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Water activity, osmotic and activity coefficients of aqueous solutions of Li_2SO_4, Na_2SO_4, K_2SO_4, $(NH_4)_2SO_4$, $MgSO_4$, $MnSO_4$, $NiSO_4$, $CuSO_4$, and $ZnSO_4$ at $T = 298.15$ K

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Abstract

The water activities for aqueous solutions of Li_2SO_4(aq), Na_2SO_4(aq), K_2SO_4(aq), $(NH_4)_2SO_4$(aq), and sulphates $MgSO_4$(aq), $MnSO_4$(aq), $NiSO_4$(aq), $CuSO_4$(aq), and $ZnSO_4$(aq) were determined experimentally at a temperature of 298.15 K with a hygrometric method, at molalities in the range from $0.1\ \mathrm{mol \cdot kg^{-1}}$ to saturation. The osmotic coefficients are calculated from these results. The coefficients of Pitzer's model was used to fit the osmotic coefficients for each salt solution. These parameters were used to predict solute activity coefficients for the salts studied.

Keywords: Aqueous solutions; Lithium; Sodium; Potassium; Ammonium; Magnesium; Manganese; Nickel; Copper; Zinc sulphate; Hygrometric method; Relative humidity; Water activity; Osmotic coefficient; Activity coefficient; Pitzer's model

1. Introduction

The thermodynamic properties of aqueous electrolyte solutions are required for atmospheric [1–3], biological [4], and industrial processes [5].

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In this work, we use the hygrometric method, described previously [6], that provides directly water activities in aqueous electrolyte solutions. This approach has been used it to study binary aqueous chlorides [7] and mixed electrolyte solutions [8,9]. In this paper we report the determination of water activities of aqueous solutions of Li_2SO_4(aq), Na_2SO_4(aq), K_2SO_4(aq), $(NH_4)_2SO_4$(aq), $MgSO_4$(aq), $MnSO_4$(aq), $NiSO_4$(aq), $CuSO_4$(aq), and $ZnSO_4$(aq). The solute activities for molalities in the range from $0.2\,\mathrm{mol \cdot kg^{-1}}$ to saturation are reported at a temperature of 298.15 K. From these data other thermodynamic properties are determined, in particularly osmotic and activity coefficients, using Pitzer's model.

2. Experimental

We have employed the hygrometric method, which is based on the measurements of the relative humidity above the solutions containing non-volatile electrolytes. The relative humidity of a salt solution is identified particular with the water activity of this solution.

The experimental apparatus and procedures have been described previously [6]. The temperature of the hygrometer was maintained to within ± 0.02 K. The droplet diameter is measured by a microscope, with an ocular equipped with a micrometric screw, with an uncertainly of 0.25 per cent.

A droplet of reference a solution NaCl(aq) was placed on a thin ($r = 0.1\,\mu$m diameter) thread is tensioned on a perspex support. This support is fixed on a cup containing the reference solution. The cup is then placed in the thermostate and the droplet diameter $D(a_{\mathrm{ref}})$ for the reference solution is measured and used to determine the relationship between droplet diameter and relative humidity. The thread and support with suspended drop of reference material drops were then fixed on to a cup containing the solution of unknown water activity. The droplet diameter $D(a_{\mathrm{w}})$, where a_{w} is relative humidity, can be used to deduce the water activity, from the variation of the ratio $K = D(a_{\mathrm{w}})/D(a_{\mathrm{ref}})$ with the water activity of the reference NaCl(aq) [6]. The relative humidity of the salt solution is the water activity.

Measurements of droplet diameter as a function of water activity were performed for aqueous solutions of Li_2SO_4(aq), Na_2SO_4(aq), K_2SO_4(aq), $(NH_4)_2SO_4$(aq), $MgSO_4$(aq), $MnSO_4$(aq), $NiSO_4O$(aq), $CuSO_4$(aq), and $ZnSO_4$(aq) at a temperature of 298.15 K with NaCl(aq) as reference electrolyte. The solutions were prepared from Merck extrapur-grade chemicals, of mass fraction purity in the range 0.98 to 0.995, and deionised distilled water with a conductivity $< 5\,\mu$s. The molality of the sample solution held in the cup was determined refractive index measurements. The uncertainties of refractive index measurements are ± 0.0002, and thus the molality of the solutes is uncertain to less than $\pm 0.01\,\mathrm{mol \cdot kg^{-1}}$. In most cases, measurements for a given solution were made on several droplets. For solutions having $a_{\mathrm{w}} < 0.98$, we use a reference water activity of 0.84. For those having $a_{\mathrm{w}} > 0.98$, we use a reference water activity of 0.98 [6,7].

TABLE 1
Ratio of growth K of the droplets and water activities a_w for Li_2SO_4(aq), Na_2SO_4(aq), K_2SO_4(aq), $(NH_4)_2SO_4$(aq), $MgSO_4$(aq), $MnSO_4 \cdot H_2O$(aq), $NiSO_4 \cdot 6H_2O$(aq), $CuSO_4 \cdot 5H_2O$(aq), and $ZnSO_4 \cdot 7H_2O$(aq) at molalities m and at $T = 298.15$ K

$m/(\text{mol}\cdot\text{kg}^{-1})$	Li_2SO_4(aq)		Na_2SO_4(aq)		K_2SO_4(aq)		$(NH_4)_2SO_4$(aq)	
	K	a_w	K	a_w	K	a_w	K	a_w
0.1	(1.640)	0.9956	(1.650)	0.9957	(1.668)	0.9958	(1.680)	0.9959
0.2	(1.318)	0.9915	(1.346)	0.9920	(1.346)	0.9920	(1.350)	0.9921
0.3	(1.182)	0.9875	(1.200)	0.9882	(1.206)	0.9884	(1.212)	0.9886
0.4	2.045	0.9833	2.120	0.9848	2.135	0.9850	2.150	0.9853
0.5	1.854	0.9793	1.920	0.9815	1.920	0.9815	1.925	0.9820
0.6	1.756	0.9753	1.823	0.9781	1.830	0.9783	1.844	0.9788
0.7	1.656	0.9710	1.746	0.9749	1.750	0.9750	1.764	0.9756
0.8	1.582	0.9667	1.674	0.9718	1.672	0.9720	1.686	0.9724
1.0	1.479	0.9585	1.572	0.9660			1.580	0.9662
1.5	1.284	0.935	1.391	0.950			1.391	0.950
2.0	1.171	0.911	1.284	0.935			1.284	0.935
2.5	1.085	0.883	1.197	0.918			1.203	0.919
3.0	1.023	0.853	1.128	0.899			1.138	0.902
3.5							1.085	0.885
4.0							1.050	0.867
4.5							1.018	0.850
5.0							0.986	0.831

$m/(\text{mol}\cdot\text{kg}^{-1})$	$MgSO_4$(aq)		$MnSO_4$(aq)		$NiSO_4$(aq)		$CuSO_4$(aq)		$ZnSO_4$(aq)	
0.2	(1.700)	0.9960	(1.710)	0.9961	(1.720)	0.9962	(1.740)	0.9963	(1.720)	0.9962
0.3	(1.468)	0.9941	(1.510)	0.9945	(1.520)	0.9946	(1.526)	0.9947	(1.520)	0.9946
0.4	(1.366)	0.9924	(1.394)	0.9929	(1.402)	0.9931	(1.410)	0.9932	(1.400)	0.9930
0.5	(1.280)	0.9906	(1.310)	0.9913	(1.322)	0.9916	(1.330)	0.9917	(1.316)	0.9914
0.6	(1.220)	0.9888	(1.250)	0.9898	(1.261)	0.9901	(1.262)	0.9901	(1.250)	0.9898
0.7	(1.166)	0.9870	(1.200)	0.9882	(1.214)	0.9887	(1.210)	0.9885	(1.204)	0.9882
0.8	(1.117)	0.9851	(1.154)	0.9866	(1.168)	0.9871	(1.160)	0.9868	(1.152)	0.9865
0.9	(1.067)	0.9832	(1.110)	0.9850	(1.124)	0.9855	(1.114)	0.9851	(1.104)	0.9847
1.0	1.920	0.9812	(1.067)	0.9832	(1.082)	0.9838	2.045	0.9833	2.024	0.9828
1.2	1.775	0.9768	1.858	0.9794	1.873	0.9800	1.860	0.9795	1.835	0.9788
1.4	1.645	0.9717	1.750	0.9750	1.770	0.9758	1.750	0.9750	1.736	0.9743
1.6	1.540	0.9660	1.644	0.9703	1.656	0.9710			1.624	0.9692
1.8	1.496	0.9598	1.556	0.9649	1.558	0.9650			1.536	0.9634
2.0	1.375	0.9529	1.425	0.9590	1.482	0.9588			1.462	0.9570
2.5	1.270	0.932	1.322	0.941	1.309	0.939			1.302	0.938
3.0	1.134	0.905	1.203	0.919					1.178	0.913
3.5			1.108	0.892						
4.0			1.040	0.862						

Numbers in parentheses are for reference water activity of 0.98.

3. Results and discussion

The experimental values of the water activities at different molalities are listed in table 1. The uncertainty in the water activity depends on the measurements accuracy of the diameter of the droplets and is approximately between ($\pm 1.5 \cdot 10^{-4}$ and $\pm 9 \cdot 10^{-4}$) over the molality range investigated.

TABLE 2
Osmotic coefficients ϕ and mean activity coefficients $\gamma_\pm$ at molalities m of Li_2SO_4(aq) at $T = 298.15$ K[a]

$m/(\mathrm{mol \cdot kg^{-1}})$	ϕ(expt.)	ϕ(calc)	ϕ [10]	$\gamma_\pm$(calc.)	$\gamma_\pm$ [10]	$\gamma_\pm$ [14]
0.1	0.816	0.815	0.818	0.475	0.478	0.468
0.2	0.790	0.792	0.792	0.405	0.406	0.398
0.3	0.776	0.781	0.780	0.368	0.369	–
0.4	0.779	0.777	0.775	0.347	0.344	–
0.5	0.774	0.773	0.772	0.325	0.326	0.323
0.6	0.771	0.773	0.773	0.313	0.313	–
0.7	0.778	0.775	0.775	0.301	0.303	–
0.8	0.783	0.779	0.778	0.297	0.298	–
1.0	0.784	0.785	0.787	0.282	0.283	0.276
1.5	0.829	0.822	–	0.270	–	0.272
2.0	0.862	0.870	0.867	0.270	0.269	0.267
2.5	0.921	0.923	0.923	0.279	0.280	–
3.0	0.981	0.977	0.984	0.292	0.294	–

[a] ϕ(expt.) are values obtained is then work and ϕ(calc.) and $\gamma_\pm$(calc.) were obtained from equations (2) and (3), respectively. For comparison, values of ϕ [10] and $\gamma_\pm$ [10] obtained from reference 10 and $\gamma_\pm$ [14] from reference 14 are listed.

TABLE 3
Osmotic coefficients ϕ and mean activity coefficients $\gamma_\pm$ at molalities m of Na_2SO_4(aq) at $T = 298.15$ K[a]

$m/(\mathrm{mol \cdot kg^{-1}})$	ϕ(expt.)	ϕ(calc.)	ϕ [10]	$\gamma_\pm$(calc.)	$\gamma_\pm$ [10]	$\gamma_\pm$ [14]	$\gamma_\pm$ [15]
0.1	0.797	0.790	0.793	0.450	0.452	0.445	0.4508
0.2	0.743	0.751	0.753	0.369	0.371	0.365	0.3702
0.3	0.732	0.725	0.725	0.323	0.325	0.322	–
0.4	0.708	0.709	0.705	0.298	0.294	–	–
0.5	0.691	0.690	0.690	0.269	0.270	0.267	0.2709
0.6	0.683	0.679	0.678	0.254	0.252	–	–
0.7	0.672	0.669	0.667	0.239	0.237	0.234	–
0.8	0.661	0.660	0.658	0.225	0.225	–	–
1.0	0.640	0.643	0.642	0.204	0.204	0.202	0.2053
1.5	0.632	0.624	–	0.173	–	0.171	0.1763
2.0	0.621	0.621	0.621	0.155	0.154	0.153	0.1559
2.5	0.633	0.626	0.635	0.143	0.144	–	0.1459
3.0	0.657	0.658	0.661	0.140	0.139	0.137	0.1409

[a] ϕ(expt.) are values obtained is this work and ϕ(calc.) and $\gamma_\pm$(calc.) were obtained from equations (2) and (3), respectively. For comparison, values of ϕ [10] and $\gamma_\pm$ [10] obtained from reference 10, $\gamma_\pm$ [14] from reference 14, and $\gamma_\pm$ [15] from reference 15 are also listed.

Using the experimental data for the water activities as a function of molality, we determined the osmotic coefficients ϕ for each sulphate from

$$\phi = -(1000/vmM) \cdot \ln a_w, \quad (1)$$

where v is the number of ions released by dissociation, m the molality, M the molar mass, and a_w the activity. The results are listed, in tables 2–10 and are shown, in figures 1 and 2. The uncertainty in the osmotic coefficient is estimated to be, at most,

TABLE 4
Osmotic coefficients ϕ and mean activity coefficients $\gamma_\pm$ at molalities m of K_2SO_4(aq) at $T = 298.15$ K[a]

$m/(\mathrm{mol \cdot kg^{-1}})$	ϕ(expt.)	ϕ(calc.)	ϕ [10]	$\gamma_\pm$(calc.)	$\gamma_\pm$ [10]	$\gamma_\pm$ [14]
0.1	0.779	0.783	0.779	0.442	0.436	0.441
0.2	0.743	0.743	0.742	0.360	0.356	0.361
0.3	0.720	0.718	0.721	0.315	0.313	0.317
0.4	0.699	0.701	0.703	0.285	0.283	–
0.5	0.691	0.687	0.691	0.263	0.261	0.264
0.6	0.676	0.676	0.679	0.245	0.243	–
0.7	0.667	0.667	0.670	0.231	0.229	0.233
0.8	0.657	0.660	–	0.219	–	–

[a] ϕ(expt.) are values obtained in this work and ϕ(calc.) and $\gamma_\pm$(calc.) were obtained from equations (2) and (3), respectively. For comparison, values of ϕ [10] and $\gamma_\pm$ [10] obtained from reference 10 and $\gamma_\pm$ [14] from reference 14 are listed.

TABLE 5
Osmotic coefficients ϕ and mean activity coefficients $\gamma_\pm$ at molalities m of $(NH_4)_2SO_4$(aq) at $T = 298.15$ K[a]

$m/(\mathrm{mol \cdot kg^{-1}})$	ϕ(expt.)	ϕ(calc.)	ϕ [10]	$\gamma_\pm$(calc.)	$\gamma_\pm$ [10]	$\gamma_\pm$ [14]	$\gamma_\pm$ [16]
0.1	0.760	0.773	0.767	0.430	0.423	0.439	0.4296
0.2	0.734	0.729	0.731	0.347	0.343	0.356	0.3469
0.3	0.707	0.708	0.707	0.305	0.300	0.311	0.3023
0.4	0.685	0.689	0.690	0.272	0.270	0.280	0.280
0.5	0.672	0.671	0.677	0.249	0.248	0.257	0.2508
0.6	0.661	0.664	0.667	0.233	0.231	0.240	0.2338
0.7	0.653	0.655	0.658	0.218	0.218	0.226	0.22202
0.8	0.647	0.648	0.652	0.207	0.206	0.214	0.2089
1.0	0.636	0.635	0.640	0.189	0.189	0.196	0.1911
1.5	0.633	0.624	–	0.160	–	0.155	–
2.0	0.622	0.623	0.623	0.144	0.144	0.149	0.1458
2.5	0.625	0.629	0.626	0.133	0.132	0.137	–
3.0	0.636	0.637	0.635	0.125	0.125	0.130	0.1269
3.5	0.646	0.648	0.647	0.120	0.119	0.124	–
4.0	0.660	0.659	0.660	0.116	0.116	0.120	0.11173
4.5	0.668	0.670	0.673	0.112	–	–	–
5.0	0.685	0.682	0.686	0.110	–	–	0.1119

[a] ϕ(expt.) were obtained is this work and ϕ(calc.) and $\gamma_\pm$(calc.) were obtained from equations (2) and (3), respectively. For comparison, values of ϕ [10] and $\gamma_\pm$ [10] from reference 10, $\gamma_\pm$ [14] from reference 14, and $\gamma_\pm$ [16] from reference 16 are also listed.

TABLE 6
Osmotic coefficients ϕ and mean activity coefficients $\gamma_\pm$ at different molalities m of $MgSO_4$(aq) at $T = 298.15\,K$[a]

$m/(\mathrm{mol \cdot kg^{-1}})$	ϕ(expt.)	ϕ(calc.)	ϕ [10]	$\gamma_\pm$(calc.)	$\gamma_\pm$ [10]	$\gamma_\pm$ [14]	$\gamma_\pm$ [13]	$\gamma_\pm$ [18]
0.2	0.556	0.557	0.562	0.1140	0.1070	0.1077	0.1157	–
0.3	0.547	0.541	0.540	0.0934	0.0874	0.0877	0.0945	–
0.4	0.529	0.531	0.529	0.0809	0.0756	0.076	0.0817	–
0.5	0.524	0.524	0.522	0.0723	0.0675	0.0678	0.0730	0.0753
0.6	0.521	0.521	0.518	0.0661	0.0616	–	0.0666	–
0.7	0.519	0.520	0.517	0.0613	0.0571	0.0574	–	–
0.8	0.521	0.521	0.518	0.0576	0.0536	–	0.0579	–
0.9	0.523	0.525	0.520	0.0546	0.0508	–	–	–
1.0	0.527	0.530	0.525	0.0523	0.0485	0.0488	0.0524	0.0544
1.2	0.543	0.546	0.542	0.0488	0.0453	–	–	–
1.4	0.569	0.568	0.567	0.0466	0.0434	–	–	–
1.6	0.600	0.597	0.597	0.0453	0.0423	–	–	–
1.8	0.632	0.630	0.630	0.0448	0.0417	–	–	–
2.0	0.670	0.665	0.666	0.0448	0.0417	0.0419	0.0419	0.0464
2.5	0.782	0.785	0.780	0.0473	0.0439	0.0441	0.0441	–
3.0	0.923	0.924	0.922	0.0529	0.0492	0.0495	0.0495	0.0549

[a] ϕ(expt.) were obtained is this work and ϕ(calc.) and $\gamma_\pm$(calc.) were obtained from equations (2) and (3). For comparison, values of ϕ [10] and $\gamma_\pm$ [10] from reference 10, $\gamma_\pm$ [14] from reference 14, $\gamma_\pm$ [17] from reference 17, and $\gamma_\pm$ [18] from reference 18 are also listed.

TABLE 7
Osmotic coefficients ϕ and activity mean coefficients $\gamma_\pm$ at molalities m of $MnSO_4$(aq) at $T = 298.15\,K$[a]

$m/(\mathrm{mol \cdot kg^{-1}})$	ϕ(expt.)	ϕ(calc.)	ϕ [10]	$\gamma_\pm$(calc.)	$\gamma_\pm$ [10]	$\gamma_\pm$ [14]	$\gamma_\pm$ [17]
0.2	0.542	0.526	0.538	0.1050	0.1050	0.1056	0.112
0.3	0.510	0.504	0.516	0.0846	0.0848	0.0850	0.090
0.4	0.494	0.490	0.501	0.0722	0.0725	0.0728	0.077
0.5	0.485	0.480	0.490	0.0638	0.0640	0.0643	0.068
0.6	0.474	0.475	0.481	0.0576	0.0578	–	0.061
0.7	0.471	0.471	0.475	0.0529	0.0530	0.0532	–
0.8	0.468	0.470	0.472	0.0493	0.0493	–	0.052
0.9	0.466	0.471	0.472				
1.0	0.470	0.474	0.475	0.0440	0.0439	0.0441	0.047
1.2	0.481	0.485	0.485	0.0404	0.0404	–	0.043
1.4	0.502	0.501	0.504	0.0380	0.0380	–	0.040
1.6	0.523	0.523	0.527	0.0364	0.0365	–	0.039
1.8	0.551	0.550	0.556	0.0354	0.0356	–	0.038
2.0	0.581	0.580	0.588	0.0348	0.0351	0.0351	0.037
2.5	0.675	0.671	0.677	0.0350	0.0349	0.0353	0.037
3.0	0.781	0.780	0.782	0.0372	0.0373	0.0375	0.040
3.5	0.906	0.904	0.909	0.0410	0.0413	0.0416	0.044
4.0	1.038	1.041	1.048	0.0469	0.0473	0.0478	0.050

[a] ϕ(expt.) obtained is this work and ϕ(calc.) and $\gamma_\pm$(calc.) were obtained from equations (2) and (3), respectively. For comparison, values of ϕ [10] and $\gamma_\pm$ [10] obtained from reference 10, $\gamma_\pm$ [14] from reference 14, and $\gamma_\pm$ [17] from reference 17 are also listed.

TABLE 8
Osmotic coefficients ϕ and mean activity coefficients $\gamma_\pm$ at molalities m of $NiSO_4$(aq) at $T = 298.15$ K[a]

$m/(\mathrm{mol \cdot kg^{-1}})$	ϕ(expt.)	ϕ(calc.)	ϕ [10]	$\gamma_\pm$(calc.)	$\gamma_\pm$ [10]	$\gamma_\pm$ [14]	$\gamma_\pm$ [17]
0.2	0.528	0.523	0.533	0.1039	0.105	0.1049	0.1077
0.3	0.501	0.498	0.508	0.0831	0.0841	0.0841	0.0864
0.4	0.480	0.481	0.488	0.0705	0.0713	0.0713	0.0732
0.5	0.468	0.469	0.475	0.0620	0.0627	0.0628	0.0644
0.6	0.465	0.461	0.465	0.0558	0.0562	–	0.0577
0.7	0.451	0.456	0.458	0.0510	0.0515	0.0516	–
0.8	0.450	0.453	0.456	0.0473	0.0478	–	0.0491
0.9	0.450	0.453	0.456				–
1.0	0.453	0.456	0.459	0.0420	0.0425	0.0426	0.0437
1.2	0.467	0.467	0.472	0.0385	0.0390	–	0.0401
1.4	0.486	0.485	0.492	0.0362	0.0368	–	0.0378
1.6	0.510	0.511	0.517	0.0347	0.0353	–	0.0363
1.8	0.549	0.544	0.551	0.0339	0.0345	–	0.0354
2.0	0.584	0.582	0.589	0.033	0.0343	0.0343	0.0352
2.5	0.699	0.702	0.708	0.0350	0.0357	0.0357	0.0367

[a] ϕ(expt.) obtained is this work and ϕ(calc.) and $\gamma_\pm$(calc.) were obtained from equations (2) and (3), respectively. For comparison, values of ϕ [10] and $\gamma_\pm$ [10] obtained from reference 10, $\gamma_\pm$ [14] from reference 14, and $\gamma_\pm$ [17] from reference 17 are also listed.

TABLE 9
Osmotic coefficients ϕ and mean activity coefficients $\gamma_\pm$ at molalities m of $CuSO_4$(aq) at $T = 298.15$ K[a]

$m/(\mathrm{mol \cdot kg^{-1}})$	ϕ(expt.)	ϕ(calc.)	ϕ [10]	$\gamma_\pm$(calc.)	$\gamma_\pm$ [10]	$\gamma_\pm$ [14]	$\gamma_\pm$ [17]
0.2	0.514	0.512	0.515	0.0993	0.104	0.1043	0.0999
0.3	0.492	0.488	0.494	0.0792	0.0829	0.0834	0.0798
0.4	0.473	0.474	0.478	0.0672	0.0704	0.0708	0.0677
0.5	0.463	0.466	0.469	0.0593	0.0620	0.0624	0.0596
0.6	0.460	0.461	0.462	0.0535	0.0559	–	0.0538
0.7	0.459	0.459	0.458	0.0491	0.0512	0.0515	–
0.8	0.461	0.460	0.457	0.0457	0.0475	–	0.0457
0.9	0.463	0.462	0.458	0.0430	0.0446	–	–
1.0	0.467	0.466	0.461	0.0408	0.0423	–	0.0407
1.2	0.479	0.480	0.473	0.0376	0.0388	–	0.0373
1.4	0.500	0.500	0.491	0.0354	0.0365	–	0.0351

[a] ϕ(expt.) obtained is this work and ϕ(calc.) and $\gamma_\pm$(calc.) were obtained from equations (2) and (3), respectively. For comparison, values of ϕ [10] and $\gamma_\pm$ [10] obtained from reference 10, $\gamma_\pm$ [14] from reference 14, and $\gamma_\pm$ [17] from reference 17 are also listed.

± 0.006. When the present results can be compared with literature data [10], the agreement is generally within the experimental uncertainty (see figures 1 and 2).

The osmotic coefficients were used to determine Pitzer's parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{ϕ} using an unweighted least-squares fit to [11]

$$\phi = 1 + |z_M z_X|\{-A_\phi(I^{1/2}/1 + 1.2I^{1/2})\} + mB^{\phi} + m^2C^{\phi}. \quad (2)$$

TABLE 10
Osmotic coefficients ϕ and mean activity coefficients $\gamma_{\pm}$ at molalities m of $ZnSO_4$(aq) at $T = 298.15$ K[a]

$m/(\mathrm{mol \cdot kg^{-1}})$	ϕ(expt.)	ϕ(calc.)	ϕ [10]	$\gamma_{\pm}$(calc.)	$\gamma_{\pm}$ [10]	$\gamma_{\pm}$ [14]	$\gamma_{\pm}$ [17]	$\gamma_{\pm}$ [19]
0.2	0.521	0.521	0.533	0.108	0.104	0.104	0.1120	0.0995
0.3	0.499	0.499	0.506	0.0863	0.0835	0.0831	0.0899	0.0798
0.4	0.486	0.486	0.492	0.0736	0.0714	0.0708	0.0768	0.0681
0.5	0.478	0.478	0.483	0.0651	0.0630	0.0628	0.0678	0.0603
0.6	0.473	0.474	0.476	0.0589	0.0569	–	0.0612	0.0546
0.7	0.472	0.472	0.473	0.0542	0.0523	0.0520	–	0.0503
0.8	0.473	0.473	0.473	0.0506	0.0487	–	0.0524	0.0469
0.9	0.475	0.476	0.474	0.0476	0.0458	–	–	0.0442
1.0	0.481	0.481	0.478	0.0454	0.0435	0.0434	0.0468	0.0420
1.2	0.496	0.496	0.489	0.0420	0.0401	–	0.0432	0.0388
1.4	0.517	0.517	0.508	0.0398	0.0378	–	0.0407	0.0366
1.6	0.543	0.543	0.533	0.0384	0.0363	–	0.0391	0.0353
1.8	0.575	0.575	0.566	0.0377	0.0356	–	0.0383	0.0345
2.0	0.610	0.610	0.602	0.0374	0.0357	0.0350	0.0384	0.0342
2.5	0.716	0.715	0.717	0.0386	0.0367	0.0360	0.0395	–
3.0	0.841	0.840	0.861	0.0421	0.0408	0.0397	0.0439	0.0396

[a] ϕ(expt.) obtained is this work and ϕ(calc.) and $\gamma_{\pm}$(calc.) were obtained from equations (2) and (3), respectively. For comparison, values of ϕ [10] and $\gamma_{\pm}$ [10] obtained from reference 10, $\gamma_{\pm}$ [14] from reference 14, $\gamma_{\pm}$ [17] from reference 17, and $\gamma_{\pm}$ [19] from reference 19 are also listed.

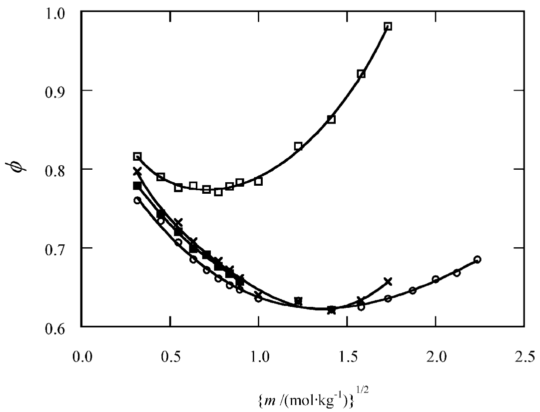

FIGURE 1. Osmotic coefficients ϕ as a function of molality $m^{1/2}$ at $T = 298.15$ K. □, Li_2SO_4(aq); ×, Na_2SO_4(aq); ■, K_2SO_4(aq); ○, $(NH_4)_2SO_4$(aq).

In equation (2), A_{ϕ} is the Debye–Hückel coefficient that has the value 0.39194 $(\mathrm{kg \cdot mol^{-1}})^{1/2}$ for water [12] at 298.15 K, I is the ionic strength, B^{ϕ} is given by $B^{\phi} = \beta^{(0)} + \beta^{(1)} \cdot \exp(-\alpha I^{1/2})$, were $\alpha = 2(\mathrm{kg \cdot mol^{-1}})^{1/2}$ for 1:2 electrolytes, and $B^{\phi} = \beta^{(0)} + \beta^{(1)} \cdot \exp(-\alpha_1 I^{1/2}) + \beta^{(2)} \cdot \exp(-\alpha_2 I^{1/2})$, were $\alpha_1 = 1.4\ (\mathrm{kg \cdot mol^{-1}})^{1/2}$ and $\alpha_2 = 12\ (\mathrm{kg \cdot mol^{-1}})^{1/2}$ for 2:2 electrolytes.

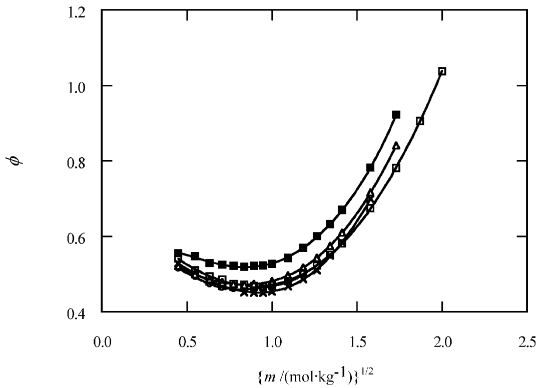

FIGURE 2. Osmotic coefficients ϕ as a function of molality $m^{1/2}$ at $T = 298.15\,\mathrm{K}$. ■, $MgSO_4$(aq); □, $MnSO_4$(aq); ×, $NiSO_4$(aq), ○, $CuSO_4$(aq); △, $ZnSO_4$(aq).

The determined parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{ϕ} with the corresponding standard deviation errors σ_s, and standard deviation of fit $\sigma(\phi)$, are listed in table 11 and compared with those reported by Pitzer and Mayorga [13].

The osmotic coefficients calculated using these parameters are listed in tables 2–10.

The parameters now obtained were used to calculate the corresponding mean activity coefficients for these sulphates using

$$\ln \gamma_{\pm} = |z_M z_X| f^{\gamma} + mB^{\gamma} + m^2 C^{\gamma}, \tag{3}$$

and

$$f^{\gamma} = -A_{\phi}\{I^{1/2}/(1 + 1.2I^{1/2}) + (2/1.2) \cdot \ln(1 + 1.2I^{1/2})\}. \tag{4}$$

The coefficient B^{γ} for 1:2 electrolyte is given by

$$B^{\gamma} = \beta^{(0)} + (2\beta^{(1)}/\alpha^2 I)\{(1 - (1 + \alpha I^{1/2} - \alpha^2 I/2) \cdot \exp(-\alpha I^{1/2})\}, \tag{5}$$

and for 2:2 electrolyte by

$$\begin{aligned} B^{\gamma} = 2\beta^{(0)} &+ (2\beta^{(1)}/\alpha_1^2 I)\{(1 - (1 + \alpha_1 I^{1/2} - \alpha_1^2 I/2) \cdot \exp(-\alpha_1 I^{1/2})\} + \\ &(2\beta^{(2)}/\alpha_2^2 I)\{(1 - (1 + \alpha_2 I^{1/2} - \alpha_2^2 I/2) \cdot \exp(-\alpha_2 I^{1/2})\}, \end{aligned} \tag{6}$$

and

$$C^{\gamma} = (3/2)C^{\phi}. \tag{7}$$

The results of this calculations are in tables 2 to 10. These mean activity coefficients agree with the literature values [10,14–19] within our experimental uncertainties. The mean activity coefficients are shown in figures 3 and 4.

TABLE 11

Pitzer's parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{ϕ} along with standard deviation $\sigma(\phi)$ of the set of equation (2) for Li_2SO_4(aq), Na_2SO_4(aq), K_2SO_4(aq), $(NH_4)_2SO_4$(aq), $MgSO_4$(aq), $MnSO_4$(aq), $NiSO_4$(aq), $CuSO_4$(aq), and $ZnSO_4$(aq) at $T = 298.15$ K[a]

	$\beta^{(0)}/(\text{kg}\cdot\text{mol}^{-1})$	$\beta^{(1)}/(\text{kg}\cdot\text{mol}^{-1})$	$\beta^{(2)}/(\text{kg}\cdot\text{mol}^{-1})$	$C^{\phi}/(\text{kg}\cdot\text{mol}^{-1})^2$	$\sigma(\phi)$
Li_2SO_4(aq)	0.13608 ± 0.00730	1.2513 ± 0.04120	–	-0.00399 ± 0.00090	0.0010
	(0.13627)	(1.2705)		(−0.00399)	(0.002)
Na_2SO_4(aq)	0.02963 ± 0.00100	1.01092 ± 0.03400	–	0.00171 ± 0.00030	0.0013
	(0.01957)	(1.11300)		(0.00497)	(0.003)
K_2SO_4(aq)	0.04318 ± 0.00210	0.81395 ± 0.009200	–	–	0.0030
	(0.04995)	(0.77925)			(0.002)
$(NH_4)_2SO_4$(aq)	0.04022 ± 0.00340	0.5911 ± 0.0512	–	-0.00106 ± 0.00030	0.0009
	(0.04087)	(0.6585)		(−0.00116)	(0.004)
$MgSO_4$(aq)	0.2305 ± 0.0015	3.267 ± 0.083	-47.93 ± 6.23	0.0232 ± 0.0022	0.003
	(0.221)	(3.343)	(−37.23)	(0.025)	(0.004)
$MnSO_4$(aq)	0.2123 ± 0.0021	2.793 ± 0.057	-48.24 ± 4.28	0.0145 ± 0.0041	0.005
	(0.213)	(2.938)	(−41.91)	(0.0155)	(0.005)
$NiSO_4$(aq)	0.1625 ± 0.0019	2.903 ± 0.103	-51.54 ± 7.81	0.0389 ± 0.0013	0.003
	(0.1702)	(2.907)	(−40.06)	(0.0366)	(0.005)
$CuSO_4$(aq)	0.2239 ± 0.0031	2.504 ± 0.112	-54.24 ± 5.87	0.0127 ± 0.0019	0.002
	(0.234)	(2.527)	(−48.33)	(0.0044)	(0.003)
$ZnSO_4$(aq)	0.2224 ± 0.0071	2.671 ± 0.2131	-38.36 ± 5.23	0.0182 ± 0.0007	0.0003
	(0.1949)	(2.883)	(−32.81)	(0.0029)	(0.004)

[a] The values in parenthesis were taken from reference 13.

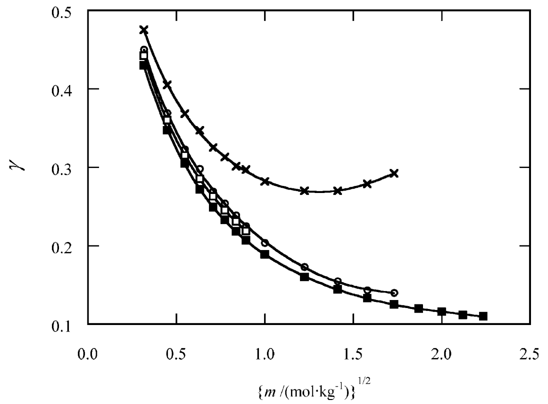

FIGURE 3. Mean activity coefficients γ as a function of molality $m^{1/2}$ at $T = 298.15\,K$. □, Li_2SO_4(aq); ×, Na_2SO_4(aq); ■, K_2SO_4(aq); ○, $(NH_4)_2SO_4$(aq).

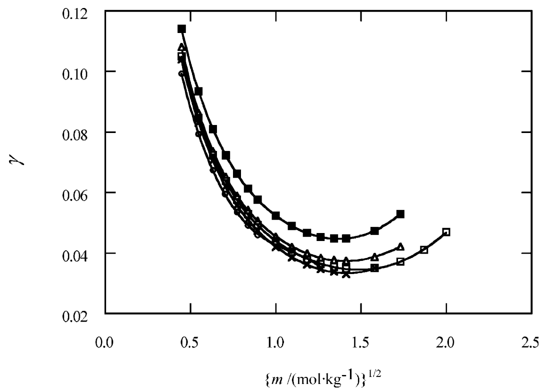

FIGURE 4. Mean activity coefficients γ as a function of molality $m^{1/2}$ at $T = 298.15\,K$. ■, $MgSO_4$(aq); □, $MnSO_4$(aq); ×, $NiSO_4$(aq), ○, $CuSO_4$(aq); △, $ZnSO_4$(aq).

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