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Apparent Molal Volumes of Sodium Fluoride in Mixed Aqueous-Ethanol Solvents

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Resumen:

Las densidades de diferentes concentraciones molales de fluoruro de sodio en mezclas de etanol/agua como solvente han sido medidas sobre el rango total de composición a tres temperaturas diferentes: 293,15; 303,15 y 313,15 ºK. De las densidades medidas los volúmenes molales aparente y límite de los electrolitos han sido evaluados. Los volúmenes molales límites para los iones sodio y fluoruro fueron estimados por desdoblamiento de las contribuciones iónicas con una asunción asimétrica

Palabras clave: Volumen molal aparente; Volumen molal parcial; Asunción asimétrica; Fluoruro de sodio.

Abstract

The densities of different molal concentrations of sodium fluoride at ethanol-water mixtures, as solvent, have been measured over the whole composition range at three different temperatures, 293.15, 303.15 and 313.15°K. From the measured densities, the apparent and limiting molal volumes of the electrolytes have been evaluated. The limiting molal volumes for sodium and fluoride ions were estimated by splitting the ionic contributions as an asymmetric assumption.

Keywords: Apparent molal volumes; partial molal volumes; asymmetric assumption; sodium fluoride.

Introduction:

The volumetric behaviour of electrolyte solutions is an important parameter for studying ion-solvent interactions as well as equilibria occurring in the solutions. The limiting apparent molar volumes of an electrolyte at infinite dilution correspond to standard partial molar volume[1].

The partial molar volume of an ionic solid can be splitted into its ionic contributions compounds[2]. A simple alternative method is to employ a reference electrolyte, like tetralkylammonium salt, whose ions are equal in size and do not have any solvation effects. Another reference electrolyte is tetraphenyl-phosphonium tetraphenylborate ($Ph_4PBPh_4^+$ $TPTB^-$)[1].

The aim of this work is to evaluate the partial molal volumes for sodium fluoride and their ionic contributions in mixtures of ethanol-water as solvent

Experimental

Sodium fluoride 99%, from Aldrich Chemicals, was used. Absolute ethanol, from Al-Gomhoria Supplements, was used and it was used without further purification.

In general, densities of NaF in mixed ethanol, water and their mixtures were done by measuring specific concentrations and their dilutions using weighing bottle (1 ml) with capillary precalibrated by means of bidistilled water. The deviation of the data is ± 0.001 g. The solutions were put in a water bath Assistant – 3193 for at least 3 hours. Four digital weighing balance (Mettler 240) was used in all weighing procedures.

Results discussion

The experimental densities (d) of dilute solutions of sodium fluoride at different concentrations in the mixtures ethanol-water at three different temperatures, 293.15, 303.15 and 313.15 K were measured and their values tabulated in Tables 1, 2 and 3.

The apparent molal volumes (V_ϕ)[3,4] of NaF were calculated by using equation (1)[5].

$$V_\phi = \frac{M}{d} - \left(\frac{d-d_o}{dd_o}\right)\frac{1000}{m} \qquad (1)$$

where M is the molar mass of NaF and m is the concentration in molality, d and d_o are the densities of solution and mixed solvent or pure solvents, respectively. The values of V_ϕ for NaF at the different temperatures in the mixtures of ethanol-water are also presented in Tables 1, 2 and 3. The partial molar volumes V_ϕ^o of sodium fluoride were obtained by linear extrapolation of V_ϕ against $\sqrt{m}$ to infinite dilution, following the Covington, equation[6]:

$$V_\phi = V_\phi^o + S_v\sqrt{m} \quad (2)$$

V_ϕ^o, the intercept, is the limiting value of the apparent molal volume and it is equal to the partial molal volumes at infinite dilution.

The values of V_ϕ^o and the proportionality constant S_v (the slope) obtained from equation (2) are given in Table 4 with standard deviation ranging from 0.11 to 0.13.

Table 1: Apparent molal volumes (V_ϕ) in cm^3/mole and densities (d) in g/cm^3 of different molal concentrations (m) for NaF at 293.15 K in ethanol-water solvents.

X_S (Ethanol)	m	d	V_Φ	X_S (Ethanol)	m	d	V_Φ
0	$9.622x10^{-4}$	0.9988	-41.289	0.316	$1.071x10^{-3}$	0.8976	-34.357
	$1.938x10^{-3}$	0.9988	-40.310		$2.157x10^{-3}$	0.8977	-39.527
	$2.027x10^{-3}$	0.9989	-41.981		$2.157x10^{-3}$	0.8977	-35.736
	$3.974x10^{-3}$	0.9989	-58.811		$4.422x10^{-3}$	0.8979	-59.848
	$5.004x10^{-3}$	0.9989	-58.050		$5.569x10^{-3}$	0.8980	-64.882
0.072	$9.917x10^{-4}$	0.9690	-42.558	0.552	$1.139x10^{-3}$	0.8441	-36.550
	$1.998x10^{-3}$	0.9692	-41.929		$2.294x10^{-3}$	0.8441	-35.912
	$2.089x10^{-3}$	0.9692	-38.213		$2.399x10^{-3}$	0.8441	-32.149
	$4.096x10^{-3}$	0.9694	-60.564		$4.703x10^{-3}$	0.8443	-54.680
	$5.158x10^{-3}$	0.9695	-55.722		$5.922x10^{-3}$	0.8444	-49.764
0.171	$1.026x10^{-3}$	0.9366	-44.049	1.0	$1.218x10^{-3}$	0.7894	-25.885
	$2.067x10^{-3}$	0.9367	-39.105		$2.453x10^{-3}$	0.7894	-31.847
	$2.162x10^{-3}$	0.9367	-39.534		$2.566x10^{-3}$	0.7894	-28.094
	$4.238x10^{-3}$	0.9669	-51.013		$5.029x10^{-3}$	0.7896	-52.089
	$5.337x10^{-3}$	0.9370	-55.544		$6.332x10^{-3}$	0.7897	-48.132

Table 2: Apparent molal volumes (V_ϕ) in cm^3/mole and densities (d) in g/cm^3 of different molal concentrations (m) for NaF at 303.15 K in ethanol-water solvents.

X_S (Ethanol)	m	d	V_Φ	X_S (Ethanol)	m	d	V_Φ
0	$9.658x10^{-4}$	0.9951	-42.112	0.363	$1.087x10^{-3}$	0.8841	-34.883
	$1.946x10^{-3}$	0.9952	-40.867		$2.190x10^{-3}$	0.8841	-34.290
	$2.035x10^{-3}$	0.9952	-42.156		$2.291x10^{-3}$	0.8842	-36.278
	$3.989x10^{-3}$	0.9954	-64.096		$4.489x10^{-3}$	0.8844	-57.904
	$5.023x10^{-3}$	0.9955	-58.285		$5.654x10^{-3}$	0.8844	-52.034
0.097	$9.958x10^{-4}$	0.9651	-42.742	0.604	$2.745x10^{-3}$	0.8351	-13.723
	$2.006x10^{-3}$	0.9652	-42.115		$2.634x10^{-3}$	0.8351	-20.477
	$2.098x10^{-3}$	0.9652	-38.322		$2.755x10^{-3}$	0.8351	-22.573
	$4.113x10^{-3}$	0.9654	-60.872		$5.400x10^{-3}$	0.8353	-48.087
	$5.169x10^{-3}$	0.9655	-55.963		$6.800x10^{-3}$	0.8354	-36.138
0.202	$1.036x10^{-3}$	0.9281	-33.237	1.0	$1.230x10^{-3}$	0.7811	-26.165
	$2.086x10^{-3}$	0.9282	-38.222		$2.479x10^{-3}$	0.7811	-32.189
	$2.182x10^{-3}$	0.9282	-39.872		$2.593x10^{-3}$	0.7811	-28.409
	$4.277x10^{-3}$	0.9282	-38.241		$5.082x10^{-3}$	0.7813	-52.637
	$5.386x10^{-3}$	0.9284	-36.608		$6.399x10^{-3}$	0.7814	-46.087

Table 3: Apparent molal volumes (V_ϕ) in cm^3/mole and densities (d) in g/cm^3 of different molal concentrations (m) for NaF at 313.15 K in mixed ethanol-water solvents.

X_S (Ethanol)	m	d	V_Φ	X_S (Ethanol)	m	d	V_Φ
0	9.685×10^{-4}	0.9923	0.3799	0.338	1.104×10^{-3}	0.8708	-35.422
	1.951×10^{-3}	0.9924	-20.135		2.223×10^{-3}	0.8708	-34.824
	2.041×10^{-3}	0.9924	-22.367		2.326×10^{-3}	0.8708	-35.699
	3.999×10^{-3}	0.9926	-51.583		4.558×10^{-3}	0.8711	-57.357
	5.036×10^{-3}	0.9927	-48.368		5.742×10^{-3}	0.8712	-60.369
0.078	9.996×10^{-4}	0.9614	-32.054	0.577	1.163×10^{-4}	0.8263	-62.515
	2.014×10^{-3}	0.9614	-36.896		2.343×10^{-3}	0.8264	-49.206
	2.107×10^{-3}	0.9615	-38.490		2.451×10^{-3}	0.8264	-44.785
	4.129×10^{-3}	0.9617	-61.107		4.804×10^{-3}	0.8266	-58.899
	5.199×10^{-3}	0.9618	-56.167		6.049×10^{-3}	0.8266	-55.669
0.185	1.044×10^{-3}	0.9208	-33.502	1.0	1.244×10^{-3}	0.7725	-26.462
	2.027×10^{-3}	0.9208	-45.743		2.506×10^{-3}	0.7725	-32.546
	2.199×10^{-3}	0.9209	-42.149		2.621×10^{-3}	0.7726	-73.473
	4.311×10^{-3}	0.9211	-60.246		5.139×10^{-3}	0.7727	-49.973
	5.428×10^{-3}	0.9212	-54.918		6.471×10^{-3}	0.7728	-59.513

The molar volumes (V_M) of NaF were obtained by dividing the molar mass by the densities and their values are listed in Tables 1, 2 and 3. The packing density (P) as reported by Kim *et al*.[7] and Gomaa *et al*.[8], i.e., the relation between Van der Waals volume (V_w) and the molar volume (V_M) of relatively large molecules, was found to be a constant value and equal to 0.661.

$$P = \frac{V_W}{V_M} = 0.661 \pm 0.017 \qquad (3)$$

The electrostriction volume (V_e) which is the volume compressed by the solvent, was calculated by using equation (4)[9].

$$V_e = V_W - V_M \qquad (4)$$

The molar, Van der Waals and electrostriction volumes of NaF in ethanol–water mixtures at the three different temperatures were tabulated in Table 4.

The data in Table 4 shows an increase in the values of V_M and V_W and decrease at the values of the third V_e. A negative increase of electrostriction values was observed for NaF solutions by increasing the proportions of ethanol in the mixtures.

It is obvious that the apparent molal volumes of electrolytes at infinite dilution, for vanishing ion-ion interactions can be considered as the sum of independent ionic contribution. It means that the simple equation[10]

$$V_\phi^o = V_\phi^o(M^+) + V_\phi^o(X^-) \qquad (5)$$

s valid for monovalent – monovalent salts and divalent – monovalent salts.

The study for limiting value of the apparent molal volumes of electrolytes as function of ion nature, size, charge, temperature and solvent is very useful for better understanding ion-solvent interactions[11].

In comparison of the different volumes of sodium and fluoride, like crystal volumes[12] and Van der Waals volumes[13], we get mean radius value for Na^+ equal 0.97 Å and 1.333 Å for F^-. Dividing the two together we get a ratio of 0.72768. This ratio can be used to split the volume of electrolyte by it to get that of sodium ion. This method is called NaF asymmetric assumption. Therefore, the partial molar volumes obtained for both Na^+ and F^- ions are evaluated and their values are listed in Table 5.

It was observed from the different volume values, that all volumes for the electrolyte (NaF) increased by increasing ethanol content in the mixed solvent due mainly to the higher solvation. Also the electrostriction volumes increase in negativity confirming the increase in solvent effect by more adding ethanol to the mixtures. The values of the slopes S_v are negative at 293.15 and 303.15 K indicating dissociation of NaF electrolyte at these temperatures. S_v values are positive at 313.15 K indicating more association process at this temperature. Both dissociation and association processes are increased by increasing the mole fraction of ethanol. S_v values increase by increasing alcohol percentage.

Table 4: Limiting partial molal volume (V_ϕ^o), molar volumes (V_M), Van der Waals volumes (V_W), electrostriction volumes (V_e) in cm^3/mole and slope values (S_V) for NaF in mixed ethanol-water solvents at different temperatures.

293.15 K

X_s (Ethanol)	$-V_\phi^o$	V_M	V_W	$-V_e$	S_V
0	43.0	43.000	27.787	14.251	-70
0.072	43.9	43.331	28.642	14.689	-400
0.171	53.1	44.859	29.617	15.207	-280
0.316	32.0	46.783	30.924	15.859	72.72
0.552	45.0	49.748	32.884	16.865	-265
1.0	52.2	53.197	35.163	18.034	-420

303.15 K

X_s (Ethanol)	$-V_\phi^o$	V_M	V_W	$-V_e$	S_V
0	43.2	42.199	27.894	14.305	-40.10
0.097	44.0	43.511	28.761	14.450	-43.47
0.202	41.2	45.246	29.907	19.768	-60.10
0.363	37.3	47.498	31.396	16.402	-69.56
0.604	34.7	50.285	33.238	17.047	-230
1.0	38.4	53.481	35.351	18.130	-170

313.15 K

X_s (Ethanol)	$-V_\phi^o$	V_M	V_W	$-V_e$	S_V
0	14.0	42.316	27.970	14.345	180
0.078	22.0	43.678	28.871	14.806	380
0.185	18.6	45.604	30.144	15.459	480
0.338	27.0	48.223	31.876	16.347	169.2
0.577	38.3	50.819	33.592	17.228	184
1.0	17	54.360	35.932	18.828	285

Table 5: Ionic partial molal volumes for Na^+ and F^- in mixed ethanol-water solvents at different temperatures (in cm^3/mole).

293.15 K

X_s (Ethanol)	$-V_\phi^o$ (Na^+)	$-V_\phi^o$ (F^-)
0	15.645	27.355
0.072	15.972	27.928
0.171	19.319	33.780
0.316	11.642	20.357
0.552	16.664	29.136
1.0	18.992	33.207

303.15 K

X_s (Ethanol)	$-V_\phi^o$ (Na^+)	$-V_\phi^o$ (F^-)
0	15.717	27.483
0.097	16.009	27.991
0.202	14.990	26.209
0.363	13.571	23.728
0.604	12.625	22.074
1.0	13.971	24.428

313.15 K

X_s (Ethanol)	$-V_\phi^o$ (Na^+)	$-V_\phi^o$ (F^-)
0	5.093	8.906
0.078	5.833	16.166
0.185	6.769	11.832
0.338	9.896	9.896
0.577	14.007	14.007
1.0	6.185	6.185

Conclusions

A new and simple method for evaluating the single ion partial molal volumes was applied using asymmetric sodium fluoride assumption. Sodium fluoride is a stable electrolyte and it is better than potassium fluoride which was used as symmetric assumption, according to the unstability of the latter.

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