Thermodynamics of Some Sodium Salts in Glycol + Water and Glycerol + Water Mixtures at Different Temperatures

P.C. MOHANTY, B.B. NANDA, C. CHAKRABORTY and P.K. MISRA*

*Department of Chemistry, Mayurbhanj Chemical Laboratory,
Ravenshaw College, Cuttack-753 003, India*

The ion solvent interaction of NaCl, NaBr and NaI in glycol + water and glycerol + water along with the data of methanol + water and dioxane + water at 10, 20 and 30% (w/w) within the temperature range of 30–40°C have been inferred from conductance data. The dissociation constants K, $\Delta G°$, ΔG_1°, $\Delta G_{t(el)}^\circ$ have been computed and the ion-solvent interactions have been inferred.

Key Words: Thermodynamics, NaCl, NaBr, NaI, Salt solutions.

INTRODUCTION

The physical properties of the mixed solvents like glycol + water and glycerol + water, *viz.*, dielectric constants, dipole moments are very much different from those of water. These organic solvents are more or less aprotic, water is both an electron donor and acceptor[1]. These and several other properties make a study of their aqueous mixtures an interesting thing to explore, particularly of the ionic processes accompanying the solution of strong electrolytes.

In the present communication, the conductivities of sodium salts in glycol + wter and glycerol + water along with the data of methanol + water and ethanol + water[2] mixture at 30–40°C have been compared to investigate the non-solvent interaction.

EXPERIMENTAL

The salts used were of E. Merck extra pure varieties. The purification of solvents, preparation of solvents and solutions and measurement of conductance have been done as reported previously[3]. The conductance measurements were performed within an accuracy of 0.002 and in the concentration range from 0.01 to 0.001 equiv. L^{-1}.

RESULTS AND DISCUSSION

The Onsagar equation[1] for a completely dissociated electrolyte is:

$$\Lambda = \Lambda° - (A + B\Lambda°)\sqrt{C} \qquad (1)$$

where A and B are independent of concentration of the electrolytes. It satisfactorily accounts for the change in the equivalent conductivities with concentration.

Correct evaluation of Λ° can be made by extrapolating to zero concentration of the line obtained by plotting Λ *vs.* $C^{1/2}$. However, the above method of extrapolation has been reported to be unreliable in cases of a number of electrolytes involving incomplete dissociation or ion association. Electrolytic conductivities have been used to study ion solvent interaction and salvation of various eations and anions in aqueous and non-aqueous solution.

The equivalent conductivity of NaCl, NaBr, NaI in glycol and glycerol (10, 20 and 30%) water mixtures at 30–40°C are found to be almost linear with $C^{1/2}$. The theoretical slope (S_T) calculated from the determined Λ° values for different electrolytes at different solvent compositions has been obtained and compared with the experimental slope (S). Dielectric constants were calculated from the data of Akerlof and Short and viscosities were determined experimentally. The S_T and S values are almost in fair agreement and differ by 2–3%. Λ° values are given in Table-1.

TABLE-1

$\Lambda_0/\Omega^{-1} cm^2$

	Temperature (°C)	Composition (%)								
		10	20	30	10	20	30	10	20	30
I	30	100	199	90	104	99	90	110	103	88
	35	105	104	95	109	104	96	115	108	94
	40	110	109	100	114	110	101	120	114	100
II	30	112	102	93	115	101	97	120	113	95
	35	118	109	100	122	106	103	128	121	100
	40	123	110	106	128	110	108	133	128	106
III	30	141	118	102	134	113	100	103	95	86
	35	144	121	105	138	116	101	109	100	90
	40	156	129	108	144	123	102	115	105	95
IV	30	195	147	126	113	97	93	115	110	108
	35	197	155	140	132	118	110	132	122	114
	40	200	162	150	130	122	118	148	144	135
V	30	175	154	80	192	136	97	124	97	96
	35	196	172	109	199	148	120	135	115	87
	40	200	178	116	200	152	126	146	120	97

The Walden product[2] $\Lambda^\circ\eta_0$ (Table-2) has been actually employed to study ion-solvent interactions in solution from conductivity data. The plot of $\Lambda^\circ\eta_0$ *vs.* t is found to be linear and is almost independent of temperature. Further, the mere constancy of the Walden product at different temperatures is most presumably due to compensating contribution of the temperature coefficient of the conductivity by the negative temperature coefficient of the viscosity of the solvent. The electrostatic charge densities of the ion play an important role in inducing ion-solvent interaction and salvation. It also appears that during these migrations of these common ions they are covered with a sheath of solvent molecules resulting in a larger size of the solvodynamic unit and a decrease in R_n (Table-2), so that the size of the solvated ions and the ion-solvent interaction is of the order

$Br^- > Cl^- > I^-$ and ethanol + water > methanol + water > dioxane + water > glycol + water > glycerol + water and is in agreement with the viscosity and apparent molar volume data.

TABLE-2

$\Lambda^\circ \eta_0 / \Omega^{-1} cm^2 \rho$

	Temperature (°C)	Composition (%)								
		10	20	30	10	20	30	10	20	30
I	30	1.07	1.16	1.17	1.14	1.15	1.15	1.14	1.15	1.16
	35	1.06	1.16	1.12	1.13	1.15	1.14	1.13	1.16	1.15
	40	1.07	1.16	1.15	1.14	1.14	1.15	1.14	1.16	1.15
II	30	1.09	1.18	1.19	1.16	1.17	1.18	1.18	1.19	1.20
	35	1.10	1.20	1.20	1.18	1.19	1.19	1.21	1.23	1.25
	40	1.20	1.21	1.22	1.20	1.20	1.20	1.30	1.30	1.30
III	30	1.24	1.24	1.23	1.19	1.18	1.18	1.31	1.32	1.35
	35	1.25	1.24	1.22	1.18	1.19	1.18	1.32	1.31	1.32
	40	1.21	1.25	1.23	1.18	1.19	1.18	1.31	1.32	1.31
IV	30	1.19	1.20	1.21	1.15	1.16	1.14	1.26	1.26	1.26
	35	1.19	1.19	1.20	1.16	1.16	1.15	1.26	1.27	1.27
	40	1.20	1.20	1.20	1.15	1.16	1.16	1.27	1.26	1.26
V	30	1.16	1.16	1.15	1.13	1.12	1.12	1.24	1.24	1.22
	35	1.16	1.16	1.16	1.13	1.13	1.13	1.23	1.23	1.23
	40	1.15	1.16	1.16	1.14	1.13	1.13	1.24	1.23	1.23

Because of the use of glycol and glycerol + water mixtures, the dielectric constant of the medium is lowered and there is more probability of ion-pair formation. Hence, the method of Fuoss and Krauss[3] and that of Shedlovsky[4] have been utilized to calculate the dissociation constant and Λ° simultaneosuly. K values calculated by both the methods are in good agreement and are recorded in Table-3. The K values decrease with the decrease in dielectric constant, i.e., with increase in non-aqueous solvent. They have been calculated in the usual manner. The plots of ΔG° and ΔS° vs. solvent composition are found to be linear. The extrapolated values give the thermodynamic parameter for water. The standard thermodynamic quantities (ΔG_t° and ΔS_t°) for transfer process from water to 10, 20 and 30% of organic solvent + water have been calculated by using Feakin's and Tuner's method[5]. ΔG_t° values are presented in Table-4. The ΔG° values are all negative, which indicates that the ion pairs are in a lower free energy state in aquo-organic solvent than in water and hence the ion pair formation is favoured by decreasing the dielectric constant of the medium.

TABLE-3

$K \times 10^2$

	Temperature (°C)	Composition (%)								
		10	20	30	10	20	30	10	20	30
I	30	18.20	12.50	9.90	14.10	11.30	9.90	8.50	7.80	5.80
	35	18.10	12.40	9.80	14.20	11.20	9.90	8.40	7.90	5.70
	40	17.80	12.20	9.70	14.30	11.40	9.90	8.20	7.70	5.80
II	30	19.70	13.10	10.80	16.20	14.80	11.30	8.90	8.10	6.00
	35	19.50	13.20	10.10	16.40	15.20	11.20	10.10	8.20	6.10
	40	19.20	13.40	10.20	16.80	15.70	11.10	10.90	8.30	6.30
III	30	21.68	14.79	11.75	18.20	17.20	14.45	10.20	8.40	6.30
	35	20.89	13.52	10.72	17.38	10.22	12.88	10.30	8.30	6.20
	40	19.99	12.38	9.77	16.60	15.14	11.22	10.30	8.20	6.10
IV	30	18.98	12.71	10.52	16.21	13.62	11.24	8.94	7.85	6.24
	35	19.81	12.81	10.51	16.58	14.78	11.95	9.98	8.12	6.14
	40	19.24	12.14	9.78	15.34	13.52	11.84	8.59	7.95	6.12
V	30	17.71	11.51	10.25	13.42	13.22	10.42	9.11	8.02	6.24
	35	18.91	11.91	10.11	15.82	15.52	10.52	9.05	7.98	6.04
	40	17.81	11.71	10.12	14.52	13.42	10.72	9.25	7.82	6.52

TABLE-4

$-\Delta G_t^\circ / J \, mol^{-1}$

	Temperature (°C)	Composition (%)								
		10	20	30	10	20	30	10	20	30
I	30	420	1271	1752	398	549	1152	384	589	765
	35	501	1360	1782	402	560	1251	394	620	820
	40	520	1358	1841	430	580	1255	420	640	904
II	30	451	1381	1932	412	630	1352	402	603	805
	35	566	1421	2060	500	780	1481	480	716	912
	40	595	1510	2110	590	799	1602	510	792	972
III	30	614	1313	2075	452	832	1414	395	612	1014
	35	743	1521	2373	552	871	1681	505	814	1012
	40	749	2074	2418	1030	1109	2083	518	915	1003
IV	30	894	1505	2360	1005	1733	2474	584	880	998
	35	843	1524	2340	976	1615	2500	605	914	1014
	40	889	1574	2350	1004	1712	2480	598	889	1002
V	30	980	1014	2418	1098	1702	2575	790	1000	1198
	35	900	1605	2415	1020	1715	2515	704	1014	1115
	40	990	1603	2498	1102	1704	2535	707	1010	1112

Since single ion values of free energies are not available presently for the solvent mixtures studied, the method adopted by Khoo[6] is followed to study ion-solvent interaction. The Boron equation may be expected to fit increasingly better as the organic solvent content is increased. It is possible to split the ΔG_t° values into two parts as suggested by Roy *et al.*[7], *i.e.*, chemical contribution denoted in

their terminology by $\Delta G^{\circ}_{t(ch)}$ and an electrostatic contribution $\Delta G^{\circ}_{t(el)}$, which has been calculated from the Boron equation,

$$\Delta G^{\circ}_{t(el)} = \frac{Ne^2}{2}\left(\frac{1}{\Sigma S} - \frac{1}{\Sigma W}\right)\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{2}$$

where, r_+ and r_- are the crystallographic radii of the cation and anion and ΣS and ΣW are dielectric constants of the mixed solvent and water respectively. To calculate the electrostatic part of the entropy of the equation (2), on differentiation and algebraic manipulation, we get

$$\Delta S^{\circ}_{t(el)} = \frac{Ne^2}{2}\left(\frac{1}{\Sigma W}\frac{d\ln\Sigma W}{dt} - \frac{1}{\Sigma S}\frac{d\ln\Sigma S}{dt}\right)\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{3}$$

where $\dfrac{d\ln\Sigma W}{dT}$ and $\dfrac{d\ln\Sigma S}{dT}$ can be evaluated from the simple empirical equation

$$\frac{d\ln\Sigma^{\circ}}{dT} = -\frac{1}{\phi} \tag{4}$$

in which ϕ is a constant characteristic of the medium; so the equation may be written as:

$$\Delta S^{\circ}_{t(el)} = -\frac{Ne^2}{2}\left(\frac{1}{\Sigma S\phi s} - \frac{1}{\Sigma w\phi w}\right)\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{5}$$

From the knowledge of $\Delta G^{\circ}_{t(ch)}$ and $\Delta S^{\circ}_{t(ch)}$ the chemical contribution of the energy transfer, $\Delta G^{\circ}_{t(ch)}$ and entropy transfer, $\Delta S^{\circ}_{t(ch)}$ could be calculated by subtracting the respective electrostatic contribution values from the molar quantities and are tabulated in Tables 5 and 6. It is evident that the chemical contribution of the free energy of transfer is negative in all cases and hence is thermodynamically favourable as far as the chemical interactions are concerned and is of the order:

Ethanol + water > methanol + water > dioxane + water > glycol + water

> glycerol + water

The $\Delta S^{\circ}_{t(el)}$ is also negative in all cases indicating chemical interaction and is of the order:

Ethanol + water > methanol + water > dioxane + water > glycol + water

> glycerol + water

The Walden product[2] may be given by the equation:

$$\lambda^{\circ}\eta_0 = (\lambda^{\circ}_+ + \lambda^{\circ}_-)\eta_0 = \frac{eF}{6\pi}\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{6}$$

where e is the electronic charge of the ion, F is the force acting on the particles, r_+ and r_- are the radii of the cation and anion respectively. Ionic Walden products $\lambda_0 + \eta_0$ and $\lambda_0 - \eta_0$ for the individual ions and hence the single ion mobilities were, therefore, estimated by plotting $\lambda^{\circ}\eta_0$ vs. inverse of radii of the anion. Linear

relations were found to exist al all solvent compositions and at all temperatures. By extrapolating the straight line to $1/r = 0$, $\lambda° + \eta_0$ for Na^+ was estimated. Then on subtracting these values from $\lambda°\eta_0$ the values of $\lambda°\eta_0$ for Cl^-, Br^- and I^- were evaluated and tabulated in Table-7 (only at 35°C).

TABLE-5

$-\Delta G_{t(ch)}^{o}/J\ mol^{-1}$

	Temperature (°C)	Composition (%)								
		10	20	30	10	20	30	10	20	30
I	30	209	280	990	702	1040	1410	332	601	808
	35	220	290	980	750	1000	1540	352	620	815
	40	250	284	960	800	980	1550	362	680	880
II	30	262	292	1010	782	1100	1510	352	701	912
	35	200	251	972	700	1068	1490	350	651	805
	40	132	201	903	630	982	1415	315	603	825
III	30	640	660	1520	786	1266	2087	440	717	1080
	35	227	291	1083	793	1101	1690	450	750	1073
	40	408	151	4085	797	1059	1523	440	780	1055
IV	30	520	810	1090	902	1098	1740	470	830	998
	35	560	781	1005	801	1114	1705	500	850	1170
	40	540	800	1040	890	1095	1770	480	840	1080
V	30	640	894	1205	998	1285	1847	570	1044	1050
	35	660	855	1104	998	1248	1890	600	950	1280
	40	670	890	1204	1004	1255	1812	580	1050	1150

TABLE-6

$-\Delta S_{t(ch)}^{o}/J\ K^{-1}\ mol^{-1}$

	Temperature (°C)	Composition (%)								
		10	20	30	10	20	30	10	20	30
I	30	3.40	7.30	8.40	2.90	6.40	8.90	1.00	2.40	4.20
	35	3.30	7.20	8.50	3.00	6.50	9.00	1.30	2.50	4.10
	40	3.20	7.10	8.30	3.10	6.40	9.00	1.50	2.60	4.20
II	30	3.90	8.10	9.10	3.10	7.10	10.10	0.80	2.80	4.80
	35	4.40	8.80	9.90	3.50	7.40	10.50	0.90	3.30	5.30
	40	4.90	9.50	10.90	4.60	8.90	10.90	1.30	3.90	6.20
III	30	5.37	10.45	13.55	4.26	10.32	12.52	1.34	4.32	6.45
	35	5.62	11.06	11.56	4.22	8.48	11.67	1.11	4.32	6.42
	40	3.12	15.00	11.09	4.24	9.35	10.55	1.45	4.45	6.65
IV	30	4.64	11.86	11.78	5.51	12.60	13.98	3.32	5.02	6.52
	35	4.72	12.82	12.42	5.62	12.15	14.42	2.12	5.42	7.42
	40	4.62	10.90	11.98	5.42	12.25	15.02	2.42	5.12	6.57
V	30	5.61	11.23	12.48	7.21	12.90	15.21	3.92	5.71	8.57
	35	5.71	11.52	13.54	6.82	13.54	15.54	3.72	6.91	8.42
	40	5.51	11.42	13.14	6.92	12.24	15.41	3.82	5.81	8.42

TABLE-7

$\lambda^{\circ}\eta_0/\Omega^{-1}$ cm^2 ρ

	Temperature (°C)	Composition (%)								
		10	20	30	10	20	30	10	20	30
I	30	0.64	0.65	0.64	0.60	0.55	0.55	0.73	0.72	0.72
	35	0.64	0.65	0.64	0.60	0.54	0.54	0.74	0.73	0.71
	40	0.64	0.64	0.64	0.61	0.55	0.55	0.74	0.72	0.71
II	30	0.65	0.65	0.64	0.60	0.52	0.53	0.73	0.73	0.72
	35	0.66	0.65	0.65	0.62	0.58	0.59	0.74	0.74	0.74
	40	0.67	0.67	0.68	0.65	0.60	0.60	0.75	0.75	0.75
III	30	0.65	0.63	0.63	0.60	0.60	0.58	0.70	0.71	0.71
	35	0.63	0.65	0.62	0.58	0.58	0.61	0.71	0.70	0.70
	40	0.63	0.65	0.64	0.62	0.62	0.59	0.71	0.70	0.71
IV	30	0.60	0.60	0.61	0.53	0.53	0.53	0.57	0.64	0.66
	35	0.60	0.60	0.60	0.53	0.53	0.53	0.57	0.65	0.67
	40	0.60	0.60	0.60	0.53	0.53	0.53	0.57	0.65	0.67
V	30	0.57	0.57	0.56	0.50	0.50	0.50	0.63	0.63	0.63
	35	0.57	0.57	0.57	0.50	0.50	0.50	0.63	0.63	0.63
	40	0.58	0.57	0.61	0.50	0.50	0.50	0.63	0.63	0.63

Then on dividing the respective ionic Walden products by the viscosity of solvents, the mobility of each ion was also estimated. Only data at 35°C are given for illustration. Table-8 shows the limiting mobilities of all the anions and ethanol + water > methanol + water > dioxane + water > glycol + water > glycerol + water and Br > Cl > Γ.

TABLE-8

$\lambda^{\circ}\eta_0/\Omega^{-1}$ cm^2 ρ (at 35°C)

	Cl			Br			I		
I	65.40	55.50	48.20	69.40	54.30	50.30	71.30	68.70	52.8
II	68.10	59.10	50.40	72.10	56.20	53.40	76.20	71.10	55.8
III	73.11	61.55	53.57	67.10	57.73	49.32	74.10	69.40	54.8
IV	68.12	58.14	50.44	63.22	53.34	46.24	70.10	60.15	52.4

REFERENCES

1. L. Onsager, *Phys. Z.,* **28,** 277 (1927).
2. N.C. Das and P.B. Das, *Electrochim. Acta,* **23,** 191 (1978).
3. T. Shedloksky, *J. Franklin, Inst.,* **225,** 439 (1938).
5. D. Feakins, D. Turner and D.J. Turner, *J. Chem. Soc.,* 4986 (1965).
6. R. Khoo and C. Chan, *Aust. J. Chem.,* **28,** 721 (1937).
7. R.N. Roy, R.L. Vernon and P.M. Bothwell, *Electrochim. Acta,* **12,** 3 (1977).