

Apparent molar volume of sodium chloride in mixed solvent at different temperatures

C.K. RATH¹, N.C. ROUT², S.P. DAS³ and P.K. MISHRA⁴

¹Department of Chemistry, Synergy Engineering College, Dhenkanal, Odisha (INDIA)

²Department of Chemistry, B.B.Mahavidyalaya, Harichandanpur, Keonjhar, Odisha (INDIA)

^{3,4}Department of Chemistry, Ravenshaw University, Cuttack, Odisha (INDIA)

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Abstract

Apparent molar volume of NaCl have been studied in Ethanol, Methanol, Propan-2-ol, Dioxane, Glycol, Glycerol water mixture at 10, 20 and 30% (w/w) within the temperature range 30⁰ -40⁰C and ion solvent interaction has been inferred.

Introduction

Ion solvent interaction studies have attracted considerable attention in recent years^{1,2,3}. The influence regarding the interaction is derived from density data. As it is the easiest and simplest thermodynamic property that can be studied, in the present communication, the apparent molar volume (ϕ) of NaCl in ethanol, methanol, propan-2-ol, dioxane, glycol, glycerol water mixture at solvent compositions 10, 20 and 30% (w/w) have been studied and nature of ion solvent interaction is derived.

Experimental

The Sodium Chloride used in the present work were analytical reagent (AR) grades with a minimum assay of 99.9%, obtained from S.D. Fine Chemicals (India) without further

purification. In all the measurements various concentrations of the solvent mixtures were prepared in terms of molarity varied from 0.1000 to 0.0010. The densities of pure liquids and liquid mixtures were determined using pycnometer at 30⁰, 35⁰ and 40⁰ C. An Oswald's viscometer with 10ml capacity was used for the viscosity measurements of pure liquids and liquid mixtures. The viscometer was calibrated with fresh conductivity water immersed in a water bath and that can be operated at various temperatures. The flow time of solvent and the flow time of solutions were measured with a digital stop clock with an accuracy of 0.01s (RACER HS-10W). For each concentration, the mass of Sodium Chloride was measured using electronic digital balance having an accuracy ± 0.1 mg. (Model : SHIMADZU AX200).

Discussion

The apparent molar volume (ϕ) of a solution is most conveniently calculated from the density data of the solution using the equation.

$$\phi = \frac{M}{\rho_0} - \frac{(\rho - \rho_0)}{\rho_0} \frac{10^3}{C} \quad (1)$$

where M is the molecular weight of the solute C is the molar concentration of the electrolyte. ρ and ρ_0 are the densities of the solution and solvent respectively. The data obtained have been found to agree with the Masson's equation on the plot of ϕ vs $C^{1/2}$ is linear. The values of the limiting apparent molar volume (ϕ^0) obtained from the extrapolation of the plot to zero concentration and the limiting slope (S_v) are reported in tablets 1 & 2. The limiting

apparent molar volume (ϕ^0) decreases slightly with the increase in temperature for the salt studied at all solvent compositions¹⁻⁷.

Dependence of ϕ^0 on temperature :

The variation of ϕ^0 with temperature can be explained on the basis of ion dipole interaction as follows as non-aqueous solvents are somewhat less hydrogen bonded than that of water, the ion dipole interaction energy will be appreciable and attachment of solvent molecules to that of ions may not loose and at the same time no structure formation would occur around the ion. The net result will be slightly less in solvation and the expansion of the solvent would be less appreciably that of pure solvent. The reason may be described due to strong ion solvent interaction together with primary and secondary solvation depending on the ionic radius.

Table 1. $\phi^0/\text{cm}^3\text{mol}^{-1}$

	Temp $^{\circ}\text{C}$	10%	20%	30%
Methanol + Water	30	23.2	27.3	30.3
	35	23.3	27.2	30.2
	40	22.4	27.1	30.1
Ethanol + Water	30	23.5	27.6	31.0
	35	23.4	27.5	31.7
	40	23.3	27.4	31.6
Propan-2-ol + Water	30	22.2	26.4	27.9
	35	22.3	26.3	28.1
	40	22.4	26.2	28.4
Dioxane + Water	30	21.3	24.6	26.6
	35	21.2	24.5	26.4
	40	21.1	24.4	26.3
Glycol + Water	30	22.5	25.6	26.5
	35	22.4	25.5	26.4
	40	22.3	25.4	26.4
Glycerol + Water	30	21.1	23.2	24.2
	35	21.3	23.1	24.2
	40	20.7	23.0	23.7

Table 2. (S_v)

	Temp $^{\circ}\text{C}$	10%	20%	30%
Methanol	30	1.15	1.26	1.34
+	35	1.14	1.17	1.32
Water	40	1.13	1.15	1.30
Ethanol	30	1.25	1.32	1.42
+	35	1.24	1.30	1.40
Water	40	1.23	1.31	1.28
Propan-2-ol	30	1.18	1.21	1.27
+	35	1.19	1.21	1.29
Water	40	1.19	1.14	1.25
Dioxane	30	1.05	1.16	1.30
+	35	1.06	1.17	1.30
Water	40	1.06	1.16	1.31
Glycol	30	1.04	1.30	1.40
+	35	1.03	1.20	1.30
Water	40	1.02	1.10	1.20
Glycerol	30	1.00	1.00	1.05
+	35	1.01	1.01	1.08
Water	40	1.02	1.02	1.07

Limiting Slope (S_v) :

At all temperatures of the present study, the limiting apparent slope (S_v) of the Masson's equation is positive (Table 2) suggesting ion-ion interaction. It may be attributed due to the change in the mobility of the ions due to the change in the dielectric constant in all the solvents. The ion-ion interaction in different solvents is of the order ethyl alcohol + water > methyl alcohol + water > propan-2-ol + water > dioxane + water > glycol + water > glycerol + water.

Dependence of ϕ^0 on aquo-organic solvents:

It is observed from Table 1 that ϕ^0 increase with the increase in non-aqueous solvent and may be attributed due to low surface charge density as a result of which the electrostatic attraction is more in a medium of low dielectric constant. Hence, ion solvent interaction would also be more and consequently will be larger and the order is ethanol + water > methanol + water > propan-2-ol + water > dioxane + water > glycol + water > glycerol + water.

Further the plot of the values of ϕ^0 vs $1/\epsilon$ reciprocal of the dielectric constant is found to be linear in all the cases and the slope values of these plots follow the order ethanol + water > methanol + water > propan-2-ol +

water > dioxane + water > glycol + water > glycerol + water indicating the dependence of the dielectric constant of the medium and is in agreement with the observation of Gopal *et al*⁴.

Partial ionic volume :

From the limiting apparent molar volume data along with KCl and KBr data of P.B.Das partial ionic volumes for the common ions have been evaluated and have been used to investigate the nature of the ion solvent interaction in solutions. For the sake of convenience, the limiting apparent molar volume ϕ^0 ($\equiv V^0$) for different salts in all the three solvent mixtures at 40°C only. Assuming the additivity law to hold good for V^0 values

for electrolytes. V^0 of the salt have been divided into ionic contribution by plotting V^0 vs r^3 assuming that for spherical ions, V^0 should be a monotonic function of the crystallographic radii.

The limiting partial molar volume of an ion can be assumed to be the sum of the major contribution namely the geometric part and electrostriction part⁴ and can be written as :

$$V_{\text{ion}}^0 = V_{\text{geom.}}^0 + V_{\text{electrostriction}}^0 \quad (2)$$

where, V_{geom}^0 taking into account the interionic volumes of the ions plus the void space effects created on introducing ions into the solvent and V_{elect}^0 the contribution due to electrostriction is due to the electrostatic ion solvent dipole interaction. A number of relations have been

Table 3. Constants A & B with K^{-1} in equ.5 at 40°C K^0

	10%		20%		30%	
	A	B	A	B	A	B
Methanol + water	7.1	10.8	7.4	13.2	6.3	14.4
Ethanol + water	8.1	11.8	8.5	14.7	7.5	16.3
Propan-2-ol + water	7.1	10.2	7.1	13.0	6.0	14.2
Dioxane + water	6.16	10.0	6.33	12.2	5.50	14.0
Glycol + water	5.1	9.2	5.8	11.1	5.0	12.0
Glycerol + water	4.9	8.9	5.4	10.5	4.5	11.8

Table 4. Disorted V^0 at 40°C/ r^3 cm mole⁻¹

	10%	20%	30%
Methanol + water	20.5	21.3	17.6
Ethanol + water	22.6	22.4	18.7
Propan-2-ol + water	20.0	20.7	17.0
Dioxane + water	19.5	20.3	16.5
Glycol + water	18.4	19.2	15.4
Glycerol + water	17.8	18.6	14.8

proposed connecting these two effects with the radius of the ion^{5,6} *i.e.*

$$V_{\text{ion}}^- = Ar^3 + B(z^2/r) \quad (3)$$

$$\text{and, } V_{\text{ion}}^0 = 2.52 r^3 + (A + 2.52 r^3) - B (z^2/\eta) \quad (4)$$

The above two equations (3) and (4) have been used to separate the geometric and electrostriction part as the plot of $V_i^0 (\eta/z^2)$ vs. (r^2/z^2) is linear. The constant B, the electrostriction part is obtained from the intercept and A, the geometric part is obtained from the slope.

The geometric part of the partial molar volume has further been divided into the intrinsic size of the ion, V_{int}^0 and void space effect V^0 disorder using equation (4). From this (table) it is concluded that the disorderliness of the mixed solvents is of the order.

ethanol + water > methanol + water > propan-2-ol + water >
dioxane + water > glycol + water > glycerol + water

Solvation number (η_s) :

The limiting apparent molar volume ϕ^0 of the solutions in all the mixed solvents (10,

20 & 30% w/w) is considered as equal to partial molar volume at zero concentration *i.e.* $\phi^0 = V^0$. This V_{int}^0 and V_{electro}^0 by the relation:

$$V^0 = V_{\text{int}}^0 + V_{\text{elect}}^0$$

due to solvation V_{elect}^0 is calculated by the method of Conway *et al.* and V_{elect}^0 is then calculated. The V_{elect}^0 is related to be number of water molecules solvated with the salts by the equation.

$$V_{\text{elect}}^0 = \eta_p (V^0 E - V_1^0)$$

Where $V^0 E$ is the molar volume of the electrostatic water and V^0 is the molar volume of bulk layer and using the value of $(VE^0 - V_1^0) = 3.3 \eta_s$ is evaluated (Table 5).

This η_s value increases with the increases with the increase in organic solvent. This shows that in presence of these solvent, there is increase in electrostriction of solvation and the order is glycerol + water > glycol + water > dioxane + water > propan-2-ol + water > methanol + water > ethanol + water and the reverse is the structure breaking order. The reason has been explained as follows :

Ethanol, methanol and propan-2-ol have got one –OH group whereas water is

Table 5. η_s at 40°C

	10%	20%	30%
Ethanol + water	3.5	3.9	4.3
Methanol + water	3.9	4.4	4.9
Propan-2-ol + water	4.0	4.6	5.2
Dioxane + water	4.2	4.9	5.4
Glycol + water	4.8	5.6	6.1
Glycerol + water	5.2	6.0	7.1

both an electron donor and acceptor. Hence, the former could accept a proton from water and hence the three dimensional water structures are easily broken down⁴⁻⁶.

The addition of small amount of dioxane to water may give rise to two effects if the dioxane is accommodated in the solvent structure, it may strengthen the water structure because dioxane is a proton acceptor if it can not be accommodated because of its bulky size then it may cause a breakdown in three dimensional water structure. Several authors have observed that dioxane + water is less ordered than pure water. It is observed that ΔE and ΔG increase with in dioxane content and hence the three dimensional water structure is broken down through the quanta is less than that of ethanol and methanol + water mixtures.

Glycol has got two –OH groups and

glycerol has got 3 –OH groups, so it should have more tendency to break hydrogen bond more readily than methyl alcohol and ethyl alcohol, but the reverse is seen to be true. This is probably due to the low ion solvent dipole interaction energy which is unable to break the strong intermolecular hydrogen bond.

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