.2
Adipic	177.1(2)	−44.3(4)	3.12(4)	−86.5(2)	20.9(4)	−1.48(2)	21.0(3)	−1.48(2)	−83.9(8)	57.0
(w/w = 40%, U_o = 1615.2 ms^{-1}, $K_s^o \times 10^{11}$ = 41.09 Pa^{-1})										
Oxalic	93.1(1)	−22.1(3)	1.56(4)	−54.5(1)	12.7(3)	−0.91(1)	12.7(3)	−0.90(3)	−53.5(6)	32.6
Malonic	113.5(2)	−27.6(3)	1.95(4)	−60.6(1)	13.9(3)	−0.99(1)	14.0(3)	−0.98(3)	−59.1(6)	36.9
Succinic	133.8(2)	−33.0(3)	2.30(4)	−70.9(1)	16.7(3)	−1.18(1)	16.7(2)	−1.18(3)	−69.0(7)	42.5
Glutaric	154.1(2)	−38.4(3)	2.73(4)	−81.4(1)	19.5(3)	−1.38(1)	19.5(2)	−1.38(3)	−79.0(8)	48.1
Adipic	174.4(2)	−43.9(4)	3.12(4)	−91.7(2)	22.2(3)	−1.57(2)	22.2(2)	−1.57(3)	−88.8(9)	53.7

The figures in parentheses in $A \times 10^2$, $B \times 10^2$, $A' \times 10^{14}$, $B' \times 10^{14}$ $A'' \times 10^{11}$ and $K_{s,o}^o \times 10^{11}$ are the standard deviations in ther order of 10^{-1}; $C \times 10^2$, $C' \times 10^{14}$ and $B'' \times 10^{11}$ are the standard deviations in the order of 10^{-2}.

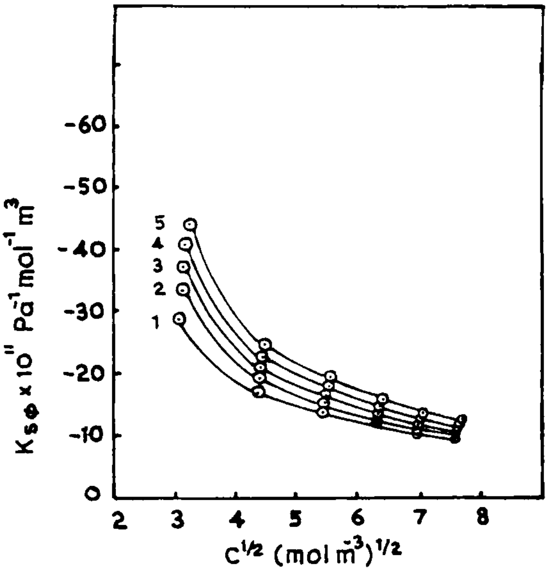

FIGURE 3 Plot of $K_{s,\phi}$ vs $c^{1/2}$ in w/w = 5% methanol (1-oxalic acid, 2-malonic acid, 3-succinic acid, 4-glutaric acid and 5-adipic acid).

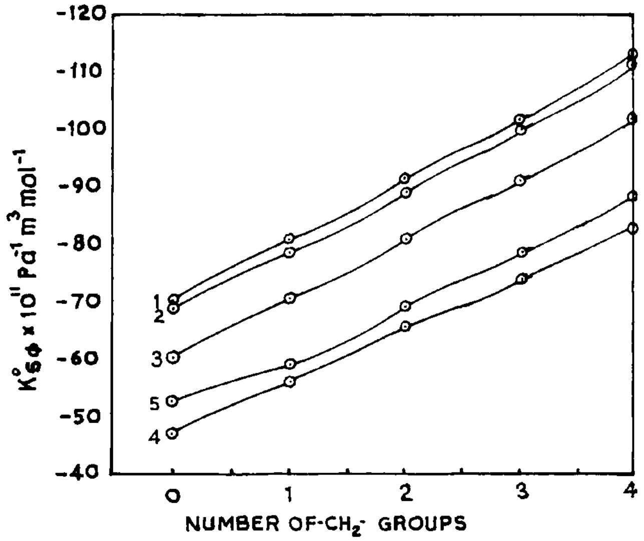

FIGURE 4 Variation $K^0_{s,\phi}$ vs number of —CH$_2$— group (1, 5 wt%, methanol, 2, 10 wt% methanol, 3, 20 wt% methanol, 4, 30 wt% methanol and 5, 40 wt% methanol).

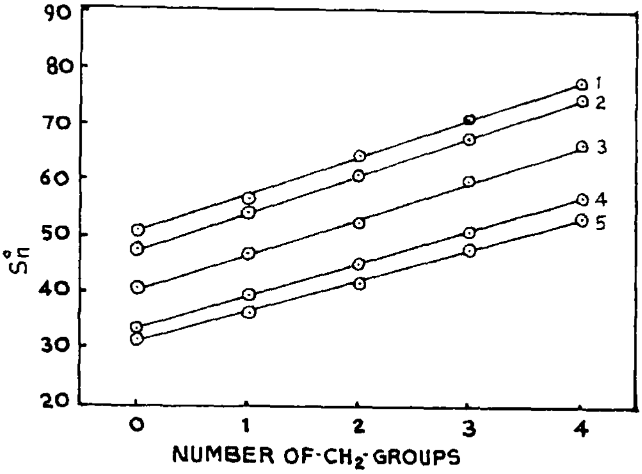

FIGURE 5 Variation of S_n^o vs number of $-CH_2-$ groups 1, 5 wt% methanol, 2, 10 wt% methanol 3, 20 wt% methanol 4, 30 wt% methanol and 5, 40 wt% methanol.

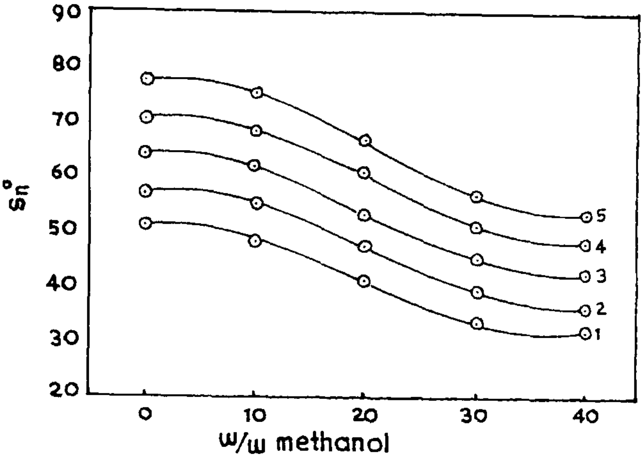

FIGURE 6 Variation of S_n^o vs w/w methanol (1, oxalic acid, 2, malonic acid, 3, succinic acid, 4, glutaric acid and 5, adipic acid).

presence of solute-solvent interaction between the molecules produces a greater structure making effect of the acids in aqueous medium than in aqueous methanol media. As expected the ϕ_v^o increases with increase in hydrophobic chain length.

The ϕ_E^o (Tab. II) increases with increase of temperature indicating the presence of caging or packing effect [8]. As is seen, the ϕ_E^o increases with increase of methanol content in the mixed solvent suggesting that the structure making effect of the acids decreases with increasing methanol content. As observed the ϕ_E^o tends to increase with increase in hydrophobic chain length indicating the increasing tendency of packing effect. The temperature dependence of ϕ_E^o for the acids in various solvents has been represented by Equation (11)

$$\phi_v^o = a' + b'T \tag{11}$$

over the temperature range, 288.15 to 318.15 K, where a' and b' are constants and are also shown in Table III.

The sound velocity increases as the methanol content in water increases and passes through a maximum in the region *w/w* methanol = 30% which means that the isentropic compressibility decreases and passes through a minimum in the same region. Such minima are also observed in other water + organic solvent mixtures like water + DMSO [9–12] and water + ethanol [13]. The decrease in isentropic compressibility may be due to the fact that the organic solvent leads to a partial break down of water rendering it less structured than in pure water. As observed (Tab. IV) the physical properties of water + methanol mixture changes with gradual addition of methanol to water and this is owing to the characteristic structural changes of water with addition of methanol. The addition of methanol leads to break down the structure of water.

The results indicate that the sound velocity increases with increase of acid concentration and with increase in the hydrophobic chain length ($—CH_2—$ groups) of the acids in all solvents. The isentropic compressibility, K_s of the acids decreases with increase of acid concentration and with increase of number of $—CH_2—$ groups of the dicarboxylic acids. This is reasonable in view of decreasing compressibility of solvation layer as we go from oxalic to adipic acids.

It has been observed that the apparent isentropic molar compressibility, $K_{s,\phi}$ increases with increase of solution concentration. The negative $K_{s,\phi}^o$ values [14, 15] may be explained in terms of two different phenomena viz. hydrophilic and hydrophobic solvation. It may be stated here that oxalic acid having no $—CH_2—$ groups can have only hydrophilic, where the higher homologues have both hydrophilic as well as hydrophobic hydration increasing with chain length. The loss of compressibility of the surrounding solvent molecules due to strong hydrophilic group-water interaction at the carboxylic group causes hydrophilic solvation.

It has been observed that the solvation number S_n decreases with increase in concentration of the solution and with increasing methanol content in water. The limiting solvation number S_n^o increases as we go from oxalic to adipic acid (Fig. 5). This is again due to the fact that oxalic acid shows hydrophilic solvation whereas the higher homologues show both hydrophilic as well as hydrophobic solvation as the size of nonpolar moiety increases. S_n^o decreases with increase of methanol content. This is owing to the fact that the solvation layer formed around the carboxylic group is thick and/or hard in water while in water + methanol mixture is thin and loose.

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