

Degrees of dissociation and hydration numbers of M_2SO_4 ($M = H, Li, Na, K, Rb, Cs$ and NH_4) in aq. solns at 25 °C

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The osmotic coefficient (ϕ) of a solution of molality m is related¹⁻³ to the degree of dissociation (α) and hydration numbers by

$$v\phi = -(55.51/m)\ln N_{Afs} = i/(1-mn_b/55.51), \quad (1)$$

where v is the number of ions into which each molecule of solute dissociates (= 3 for monovalent sulphates), 55.51 is the number of moles of water in one kg, $N_{Afs} = a_A$, the activity of the solvent (A), is the mole fraction of free water, $n_{Afs}/(n_{Afs}+n_B)$ at the solution/vapour interface, n_s and n_b are the surface (s) and bulk (b) hydration numbers respectively¹⁻³, $i = 1+(v-1)\alpha$ is the van't Hoff factor, $n_{Afs} = 55.51-mn_s$ is the number of moles of free water and $n_B = im$ is the number of moles of solute (B) in the solution.

The values of α , n_s and n_b can be evaluated from the ϕ -data by using the method described recently^{1a,c,2,3}. The data for 44 uni-univalent strong electrolytes in aq. solutions at 25 °C are in^{1a,2,3}. In this work, the values evaluated from the ϕ -data⁴ for seven monovalent sulphates are presented in Tab.I. It is pointed out that these values of α and those in refs.^{1a,2,3} are different from the data in refs.^{5,6} since the hydration numbers used for calculating α are different.

The linear relation, $n_s = 0.99n_b + 1.0$ for the 1:1 electrolytes^{2,3} also holds for the monovalent sulphates.

The linear dependence of the emf (ΔE) of concentration cells on the logarithm of the ratio of ionic molality (αm) to the molality of free water ($n_{Afx} = 55.51-mn_x$, $x = s$ or b) is given by^{1a,c,2,3},

$$-nF(\Delta E)/vRT = \ln(m\gamma_{\pm}) = \delta_A \ln(\alpha m/n_{Afx}/r^0), \quad (2)$$

where γ_{\pm} is the molal mean ionic activity coefficient, the product $m\gamma_{\pm} = a_{\pm}$ is the molal mean ionic activity, δ_A is a solute-solvent polarization constant, obtained from the slope of the $\ln(a_{\pm})$ vs $\ln(\alpha m/n_{Afx})$ plots and $r^0 = (\alpha m/n_{Afx})^0$ when $\Delta E = 0$ (i.e., $a_{\pm} = 1$). The values of δ_A and $\Delta E^0 = -(\delta_A vRT/nF)\ln r^0$ are also given in Tab.I.

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Table I: Degrees of dissociation ($\bullet \pm 0.001$) of sulphates of monovalent cations in aqueous solutions at 25 °C, hydration numbers $n(s)$ and $n(b)$ and \bullet_A and \bullet_{E^0} (n_{Afx} : see Eq. 2).

m	M=H	Li	Na	K	Rb	Cs	(NH ₄)
0.0	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.1	0.509	0.717	0.699	0.693	0.715	0.695	0.648
0.2	0.481	0.667	0.648	0.659	0.677	0.637	0.591
0.3	0.470	0.639	0.614	0.649	0.655	0.595	0.552
0.4		0.622	0.592	0.642	0.644	0.567	0.524
0.5	0.460	0.607	0.577	0.645	0.642	0.545	0.502
0.6		0.598	0.566	0.646	0.642	0.526	0.484
0.7	0.458	0.591	0.557	0.652	0.645	0.510	0.468
0.8		0.584	0.550		0.647	0.494	0.456
0.9		0.580	0.545		0.653	0.479	0.445
1.0	0.467	0.576	0.540		0.658	0.466	0.433
1.2		0.572	0.537		0.679	0.443	0.416
1.4		0.571	0.542		0.706	0.425	0.404
1.5	0.485						
1.6		0.571	0.551		0.738	0.408	0.393
1.8		0.567	0.564		0.776	0.394	0.386
2.0	0.501	0.569					0.380
2.5	0.512	0.577					0.370
3.0	0.517	0.583					0.368
3.5	0.513						0.370
4.0							0.373
4.5							0.376
5							0.377
5.5							0.378
5.843							0.378
n(s)	6.84	5.99	-3.40-10.42	-6.26	6.28	2.49	
n(b)	5.85	4.94	-4.45	-11.56	-7.495.40	1.65	
\bullet_A	0.720	0.806	0.726	0.737	0.712	0.812	0.731
St.Er	0.010	0.003	0.012	0.010	0.012	0.002	0.008
\bullet_{E^0}	-0.105	-0.178	-0.139	-0.142	-0.132	-0.180	-0.144
St.Er	0.003	0.001	0.002	0.001	0.003	0.000	0.002
$n_{Afx,x}$: s	s	s	b	b	b	s	b

* up to saturation