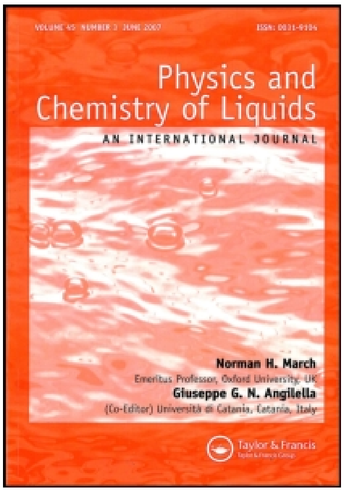

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Dash, U. N. and Mohanty, B. K.(1999) 'Partial Molar and Ultrasonic Properties of Benzoic and Phenyl Acetic Acids in Water and Water Alcohol Mixtures', Physics and Chemistry of Liquids, 37: 4, 443 — 453

To link to this Article: DOI: 10.1080/00319109908031448

URL: http://dx.doi.org/10.1080/00319109908031448

Phys. Chem. Liq., 1999, Vol. 37, pp. 443–453
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PARTIAL MOLAR AND ULTRASONIC PROPERTIES OF BENZOIC AND PHENYL ACETIC ACIDS IN WATER AND WATER + ALCOHOL MIXTURES

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(Received 23 December 1997)

Partial molar volumes of Benzoic and Phenylacetic acids have been determined in water and water + alcohol (5 wt% each of methanol, ethanol and propanol) mixtures from density measurements in varying ranges of concentration at four different temperatures in the interval of 10° from 288.15 to 318.15 K. The density data have been used to obtain partial molar volumes, co-efficients of thermal expansion and partial molar expansibilities of the acids in these solvents. Studies on sound velocity have been made in aqueous and aqueous alchohol solutions of these two acids to evaluate various acoustic parameters at 303.15 K. The solvation numbers of these acids have been determined in these solvents. The results are discussed in terms of ion – ion and ion-solvent interactions and of structural effects on the solvent in solution.

Keywords: Partial molar properties; acoustic parameters; aqueous alcohol solutions

INTRODUCTION

In continuation of our studies on the various aspects of solvation of solutes [1–4] we now report the partial molar properties of benzoic and phenylacetic acids in water and water + 5 wt% each of methanol, ethanol and propanol solutions at four different temperatures at an interval of 10° from 288.15 K to 318.15 K. The apparent molar

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isentropic compressibilities ($K_{s,\phi}$) of these two acids in aqueous and aqueous alcohol solutions have been determined at 303.15 K from sound velocity measurements. The limiting apparent molar adiabatic compressibilities ($K^o_{s,\phi}$) and solvation numbers (S^o_n) have been determined for benzoic and phenylacetic acids and the contribution of — CH_2 — group towards these values has been discussed in various water + alcohol mixtures.

MATERIALS AND METHODS

Benzoic (E Merck) and phenylacetic acids (BDH, AnalaR) were kept in a vacuum desiccator over anhydrous calcium chloride until required. Conductivity water (sp. cond. $\approx 10^{-6}\,\mathrm{s\,cm^{-1}}$) was used for preparing water + 5 wt% each of methanol, ethanol and propanol mixtures. The alcohol content in the mixed solvents was accurate to within ± 0.01%. The solutions of the acids in water and water + alcohol mixtures were prepared by weight. The densities were determined pycnometrically [5] (uncertainty, $\pm\ 1 \times 10^{-2}\ \mathrm{kg\,m^{-3}}$). The density measurements were made in a water bath whose temperature was controlled to ± 0.05 K.

Sound velocities of the acid solutions were measured with a multifrequency ultrasonic interferometer (M-84, Mittal Enterprises, New Delhi) at a frequency of 3 MHz at 303.15 ± 0.05 K. The uncertainty in sound velocity was within $\pm 0.5\,\mathrm{m\,s^{-1}}$.

RESULTS AND DISCUSSION

The densities, d of the acid solutions determined in the solvents concerned were used to convert molalities, into molarities, c of the acid solutions by the usual relation [6]. The apparent molar volume, ϕ_v of the acids was calculated by using the relation [7]

$$\phi_v = 1000(c\,d_o)^{-1}\,(d_o - d) + M_2\,d_o^{-1} \qquad (1)$$

where d_o is the density of the solvent, and M_2 is the molecular weight of the acid concerned. The ϕ_v data were fitted by a method of least squares to Masson equation

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

to obtain ϕ_v^o and S_v.

The apparent molar expansibility ϕ_E of the acids was calculated using the relation

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

The ϕ_E data were also fitted by a method of least squares to an equation of the form,

$$\phi_E = \phi_E^o + S_E c^{1/2} \tag{4}$$

α_o and α are the co-efficients of thermal expansion of solvent and solution, respectively. The values of ϕ_v^o, S_v, ϕ_E^o and S_E are presented in Table I at different temperatures.

The positive values of S_v for the acids in all solvents at the experimental temperatures indicate the presence of ion–ion interaction varying with change of temperature and acid. The ϕ_v^o values are also positive for the acids in all solvents at the four temperatures indicating the presence of ion-solvent interaction at infinite dilution (as the ion–ion interaction vanishes at infinite dilution). As observed ϕ_v^o increased with increase of temperature. The temperature dependence of ϕ_v^o for the acids in various solvents can be represented as,

$$\phi_v^o = a + bT \tag{5}$$

over the temperature range 288.15–318.15 K, where a and b are the constants and given in Table II. The ϕ_v^o values of the acids in various solvents follow the order: water > 5 wt% methanol > 5 wt% ethanol > 5 wt% propanol. As the ϕ_v^o is a measure of ion-solvent interaction, the higher ϕ_v^o value in water indicates that ion-solvent interaction is more in aqueous medium than in aqueous alcohol media, and the ion-solvent interaction decreases with increase in — CH_2 — group in the co-solvent, alcohol. In other words, hydrophobic solvation predominates over the hydrophilic solvation in aqueous alcohols and increases as the hydrophobic (*i.e.*, — CH_2 —) group

TABLE I Values of ϕ_v^o (m^3 mol^{-1}), S_v ($m^{9/2}$ $mol^{-3/2}$), ϕ_E^o (m^3 mol^{-1}) and S_E ($m^{9/2}$ $mol^{-3/2}$) for benzoic and phenylacetic acids in water and water + alcohol (5 wt%, each of methanol, ethanol and propanol) mixtures

wt% alcohol (1)	*Temp./K* (2)	10^3 ϕ_v^o (3)	10^5 S_v (4)	10^5 ϕ_E^o (5)	10^7 S_E (6)
			Benzoic acid		
0.00	288.15	69.46(7)	48.74(5)	21.24(4)	8.13(1)
	298.15	71.41(5)	51.26(5)	21.33(4)	7.98(1)
	308.15	73.48(8)	52.01(6)	21.46(3)	8.02(1)
	318.15	75.60(8)	52.43(5)	21.54(4)	6.77(1)
5 wt% methanol	288.15	63.41(6)	51.39(4)	21.43(3)	7.84(1)
	298.15	65.43(7)	52.45(5)	21.36(4)	8.05(1)
	308.15	67.52(7)	52.93(5)	21.70(4)	8.02(1)
	318.15	68.9(7)	53.73(5)	21.86(4)	8.13(1)
5 wt% ethanol	288.15	61.34(7)	52.09(4)	17.91(3)	8.36(1)
	298.15	63.35(6)	53.08(4)	18.03(3)	8.51(1)
	308.15	65.61(6)	53.37(5)	18.16(4)	8.47(1)
	318.15	66.52(7)	53.52(5)	18.26(3)	8.40(1)
5 wt% propanol	288.15	59.31(5)	52.07(5)	17.56(3)	8.46(1)
	298.15	61.33(7)	52.40(5)	17.78(3)	8.48(1)
	308.15	63.40(6)	52.82(5)	17.99(3)	8.45(1)
	318.15	64.40(6)	54.11(6)	18.21(4)	8.53(1)
			Phenylacetic acid		
0.00	288.15	79.08(7)	54.41(6)	21.33(4)	8.32(1)
	298.15	81.70(7)	50.72(5)	21.43(4)	7.93(1)
	308.15	83.58(8)	50.67(6)	21.64(4)	7.75(1)
	318.15	85.72(7)	51.33(6)	21.78(4)	7.77(1)
5 wt% methanol	288.15	72.48(7)	50.98(6)	21.63(4)	7.86(1)
	298.15	74.59(7)	50.07(6)	21.76(4)	8.09(1)
	308.15	76.64(8)	51.66(6)	21.89(4)	7.78(1)
	318.15	78.78(7)	52.36(5)	22.06(4)	7.81(1)
5 wt% ethanol	288.15	70.44(6)	50.78(6)	18.10(3)	8.17(1)
	298.15	72.50(7)	51.13(6)	18.22(4)	8.18(1)
	308.15	74.58(7)	51.69(7)	18.34(3)	8.18(1)
	318.15	76.71(7)	51.93(6)	18.49(3)	8.17(1)
5 wt% propanol	288.15	68.41(7)	50.66(6)	17.76(3)	8.71(1)
	298.15	70.12(8)	53.34(5)	17.94(3)	8.04(1)
	308.15	72.28(8)	54.62(5)	18.18(3)	8.25(1)
	318.15	74.49(8)	55.49(6)	18.42(4)	8.25(1)

The figures in parentheses are the standard deviations in the order of 10^{-2}.

increases in the homologous alcohol. The higher ϕ_v^o values of phenylacetic acid in all solvents as compared to those of benzoic acid may be attributed to the greater hydrophilic character of phenylacetic acid.

The ϕ_v^o (Tab. I) increases with increase in temperature indicating the presence of caging or packing effect [8]. As is seen the ϕ_E^o values of the acids at any temperature follow the order: water < 5 wt% metha-

TABLE II Values of constants a and b of Eq. (5) and a', b' of Eq. (6) for benzoic and phenylacetic acids in water and water + alcohol mixtures

wt% alcohol	$10^3\,a$	$10^4\,b$	$10^5\,a'$	$10^7\,b'$
		Benzoic acid		
0	10.37(3)	2.04(2)	18.27(4)	1.03(1)
5 wt% methanol	10.12(2)	2.00(2)	17.30(4)	1.43(2)
5 wt% ethanol	10.20(3)	1.78(2)	14.51(3)	1.18(2)
5 wt% propanol	9.44(2)	1.73(2)	11.34(2)	2.16(3)
		Phenylacetic acid		
0	16.33(4)	2.18(2)	16.81(3)	1.56(2)
5 wt% methanol	15.06(4)	2.01(2)	17.53(3)	1.42(2)
5 wt% ethanol	10.22(4)	2.09(3)	14.37(2)	1.29(2)
5 wt% propanol	9.48(3)	2.04(3)	11.34(2)	2.22(4)

The figures in parentheses are the standard deviations in the order of 10^{-2}.

nol < 5 wt% ethanol < 5 wt% propanol, which is reverse to that of the ϕ_V^o values.

The temperature dependence of ϕ_E^o for the acids in various solvents can be represented as

$$\phi_E^o = a' + b'T \tag{6}$$

over the temperature range 288.15 to 318.15 K, where a' and b' are the constants and given in Table II. The sound velocity, U is related to the density, d of the solution and isentropic compressibility, K_s by the relation

$$U = (K_s d)^{-1/2} \tag{7}$$

The values of K_s obtained for solutions of different concentrations can be fitted to an equation of the form

$$K_s = K_s^o + A'c + B'c^{3/2} + C'c^2 \tag{8}$$

where A', B' and C' are constants. The values of K_s^o and the constants are given in Table III. Typical plots of $(K_s - K_s^o)/c$ *vs* $c^{1/2}$ are shown in Figure 1.

The apparent isentropic molar compressibility, $K_{s,\phi}$ of the acid solution in different concentrations has been computed using the

TABLE III The constants A', B', C' of Eq. (8), and A'', B'' of Eq. (10), $K^o_{s,\phi}$ (Pa^{-1}) and S^o_n of benzoic and phenylacetic acids in water and water + alcohol mixtures at 303.15 K

Acid	$A' \times 10^{14}$	$B' \times 10^{14}$	$C' \times 10^{14}$	$A'' \times 10^{11}$	$B'' \times 10^{11}$	$K^o_{s,\phi} \times 10^{11}$	S^o_n
			(*water*, $U_o = 1509.2$ m sec^{-1}, and $K^o_s = 44.09$ Pa^{-1})				
Benzoic acid	−56.21(3)	12.30(2)	−0.839(1)	12.31(2)	−0.837(2)	−52.97(4)	41.89
Phenylacetic acid	−74.06(4)	16.75(3)	−1.153(2)	16.42(1)	−1.155(2)	−69.82(5)	53.63
			(5 *wt% methanol*, $U_o = 1532.6$ m sec^{-1}, $K^o_s = 43.15$ Pa^{-1})				
Benzoic acid	−51.14(3)	10.85(2)	−0.734(1)	10.85(2)	−0.732(1)	−48.22(4)	38.95
Phenylacetic acid	−68.28(5)	15.29(4)	−1.045(2)	14.67(3)	−0.985(2)	−63.85(5)	49.90
			(5 *wt% ethanol*, $U_o = 1544.6$ m sec^{-1}, $K^o_s = 42.49$ Pa^{-1})				
Benzoic acid	−49.06(3)	10.48(2)	−0.719(1)	10.47(2)	−0.718(1)	−46.23(4)	37.15
Phenylacetic acid	−64.31(4)	14.36(3)	−0.983(1)	14.36(3)	−0.981(1)	−61.13(5)	47.34
			(5 *wt% propanol*, $U_o = 1552.6$ m sec^{-1}, $K^o_s = 42.03$ Pa^{-1})				
Benzoic acid	−47.67(3)	10.24(2)	−0.700(1)	10.22(2)	−0.696(1)	−44.95(4)	36.23
Phenylacetic acid	−60.30(4)	13.58(2)	−0.942(2)	13.27(3)	−0.909(2)	−56.52(5)	44.14

The figures in parentheses are the standard deviations in the order of 10^{-2}.

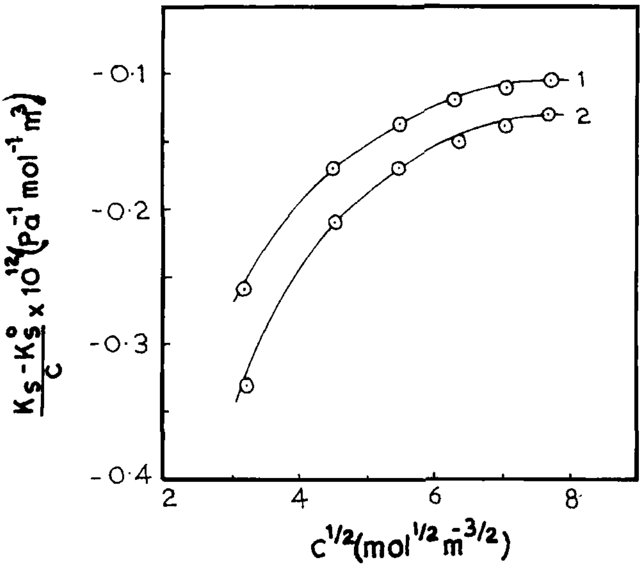

FIGURE 1 Plot of $K_s - K_s^o/c$ vs $c^{1/2}$ (1. benzoic acid and 2. phenylacetic acid) in water at 303.15K.

relation,

$$K_{s,\phi} = 1000\,K_s c^{-1} - K_s^o d_0^{-1}(1000\;c^{-1} d - M_2) \tag{9}$$

The $K_{s,\phi}$ data can be fitted to an equation of the form

$$K_{s,\phi} = K_{s,\phi}^o + A''\,c^{1/2} + B''\,c \tag{10}$$

to obtain $K_{s,\phi}^o$ (the limiting apparent isentropic molar compressibility of the acid). The values of constants A'' and B'' alongwith $K_{s,\phi}^o$ are given in Table III. Typical plots of $K_{s,\phi}$ *vs* $c^{1/2}$ are shown in Figure 2.

The molar sound velocity, R, and the specific acoustic impedance Z, have been determined from the sound velocity and density of the solutions by the following equations.

$$R = \overline{M} d^{-1}\,U^{1/3} \tag{11}$$

and $Z = Ud$ respectively.

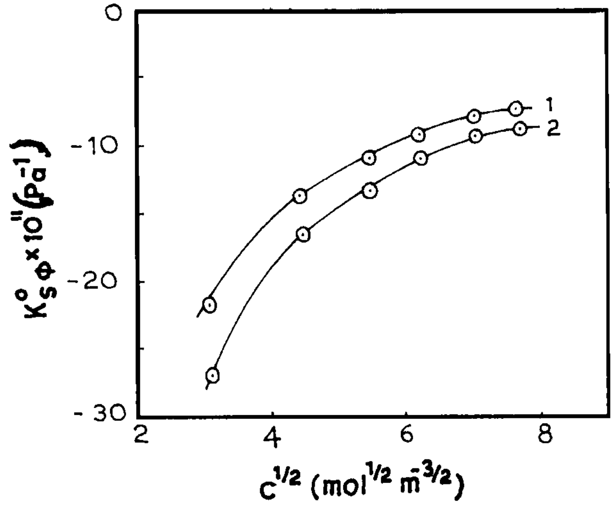

FIGURE 2 Plot of $K^o_{s,\phi}$ *vs* $c^{1/2}$ (1. benzoic acid and 2. phenylacetic acid) in 5 wt% methanol at 303.15 K.

Where $\overline{M}$ is the average molecular weight of the solution, and is given by $\overline{M} = \Sigma(n_1 m_1/n_1)$. The values of R and Z are plotted against the square root of molar concentration of the acids in Figures 3 and 4, respectively.

The solvation number, S_n of a solute related to the isentropic compressibility, K_s by Eq. (12)

$$S_n = n_1 n_2^{-1}[1 - VK_s(n_1 V_1^o K_s^o)^{-1}] \tag{12}$$

where V is the volume of the solution containing n_2 moles of solute (acid), V_1^o is the molar volume of the solvent, and n_1 is the number of moles of the solvent. The variation of the solvation number with the molar concentration of the acid leads to the limiting solvation number, S_n^o and can be obtained from the relationship

$$\lim_{c \to o} K_{s,\phi} = -S_n^o V_1^o K_s^o \tag{13}$$

The values of S_n^o are presented in Table III.

As expected, the sound velocity increases with increase in concentrations of the solutions in all solvents and are in the order:

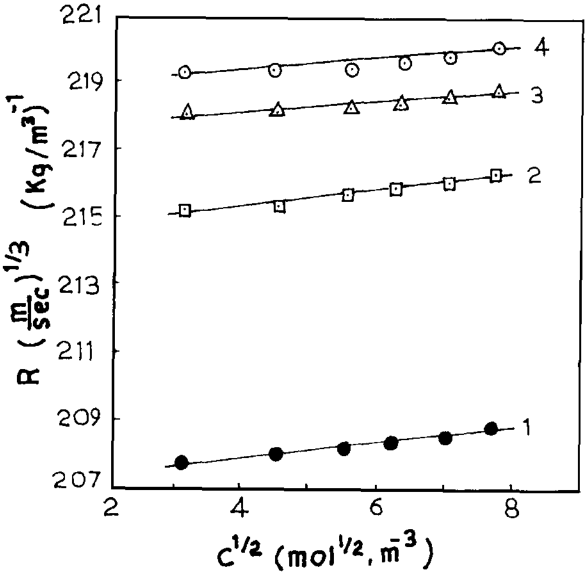

FIGURE 3 Plot of R *vs* $c^{1/2}$ of benzoic acid (1. water, 2. 5 wt% methanol, 3. 5 wt% ethanol and 4. 5 wt% propanol) at 303.15 K.

water < 5 wt% methanol < 5 wt% ethanol < 5 wt% propanol. The sound velocity increases with increase of molecular weight of the acid.

The isentropic compressibility, K_s decreases with the concentration of the solution. It follows that the isentropic compressibility of the solvation layer is smaller than that of the solvent in bulk. The decrease in compressibility may be due to the fact that the interstitial spaces of water molecules are filled up by the organic co-solvent, alcohol molecules.

As observed the values of K_s for any acid solutions are in the order: water > 5 wt% methanol > 5 wt% ethanol > 5 wt% propanol. This may be owing to the ions (produced from the acids in solution) and water molecules in immediate contact in the mixed solvents are incompressible due to filled up interstitial spaces of water molecules by the organic co-solvent molecules.

It is found that the apparent isentropic molar compressibility, $K_{s,\phi}$ increases with increase of solution concentration. The negative $K^o_{s,\phi}$ values [9, 10] may be explained in terms of two different phenomena *viz.*, electrostriction and hydrophobic solvation. The loss of compres-

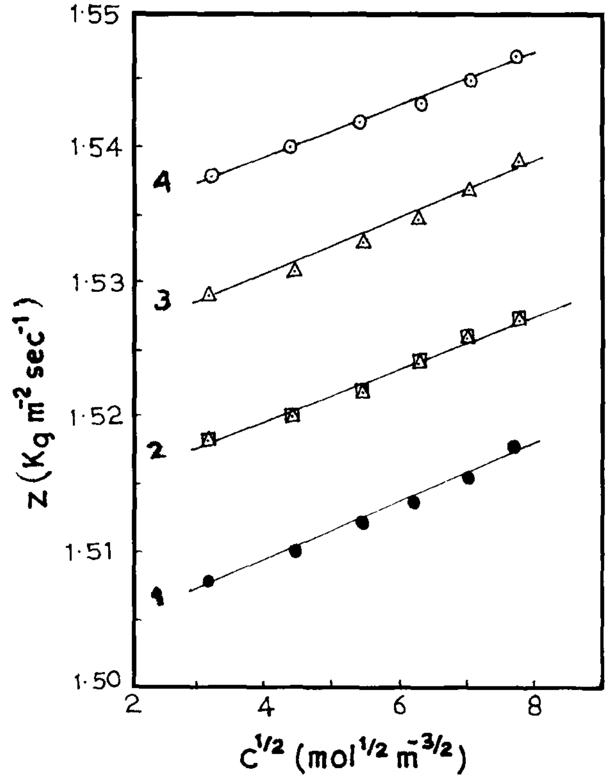

FIGURE 4 Plot of Z *vs* $c^{1/2}$ of phenylacetic acid (1. water, 2. 5 wt% methanol, 3. 5 wt% ethanol and 4. 5 wt% propanol) at 303.15 K.

sibility of the surrounding solvent molecules due to strong electrostrictive forces at the anionic end causes electrostrictive solvation. However, for the case of phenylacetic acid the hydrophobic solvation predominates over the electrostrictive solvation because of the greater size of the hydrophobic moieties of the acid molecules. As observed, the $K^o_{s,\phi}$ value decreases with increasing number of *C-atom* in the organic co-solvent, alcohols indicating the increased electrostrictive solvation of anions.

As previously [1–4], the solvation number, S_n decreases with increase in concentration of the solution as well as with increase of — CH_2 — groups in homologous organic co-solvent, alcohols in water. The higher limiting solvation number, S^o_n for phenylacetic as compared to that for benzoic acid in all solvents maybe due to the greater hydrophobic solvation provided by phenylacetic acid containing the large sized non-polar moiety. A perusal of Table III shows that the solvation number, S_n^o of both the acids is larger in water than in water + alcohol solvents and decreases with increase in —CH_2— groups in the homologous organic co-solvent alcohols. It means that the solvation layer formed around the anion is thick and/or hard in water medium while that in mixed solvents is thin and/or loose.

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