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Density and Speed of Sound of Sodium Nitroprusside with Aqueous Alcohols

Upendra Nath Dash, Sujata Mishra and Biswajit Samantray
Department of Chemistry, ITER, SOA University, Jagamohan Nagar, Bhubaneswar-751030,Odisha, India.

STUDIES on apparent molar volumes for the solutions of sodium nitroprusside in aqueous solutions of methanol, ethanol and propanol in the temperature range 298.15 to 313K at 5K intervals have been determined from the density measurements of the solutions. Speed of sound of solutions of sodium nitroprusside in aqueous solutions of alcohols has also been experimentally determined at 303.15K.Molar isentropic compressibilities and apparent molar isentropic compressibilities have been calculated from the speed of sound data. These results have been used to calculate the following partial molar quantities :

$$V_{\phi}, E_{\Phi}^{0}, K_{s\Phi}^{0}$$

Various acoustic parameters and solvation number have been evaluated for sodium nitroprusside in different aqueous solutions of alcohols. The results are discussed in the light of solute- solvent and solute –solute interactions.

Keywords: Water, Alcohols**,** Sodium nitroprusside, Apparent molar volume, Density, Solvation number, Ultrasonic velocity, Molar isentropic compressibilities and Apparent molar isentropic compressibilities.

Physico-chemical studies involving determination of partial molar properties, acoustical properties(1-5)…, etc. have gained much importance during last two decades for studying ion-ion and ion-solvent interactions in aqueous, non-aqueous and mixed solvent media. Since density measurements can provide interesting information about the ion-ion, ion-solvent and solvent-solvent interactions(6,7), we now report the partial molar and thermal expansibility values based on density measurements of sodium nitroprusside in different compositions of water + methanol + ethanol and + propanol mixtures in the temperatures ranging from 298.15K to 313.15K at an interval of 5K. Ultrasonic velocity leading to isentropic compressibility and isentropic molar compressibility is also measured in water and in aqueous solutions of methanol, ethanol and propanol at 303.15K only to study the structural effect of solute and solvent molecules in solutions.

Experimental

Methanol, ethanol and propanol (SRL extra pure samples) were purified by methods available in literature(4). Conductivity water (specific conductivity, 10^{-6} S cm^{-1}) was used for preparation of various compositions of water and alcohol mixtures. The solutions of sodium nitroprusside were made by weight and conversion of molality to molarity was done by using standard expression(8). Density and ultrasonic velocity measurements were done, respectively, by a bicapillary pyknometer with an accuracy of ±0.1kgm^{-3}and single frequency ultrasonic interferometer (Mittal Enterprises, New Delhi) at a frequency of 2 MHz with an accuracy of ± 0.5 ms^{-1}.

The electrolyte content in the solutions varied over a range of 0.01M to 0.1M in various solvents. At least five observations were taken for each solution in each determination and differences in any two readings did not exceed 0.02%. Measurements of densities and speed of sound of the solutions of sodium nitroprusside in the range of temperature 298.15K to 313.15K (but speed of sound at 303.15Konly) were taken as a function of the concentrations. A thermostatistically controlled well-stirred water bath whose temperature was controlled to ± 0.01K was used for all the measurements.

Results and Discussion

The concentrations c (mol dm^{-3}) of solutions of sodium nitroprusside in water and in different water + alcohols mixtures were computed from the molalities, m by the relation(8):

$$c = md\,(1 + 0.001\,m\,M_2)^{-1} \tag{1}$$

where M_2 is the molecular weight of sodium nitroprusside. From the density data, the apparent molar volume V_ϕ was calculated by using Equation (2)(9):

$$V_\phi = 1000\,(cd_0)^{-1}\,(d_0 - d) + M_2 d_0^{-1} \tag{2}$$

where d_0 is the density of water + alcohol mixture. It was found that the V_ϕ varied linearly with concentration $c^{1/2}$ (typical plots are shown in Fig. 1). The V_ϕ data were fitted by a method of least squares to Masson Equation (9).

$$V_\phi = V_\phi^0 + S_v c^{1/2} \tag{3}$$

to obtain V_ϕ^0 (the limiting apparent molar volume) and the slope, S_v. The values of V_ϕ^0 and S_v are given in Table 1.

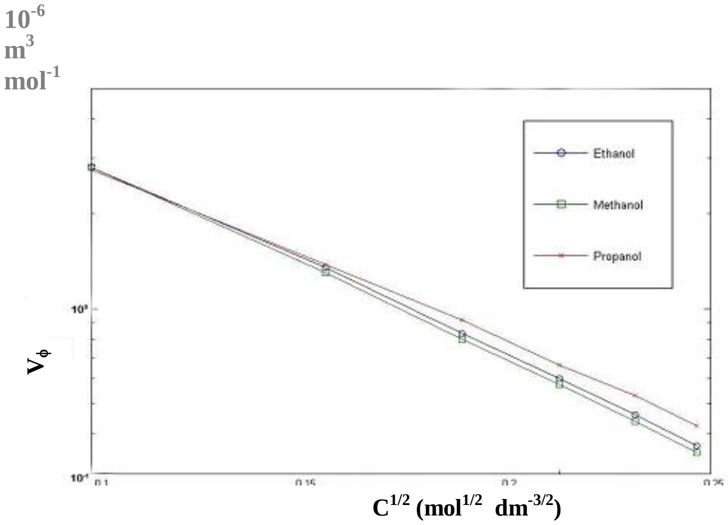

Fig. 1. Plot of V_Φ Vs. $C^{1/2}$ for sodium nitroprusside in 5 weight % of methanol, ethanol and propanol at 298.15K.

TABLE 1. Different density parameters d_0 (Kg m^{-3}), V^0_Φ(m^3 mol^{-1}), S_v ($m^{3/2}mol^{-3/2}$), E^0_Φ ($m^3mol^{-1}K^{-1}$) and S_E($m^{3/2}mol^{-3/2}K^{-1}$), for sodium nitroprusside in various aqueous solutions of methanol, ethanol and propanol at different temperatures.

Solvent	Weight %	T(K)	$(10^{-3})d_0$	$(10^{-4})V^0_\Phi$	Sv	$(10^{-6})E^0_\Phi$	$(10^{-3})S_E$
Water		298.15	0.9970	14.42(6)	-44.81(9)	43.72(6)	149.00(6)
		303.15	0.9956	16.58(5)	-44.01(9)	43.72(7)	362.55(8)
		308.15	0.9940	82.91(8)	-25.88(9)	5.87(8)	369.85(3)
		313.15	0.9922	53.40(4)	-27.58(9)	2.47(2)	10587.42(5)
Methanol	5	298.15	0.9877	39.393(9)	-15.896(8)	30.100(6)	-107.691(14)
		303.15	0.9867	40.817(9)	-16.403(9)	26.012(8)	-107.216(9)
		308.15	0.9857	42.041(9)	-16.908(9)	4.947(3)	-29.791(4)
		313.15	0.9827	42.157(9)	-17.003(9)	20.721(5)	-83.035(8)
	10	298.15	0.9799	37.058(8)	-14.687(8)	62.751(14)	-245.571(9)
		303.15	0.9769	40.010(9)	-15.842(9)	28.037(9)	-130.596(9)
		308.15	0.9749	41.295(9)	-16.446(9)	13.895(4)	-52.697(4)
		313.15	0.9719	41.848(9)	-16.653(9)	35.868(8)	-146.878(6)
	15	298.15	0.9722	86.473(20)	-34.092(19)	36.138(9)	-153.842(35)
		303.15	0.9712	88.086(20)	-34.781(20)	27.477(9)	-116.855(17)
		308.15	0.9702	89.289(20)	-35.295(20)	8.341(4)	-34.385(16)
		313.15	0.9662	89.585(20)	-35.418(20)	24.216(6)	-102.659(22)
	20	298.15	0.9644	89.996(20)	-35.463(20)	123.854(35)	-565.638(7)
		303.15	0.9634	95.707(22)	-38.077(20)	95.144(17)	-313.163(9)
		308.15	0.9624	100.045(22)	-39.494(22)	78.539(16)	-286.849(2)
		313.15	0.9544	103.597(23)	-40.787(23)	100.509(22)	-393.679(5)

TABLE 1. Cont.

Solvent	Weight %	T(K)	$(10^{-3})d_0$	$(10^{-4})V_\Phi^0$	Sv	$(10^{-6})E_\Phi^0$	$(10^{-3})S_E$
Ethanol	5	298.15	0.9867	39.215(9)	-15.928(9)	45.775(7)	-143.453(4)
		303.15	0.9861	41.417(9)	-16.614(9)	28.034(9)	-104.970(6)
		308.15	0.9854	42.748(9)	-17.111(9)	7.012(2)	-11.035(5)
		313.15	0.9836	43.012(9)	-17.133(9)	27.119(5)	-86.959(5)
	10	298.15	0.9804	42.159(9)	-16.937(9)	21.657(4)	-71.7069(7)
		303.15	0.9792	43.159(9)	-17.264(9)	17.338(6)	-85.293(9)
		308.15	0.9778	43.940(10)	-17.654(10)	14.787(5)	-73.615(2)
		313.15	0.9762	44.588(10)	-17.983(10)	18.205(5)	-78.033(5)
	15	298.15	0.9734	37.687(8)	-15.171(8)	122.238(7)	-490.398(22)
		303.15	0.9714	43.570(10)	-17.530(10)	40.893(9)	-177.892(14)
		308.15	0.9694	45.469(10)	-18.358(10)	8.566(2)	-16.008(8)
		313.15	0.9664	45.749(10)	-18.381(10)	58.506(5)	-233.130(14)
	20	298.15	0.9724	53.521(12)	-21.224(12)	99.162(22)	-397.902(17)
		303.15	0.9704	58.192(13)	-23.098(13)	56.568(14)	-204.572(6)
		308.15	0.9684	60.791(13)	-24.032(13)	39.228(8)	-157.041(2)
		313.15	0.9664	62.550(14)	-24.737(13)	66.245(14)	-258.058(8)
Propanol	5	298.15	0.9882	38.475(8)	-15.158(8)	57.204(17)	-266.307(14)
		303.15	0.9872	41.221(9)	-16.439(9)	30.645(6)	-119.968(4)
		308.15	0.9862	42.669(9)	-17.006(9)	7.75092)	-25.087(4)
		313.15	0.9843	42.968(9)	-17.096(11)	32.144(8)	-138.31716)
		303.15	0.9781	50.262(11)	-20.074(11)	44.833(4)	-197.881(4)
		308.15	0.9775	52.395(12)	-21.016(11)	26.209(4)	-102.790(4)
		313.15	0.9763	53.595(12)	-21.486(12)	44.193(6)	-175.990(6)
	15	298.15	0.9742	43.876(10)	-17.471(10)	42.522(14)	-202.997(14)
		303.15	0.9715	45.873(10)	-18.430(10)	16.358(4)	-83.285(4)
		308.15	0.9691	46.589(10)	-18.803(10)	2.595(4)	-12.237(4)
		313.15	0.9676	46.608(10)	-18.819(10)	20.909(6)	-101.336(6)
	20	298.15	0.9672	43.373(10)	-17.420(10)	33.398(12)	-155.361(12)
		303.15	0.9644	44.866(10)	-18.123(10)	27.339(9)	-122.043(9)
		308.15	0.9628	46.101(10)	-18.678(10)	15.095(7)	-29.421(7)
		313.15	0.9570	46.740(10)	-18.782(10)	206.020(47)	-815.221(47)

Values in parenthses are the uncertainties of the respective parameters. The uncertainties of V_ϕ^0 are of the order of 10^{-6}, Sv , 10^{-3} ; E_φ^0 , 10^{-8} and $S_{E,}$ 10^{-6}

The densities, d of ternary solutions have been represented by the relation (4),

$$d = d_0 + Ac + Bc^{3/2} \tag{4}$$

where A= 10^{-3} ($M_2 - d_0 V_\phi^0$) and B = 10^{-3} $S_v d_0$

Typical plots of $(d-d_0)/c$ versus $c^{\frac{1}{2}}$ are shown in Fig. 2. The values of d_0 of aqueous binary solvents are presented in Table 1.

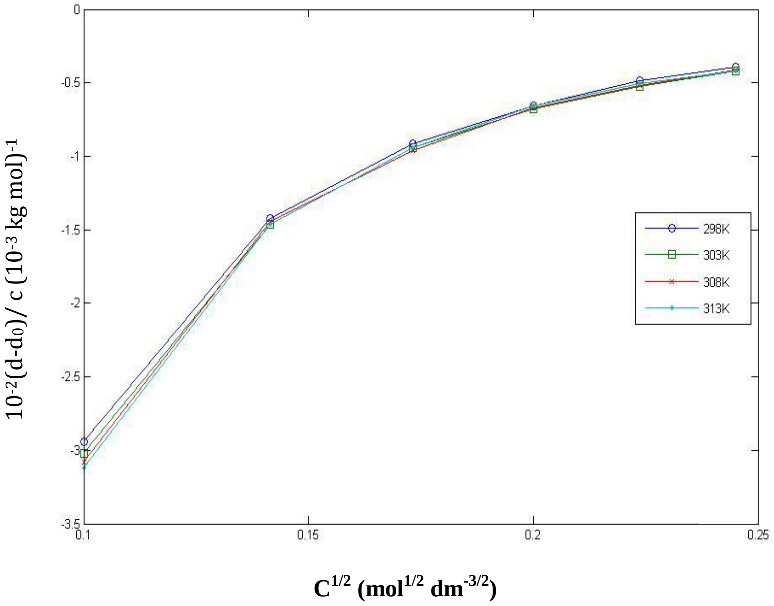

Fig. 2. Plot of $(d-d_0)/C$ Vs. $C^{1/2}$ for sodium nitroprusside at different temperatures for 5% weight of methanol.

The partial molar expansibility, $\bar{E}_2$ of sodium nitroprusside has been evaluated by using Equation (5)(9).

$$\bar{E}_2 = E_\phi + (1000 - c\,E_\phi)\,(2000 + S_E c^{3/2})^{-1}\, S_E c^{1/2} \qquad (5)$$

where E_ϕ is the apparent molar expansibility and its value was determined from Equation (6)(8)

$$E_\phi = \alpha_0 V_\phi + (\alpha - \alpha_0)\,1000c^{-1} \qquad (6)$$

and S_E is the slope of the plot of E_ϕ versus $c^{\frac{1}{2}}$, (typical plots are shown in Fig. 3, *i.e.*

$$E_\phi = E_\phi^0 + S_E\, c^{\frac{1}{2}} \qquad (7)$$

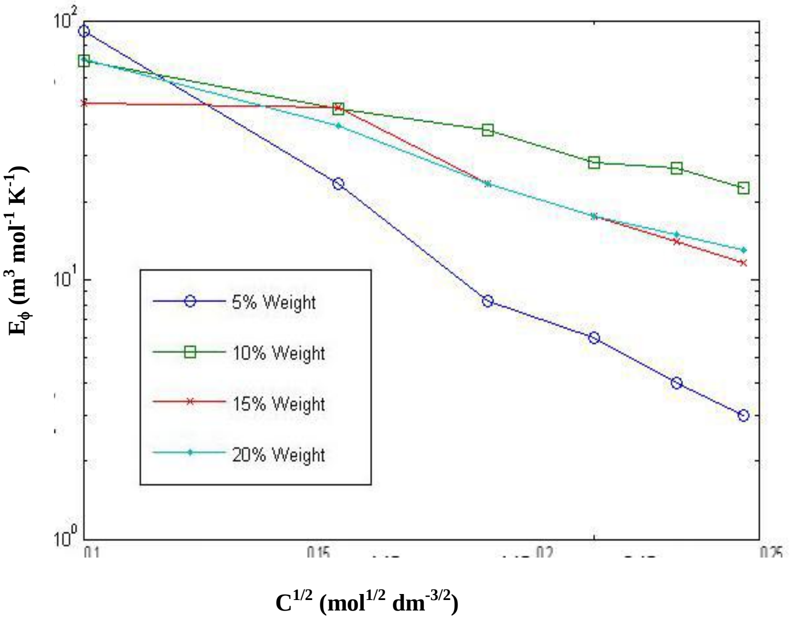

Fig. 3. Plot of E_Φ Vs. $C^{1/2}$ for sodium nitroprusside in various composition of methanol at different temperatures for 5% weight.

The values of E_ϕ^0 and S_E are recorded in Table 1. In Equation (6), α_0 and α are the coefficients of thermal expansion of solvent and solution, respectively, and are obtained by the relation

$$\alpha_0 = -1/d_0(\delta d_0/\delta t)_p \text{ and } \alpha = -1/d(\delta d/\delta t)_p \qquad (8)$$

reported in the literature (9).

The ultrasonic velocities U of the solutions of sodium nitroprusside in mixed solvents at different concentrations were fitted to an equation of the form(10).

$$U = U_0 + Fc + Gc^{3/2} + Hc^2 \qquad (9)$$

over the concentration range studied for sodium nitroprusside in the mixed solvents concerned, where U_0 is the sound velocity in pure water and mixed solvent, F, G and H are the constants. Typical plots of $(U - U_0)/c$ versus $c^{\frac{1}{2}}$ are shown in Fig. 4. The values of U_0, F, G and H are recorded in Table 2.

TABLE 2. Values of U_0 (ms^{-1}), and the constants F, G, H of Equation (9) for sodium nitroprusside in different compositions of methanol, ethanol and propanol at 303.15K.

Solvent	Weight %	U_0	$(10^{-3})F$	$(10^{-4})G$	$(10^{-4})H$
Water		1470	7.09	-5.53	1.19
Methanol	5	1500	17.7321	-13.6891	28.7705
	10	1580	6.2822	-5.0177	10.8838
	15	1600	4.3809	-3.0511	6.3402
	20	1620	16.2780	-13.1686	28.6834
Ethanol	5	1530	12.7975	-10.5367	23.5380
	10	1590	8.9691	-7.0123	15.1200
	15	1620	6.2220	-4.1471	8.7643
	20	1650	11.0938	-8.4478	17.7535
Propanol	5	1550	9.2485	-7.4667	16.4415
	10	1600	26.9797	-22.0660	48.8353
	15	1700	26.8767	-21.8986	48.5912
	20	1790	12.1371	-9.0210	18.4765

Uncertainties in U_0 values are of the order 0.5

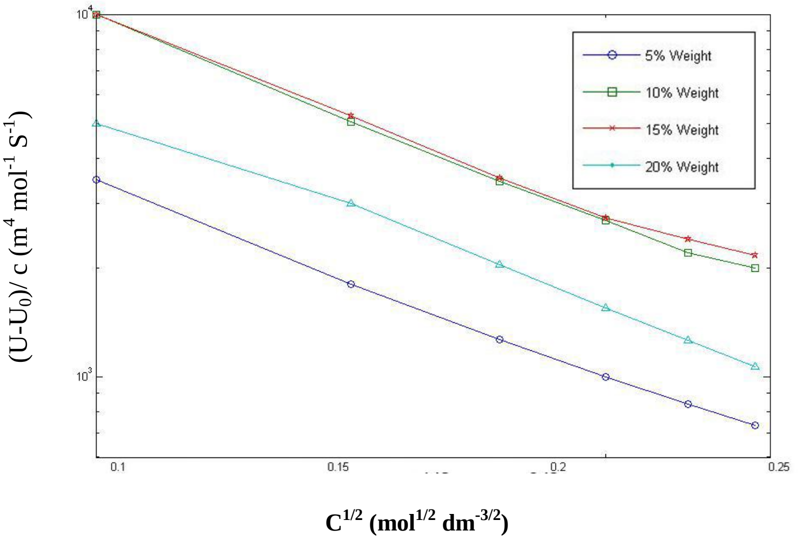

Fig. 4. Plot of $(U-U_0)/C$ Vs $C^{1/2}$ for sodium nitroprusside in various composition of propanol at 303.15K for 5% weight.

The ultrasonic velocity, U is related to the density, d of the solution and isentropic compressibility K_s, by the relationship(11)

$$U = (K_s d)^{-\frac{1}{2}} \tag{10}$$

The values of K_s obtained for solutions of different concentrations were filtted to an equation of the form,

$$K_s = K_s^0 + A'c + B'c^{\frac{3}{2}} + C'c \qquad (11)$$

where A', B' and C' are the constants. The values of K_s^0 and constants are presented in Table 3. Typical plots of $(K_s - K_s^0)/c$ versus $c^{\frac{1}{2}}$ are shown in Fig. 5.

TABLE 3. Values of K_s^0 (pa^{-1}) and the constants A', B', C' of Equation(11) for sodium nitroprusside in different compositions of methanol, ethanol and propanol at 303.15K.

Solvent	Weight %	$(10^{-7})K_s^0$	$(10^{-6})A'$	$(10^{-6})B'$	$(10^{-6})C'$
Water		-6.55	-4.36	3.41	-7.3
Methanol	5	4.63(1)	-10.307	7.997	-16.863
	10	4.22(1)	-3.284	2.624	-5.692
	15	4.28(5)	-2.318	1.621	-3.364
	20	4.23(8)	-8.100	6.560	-14.300
Ethanol	5	4.45(1)	-7.135	5.871	-13.093
	10	4.16(3)	-4.564	3.575	-7.707
	15	4.04(9)	-3.062	2.059	-4.326
	20	3.94(3)	-5.130	3.920	-8.240
Propanol	5	4.34(1)	-5.022	4.057	-8.930
	10	4.13(1)	-5.022	4.057	-8.930
	15	3.67(3)	-10.692	8.710	-19.284
	20	3.33(5)	-4.380	3.280	-6.750

Values in parentheses are the uncertainties of the the order of 10^{-7}

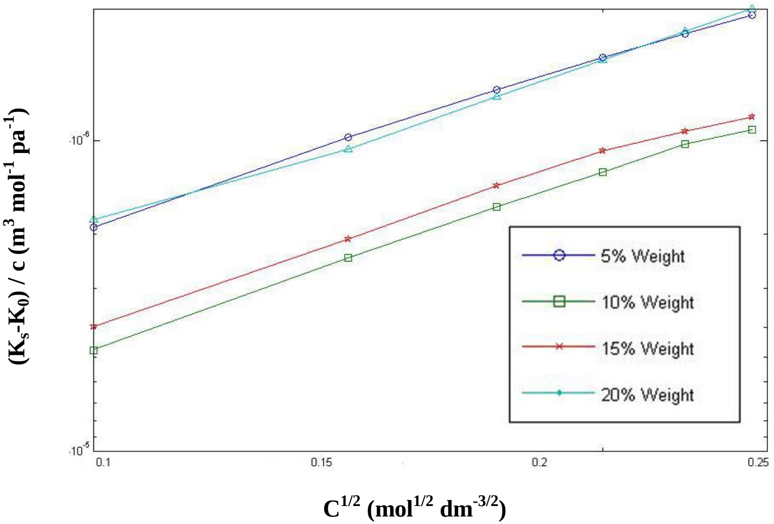

Fig. 5. Plot of $(K_s - K_s^0)/C$ Vs. $C^{1/2}$ for sodium nitroprusside in various composition of propanol at 303.15K.

The apparent molar properties are found to depend on the concentrations of the solution. The apparent isentropic molar compressibility $K_{s,\Phi}$ has been computed from$^{(12)}$ Equation 12,

$$K_{s\phi} = 1000 K_S c^{-1} - K_S^0 d_0^{-1} \left(1000 c^{-1} d - M_2\right) \tag{12}$$

The $K_{s,\Phi}$ data were fitted to Equation (13),

$$K_{S,\Phi} = K^0{}_{S,\Phi} + F'c^{1/2} + G'c \tag{13}$$

to obtain $K_{S\ \Phi}^0$ (the limiting apparent isentropic molar compressibility of sodium nitroprusside). Typical plots of $K_{s\ \Phi}$ versus $c^{\frac{1}{2}}$ are displayed in Fig.6. The values of $K_{S\ \Phi}^0$ and the constants F' and G' are given in Table 4.

x10^{-3}

$K_{S\phi}$ (m^3 mol^{-1} Pa^{-1})

$C^{1/2}$ ($mol^{1/2}$ $dm^{-3/2}$)

Fig. 6. Plot of $K^0_{s\Phi}$ Vs. $C^{1/2}$ for sodium nitroprusside in 5 weight % of methanol, ethanol, propanol and water at 303.15K.

The solvation number, S_n of a solute can be related to the isentropic compressibility by Equation (14)$^{(13)}$

$$S_n = n_1 n_2^{-1} \left[1 - V K_S (n_1 V_1^0 K_S^0)^{-1}\right] \tag{14}$$

where V is volume of the solution containing n_2 moles of solute. V_1^0 is the molar volume of solvent and n_1 is the number of moles of solvent. The variation of solvation number with molar concentration of the solute leads to the limiting solvation number, S_n^0 which was also obtained from the relation (15).

$$\lim_{C \to 0} K_{s\,\Phi} = -S_n^0 V_1^0 K_s^0 \tag{15}$$

The values of S_n^0 are presented in Table 4.

TABLE 4. Values of $K_{s\Phi}^0$ (m^3 mol^{-1} pa^{-1}) and the constant F' and G' of Equation (12) and S_n^0 for Sodium nitroprusside in various aqueous solutions of methanol, ethanol and propanol at 303.15K.

Solvent	Weight %	$(10^{-4})K_{s,\Phi}^0$	(10^{-4})F’	(10^{-4})G’	S_n^0
Water		-65.54(2)	488.79	-1006.4	19
Methanol	5	-65.5429(1)	488.7969	-1006.4779	18
	10	-0.1750(2)	-3.7327	7.9104	47
	15	50.2765(5)	-437.5118	967.3529	17
	20	0.0434(8)	-15.5791	46.3226	13
Ethanol	5	-35.0000(1)	289.0000	-661.0000	10.
	10	-10.1394(3)	64.3715	130.5729	11
	15	5.0000(3)	-91.0000	222.0000	17
	20	-7.0000(2)	27.0000	-33.0000	13
Propanol	5	-14.5845(3)	110.4074	-244.7521	7
	10	-86.8988(4)	708.7945	-1576.9548	8.
	15	-73.0890(3)	588.8809	-1307.5000	8
	20	-13.5412(5)	74.1562	-115.2908	11

Values in parentheses are the uncertainties of the the order of 10^{-6}

The values of density and sound velocity enable us to estimate the magnitude of the relative association, R_A from the relation (16)$^{(3)}$.

$$R_A = d/d_0\,(U_0/U)^{\frac{1}{3}} \tag{16}$$

Typical plots of the variation of R_A with concentration are shown in Fig 7. As expected, the experimental density increased with increase of concentration of sodium nitroprusside at each temperature in all solvents (Fig. 2). But the density decreases with temperature at the same concentration. A perusal of Table 1 shows that the S_v values for the sodium nitroprusside are negative in all the mixed solvents at all temperatures and decreases with increase in temperature and with increase in alcohol content, (except in 15 wt % propanol) in aqueous mixtures. The negative values of S_v indicate the presence of weak ion-ion interactions varying with the change of temperature and the organic co – solvent. The limiting apparent partial molar volume, V_Φ^0 values (Table 1) are however, positive and large in all the mixed solvents at the experimental temperatures indicating the presence of strong ion- solvent interaction at infinite dilution. As observed, the V_{Φ}^{0} shows an increasing trend with increasing temperature and the alcohol content in the mixed solvent. The ion- solvent interactions for the sodium nitroprusside in water and the various mixed solvents follow the order: water <water + propanol < water + ethanol < water + methanol. The higher V_{Φ}^{0} values for sodium nitroprusside in water+methanol mixtures suggest that it is more solvated in water+methanol mixtures than in other aqueous alcohol mixtures. This may be due to the fact that with increase in the $–CH_2$ group in the homologous alcohol molecules the solute solvent interaction decreases. These results can be explained by strong hydrogen bonds that are possible between the hydroxyl groups of methanol and water. It is seen from the data in Table 1 that the limiting apparent molar expansibility, E_{Φ}^{0} values are positive in all solvents and vary irregularly with temperature and solvent composition. But in almost all the solvents E_{Φ}^{0} shows a decreasing trend with increasing temperature .These results indicate the presence of caging or packing effect(14) in water + alcohol mixtures. The increase in alcohol contents in the mixed solvents has a suppressive effect on the expansibility of sodium nitroprusside, which may probably be due to cooperative fluctuations of the H-bond network in the system.

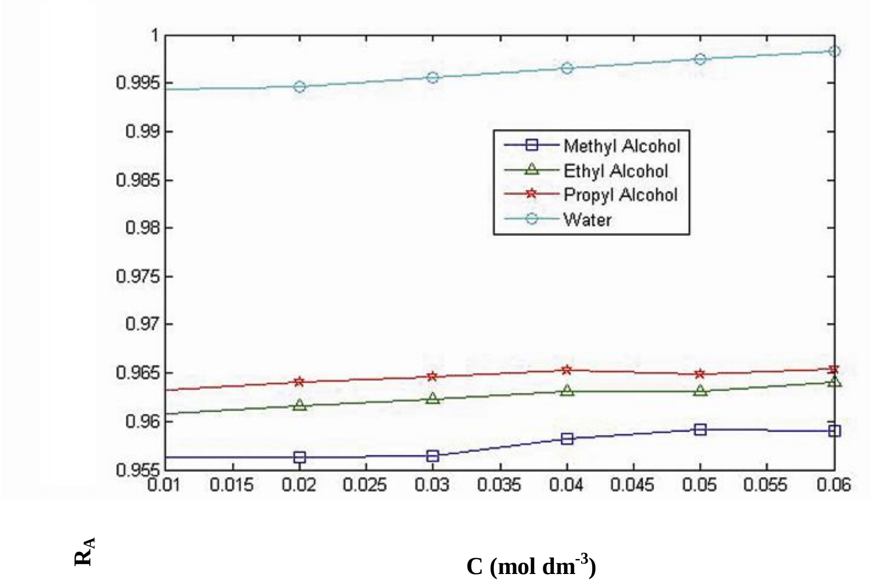

Fig. 7. Plot of R_A Vs. C for sodium nitroprusside in water and 5 weight % of methanol, ethanol, propanol and water at 303.15K.

The experimental speed of sound displayed in Fig. 4 increases with increase in concentration of nitroprusside, in alcohol content and also in increase of the $–CH_2$ group in the homologous alcohol series. The isentropic compressibility K_s decreases as the proportion of alcohol (methanol, ethanol or propanol) increases in water. Such changes are also reported by other workers(4) in water + methanol, water + ethanol and water + DMSO(1,3) which may be due to the fact that the interstitial space of water molecules are filled by the organic co solvent molecules, *e.g.* alcohols.

The data on differential sound velocity, *i.e.* $(U - U_0)/c$, (Fig. 4), show an increasing trend of negative values of the first derivative with increase in alcohol content in the mixed solvent. The increasing values of the second derivation (Table 2) suggest a strong ion- solvent interaction, and the third derivative indicates the ion- ion interaction. As discussed earlier because of weak ion- ion interactions the third derivative is not considered here. It has been observed that the apparent isentropic molar compressibility, $K_{s,\Phi}$ increases with increase in solution concentration. The values of $K_{s,\Phi}$ are almost negative and also $K^0_{s\Phi}$ values (Table 4). The negative $K^0_{s\Phi}$ values can be explained in terms of loss of compressibility of the surrounding solvent molecules due to strong electrostrictive solvation of the solute. As observed $K^0_{s\Phi}$ varies irregularly with the organic co- solvent (alcohol) composition and also with the change in the number of $-CH_2$ group in the alcohol. This indicates that the electrostrictive solvation of nitroprusside ions (a larger anion) probably changes irregularly (as stated above) due to cooperative fluctuation of the H-bond network in the systems involving alcohol and water molecules.

The solvation number decreases with increase in concentration of the solution as well as with the alcohol content in water. Similar is the case with the limiting solvation number, $\mathbf{S^0_n}$. It was found that the $\mathbf{S^0_n}$ of sodium nitroprusside is larger in water than in water + alcohol mixtures. Since sodium nitroprusside shows strong electrostriction in water as compared to that in water + alcohol mixtures. It is considered that the solvation layer formed around the ions is thick and / or hard in water while that in water + alcohol mixtures is thin and/ or loose. However, any change in S^0_n from one solvent to another is regarded as a measure of the degree of hard electrostrictive solvation. As observed, the relative association (R_A) is a function of ultrasonic velocity. The relative association is influenced by two factors (i) The breaking- up of the solvent structure on addition of solute to it and (ii) the solvation of solute .The former results in decrease and the latter results in increase in R_A. The increase in R_A with concentration (Fig.7) suggests that The solvation of sodium nitroprusside predominates over breaking –up the solvent structure. It is observed, that R_A increases linearly with concentration for sodium nitroprusside.

Conclusion

The apparent molar volumes at infinite dilution show linear dependence on temperature. The high positive value of V^0_Φ indicates the presence of strong ion-solvent interaction at infinite dilution, and a greater partial molar volumes increase with temperature indicates a greater structural sensitivity. The increase in the magnitude of the relative association, RA ,with concentration points to the fact that the solvation of sodium nitroprusside predominates over the breaking-up the solvent structure.

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كثافة وسرعة الصوت فى محاليل الكحولات المخففة من نتروبروسيد الصوديوم

أبندراناث داش وسوجاتامشرا وبسواجيت سامانترى
قسم الكيمياء– ايتر– جامعة سوا – جاجاموهان ناجار – بوبانيسوار – 751030 –
اوديشا – الهند.

قدم هذا البحث دراسات على الحجوم (الأحجام) الجزيئية الظاهرية لمحاليل نتروبروسيد الصوديوم فى درجة حرارة تتراوح بين 13و298 – 313 كالورى لتقدير كثافة القياسات فى المحاليل كما أمكن تقدير سرعة الصوت فى هذه المحاليل عند درجة حرارة 15و303 كالورى وتم تقديم الحسابات الرياضية لهذه القياسات كما نوقشت نتائج هذه الدراسات فى ضوء التداخلات من نوع ذائب – مذيب ومذيب – مذيب .