[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, AUCKLAND UNIVERSITY COLLEGE]

The Activity Coefficients of the Alkali Bromides and Iodides in Aqueous Solution from Vapor Pressure Measurements

BY ROBERT A. ROBINSON

In a previous communication[1] a method has been described whereby solutions of two salts can be distilled from one to the other until the two solutions are in equilibrium under the same vapor pressure, the concentrations of these isopiestic solutions being found from the weight of water distilled from or condensed onto the solutions. The calculation of activity coefficients from such data has also been described and applied to the alkali chlorides and to lithium iodide. This paper describes a similar investigation of the remaining alkali bromides and iodides.

Experimental

Only two points supplementary to the previous description of the apparatus require mention. Considerable difficulty was experienced in the case of potassium, rubidium and cesium iodide by corrosion of the silver dishes. This was overcome successfully in the case of the potassium salts by chromium plating the silver dishes. This was also successful with rubidium and cesium iodide, provided the solution was allowed to remain in the dishes only for a short time. By adjusting the concentrations of rubidium or cesium iodide and potassium chloride so that the solutions were almost isopiestic and therefore required only a few hours to come to equilibrium and using the solution for not more than two runs it is believed that the corrosion was reduced to a negligible amount. Nevertheless, it is proper to state that the same confidence is not to be placed in the results with these two iodides as in those with other salts.

In addition to using the set of four silver boxes previously described, a set of eight boxes has been used, each 3.8 cm. by 1.9 cm. and 2 cm. deep, the weight of a single box being approximately 20 g. Two of these contained a solution of potassium chloride as a standard and the other three pairs solutions of three different salts. Experience showed that with these boxes the time required to attain equilibrium was somewhat longer, it being advisable to rock them in the thermostat for thirty-six to forty-eight hours unless the solutions were very dilute, when three days were allowed. Since, however, results could be obtained with three salts at a time, the completion of a series was accelerated in spite of the somewhat longer time required for equilibrium.

As before, all measurements were made at 25°. The majority of the salts were purchased in a pure condition and recrystallized.

Experimental Results

The tables give the results obtained, m_1 being the concentration of potassium chloride and m_2 the concentration of the isopiestic salt solution.

TABLE I

CONCENTRATIONS OF ISOPIESTIC SOLUTIONS

m_1	m_2	m_1	m_2	m_1	m_2
		Lithium Bromide			
0.1704	0.1657	0.7169	0.6520	2.395	1.879
.2197	.2128	.8886	.7909	2.458	1.922
.2653	.2564	.9851	.8667	2.621	2.023
.3015	.2863	1.126	.9799	2.664	2.052
.3794	.3581	1.150	.9969	3.117	2.339
.4260	.4024	1.487	1.248	3.577	2.624
.4803	.4489	1.502	1.257	3.917	2.829
.5212	.4835	1.585	1.316	4.076	2.921
.5404	.5000	1.725	1.419	4.173	2.974
.6156	.5653	1.917	1.555	4.216	2.998
.6201	.5686	1.952	1.578	4.350	3.077
.6410	.5871	1.997	1.610	4.808	3.325
		Sodium Bromide			
0.1240	0.1226	1.185	1.104	2.805	2.460
.1368	.1351	1.385	1.278	3.203	2.767
.1510	.1492	1.491	1.370	3.492	2.998
.1611	.1591	1.891	1.713	3.610	3.089
.1919	.1895	1.975	1.786	3.671	3.137
.3570	.3470	2.144	1.926	3.903	3.310
.5771	.5529	2.248	2.002	3.911	3.321
.6738	.6431	2.520	2.228	4.125	3.474
.8214	.7818	2.631	2.317	4.265	3.589
.9181	.8664	2.651	2.335	4.717	3.913
.9587	.9014	2.797	2.451	4.81	3.992
		Potassium Bromide			
0.2356	0.2347	0.8002	0.7958	2.708	2.673
.3252	.3237	1.053	1.045	3.326	3.292
.3587	.3561	1.340	1.330	3.788	3.742
.5567	.5535	1.410	1.395	4.114	4.069
.5651	.5621	1.564	1.545	4.731	4.675
.5977	.5926	1.865	1.846	4.810	4.755
		2.040	2.016		

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[1] Robinson and Sinclair, THIS JOURNAL, **56**, 1830 (1934).

TABLE I (*Concluded*)

m_1	m_2	m_1	m_2	m_1	m_2
		Rubidium Bromide			
0.2692	0.2712	1.388	1.419	2.708	2.789
.5738	.5813	1.766	1.809	3.047	3.155
.8313	.8441	1.764	1.810	3.687	3.854
.8776	.8936	1.888	1.933	4.213	4.413
.8798	.8930	2.202	2.263	4.457	4.688
1.030	1.048	2.465	2.540	4.518	4.758
1.338	1.364			4.612	4.861
		Cesium Bromide			
0.2021	0.2060	1.692	1.805	3.605	3.888
.2945	.3011	1.954	2.090	3.974	4.287
.5978	.6240	2.302	2.470	4.061	4.366
.8222	.8614	2.841	3.057	4.214	4.535
1.184	1.257	3.054	3.284	4.469	4.799
1.554	1.658	3.244	3.504	4.768	5.104
		Sodium Iodide			
0.1158	0.1146	0.8944	0.8208	2.909	2.425
.2014	.1969	1.078	.9826	2.985	2.479
.2029	.1986	1.112	1.010	3.096	2.573
.2708	.2616	1.245	1.120	3.229	2.655
.4010	.3834	1.314	1.176	3.344	2.738
.4031	.3858	1.448	1.289	3.569	2.905
.5590	.5271	1.622	1.431	3.823	3.074
.6880	.6409	1.938	1.680	4.139	3.292
.7132	.6650	2.214	1.898	4.290	3.388
.7615	.7078	2.313	1.974	4.564	3.577
.8900	.8199	2.565	2.165	4.81	3.740
		Potassium Iodide			
0.1042	0.1035	1.224	1.179	3.111	2.969
.1053	.1047	1.278	1.232	3.131	2.992
.1708	.1691	1.715	1.647	3.470	3.324
.3109	.3068	1.857	1.779	3.498	3.355
.5536	.5426	2.157	2.066	3.666	3.499
.7025	.6852	2.555	2.445	3.931	3.748
1.022	.9892	2.600	2.494	4.400	4.198
1.217	1.175	2.807	2.689	4.81	4.581
		Rubidium Iodide			
0.2692	0.2727	1.387	1.429	2.638	2.739
.5738	.5859	1.952	2.016	2.965	3.094
.8313	.8489	2.307	2.392	3.420	3.574
1.125	1.152	2.325	2.414	3.733	3.937
1.202	1.236	2.337	2.424	4.053	4.288
1.330	1.369	2.374	2.463	4.276	4.514
1.372	1.413			4.81	5.102
		Cesium Iodide			
0.2053	0.2090	1.411	1.609	1.706	2.000
.3777	.3910	1.584	1.838	1.762	2.049
.5145	.5376	1.598	1.862	1.860	2.184
.6526	.6954	1.618	1.886	2.092	2.473
1.000	1.096	1.662	1.943	2.315	2.738
1.181	1.322			2.552	3.032

The activity coefficients of these salts have been calculated and are given in Table II. The plot of log γ against the square root of the salt molality is illustrated in Fig. 1.

Discussion

By the method of comparing isopiestic solutions the activity coefficients of fifteen alkali halides have now been determined and a comparison can be made with the values of these activity coefficients determined from other sources. Landolt–Börnstein's "Tabellen"[2] give the activity coefficients of a number of alkali halides calculated by Redlich and Rosenfeld. These have been compiled from freezing point data with the aid of the molal heat of dilution and the specific heats and are collected together in the following tables under the heading F. Harned[3] has deduced these activity coefficients in a number of cases from e. m. f. measurements (column H.) and Scatchard and Prentiss[4] have obtained similar data from their freezing point measurements. The latter have been corrected to 25° with the aid of the molal heats of dilution and specific heats taken from a number of sources.[5] The values obtained in this way are given in column S. The activity coefficients calculated from the present results and those of the previous investigation[1] are given in the column headed R. In the case of potassium chloride Spencer[6] has calculated values from freezing point data; these are given in the column headed Sp. In addition Harned and Nims[7] have calculated values for sodium chloride from their e. m. f. data. These are recorded in the column headed N.

To facilitate comparison the activity coefficients of any one salt derived by these different methods have all been referred to the same value at 0.1 *M* concentration, namely, that obtained in this investigation.

In the case of the chlorides and bromides of sodium and potassium the agreement between the different determinations is excellent except in the case of potassium bromide above 3.5 *M*. Sodium and potassium iodide also exhibit satisfactory agreement up to the highest concentrations employed in the e. m. f. determinations. For lithium chloride and bromide the accord between

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(2) Fifth Edition, Zweiter Ergänzungsband, 1931, p. 1112.

(3) Harned, THIS JOURNAL, **51**, 416 (1929).

(4) Scatchard and Prentiss, *ibid.*, **55**, 4355 (1933).

(5) Richards and Rowe, *ibid.*, **43**, 770 (1921); Wüst and Lange, *Z. physik. Chem.*, **116**, 161 (1925); Lange and Monheim, *Z. Elektrochem.*, **35**, 29 (1929); Lange and Dürr, *Z. physik. Chem.*, **121**, 361 (1926); Lange and Schwartz, *ibid.*, **133**, 129 (1928); Lipsett, Johnson and Maass, THIS JOURNAL, **49**, 1940 (1927); Randall and Rossini, *ibid.*, **51**, 323 (1929); Rossini, *Bur. Stand. J. Res.*, **6**, 791 (1931); **7**, 47 (1931).

(6) Spencer, THIS JOURNAL, **54**, 4490 (1932).

(7) Harned and Nims, *ibid.*, **54**, 423 (1932).

TABLE II

ACTIVITY COEFFICIENTS OF ALKALI BROMIDES AND IODIDES

m	LiBr	NaBr	KBr	RbBr	CsBr	NaI	KI	RbI	CSI
0.1	0.791	0.780	0.769	0.760	0.751	0.785	0.774	0.757	0.749
.2	.761	.739	.720	.706	.689	.749	.729	.701	.688
.3	.754	.717	.691	.671	.649	.734	.702	.666	.648
.5	.752	.698	.657	.632	.600	.723	.675	.623	.597
.7	.767	.689	.635	.605	.568	.726	.658	.597	.558
1.0	.808	.688	.615	.579	.536	.736	.645	.569	.514
1.5	.895	.704	.596	.553	.503	.769	.636	.541	.468
2.0	1.012	.732	.589	.536	.482	.821	.636	.524	.428
2.5	1.161	.770	.587	.528	.471	.885	.640	.515	.406
3.0	1.347	.814	.590	.524	.463	.963	.649	.511	.391
3.5		.868	.594	.520	.459	1.056	.659	.506	
4.0		.928	.599	.518	.457		.671	.504	
4.5			.610	.518	.458		.685	.503	
5.0				.519	.462			.503	

TABLE III

COMPARISON OF ACTIVITY COEFFICIENTS DEDUCED FROM VARIOUS SOURCES

	LiCl				NaCl				
m	F.	H.	S.	R.	F.	H.	N.	S.	R.
0.1	0.789	0.789	0.789	0.789	0.776	0.776	0.776	0.776	0.776
.2	.752	.766	.754	.758	.730	.730	.730	.732	.731
.3	..	..	.739	.745	..	..	..	.708	.708
.5	.727	.734	.732	.739	.672	.676	.678	.679	.679
.7	..	..	.739	.751	..	..	..	.663	.665
1.0	.751	.767	.764	.778	.648	.654	.655	.653	.655
1.5	..	.830	..	.838	..	.656	.654	..	.655
2.0	.905	.931	..	.927	.656	.668	.668	..	.669
2.5	..	1.056	..	1.039	..	.688	.689	..	.691
3.0	1.164	1.189	..	1.169	.697	.712	.718	..	.716
3.5	..	1.376	..	..	..	.747	.750	..	.753
4.0	1.464	1.574	..	..	.754	.777	.789	..	.789

	KCl					LiBr		
m	F.	H.	S.	R.	Sp.	H.	S.	R.
0.1	0.766	0.766	0.766	0.766	0.766	0.791	0.791	0.791
.2	.717	.714	.716	.715	.717	.766	.764	.761
.3	..	..	.686	.684	..	..	.755	.754
.5	.657	.646	.650	.648	.652	.755	.759	.752
.7	..	..	.627	.624	..	..	.778	.767
1.0	.608	.599	.604	.602	.609	.803	.818	.808
1.5	..	.577	..	.581	.591	.887	..	.895
2.0	.579	.570	..	.572	..	.995	..	1.012
2.5	..	.569	..	.569	..	1.148	..	1.161
3.0	.576	.572	..	.570	..	1.288	..	1.347
3.5	..	.572	..	.573	..	1.513	..	..
4.0	..	.583	..	.578	..	1.822	..	..

	NaBr				KBr			
m	F.	H.	S.	R.	F.	H.	S.	R.
0.1	0.780	0.780	0.780	0.780	0.769	0.769	0.769	0.769
.2	.744	.738	.745	.739	.723	.719	.723	.720
.3	..	..	.724	.717	..	..	.693	.691
.5	.714	.697	.705	.698	.664	.656	.660	.657
.7	..	..	.699	.689	..	..	.637	.635
1.0	.715	.688	.697	.688	.624	.615	.616	.615
1.5	..	.697	..	.704	..	.598	..	.596
2.0	.782	.733	..	.732	.608	.592	..	.589
2.5	..	.774	..	.770	..	.592	..	.587
3.0	..	.824	..	.814	.610	.593	..	.590
3.5	..	.872	..	.868	..	.602	..	.594
4.0	..	.934	..	.928	..	.612	..	.599

TABLE III (*Concluded*)

	NaI		KI			RbCl	
m	H.	R.	F.	H.	R.	F.	R.
0.1	0.785	0.785	0.774	0.774	0.774	0.761	0.761
.2	.751	.749	.739	.729	.729	.709	.708
.5	.718	.723	.696	.677	.675	.633	.637
1.0	.731	.736	.671	.648	.645		
1.5	..	..	..	.645	.636		
2.0	..	..	.678	.645	.636		
3.0	..	..	.708	..	.649		
4.0	..	..	.736	..	.671		

the data, although not so good, is yet within the experimental error of ±1 mv. allowed by Harned in his e. m. f. measurements with these solutions.

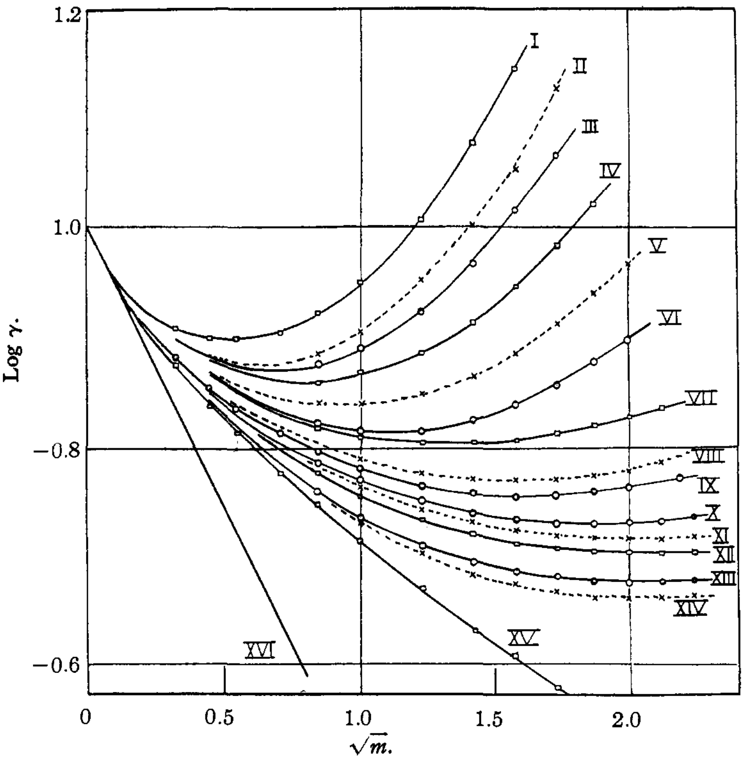

Fig. 1.—Activity coefficients of alkali halides: I, LiI; II, LiBr; III, LiCl; IV, NaI; V, NaBr; VI, NaCl; VII, KI; VIII, KBr; IX, KCl; X, RbCl; XI, RbBr; XII, RbI; XIII, CsCl; XIV, CsBr; XV, CsI; XVI, limiting Debye–Hückel slope.

The data for rubidium chloride can be checked only up to 0.5 *M* against freezing point determinations; within this range the agreement is excellent. As has been pointed out in the previous paper, the agreement with the e. m. f. data is also satisfactory in the case of cesium chloride. There are no comparable measurements to confirm the activity coefficients of lithium iodide, rubidium and cesium bromides and rubidium and cesium iodides.

TABLE IV

OSMOTIC COEFFICIENTS AT 1 *M* CONCENTRATION

$$\begin{tikzcd}
 & \text{Li} & \text{Na} & \text{K} & \text{Rb} & \text{Cs} \\
\text{Cl} & 0.99_9 \arrow[d] & 0.91_9 \arrow[l] \arrow[d] & 0.88_0 \arrow[l] \arrow[d] & 0.86_9 \arrow[l] & 0.84_0 \arrow[l] \\
\text{Br} & 1.10_9 \arrow[d] & 0.94_1 \arrow[l] \arrow[d] & 0.88_9 \arrow[l] \arrow[d] & 0.86_6 \arrow[l] \arrow[u] & 0.83_4 \arrow[l] \arrow[u] \\
 & 1.05_7 & 0.97_1 \arrow[l] & 0.90_9 \arrow[l] & 0.85_9 \arrow[l] \arrow[u] & 0.80_9 \arrow[l] \arrow[u]
\end{tikzcd}$$

With a knowledge of the molalities of isopiestic solutions of a salt and potassium chloride it is possible to calculate the osmotic coefficients of the salt. This has been done and the osmotic coefficients of fifteen salts at 1 *M* concentration are collected in Table IV, which may be compared with similar tables given by Scatchard and Prentiss[8] and by Fajans.[9]

The agreement with the data tabulated by Scatchard and Prentiss is satisfactory in view of the difference of 25° between the temperatures at which the two sets of data were recorded.

It is significant that the order of activity coefficient curves, I > Br > Cl, which holds for the lithium, sodium and potassium salts, is reversed in the case of the rubidium and cesium salts.

I wish to thank the Chemistry Department of Sydney University for the loan of cesium salts.

Summary

1. Measurements of the concentrations of lithium, sodium, potassium, rubidium, cesium bromide solutions and sodium, potassium, rubidium and cesium iodide solutions, isopiestic with solutions

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[8] Scatchard and Prentiss, THIS JOURNAL, **56**, 810 (1934).

[9] Fajans, "Chemistry at the Centenary Meeting of the British Association," **1931**, p. 50.

of known strength of potassium chloride at 25°, have been reported.

2. From these the activity coefficients of alkaline bromides and iodides have been computed at concentrations of from 0.1 to 4 *M*.

3. Activity coefficients determined by this method are found to be in good agreement with the best electromotive force and freezing point data.

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The Activity Coefficients of Alkali Nitrates, Acetates and *p*-Toluenesulfonates in Aqueous Solution from Vapor Pressure Measurements

BY ROBERT A. ROBINSON

The isopiestic method of determining the vapor pressure of a solution (and thence the activity coefficient of the solute), previously described[1] with reference to the alkali halides has now been applied to other alkali salts. Measurements have been made on the nitrates of lithium, sodium and potassium which are of interest because of the very low activity coefficient of the latter salt[2] and on the corresponding *p*-toluenesulfonates, the potassium salt of which Sinclair[3] has found to resemble potassium nitrate in respect of its vapor pressure lowering.

Harned and Robinson[4] have found that the plots of the activity coefficient of acetic acid in solutions of lithium, sodium and potassium chloride against salt concentration are in the order K>Na>Li, exhibiting a reversal of the order characteristic of hydrochloric acid in these alkali chloride solutions, namely, Li>Na>K. Scatchard and Prentiss[5] have recently shown by measurements of the freezing point of alkali acetate solutions that the order of the activity coefficient curves is also the reverse of that which obtains for the alkali halides. To confirm this important observation at another temperature a series of measurements have been made on three alkali acetates.

Experimental Results

The experimental procedure as well as the derivation of the activity coefficient have already been described. The three nitrates and lithium and sodium acetates were recrystallized several times. Potassium acetate was made by neutralization of the carbonate with the calculated amount of acetic acid and subsequent crystallization. The toluenesulfonates were made by simi-

TABLE I

ISOPIESTIC SOLUTIONS OF POTASSIUM CHLORIDE AND SOME ALKALI SALTS

m_1 = concentration of potassium chloride. m_2 = concentration of alkali salt in the isopiestic solution.

m_1	m_2	m_1	m_2	m_1	m_2
Lithium Acetate					
0.1263	0.1252	1.232	1.145	2.839	2.499
.1621	.1598	1.241	1.147	2.896	2.545
.2118	.2082	1.565	1.431	3.113	2.719
.3397	.3319	1.741	1.579	3.253	2.828
.5922	.5678	1.793	1.622	3.821	3.294
.7327	.6951	2.015	1.815	4.067	3.501
.8090	.7665	2.365	2.107	4.480	3.840
1.017	.9490	2.479	2.199	4.516	3.869
1.103	1.028	2.527	2.239	4.810	4.091
		2.565	2.272		
Sodium Acetate					
0.1263	0.1238	1.461	1.279	2.691	2.247
.1621	.1586	1.594	1.390	2.735	2.281
.2118	.2050	1.741	1.510	2.866	2.373
.3397	.3266	1.793	1.548	2.896	2.397
.5922	.5516	1.819	1.570	2.998	2.474
.7327	.6733	2.015	1.721	3.113	2.559
.8090	.7408	2.287	1.930	3.375	2.754
1.017	.9164	2.365	2.003	3.583	2.909
1.103	.9873	2.409	2.030	4.480	3.572
1.232	1.100	2.479	2.088	4.516	3.593
1.241	1.102	2.565	2.150	4.810	3.813
1.453	1.278	2.671	2.231		
Potassium Acetate					
0.1263	0.1230	1.017	0.9012	2.244	1.855
.1621	.1575	1.103	.9766	2.365	1.947
.1872	.1821	1.232	1.085	2.479	2.035
.2118	.2037	1.241	1.088	2.896	2.336
.3397	.3233	1.435	1.236	3.113	2.487
.3593	.3417	1.442	1.245	3.568	2.810
.5185	.4830	1.741	1.480	3.630	2.854
.5922	.5496	1.793	1.518	3.983	3.099
.8090	.7326	2.015	1.685	4.480	3.458
.9231	.8295	2.060	1.716	4.516	3.475

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[1] (a) Robinson and Sinclair, THIS JOURNAL, **56**, 1830 (1934); (b) Robinson, *ibid.*, **57**, 1161 (1935).

[2] Scatchard, Prentiss and Jones, *ibid.*, **54**, 2690 (1932).

[3] Sinclair, *J. Phys. Chem.*, **37**, 495 (1933).

[4] Harned and Robinson, THIS JOURNAL, **50**, 3157 (1928).

[5] Scatchard and Prentiss, *ibid.*, **56**, 807 (1934).