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Activity and Osmotic Coefficients in Dilute Aqueous Solutions of Uni-Univalent Electrolytes at 25 °C

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Activity and osmotic coefficients in dilute aqueous solutions of some uni-univalent electrolytes are calculated from the simplified forms of the Stokes and Robinson equation. The required hydration parameters in these equations are taken from Guggenheim and Stokes. Electrolytes studied in this article include HCl, HBr, HI, $HClO_4$, $LiClO_4$, $NaClO_4$, LiCl, LiBr, LiI, NaCl, NaBr, NaI, KCl, KBr, KI, RbCl, RbBr, and RbI over the concentration range 0.0001–0.1 *m*.

In nonassociative dilute electrolyte solutions, the Stokes and Robinson two-parameter equation reduces to a simpler form (*1*). Activity coefficients in dilute hydrochloric acid solutions and sodium solutions calculated from the simplified equation are in agreement with the existing data (*1*). By use of the Gibbs–Duhem relation, a corresponding equation for calculating osmotic coefficients is also derived. The activity and osmotic coefficients in dilute solutions of bi-univalent electrolytes have been calculated from these equations and compiled in a previous paper (*2*). The hydration parameters, å and *h*, required in the calculations are obtained experimentally from the measurements of solutions at higher concentrations. They are used to evaluate thermodynamic properties of solutions in dilute regions where experimental difficulties are encountered. Detailed thermodynamic data in dilute solutions of uni-univalent electrolytes have not been reported, in general, except some limited information by Hamer and Wu (*3*). The present article is an attempt to remove this deficiency.

The simplified forms of the Stokes and Robinson equation for activity and osmotic coefficients of 1–1 electrolytes (*2*) are

$$\ln \gamma_\pm = \frac{K_1 m^{1/2}}{1 + K_2 m^{1/2}} + 0.036(h - 1)m \qquad (1)$$

$$\phi = 1 + \frac{K_1}{K_2^3 m}[(1 + K_2 m^{1/2}) - 2\ln(1 + K_2 m^{1/2}) - (1 + K_2 m^{1/2})^{-1}] + 0.018(h - 1)m \qquad (2)$$

in which $\gamma_\pm$ is the mean molal activity coefficient, ϕ is the molal osmotic coefficient, $K_1 = -1.17604$, $K_2 = 0.328618å$, *h* is the hydration number, å is the ion-size parameter in Å units, and *m* is the molality of the solution.

The values of å and *h* for 18 different kinds of 1–1 electrolytes are taken from Guggenheim and Stokes (*4*). These values (å and *h*) are as follows: HCl (4.47 Å, 8.0), HBr (5.18 Å, 8.6),

Table I. Activity and Osmotic Coefficients in Dilute Solutions of Uni-Univalent Electrolytes at 25 °C

	HCl		HBr		HI	
m	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ
0.0001	0.9885	0.9963	0.9885	0.9962	0.9886	0.9961
0.0005	0.9750	0.9917	0.9751	0.9918	0.9752	0.9918
0.001	0.9653	0.9886	0.9656	0.9887	0.9658	0.9888
0.002	0.9523	0.9843	0.9528	0.9846	0.9533	0.9848
0.003	0.9383	0.9812	0.9436	0.9816	0.9442	0.9820
0.004	0.9351	0.9788	0.9361	0.9793	0.9369	0.9797
0.005	0.9286	0.9768	0.9297	0.9773	0.9308	0.9779
0.006	0.9229	0.9749	0.9242	0.9756	0.9254	0.9763
0.007	0.9177	0.9733	0.9192	0.9741	0.9207	0.9747
0.008	0.9131	0.9719	0.9148	0.9728	0.9164	0.9736
0.009	0.9088	0.9706	0.9107	0.9716	0.9124	0.9725
0.01	0.9048	0.9693	0.9069	0.9705	0.9088	0.9715
0.02	0.8758	0.9609	0.8793	0.9628	0.8828	0.9646
0.03	0.8566	0.9556	0.8615	0.9583	0.8663	0.9609
0.04	0.8422	0.9520	0.8483	0.9553	0.8544	0.9586
0.05	0.8308	0.9494	0.8380	0.9532	0.8452	0.9572
0.06	0.8214	0.9474	0.8295	0.9518	0.8379	0.9564
0.07	0.8135	0.9460	0.8225	0.9508	0.8320	0.9560
0.08	0.8067	0.9448	0.8166	0.9502	0.8270	0.9559
0.09	0.9007	0.9440	0.8115	0.9498	0.8229	0.9561
0.1	0.7955	0.9434	0.8070	0.9496	0.8194	0.9565

Table II. Activity and Osmotic Coefficients in Dilute Solutions of Uni-Univalent Electrolytes at 25 °C

	$HClO_4$		$LiClO_4$		$NaClO_4$	
m	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ
0.0001	0.9885	0.9961	0.9885	0.9962	0.9885	0.9960
0.0005	0.9751	0.9918	0.9752	0.9918	0.9748	0.9916
0.001	0.9655	0.9887	0.9657	0.9888	0.9650	0.9884
0.002	0.9527	0.9845	0.9531	0.9847	0.9516	0.9840
0.003	0.9434	0.9815	0.9440	0.9819	0.9418	0.9807
0.004	0.9358	0.9792	0.9366	0.9790	0.9338	0.9781
0.005	0.9294	0.9772	0.9304	0.9777	0.9270	0.9759
0.006	0.9238	0.9754	0.9250	0.9760	0.9209	0.9739
0.007	0.9188	0.9739	0.9201	0.9746	0.9155	0.9722
0.008	0.9142	0.9725	0.9157	0.9733	0.9105	0.9706
0.009	0.9101	0.9713	0.9117	0.9721	0.9060	0.9691
0.01	0.9062	0.9701	0.9080	0.9711	0.9017	0.9677
0.02	0.8782	0.9621	0.8814	0.9638	0.8700	0.9577
0.03	0.8598	0.9573	0.8642	0.9597	0.8484	0.9510
0.04	0.8462	0.9541	0.8516	0.9570	0.8317	0.9459
0.05	0.8354	0.9517	0.8418	0.9552	0.8181	0.9419
0.06	0.8265	0.9500	0.8339	0.9541	0.8065	0.9386
0.07	0.8191	0.9488	0.8274	0.9533	0.7965	0.9358
0.08	0.8127	0.9479	0.8219	0.9529	0.7877	0.9334
0.09	0.8072	0.9473	0.8171	0.9527	0.7798	0.9313
0.1	0.8024	0.9468	0.8131	0.9527	0.7726	0.9294

0021-9568/81/1726-0183$01.25/0

Table III. Activity and Osmotic Coefficients in Dilute Solutions of Uni-Univalent Electrolytes at 25 °C

	LiCl		LiBr		LiI	
m	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ
0.0001	0.9885	0.9962	0.9885	0.9961	0.9885	0.9962
0.0005	0.9749	0.9917	0.9750	0.9917	0.9752	0.9918
0.001	0.9652	0.9885	0.9653	0.9884	0.9657	0.9887
0.002	0.9522	0.9842	0.9524	0.9843	0.9531	0.9847
0.003	0.9426	0.9812	0.9429	0.9813	0.9440	0.9818
0.004	0.9348	0.9787	0.9352	0.9788	0.9366	0.9796
0.005	0.9282	0.9766	0.9287	0.9768	0.9304	0.9777
0.006	0.9224	0.9747	0.9229	0.9750	0.9250	0.9760
0.007	0.9172	0.9731	0.9178	0.9734	0.9201	0.9746
0.008	0.9125	0.9716	0.9131	0.9720	0.9157	0.9733
0.009	0.9081	0.9703	0.9089	0.9706	0.9117	0.9721
0.01	0.9041	0.9690	0.9049	0.9694	0.9081	0.9711
0.02	0.8745	0.9602	0.8759	0.9609	0.8814	0.9639
0.03	0.8548	0.9547	0.8568	0.9560	0.8643	0.9597
0.04	0.8340	0.9508	0.8424	0.9521	0.8518	0.9571
0.05	0.8281	0.9479	0.8310	0.9495	0.8421	0.9554
0.06	0.8183	0.9456	0.8216	0.9475	0.8342	0.9543
0.07	0.8099	0.9439	0.8137	0.9460	0.8277	0.9535
0.08	0.8027	0.9425	0.8069	0.9448	0.8222	0.9532
0.09	0.7964	0.9415	0.8009	0.9440	0.8176	0.9530
0.1	0.7908	0.9406	0.7957	0.9434	0.8136	0.9530

Table IV. Activity and Osmotic Cöefficients in Dilute Solutions of Uni-Univalent Electrolytes at 25 °C

	NaCl		NaBr		NaI	
m	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ
0.0001	0.9885	0.9963	0.9885	0.9962	0.9885	0.9963
0.0005	0.9748	0.9917	0.9749	0.9917	0.9749	0.9917
0.001	0.9650	0.9884	0.9651	0.9884	0.9652	0.9885
0.002	0.9517	0.9840	0.9519	0.9841	0.9522	0.9842
0.003	0.9419	0.9808	0.9422	0.9809	0.9426	0.9811
0.004	0.9339	0.9782	0.9344	0.9784	0.9348	0.9786
0.005	0.9271	0.9760	0.9276	0.9762	0.9282	0.9765
0.006	0.9211	0.9740	0.9217	0.9743	0.9224	0.9747
0.007	0.9157	0.9722	0.9164	0.9726	0.9171	0.9730
0.008	0.9108	0.9707	0.9115	0.9711	0.9124	0.9715
0.009	0.9062	0.9692	0.9071	0.9697	0.9080	0.9702
0.01	0.9020	0.9679	0.9030	0.9684	0.9040	0.9689
0.02	0.8706	0.9580	0.8723	0.9589	0.8742	0.9600
0.03	0.8492	0.9515	0.8516	0.9528	0.8543	0.9543
0.04	0.8328	0.9466	0.8358	0.9483	0.8392	0.9502
0.05	0.8195	0.9428	0.8230	0.9448	0.8271	0.9471
0.06	0.8082	0.9397	0.8123	0.9420	0.8170	0.9447
0.07	0.7985	0.9371	0.8031	0.9397	0.8084	0.9428
0.08	0.7900	0.9349	0.7950	0.9378	0.8009	0.9412
0.09	0.7823	0.9330	0.7879	0.9362	0.7943	0.9400
0.1	0.7755	0.9313	0.7814	0.9348	0.7884	0.9389

HI (5.69 Å, 10.6), $HClO_4$ (5.09 Å, 7.4), $LiClO_4$ (5.63 Å, 8.7), $NaClO_4$ (4.04 Å, 2.1), LiCl (4.32 Å, 7.1), LiBr (4.56 Å, 7.6), LiI (5.60 Å, 9.0), NaCl (3.97 Å, 3.5), NaBr (4.24 Å, 4.2), NaI (4.47 Å, 5.5), KCl (3.63 Å, 1.9), KBr (3.85 Å, 2.1), KI (4.16 Å, 2.5), RbCl (3.49 Å, 1.2), RbBr (3.48 Å, 0.9), RbI (3.56 Å, 0.6). Activity and osmotic coefficients are calculated from eq 1 and 2. They are presented in Tables I–VI.

Scatchard et al. (*5*, *6*) offered excellent freezing-point data for $LiClO_4$, $NaClO_4$, LiCl, LiBr, NaCl, NaBr, KCl and KBr. Activity coefficients in these solutions at their freezing points have been calculated and compiled by Robinson and Stokes (*7*). In comparison with these values derived from Scatchard's data, even though at different temperatures, the results reported in this article are quite satisfactory.

Table V. Activity and Osmotic Coefficients in Dilute Solutions of Uni-Univalent Electrolytes at 25 °C

	KCl		KBr		KI	
m	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ
0.0001	0.9884	0.9964	0.9885	0.9961	0.9885	0.9962
0.005	0.9747	0.9915	0.9748	0.9916	0.9748	0.9916
0.001	0.9648	0.9883	0.9649	0.9883	0.9650	0.9884
0.002	0.9513	0.9838	0.9515	0.9839	0.9517	0.9840
0.003	0.9413	0.9805	0.9417	0.9807	0.9420	0.9808
0.004	0.9332	0.9778	0.9336	0.9780	0.9340	0.9782
0.005	0.9262	0.9755	0.9267	0.9757	0.9272	0.9760
0.006	0.9200	0.9735	0.9206	0.9737	0.9212	0.9741
0.007	0.9144	0.9717	0.9151	0.9720	0.9158	0.9723
0.008	0.9094	0.9700	0.9101	0.9703	0.9109	0.9708
0.009	0.9047	0.9685	0.9055	0.9688	0.9064	0.9693
0.01	0.9003	0.9671	0.9012	0.9674	0.9022	0.9680
0.02	0.8674	0.9565	0.8691	0.9572	0.8708	0.9581
0.03	0.8447	0.9494	0.8471	0.9503	0.8495	0.9516
0.04	0.8271	0.9440	0.8302	0.9451	0.8331	0.9468
0.05	0.8127	0.9396	0.8163	0.9409	0.8198	0.9429
0.06	0.8003	0.9359	0.8045	0.9375	0.8060	0.9397
0.07	0.7896	0.9328	0.7943	0.9345	0.7987	0.9371
0.08	0.7800	0.9301	0.7852	0.9320	0.7901	0.9348
0.09	0.7714	0.9277	0.7771	0.9298	0.7824	0.9328
0.1	0.7636	0.9255	0.7698	0.9278	0.7755	0.9311

Table VI. Activity and Osmotic Coefficients in Dilute Solutions of Uni-Univalent Electrolytes at 25 °C

	RbCl		RbBr		RbI	
m	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ
0.0001	0.9884	0.9959	0.9884	0.9962	0.9884	0.9962
0.0005	0.9747	0.9916	0.9747	0.9915	0.9747	0.9916
0.001	0.9648	0.9883	0.9647	0.9883	0.9648	0.9882
0.002	0.9512	0.9837	0.9512	0.9837	0.9512	0.9838
0.003	0.9412	0.9804	0.9412	0.9804	0.9412	0.9804
0.004	0.9330	0.9777	0.9330	0.9777	0.9330	0.9777
0.005	0.9260	0.9754	0.9259	0.9753	0.9260	0.9754
0.006	0.9198	0.9733	0.9197	0.9733	0.9198	0.9733
0.007	0.9142	0.9715	0.9141	0.9714	0.9142	0.9715
0.008	0.9091	0.9698	0.9090	0.9697	0.9091	0.9698
0.009	0.9043	0.9682	0.9042	0.9681	0.9043	0.9682
0.01	0.8999	0.9668	0.8998	0.9667	0.8999	0.9668
0.02	0.8668	0.9559	0.8665	0.9558	0.8668	0.9559
0.03	0.8439	0.9485	0.8436	0.9483	0.8438	0.9484
0.04	0.8261	0.9428	0.8257	0.9425	0.8260	0.9427
0.05	0.8114	0.9382	0.8109	0.9379	0.8113	0.9380
0.06	0.7987	0.9343	0.7983	0.9339	0.7987	0.9341
0.07	0.7880	0.9309	0.7873	0.9305	0.7877	0.9307
0.08	0.7783	0.9280	0.7775	0.9275	0.7780	0.9276
0.09	0.7696	0.9253	0.7687	0.9248	0.7692	0.9250
0.1	0.7617	0.9230	0.7607	0.9224	0.7612	0.9225

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