Molar Solubility, Solvation and Conductivity Association Parameters of Sodium Fluoride in Mixed Aqueous-Ethanol Solvents at Different Temperatures

Esam A. Gomaa[*]**, R. M. Galal**

Chemistry Department, Faculty of Science, Mansoura University, Mansoura, 35516, Egypt

Abstract   This paper reports the results on the molar solubility (MS), refractive index (RIN) and molar electrical conductance (EC) of the saturated NaF at different temperatures (293.15, 303.15 and 313.15 K) in mixed ethanol (ETOH) –water solvents. From the experimental part, the molar refraction (RM), limiting molar conductance (LEC), association constants (KASS), free energies of association (GASS) were determined for all solutions by using simple equation from the Shedlovslay model of conductivity.Results predicted the exothermic behaviour of the process in most of the cases. All the measured and calculated parameters for solvation (solubility parameters) and association (conductivity parameters) are increased by increasing the mole fraction of ethanol in the mixtures. This indicates more solute-solvent interaction by more adding ethanol in the mixed solvents.The solubility; conductivity and different thermodynamic data calculated here can easily used for the industial determination of sodium fluoride.

Keywords   Molar Solubility, Refractive Index, Conductance, Association Constant, Free Energies of Association

1. Introduction

Fluoride in drinking water was originally added to prevent tooth decay. Studies hve now shown that fluoride causes dental decay. Studies have now shown that fluoride causes dental fluorosis in 10% of the population. Research is also linking fluoride to increased risk of cancer (particularly bone cancer), gene mutations , reproductive problems neurotoxicity (hyper or depressed activity) bone fuorosis (decreasing density) . Fluoride exposure disrupt the synthesis of collagen and leads to breakdown of collagen in bone , muscle. skin, cartilage , lungs , kidney and trachea[1-4] . For industrial uses sodium fluoride is commonly uses in pesticides, including fungicides and insecticides. Various types of adhesives and glues use sodium fluoride as a preservative. Sodium fluoride is also used in making steel and aluminium products. Other industrial uses for sodium fluoride include glass frosting, stainless steel pickling and wood preservation[5].Our purpose is to give new data for solubility and conductivity of sodium fluoride in different ethanol water solvents which can help for the industrial, analytical and biological determination of it.

The solubility of an electrolyte is influenced by a wide range of factors, including ion association ,variation in ionic activity coefficients , complexation and temperature. Solubility is an equilibrium property enable to thermodynamic analysis provided that sufficient information is available[6].

Conductivity explains the ion aggregation and the ion solvation and the competition between them .Two ascpects determine the role of the solvent, its bulk properties and its electron – pair donor and electron – pair acceptor abilities[7].

Molar solubility (MS) and electrical conductance (EC) is very important in elucidating not only the behaviour of ions in solution but also in the study of solution structured effects and the preferential solvation of ions by a solvent[8,9].

Recently, electrical conductance (EC) studies were done in non-aqueous solvents with the intension of investigation ion-ion and ion-solvent interactions[10,11]. In continuation of this we studied the conducting behaviour of NaF in water, ethanol[EtOH] and their mixtures at different temperatures to elucidate the solvation and association behaviours of NaF under prevailing conditions.

2. Experimental

Sodium fluoride 99%, from Aldrich chemicals Co. Ltd., Gillincham, Dorest – England was used. Absolute ethanol of Al-Gomhoria supplements was used, without further purification.

The saturated solutions of sodium fluoride were prepared by dissolving it in H_2O-ETOH mixtures in test tubes. The tubes were placed in a shaken thermostat of the type Assistant for a period of four days, followed by another two days without shaking to reach the necessary equilibrium.

The solubility of sodium fluoride were determined gravimetrically, at least three measurements for each solution, by taking 2 ml of each saturated solution and subjecting it to complete evaporation using small aluminium disks heated by I.R Lamp. The conductance of saturated and different concentrations of NaF solutions were measured by using Digital Conductance K120 Conductivity Bridge with cell constant equal 0.991. The refractive indices of the different solutions were measured by using Abbe refractrometer of the type ATAGO 3T, No: 52507, Japan. Weighing four digits Mettler AE 240 balance was used.

3. Results and Discussion

The experimental molar solubility (MS) for NaF in aqueous ethanol solutions were measured in molar scale and tabulated in Tables 1,2,3 at 293.15, 303.15 and 313.15 K. The values of refractive index (RIN) were also measured and tabulated also in these tables at the different temperatures. The salt activity coefficients (log $\gamma_{\pm}$) in each solution were calculated using Debye-Huckel equation[12]

$$\log \gamma_{\pm} = -0.5062 \sqrt{m} \qquad (1)$$

The free energy of solvation GSOL were calculated by using equation (2)

$$GSOL = -2.303 \ RT \ pKsp \qquad (2)$$

Where pK_{sp} is the solubility product calculated by equation (3)

$$pK_{sp} = -2\log \gamma_{\pm} - 2 \log m \qquad (3)$$

From the experimental refractive indices (RIN), the molar refraction (RM) were calculated[14,15] by applying equation (4),

$$RM = \frac{RIN - 1}{(RTN)^2 + 2} \ VM \qquad (4)$$

Where VM is the molar volume of NaF in the mixed solvents, calculated by dividing the molecular weight of the salt by the density of solution. VM values ranging from 42.20 cm^3/mole to 54.40 cm^3/mole for whole the solutions at different temperatures. All the solvation parameters explained before are cited in Tables 1-3 for NaF solutions at different temperatures.

The association constant KASS for 1:1 (symmetric) electrolytes can be estimated by applying Fuoss-Sheldovsky equation[16,17]

$$\frac{1}{EC.S(Z)} = \frac{1}{LEC} + \left(\frac{KASS}{(LEC)^2} \right)(m.EC.\gamma_{\pm}^2.S(Z)) \ (5)$$

Where EC, molar conductane, LEC, limiting molar conductance and S(Z) is the Fuoss-Sheldorsky factor. This equation is long enough and therefore another simple equation was used as given in equation (6)

$$KASS = \frac{LEC\left[LEC - EC.S(Z)\right]}{m \ S(Z)^2 \ LE^2 \ \gamma_{\pm}^2} \qquad (6)$$

Last equation can be easily applied, knowing that S(Z) factor for NaF and similar salts were found to be approximately one[17].

The limiting molar conductance (LEC) was obtained by extrapolating the relation between A and $\sqrt{m}$ for different solutions to zero concentration.

All, the measured and calculated EC , LEC & KASS data are given in Tables 4, 5,& 6 for NaF in the mixed solvents under consideration at different temperatures for different concentrations (m) of the electrolyte.

From the association constants KASS the free energy of association GASS were also calculated using equation (7) for NaF solution at different temperatures

$$GASS = -RT \ ln \ KASS \qquad (7)$$

From all the results it was concluded that all the measured and calculated parameters for solvation (solubility parameters) and association (conductivity parameters) are increased by increasing the mole fraction of ethanol in the mixtures[18-22]. This indicates more solute-solvent interaction by more adding ethanol in the mixed solvents.

4. Conclusions

This work introduces a lot of data for NaF which help for its industrial determination. Adding ethanol followed by increase of all the solubility and the thermodynamic parameters, which facilitate the analyst, biochemical analyst and engineering analyst works.

Table 1. Molar solubility (MS), refractive indices (RIN), molar refraction (RM),to activity coefficient (log $\gamma_{\pm}$, solubility product (pK_{sp}) and free energy of solvation (GSOL) for NaF in mixed ethanol solvents at 293.15 K.

X_s of ethanol	MS	RIN	RM	log $\gamma_{\pm}$	pK_{sp}	GSOL (k.J/mole)
0	1.0238	1.33728	8.76008	-0.5121	-1.0445	5.63109
0.0715	0.5954	1.34373	9.17281	-0.39059	-1.23148	6.9086
0.1703	0.2191	1.35135	9.68601	-0.2369	1.3197	-7.3979
0.3160	0.0555	1.35515	10.1997	-0.11925	2.2739	-12.7509
0.550	0.0682	1.36192	11.03206	-0.13219	2.06872	-11.6015
1.0	0.2016	1.3618	11.79367	-0.22723	0.93654	-5.2539

Table 2. Molar solubilities (MS), refractive indices (RIN), molar refraction (RM), log activity coefficient log $\gamma_\pm$, solubility product (pK$_{sp}$) and free energy of solvation (GSOL) for NaF in mixed ethanol-water solvents at 303.15 K.

X$_s$ of ethanol	MS	RIN	RM	log $\gamma_\pm$	pK$_{sp}$	GSOL (k.J/mole)
0	1.132	1.33203	8.65719	-0.5385	0.9694	5.6145
0.0869	0.657	1.341055	9.14598	-0.41588	0.49046	2.8406
0.2024	0.321	1.34411	9.58764	-0.2867	-0.4136	-2.3896
0.3635	0.078	1.35521	10.35736	-0.14137	-1.93396	-11.1958
0.6036	0.082	1.361181	11.13052	-0.1449	-1.8825	-10.903
1.00	0.243	1.361185	11.838009	-0.24953	-0.7295	-4.2259

Table 3. Molar solubilities (MS), refractive indices (RIN), molar refraction (RM), log activity coefficient log $\gamma_\pm$, solubility product (pK$_{sp}$) and free energy of solvation (GSOL) for NaF in mixed ethanol-water solvents at 313.15 K.

X$_s$ of ethanol	MS	RIN	RM	log $\gamma_\pm$	pK$_{sp}$	GSOL (k.J/mole)
0	1.2238	1.3316	8.6566	-0.5599	-1.2352	-7.40255
0.0786	0.7604	1.3340	9.01015	-0.4414	-1.12071	-6.7164
0.1852	0.5430	1.35212	9.86655	-0.373	-1.2754	-7.6494
0.3384	0.1021	1.3554	10.52084	-0.1617	-2.3053	-11.8156
0.577	0.091	1.036017	11.22073	-0.1527	-2.3873	-14.3071
1.0	0.3169	1.35531	11.86548	-0.2849	-1.5678	-9.3938

Table 4. Molar electrical conductance (EC), limiting molar conductance (LEC), association constants (KASS) and free energies of association (GASS) for different NaF concentrations (M) in mixed aqueous-ethanol solvents at 293.15 K.

X$_s$ mole of fraction	M	EC (m Sem)	LEC (m Sem)	KASS x10^{-6}	GASS(k.J/mole)
0	9.61x10^{-4}	180	903.688	49.1656	-9.495
	1.936x10^{-3}	283.33		44.7788	-9.267
	2.025x10^{-3}	443.925		18.8812	-7.162
	3.969x10^{-3}	600.6		3.0567	-2.723
	4.998x10^{-3}	882.35		1.0455	-0.108
	5.9907x10^{-3}	1217.039		0.5412	+1.496
0.0715	9.61x10^{-4}	150	716.361	96.4945	-11.138
	1.936x10^{-3}	216.66		10.1283	-5.644
	2.025x10^{-3}	280.373		6.9159	-4.714
	3.969x10^{-3}	330.33		2.4369	-2.171
	4.998x10^{-3}	347.82		2.1458	-1.861
	5.9907x10^{-3}	404.411		1.8112	-1.447
0.17030	9.61x10^{-4}	100	625.3219	53.2847	9.692
	1.936x10^{-3}	233.33		31.9665	-8.445
	2.025x10^{-3}	280.273		27.4221	-8.072
	3.969x10^{-3}	330.33		9.1013	-5.383
	4.998x10^{-3}	391.304		2.8087	-2.517
	5.9907x10^{-3}	404.411		1.4926	-0.976
0.3160	9.61x10^{-4}	133.33	505.659	14.9439	-6.592
	1.936x10^{-3}	207.468		8.2681	-5.149
	2.025x10^{-3}	420.42		6.7281	-4.646
	3.969x10^{-3}	588.235		4.1539	-3.471
	4.998x10^{-3}	739.13		0.3606	-1.273
	5.9907x10^{-3}				
0.552	9.61x10^{-4}	80	229.274	496.1692	-1.513
	1.936x10^{-3}	116.66		38.7865	-8.917
	2.025x10^{-3}	210.28		27.9545	-8.118
	3.969x10^{-3}	330.33		16.992	-6.820
	4.998x10^{-3}	477.94		14.9927	-6.600
	5.9907x10^{-3}	565.217		13.082	-6.267
1.0	9.61x10^{-4}	20	206.0889	545.0519	-9.726

	1.936x10⁻³	100		220.0378	-7.945
	2.025x10⁻³	140.186		26.5983	-7.705
	3.969x10⁻³	150.15		23.7721	-7.619
	4.998x10⁻³	173.913		17.8529	-7.025
	5.9907x10⁻³	183.82		4.4521	-3.640

Table 5. Molar electrical conductance (EC),limiting molar conductance (LEC), association constants (KASS) and free energies of association (GASS) for different NaF concentrations (M) in mixed ETOH-H₂O solvents at 303.15K.

X_s mole of fraction	M	EC(m Sem)	LEC (m Sem)	KASS x10⁻⁶	GASS k.J
0	9.61x10⁻⁴	180	1450.037	741.008	-16.657
	1.936x10⁻³	283.33		165.203	-12.874
	2.025x10⁻³	443.925		119.463	-12.057
	3.969x10⁻³	600.6		8.8168	-5.487
	4.998x10⁻³	882.35		8.1709	-5,269
	5.9907x10⁻³	1217.39		7.570	-5.104
0.0809	9.61x10⁻⁴	150	675.131	255.42	-13.972
	1.936x10⁻³	216.66		194.806	-13.289
	2.025x10⁻³	280.373		172.926	-12.989
	3.969x10⁻³	330.33		165.562	-12.879
	4.998x10⁻³	347.82		14.228	-6.693
	5.9907x10⁻³	404.411		10.444	-5.914
0.20211	9.61x10⁻⁴	100	629.502	458.35	-15.591
	1.936x10⁻³	233.33		274.65	-14.155
	2.025x10⁻³	280.273		205.35	-13.422
	3.969x10⁻³	330.33		122.121	-12.112
	4.998x10⁻³	391.304		76.221	-10.9214
	5.9907x10⁻³	404.411		50.300	-9.878
0.3635	9.61x10⁻⁴	50	499.707	127.93	-12.229
	1.936x10⁻³	133.33		46.62	-9.6855
	2.025x10⁻³	207.468		44.85	-9.5877
	3.969x10⁻³	420.42		41.991	-9.4118
	4.998x10⁻³	588.235		3.652	-3.2656
	5.9907x10⁻³	793.13		3.24	-2.9673
0.6036	9.61x10⁻⁴	80	411.592	248.00	-13.8985
	1.936x10⁻³	116.66		38.18	-9.1818
	2.025x10⁻³	210.28		24.30	-8.0436
	3.969x10⁻³	330.33		7.751	-5.1630
	4.998x10⁻³	477.94		1.400	-0.84.85
	5.9907x10⁻³	565.240		1.0691	-0.1684
1.00	9.61x10⁻⁴	20	369.145	92.146	-11.4027
	1.936x10⁻³	100		37.151	-9.1128
	2.025x10⁻³	140.186		18.320	-7.3306
	3.969x10⁻³	150.15		3.647	-3.2616
	4.998x10⁻³	173.913		2.044	-3.262
	5.9907x10⁻³	183.82		0.2421	-1.8021
					+3.5734

Table 6. Molar electrical conductance (EC), limiting molar conductance(LEC), association constants (KASS) and free energies of association (GASS) for different NaF concentrations (M) in mixed ETOH-H₂O solvents at 313.15 K.

X_s mole of fraction	M	EC(m Sem)	LEC (m Sem)	KASS x10⁻⁶	GASS(k.J/mole)
0	9.61x10⁻⁴	460	2414.716	297.56	-14.826
	1.936x10⁻³	569.948		57.26	-10.529
	2.025x10⁻³	800		47.8316	-10.0714
	3.969x10⁻³	1261.682		8.7749	-5.655
	4.998x10⁻³	1531.153		3.0462	-2.9005
	5.9907x10⁻³	1695.65		1.2049	-0.4853
0.0786	9.61x10⁻⁴	100	569.288	63.2628	-10.7987
	1.936x10⁻³	110.294		16.6628	-7.3255
	2.025x10⁻³	133.33		15.2272	-7.0900

	3.969x10⁻³	173.913		6.7822	-4.9848
	4.998x10⁻³	180.294		2.8672	-2.7609
	5.9907x10⁻³	257.009		2.5966	-2.4787
0.1852	9.61x10⁻⁴	110	431.279	495.867	-16.1612
	1.936x10⁻³	150		153.6612	-13.1002
	2.025x10⁻³	210.28		49.9358	-10.1835
	3.969x10⁻³	280.273		28.2645	-8.7217
	4.998x10⁻³	330.33		13.7420	-6.8236
	5.9907x10⁻³	514.705		2.9846	-2.847
0.3384	9.61x10⁻⁴	120	370.506	994.897	-17.9744
	1.936x10⁻³	166.607		303.059	-14.8790
	2.025x10⁻³	210.667		66.9891	-10.9485
	3.969x10⁻³	280.273		35.7653	-9.3159
	4.998x10⁻³	230.33		8.4775	-5.5658
	5.9907x10⁻³	514.705		3.3678	-4.3758
0.5770	9.61x10⁻⁴	90	352.298	516.5028	-16.2674
	1.936x10⁻³	100		255.1022	-14.4304
	2.025x10⁻³	210.210		24.9736	-8.3791
	3.969x10⁻³	257.009		17.3687	-7.4335
	4.998x10⁻³	294.117		7.7073	-5.3178
	5.9907x10⁻³	347.82		3.5792	-3.3208
1.0	9.61x10⁻⁴	60	111.6949	408.163	-15.6543
	1.936x10⁻³	83.33		119.399	-12.4535
	2.025x10⁻³	116.822		38.0233	-9.4738
	3.969x10⁻³	173.913		7.1179	-5.1106
	4.998x10⁻³	210.21		7.6428	-4.9979
	5.9907x10⁻³	220.588		3.1179	-2.9611

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