Activities in Alkali-Ammonia Solutions

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SOME THIRTY YEARS ago Johnson and Meyer (*8*) calculated the relative activities of lithium and potassium solutions in liquid ammonia. These calculations were limited by the fact that suitable information was available only for concentrated solutions and only for these two of the alkali metals. They observed an extremely large change in the metal activity over a relatively small concentration range and suggested that further investigation of this problem would be profitable.

There was no great rush to fulfill this suggestion, for in the intervening time only Hodgins (7) in 1949 and Marshall and Hunt (*13*) in 1956 have reported work on the vapor pressures of metal-ammonia solutions. Hodgins used only cesium and made no activity calculations. Marshall and Hunt used only sodium and lithium of the alkali metals and their measurements were neither sufficiently precise nor in sufficiently dilute solutions to permit calculation of actual values of the activities. The relative activities obtained were in agreement with those of Johnson and Meyer but displayed some most unusual characteristics.

Accordingly, it was determined to measure the vapor pressures of lithium, sodium, potassium, rubidium, and cesium solutions in liquid ammonia as functions of concentration and of temperature. This report covers one temperature, −35.00° C., for all five of these metals. The concentration range was from saturation to as dilute a solution as could be measured with satisfactory precision. The most dilute solution actually measured was a lithium solution of 0.000292 mole fraction. In other terms this is about 0.017 molal. The solutions of the other metals were somewhat less dilute.

MATERIALS

The ammonia used was Matheson, anhydrous ammonia, listed as 99.99% minimum purity. This was distilled from a sodium solution and stored in the vacuum line as a sodium solution. Whenever used, the required amount was transferred to a bulb on the line and pumped at −80° C. to remove noncondensable gases. It was then measured either as a gas or as a liquid and a gas in calibrated bulbs on the vacuum line and transferred to the reaction system.

The metals were reagent grade containing less than 0.1% impurity in each case. The impurities were principally the other alkali metals. The metals, except lithium, were further purified by repeated distillations in a vacuum line and varying amounts collected in small sealed glass tubes. The lithium was carefully cleaned in a dry box under argon, and small pieces cut and inserted in a small tube sealed to a glass apparatus. The latter was so constructed that it could be sealed to a vacuum line, the line and then the apparatus evacuated, while the lithium was at all times exposed only to argon. When the system had been evacuated, the small tube containing the lithium was sealed off.

TEMPERATURE CONTROL

The metal solutions were held at −35.00° ± 0.02° C. by the following means: The solutions tube and its companion pure ammonia tube were immersed in methyl Cellosolve in a large Dewar. An aluminum can, surrounding the two ammonia tubes, divided the bath into two compartments. Rotary stirrers were used both inside and outside of the can. The outer compartment also contained heating and cooling coils and the temperature control element, a thermistor in conjunction with a Sargent Thermonitor. A mechanical two-stage refrigerator kept 15 gallons of methyl Cellosolve at −42 ± 1° C. This coolant was pumped through the cooling coils in the Dewar. Unfortunately, none of the several thermistors tried gave quite the desired performance. That is, the temperature was not maintained at −35.00° C. Rather, as the cooolant warmed from −43° to −41° C. and then was cooled again, the bath temperature followed to some extent. The range was normally ±0.01° C. but occasionally became as great as ±0.02° C. Such a difference between the temperature of the solution and that of the pure ammonia could not, of course, be tolerated. Yet careful examination revealed that the temperature differential appeared to be less than 0.0001° C. With pure ammonia in both tubes a differential manometer connecting the two tubes was not found to change perceptibly. The manometer used was a multiplying manometer in which an air bubble in a mercury column was followed in a capillary tube along a steel meter bar. A temperature differential of as much as 0.0001° C. would have meant a movement of about 0.4 mm. on the part of the air bubble. No discernible movement was observed through several cycles of the mechanical refrigerator. Similar results were obtained when using a metal-ammonia solution in one tube and pure ammonia in the other except that now the pressure differential changed slightly but with no significant difference detected in the ratio $\Delta P/P^0$. Although this situation was tolerable, it removed the use of constant pressure differential as a simple condition of equilibrium. Although an hour or more was allowed between readings, a few values were obtained before true equilibrium had been reached. Since pressure readings took considerable time, stopcocks had to be inserted in the line to close off the liquids from the manometers while the latter were being read.

PROCEDURE

The solutions were prepared by: evacuating the system to a pressure of less than 10^{-6} mm., transferring a measured amount of ammonia to the solution tube, attaining temperature equilibrium, and introducing the metal by means of a tube breaker just above the solution vessel. The metal and glass fragments fell into the liquid ammonia, and the resulting solution was stirred by means of a solenoid-activated vertical stirrer.

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A second tube, adjacent to the solution tube, contained pure ammonia. The temperature was determined by means of the vapor pressure of the pure ammonia using the values of Henning and Stock (*6*). When the solution had reached equilibrium the vapor pressure of the pure ammonia was read using a closed end manometer and a cathetometer with a precision of 0.005 cm. The difference between the vapor pressure of the solution and that of the pure ammonia was read using one of the three manometers integrated into the vacuum line. For the large differences in more concentrated solutions the manometer used was of 12-mm. bore and the aforementioned cathetometer with 0.005-cm. precision was used. For such concentrated solutions the values of P and P^0 were measured directly using closed end manometers and ΔP obtained by difference. With more dilute solutions (ΔP less than 2.5 cm.) a low range cathetometer reading to 0.001 cm. was employed with a differential manometer while for very dilute solutions the more precise multiplying differential manometer was used. The bore of the first differential manometer, read to 0.001 cm., was 25 mm. and the bore of the multiplying differential manometer, read to 0.0001 cm., was 30 mm. All pressure readings were corrected for thermal expansion. The corrections for the shape of the menisci were negligible for the bore of the manometers used. The pressure values are reported for a gravitational acceleration of 9.803 meters per square sec.

Following each pressure reading a measured amount of ammonia was moved, and the above procedure repeated on the resulting, more concentrated, solution. In all calculations concerning the quantity of ammonia, allowance was made for the ammonia in the vapor state including the changes in volume caused by manipulation of the manometers. An average of about six different pressure-concentration points were obtained during each run. At the conclusion of each run the vapor from the solution and from the pure ammonia was introduced into another portion of the vacuum line. This portion was closed off, the ammonia frozen out and a fourth manometer used to check for residual hydrogen in the vapor above the metal solution. This method for detecting solution decomposition was sensitive to approximately 0.1% decomposition of the most concentrated and 5% decomposition of the most dilute solutions.

The ammonia was then removed to the storage bulb, the remaining ammonia pumped out of the line and air introduced. The metal was dissolved in alcohol and the alcoholate solution collected. The tube was washed several times with water. The water-alcohol solution was evaporated to a small volume to drive off any traces of ammonia and titrated with hydrochloric acid to a methyl orange endpoint.

RESULTS

A total of more than 40 runs were made. About 10 of these were preliminary runs during which the characteristics of the apparatus, primarily the bath, were being tested. One run was made on an ammonium chloride solution in liquid ammonia. It gave the expected results as shown in Table I and Figure 2. An additional 31 runs were made on the various alkali metal solutions. One run showed residual hydrogen and was discarded entirely. In a second run (on rubidium) very erratic results were obtained. Subsequent comparison with other runs on rubidium gave justification for eliminating this run. It is shown as run *C* in the rubidium section in Table II. For the remaining 29 runs there were 189 points. The results in Table I and II are given in terms of mole fraction of metal, relative pressure lowering and the ratio of the latter to the former. A plot of this ratio *vs.* mole fraction of metal was made for each of the alkali metals from the values in Table II. A quasistatistical analysis of these plots, using Chauvenet's criterion, was used as a basis for discarding 13 of the points.

The saturated solution pressures and corresponding concentrations (in molality) are shown in Table III. Some difficulty was experienced in achieving equilibrium with the rubidium solutions although no such difficulty had been observed with lithium, sodium, or potassium. In some runs with this metal, part of the ammonia was taken off and readded several times with rapid stirring before the solutions appeared to react normally. With cesium this situation was compounded greatly. An equilibrium pressure for the saturated solution was never observed with this metal, let alone repeated. Although one would certainly expect a saturated solution with its attendant constant pressure, there is no conclusive evidence that such a situation actually exists. Rather, the value shown in Table III was obtained from the maximum of the plot of the relative lowering of ammonia pressure per mole fraction of cesium *vs.* the mole fraction of cesium. Although these plots began to level off for some of the metals in the concentrated regions, none were observed to reach a maximum and then decrease. On this basis, for cesium solutions (which did show a decrease) the maximum was considered to be the best possible choice for the saturated solution. It is apparent that Hodgins (*7*) experienced similar difficulties with cesium solutions.

The fugacity of the ammonia in the various solutions was obtained from the observed pressure readings and the assumption that the ammonia vapor obeys van der Waals' equation.

Table I. Vapor Pressure Lowering in Ammonium Chloride Solutions

X_{NH_4Cl}	$\Delta P/P^0$	$\dfrac{\Delta P/P^0}{X_{NH_4Cl}}$
0.001294	0.001945	1.503
0.001819	0.002354	1.294
0.003029	0.003436	1.134
0.00887	0.008016	0.904

Although it was intended to calculate the metal activities on the basis of a standard state of a 1–1 electrolyte at infinite dilution, the observed behavior of all of the metals except lithium (Figure 2) made this impossible. Instead, relative ionic activity coefficients were calculated such that $k\gamma_\pm$ was 1.00 for each metal at unit molality. The relative activity coefficients were determined graphically by means of the Gibbs-Duhem equation according to the method of Randall and White (*14*).

DISCUSSION

These solutions have been described as being 1–1 electrolytes, at least in the dilute region. However, any equilibrium, as for example the ionization of Na to give Na$^+$ and e^-, which occurs in dilute solution must also be present in concentrated solutions. Any observed deviations from the expected behavior are usually explained in terms of other equilibria set up in the same solution. Hence, many writers have used electron pairing, metal ion pairing, metal atom pairing, solvation, etc., in an attempt to derive a suitable theory. This is similar to aqueous solutions of the alkali chlorides, bromides, and acetates, in which double and triple ions, hydration, etc., are used to explain the observed results.

Table II. Vapor Pressure Lowering in Metal-Ammonia Solutions

Run	X	$\Delta P/P^\circ$	$\frac{\Delta P/P^\circ}{X}$	Run	X	$\Delta P/P^\circ$	$\frac{\Delta P/P^\circ}{X}$
(Lithium)							
E	0.000292	0.000549	1.880	B	0.04274	0.02478	0.580
E[a]	0.000394	0.000867	2.450	A	0.04832	0.02817	0.583
E	0.000602	0.001133	1.882	B	0.06192	0.03617	0.584
E	0.001272	0.002220	1.745	B	0.07062	0.04567	0.647
E	0.001694	0.002822	1.666	B	0.08118	0.06200	0.764
D[a]	0.002034	0.004311	2.119	B	0.09040	0.08650	0.957
E	0.002489	0.003615	1.452	A	0.1035	0.1255	1.213
D	0.002799	0.004278	1.528	B	0.1308	0.2265	1.732
D	0.004468	0.005890	1.318	A	0.1458	0.3185	2.185
E	0.004757	0.006033	1.268	B	0.1635	0.4324	2.645
D	0.008206	0.007833	0.954	A	0.1737	0.5287	3.044
D	0.01077	0.009161	0.851	A	0.1889	0.6803	3.601
A	0.01138	0.008851	0.779	B	0.1982	0.8018	4.045
A	0.01414	0.01109	0.784	A	0.2054	0.8963	4.364
D	0.01565	0.01212	0.774	B	0.2073	0.9373	4.521
A	0.01862	0.01414	0.759	A[a]	0.2148	0.9679	4.506
B	0.02589	0.01768	0.683	A[a]	0.2291	0.9882	4.313
A	0.02704	0.01934	0.716	C	0.2110	0.9958	(sat)
B	0.03227	0.02084	0.646	A	. . .	0.9960	(sat)
(Sodium)							
A	0.000650	0.000141	0.217	E	0.03617	0.01505	0.416
A	0.000970	0.000239	0.246	H	0.03983	0.01514	0.380
B	0.001733	0.000831	0.480	G	0.04271	0.01553	0.364
B	0.002154	0.001151	0.534	H	0.04783	0.01637	0.342
C[a]	0.002781	0.000913	0.328	E	0.05131	0.01662	0.324
B	0.002848	0.001673	0.587	F	0.05511	0.01868	0.339
C	0.003388	0.002418	0.714	G	0.05684	0.01951	0.343
B	0.004207	0.002658	0.632	H	0.05964	0.02066	0.346
C	0.004334	0.003075	0.710	H	0.07746	0.04200	0.542
D	0.005360	0.003480	0.649	G	0.08030	0.04649	0.579
C	0.005997	0.004163	0.694	H	0.1015	0.1134	1.117
F	0.006189	0.004238	0.685	G	0.1104	0.1582	1.433
D	0.006445	0.004746	0.736	H	0.1257	0.2459	1.956
B	0.007978	0.005095	0.639	F[a]	0.1279	0.2076	1.623
F	0.008244	0.005711	0.693	G	0.1279	0.3181	2.332
F	0.01249	0.008540	0.684	G	0.1416	0.3742	2.643
E	0.01908	0.01075	0.563	H	0.1437	0.3972	2.764
F	0.02047	0.01263	0.617	G	0.1476	0.4258	2.885
E	0.02270	0.01263	0.570	G	0.1532	0.4719	3.080
E	0.02792	0.01396	0.500	G	0.1667	0.4955	(sat)
G	0.02841	0.01396	0.491	H	0.1730	0.4954	(sat)
G	0.03414	0.01467	0.430				
(Potassium)							
A	0.002442	0.000739	0.303	D	0.04826	0.03596	0.745
B	0.002657	0.000920	0.346	E	0.05116	0.03911	0.764
A	0.003042	0.001276	0.419	D	0.05845	0.05847	1.000
B	0.003118	0.001515	0.486	D	0.06226	0.06751	1.084
B	0.003774	0.002230	0.591	E	0.07054	0.08241	1.168
A	0.004032	0.002296	0.569	D	0.07826	0.1242	1.587
B	0.004776	0.003031	0.635	E	0.09407	0.1909	2.029
A	0.005976	0.004053	0.678	D	0.09636	0.2153	2.234
B	0.006507	0.004474	0.688	D	0.1015	0.2501	2.464
C	0.007838	0.005687	0.726	E	0.1144	0.3380	2.955
C	0.009246	0.006985	0.755	D	0.1221	0.4037	3.306
B[a]	0.01013	0.01072	1.058	E	0.1303	0.4810	3.691
A	0.01142	0.008941	0.783	D	0.1381	0.5484	3.971
C	0.01298	0.009902	0.763	E	0.1446	0.6227	4.306
C	0.01880	0.01417	0.754	D	0.1518	0.6609	4.354
C	0.02348	0.01683	0.717	E	0.1565	0.7291	4.659
E	0.03137	0.02159	0.688	D	0.1635	0.7488	4.580
C	0.03339	0.02307	0.691	E	0.1714	0.7891	(sat)
E	0.03914	0.02760	0.705	D	0.2058	0.7891	(sat)
(Rubidium)							
D[a]	0.00314	0.000474	0.151	E	0.03340	0.03130	0.937
A	0.00335	0.001262	0.377	E	0.04635	0.05121	1.105
B	0.00383	0.001635	0.427	D	0.04909	0.05509	1.122
A	0.00401	0.001782	0.444	G[a]	0.06296	0.06744	1.071
D	0.00425	0.001741	0.410	G	0.07332	0.1025	1.398

Table II. Vapor Pressure Lowering in Metal-Ammonia Solutions (*Continued*)

Run	X	$\Delta P/P^\circ$	$\frac{\Delta P/P^\circ}{X}$	Run	X	$\Delta P/P^\circ$	$\frac{\Delta P/P^\circ}{X}$
B	0.00483	0.002757	0.571	E	0.07846	0.1237	1.577
A	0.00498	0.003101	0.623	G	0.08548	0.1586	1.855
B	0.00655	0.004472	0.683	F	0.08956	0.1998	2.231
D	0.00665	0.004551	0.684	G	0.09882	0.2349	2.377
A	0.00672	0.004676	0.696	E	0.1046	0.2748	2.627
C[a]	0.00685	0.003505	0.512	G	0.1121	0.3279	2.925
C[a]	0.00934	0.004824	0.516	F	0.1136	0.3492	3.074
A[a]	0.00992	0.008954	0.903	G	0.1247	0.4250	3.408
B	0.01015	0.007827	0.771	F	0.1348	0.4978	3.693
D	0.01162	0.008853	0.762	G	0.1394	0.5394	3.869
C[a]	0.0134	0.01032	0.770	F	0.1492	0.6014	4.031
C[a]	0.0145	0.01327	0.915	G	0.1530	0.6340	4.144
D	0.01505	0.01177	0.782	F	0.1647	0.7031	4.269
D	0.02027	0.01849	0.912	G	0.1668	0.7069	4.238
E[a]	0.02561	0.01858	0.725	G	0.1848	0.7513	(sat)
D	0.02935	0.02856	0.973	F	0.1853	0.7514	(sat)
			(Cesium)				
A	0.00115	0.000126	0.110	D[a]	0.0384	0.06176	1.608
A	0.00208	0.000488	0.235	E	0.0509	0.06114	1.201
B	0.00364	0.001113	0.306	D	0.0602	0.1037	1.723
C	0.00484	0.002101	0.434	E	0.0671	0.09804	1.461
C	0.00576	0.003145	0.546	E	0.0842	0.1579	1.875
E	0.00659	0.003243	0.492	E	0.1017	0.2189	2.152
C	0.00710	0.004095	0.577	D	0.1103	0.2393	2.170
E	0.00820	0.005712	0.697	E	0.1140	0.2827	2.480
C	0.00914	0.004928	0.539	E	0.1252	0.3461	2.764
E	0.01086	0.008934	0.823	D	0.1414	0.4493	3.178
B	0.01170	0.01000	0.855	E	0.1525	0.5165	3.387
C[a]	0.0133	0.007230	0.544	D	0.1629	0.5819	3.572
E	0.0162	0.01489	0.919	E	0.1764	0.6401	3.629
E	0.0188	0.01731	0.921	E	0.2255	0.7538	3.343
D	0.0275	0.02490	0.905	E	0.284	0.8295	2.921
E	0.0379	0.04120	1.087	E	0.543	0.8730	1.608

[a] Discarded points.

Table III. Vapor Pressures of Saturated Metal-Ammonia Solutions

Metal	Molality	Vapor Pressures
Lithium	15.70 ± 0.20[a]	0.295 ± 0.010 cm.
Sodium	10.84 ± 0.15	35.295 ± 0.010
Potassium	11.84 ± 0.20	14.755 ± 0.010
Rubidium	12.50 ± 0.4	17.39 ± 0.01
Cesium	13.0 ± 1.0	24 ± 2

[a] All values of precision estimated.

In such uni-univalent solutions certain characteristics have been observed. For example, when $\ln k\gamma_\pm$ is plotted against $m^{1/2}$ for the alkali chlorides and k chosen so that the curves intersect at $m^{1/2} = 1.00$, it is found that to the right of the intersection, the order is Li > Na > K > Rb > Cs and to the left this order is reversed. The bromides and iodides are similar but for the acetates, hydroxides, and fluorides the above order is exactly reversed. No cases of partial reversal have been found (*5*).

The curves in Figures 1 and 2 seem to indicate that these solutions display considerable deviation from normal 1-1 electrolytic behavior. The $\ln k\gamma_\pm$ curves differ from the prescribed behavior in that they cross at other than the reference point and in fact do so several times. In other words a partial reversal is observed. Only in the region of $m^{1/2} \approx 0.5$ is the proper order found. However, the $\ln k\gamma_\pm$ curve for any single metal displays the expected form. It is only in comparison to the other metals that any discrepancies are found.

Becker, Lindquist, and Alder (*1*) calculated values for the equilibrium constants for

$$M = M^+ + e^- \qquad K_1 = \frac{[M^+][e^-]}{M} \tag{1}$$

$$2M = M_2 \qquad K_2 = \frac{[M_2]}{[M]^2} \tag{2}$$

Becker, and others using magnetic data, and Kraus (*10*) using conductance work obtained values of about 0.05 for K_1 for potassium. K_2 was found to be about 10^3 by Becker and others but changed rapidly with temperature. For sodium solutions Dye, Sankuer, and Smith with transference data (*2*) and Evers and Frank using conductance data (*4*) obtained values of about 9×10^{-3} and 20 for K_1 and K_2. The curves in Figure 2 would indicate that, according to the equilibria in Equations 1 and 2, the ionic forms are much more important for lithium than for the other metals in fairly dilute solutions. This seems reasonable in view of the extreme solvation which should obtain in the case of the very small lithium ion. Even if the same values of K_1 and

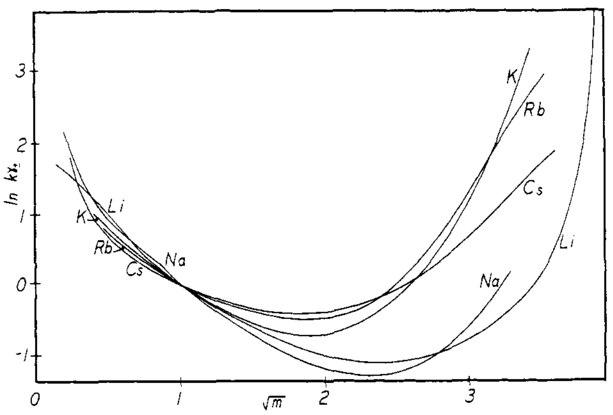

Figure 1. The ln of the relative mean ionic activity coefficient vs. the square root of the molality

The alkali metals in liquid ammonia at −35.00° C.

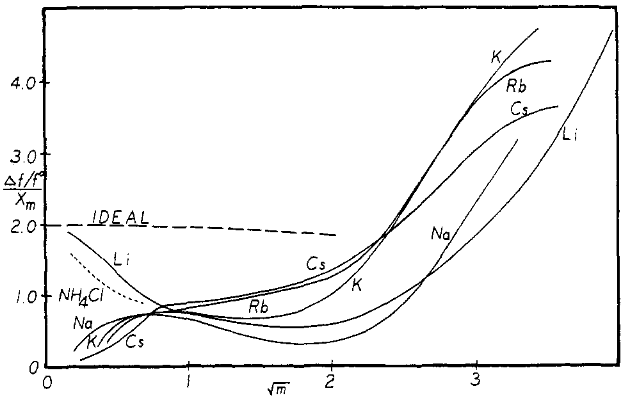

Figure 2. The relative lowering of the fugacity per mole fraction of metal vs. the square root of the molality

The alkali metals in liquid ammonia at −35.00° C.

K_2 hold for lithium as for sodium, approximate calculations from the data in Table IV indicate that lithium solutions at $m = 0.04$ would have about twice as much metal in the ionic form as would a corresponding sodium solution. Presumably, if the therory is correct, the true values of K_1 and K_2 would make this difference even more pronounced.

In view of Table V and Figure 2, the values of $k\gamma_\pm$ for the various metals are surprising. But Figure 1 does not show that the activity coefficient of sodium is greater than that of lithium in dilute solution, but only that it is increasing more rapidly between $1m$ and $0.04m$. In addition, the two figures together emphasize that "effective concentration" is not a good definition for activity.

The activities obtained in this work may be compared to those recently obtained for sodium solutions by another method. Using experimentally determined transference numbers (2) and the e.m.f. data of Kraus (9), Dye, Smith, and Sankuer (3) determined molar activity coefficients for sodium in dilute ammonia solutions. Using an interpolation method these results were combined with the vapor pressure data of Kraus, Carney, and Johnson for concentrated sodium-ammonia solutions (11), thus obtaining molar activity coefficients over the entire range of concentrations. In Table VI the results obtained in that work are compared with those found here. The activity coefficients cannnot be compared directly since one set is for molar concentrations and the other for molal solutions. Rather, it was necessary to determine the molal concentrations corresponding to the molarities listed in the table given by Dye and then to calculate the activities for each solution. The densities obtained by Kraus, Carney, and Johnson for sodium solutions (11) were used here. The activity coefficients obtained in the present research contain an undetermined constant and for the purposes of the comparison k^2 was assumed to be 282. This was done to make the activity values obtained by the two methods identical for the saturated solution. In the last column of Table VI the ratio of the activities obtained by the two procedures is shown for each concentration.

Table IV. Relative Activity Coefficients in Metal-Ammonia Solutions

	$k\gamma_\pm$				
Molality	Na		K	Rb	Cs
0.02	5.54	...	...	...	...
0.03	5.15	...	...	...	...
0.04	4.97	8.52	...	...	...
0.06	4.68	6.36	...	...	6.06
0.08	4.38	5.23	...	...	4.70
0.10	4.11	4.58	...	...	3.88
0.15	3.48	3.48	2.87	...	2.78
0.20	3.02	2.92	2.50	2.31	2.24
0.30	2.42	2.30	2.02	1.92	1.72
0.40	1.99	1.93	1.71	1.65	1.47
0.60	1.46		1.36	1.31	1.26
0.80	1.17	1.18	1.15	1.12	1.12
1.00	1.00	1.00	1.00	1.00	1.00
1.50	0.745	0.715	0.745	0.827	0.822
2.00	0.564	0.527	0.608	0.732	0.726
3.00	0.434	0.372	0.482	0.643	0.652
4.00	0.357	0.296	0.474	0.613	0.658
6.00	0.327	0.270	0.723	0.870	0.848
8.00	0.393	0.387	1.72	2.06	1.37
10.00	0.553	0.786	5.92	5.77	2.56
10.84	...	1.14	...	...	...
11.84	...	...	25.2	...	...
12.00	0.987	...	...	14.7	4.69
12.50	...	...	...	18.1	...
13.00	...	...	...	...	6.14
14.00	3.64	...	...	...	...
15.70	8.750	...	...	...	...

Table V. Relative Fugacity Lowering Per Mole Fraction of Metal

	$(\Delta f/f°/X_m)$				
Molality	Li	Na	K	Rb	Cs
.02	1.924	...	...	...	...
.03	1.892	...	...	...	...
.04	1.860	0.196	...	...	...
.06	1.774	0.328	...	...	0.112
.08	1.728	0.416	...	...	0.140
.10	1.666	0.476	...	...	0.168
.15	1.518	0.548	0.328	...	0.234
.20	1.396	0.608	0.510	0.350	0.300
.40	1.078	0.692	0.696	0.596	0.434
.60	0.880	0.682	0.762	0.744	0.808
.80	0.794	0.662	0.784	0.792	0.882
1.00	0.758	0.632	0.778	0.834	0.910
1.50	0.692	0.542	0.704	0.914	0.968
2.00	0.638	0.442	0.684	0.984	1.012
3.00	0.566	0.336	0.772	1.128	1.188
4.00	0.594	0.368	1.058	1.272	1.414
6.00	0.968	0.822	2.06	2.10	2.02
8.00	1.554	1.754	3.22	3.24	2.70
10.00	2.18	2.80	4.18	4.00	3.30
10.84	...	3.18	...	...	...
11.84	...	...	4.72	...	...
12.00	2.90	...	...	4.28	3.60
12.50	...	...	...	4.28	...
13.00	...	...	...	...	3.66
14.00	3.82	...	...	...	...
15.70	4.72	...	...	...	...

Table VI. Comparison of Calculated Activities

Data from Dye[a]			Data from This Work[b]			
M	$\gamma_{\pm}$[c]	$a \times 10^3$	m	$k\gamma_{\pm}$[c]	$a' \times 10^3$	a/a'
4.97	0.148	542	10.84	1.14	542	1.000
4.65	0.0860	160	9.71	0.695	161	0.993
4.16	0.0516	46.0	8.42	0.431	46.6	0.987
3.43	0.0328	12.6	6.58	0.283	12.3	1.023
2.93	0.0296	7.52	5.38	0.264	7.16	1.049
2.27	0.0304	4.76	3.91	0.299	4.86	0.980
1.77	0.0322	3.25	2.92	0.381	4.39	0.740
1.07	0.0354	1.44	1.69	0.623	3.93	0.367
0.762	0.0379	0.834	1.18	0.872	3.76	0.222
0.641	0.0396	0.645	0.981	1.03	3.62	0.178
0.399	0.0468	0.349	0.600	1.52	2.95	0.121
0.200	0.0647	0.168	0.303	2.32	1.76	0.0955
0.100	0.095	0.0903	0.148	3.48	0.943	0.0957
0.0631	0.125	0.0623	0.0928	4.74	0.684	0.0912
0.0398	0.166	0.0437	0.0585	6.57	0.511	0.0856
0.0251	0.216	0.0294	0.0369	8.80	0.375	0.0784

[a] Data from Tables II and III, (*12*, p. 1806). [b] The Values of molality m, for a given molarity M, were calculated using the density values of Kraus, Carney, and Johnson (*13*), which were measured at −33.8° C. The temperature of this work was −35.0° C. and that for Dye's was −37.0° C. The values of a' were obtained using the equation $a' = (\gamma_{\pm} m)^2$ with $k^2 = 282$. [c] Values in column 2 are mean molar ionic activity coefficients while those in column 5 are relative mean molal ionic activity coefficients.

It is immediately evident that the activity values do not agree over the entire range of concentrations. However, the activity ratios are very nearly constant from a molarity of just over 2 to saturation and are also fairly constant for the dilute solutions. The differences in the concentrated region are minor and may be partially due to the small differences in temperature at which the various measurements were made (−33.8° for the density determinations, −35.0° for this work, −37° for the work of Dye). In any case the maximum deviation for the activity coefficients is less than 2%. The differences in the dilute region are larger, the maximum being observed for the most dilute solution. For this solution, a 9% variation in one or the other of the activity coefficients will give agreement with the activity ratios found at 0.100 and 0.200M. Again, part of the deviation may be due to the different conditions of measurement. Yet, even if it is primarily due to experimental error such discrepancy is not surprising considering the difficulty in obtaining accurate activity coefficient measurements in dilute solutions.

The agreement in these regions must be considered good. This, then, lends support to both sets of determinations. The gross differences lie in the region for which experimental data was not available to Dye and others. However, there is no reason to believe that the relative activity coefficient values determined for sodium solutions of intermediate concentrations by vapor pressure lowering are not as good as those in the dilute or concentrated regions. Hence, the discrepancy between this work and that of Dye, Smith, and Sankuer undoubtedly lies in the interpolation as applied by the latter workers in this intermediate region. The method is certainly correct but it is fraught with many pitfalls. It is strongly dependent on the curvature at the boundaries of the experimentally determined concentrations and even more strongly dependent on the assumptions made as to the nature of the curve for the experimentally unknown range of concentrations. The authors gave too little weight to the two phase separation which occurs at a temperature [−41.6° according to Kraus and Lucasse (*12*)] only 4.6° below that at which their transference measurements were made. As shown in column 6 of Table VI, the activities actually measured in the present work change very little in the vicinity of 1M.

The form of the fugacity lowering curves, as shown in Figure 2, is more damaging to the current theories. Only the lithium curve gives any indication of behavior in the prescribed manner as the concentration decreases toward 0. Even employing the equilibria of Equations 1 and 2, the curves for sodium, potassium, rubidium, and cesium seem impossible to explain. The decrease in the value of the ordinate as the solutions become more dilute below unit molality is incredible on the basis of the theories which have been proposed. Since the number of solute particles should be increasing, it is to be expected that the curves for all of these metals should rise as 0 concentration is approached.

The behavior is little better in the concentrated region. Since the anions are considered to be identical in the various solutions they cannot cause the observed differences. Yet the relative values of lithium, sodium, and potassium at $m^{1/2} = 3$ are in contradiction to the accepted theory that the amount of solvation is greater the smaller the cation. In addition, the proposed equilibria indicate that an extremely small part of the metal will be ionic. The probability that equilibria of the type shown in Equations 1 and 2 can account for the variations appears to be small indeed. Such behavior would seem to indicate that these solutions cannot be regarded as simple ionic solutions in either the moderately dilute or the concentrated regions (the range investigated in this work). The disagreement with the current theories seems to be not only quantitative but qualitative as well.

The solvated electron theory or its modified forms have yielded discrepancies before and even outright contradictions. It may well be that the basic assumptions should be reevaluated for they are at best oversimplified and at worst incorrect.

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