Osmotic and Activity Coefficients of Aqueous Ammonium Bromide Solutions at 25°C

ARTHUR K. COVINGTON and DONALD E. IRISH[1]

School of Chemistry, The University, Newcastle upon Tyne, England

Osmotic coefficients of aqueous solutions of ammonium bromide at 25°C have been measured by the isopiestic method. Activity coefficients were calculated and are compared with available data.

Interest in the activity coefficients of ammonium bromide solutions resulted from spectral studies of the effects of 1:1 salts on the ionization of the acid bisulfate (*1*). Data have been presented by Shul'ts and Simanova (*6*) and by Kirgintsev and Luk'yanov (*3*), although the latter did not compute activity coefficients. Accurate data have been obtained for NH_4Cl by Wishaw and Stokes (*7*); these provide a standard against which the quality of other work can be tested. The difference in osmotic coefficients, $\Delta = \phi_{NH_4Br} - \phi_{NH_4Cl}$, is expected to be a smooth function of molality, m. The differences computed from the data of Shul'ts and Simanova exhibit considerable scatter (Figure 1). New measurements have been made over a somewhat greater concentration range; activity coefficients have been computed and are compared with those previously reported.

METHOD

Ammonium bromide, potassium chloride, and sodium chloride were B.D.H. Analar reagent. They were dried at 115°C and stored over calcium sulfate. Salts were either weighed directly into the dishes and distilled water was added or, especially for the dilute solutions, made into stock solutions and diluted. Solutions were contained in spun, seamless silver dishes of circular shape. Eight dishes, in contact with a thick brass or aluminum plate, were contained in a heavy glass desiccator vessel. After evacuation to about 15-mm pressure (water pump) four desiccators were gently rocked in a constant temperature bath (25°C) for periods up to 10 days. Each desiccator contained four dishes of the standard or two dishes of NaCl solution and two dishes of KCl solution (a double standard). The molalities in Table I are averages of four values for the bromide and either two or four values for the standard. The osmotic coefficient is an average value, based on both standards when applicable. In general, the average deviation from the mean was less than 0.1%. Data provided by Robinson and Stokes (*5*) were used for the standards.

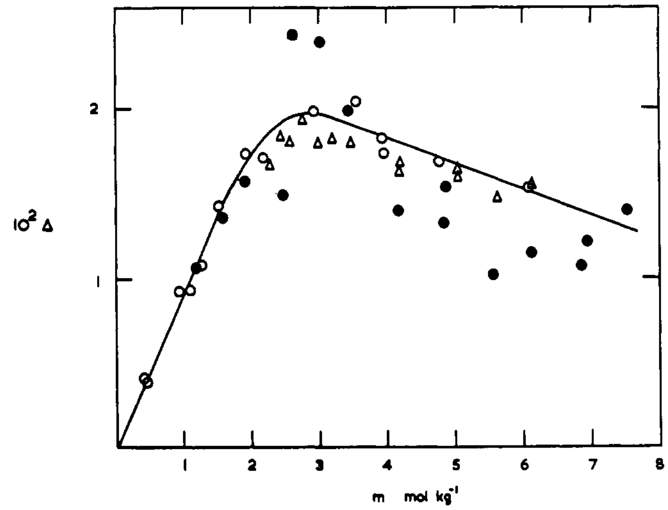

Figure 1. Variation of difference in osmotic coefficients ($\Delta = \phi_{NH_4Br} - \phi_{NH_4Cl}$) with molality ($m$)

○ This work. ● Ref. 6. △ Ref. 3

Table I. Experimental Data and Osmotic Coefficients

m_{NH_4Br}	m_{KCl}	m_{NaCl}	ϕ_{NH_4Br}
0.4145	0.4161	...	0.9047
0.4736	0.4756	...	0.9031
0.9223	0.9307	...	0.9054
1.0913	1.1030	...	0.9074
1.2595	...	1.2140	0.9092
1.5090	1.5288	1.4495	0.9155
1.9190	1.9506	1.8213	0.9248
2.1874	2.2140	2.0616	0.9292
2.9257	2.9513	2.6993	0.9450
3.5398	3.5583	3.1975	0.9569
3.9283	3.9220	3.5022	0.9616
3.9520	3.9431	3.5170	0.9613
4.7955	4.7289	4.1440	0.9730
6.0962	...	5.0300	0.9851
7.7647	...	6.0575	0.9947

RESULTS AND DISCUSSION

The primary data and the osmotic coefficients are given in Table I. Activity coefficients were computed by two different methods. The first is a direct comparison with the ammonium chloride data of Wishaw and Stokes (*7*). The ratio of activity coefficients is given by an equation derived from the equation for $\ln \gamma_B$ in ref. *5*.

$$\ln \frac{\gamma_B}{\gamma_C} = (\phi_B - \phi_C) + \int_0^m \frac{(\phi_B - \phi_C)}{m} dm \qquad (1)$$

The subscripts B and C indicate ammonium bromide and chloride, respectively. For certain pairs of salts of the 1:1 charge type $\Delta = \phi_B - \phi_C$ is directly proportional to m up to moderate concentrations, i.e., $\phi_B - \phi_C = km$ (*2*). The proportionality constant, k, is characteristic of the salt pair in question. The integral is also km and $\ln(\gamma_B/\gamma_C) = 2\ km$. For NH_4Br-NH_4Cl, the linearity holds up to 1.5 m, and $k = 0.0090$ kg mol^{-1} from the slope in Figure 1. At higher concentrations, the integral

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[1] Permanent address, Department of Chemistry, University of Waterloo, Ont., Canada. To whom correspondence should be addressed.

Table II. Activity Coefficients, Osmotic Coefficients, and Water Activity for Aqueous NH_4Br Solutions

m_{NH_4Br}	$\gamma_B{}^a$	$\gamma_B{}^b$	$\gamma_B{}^c$	ϕ^d	a_W
0.1	0.771	0.771		0.928	0.997
0.2	0.721	0.721		0.915	0.993
0.3	0.691	0.692		0.908	0.990
0.4	0.670	0.671		0.905	0.987
0.5	0.655	0.655		0.903	0.984
0.6	0.643	0.644		0.903	0.981
0.7	0.633	0.634		0.903	0.977
0.8	0.626	0.627		0.904	0.974
0.9	0.619	0.620		0.905	0.971
1.0	0.614	0.615		0.906	0.968
1.5	0.597	0.597	0.600	0.915	0.952
2.0	0.590	0.590	0.594	0.925	0.936
2.5	0.587	0.587	0.592	0.936	0.919
3.0	0.586	0.586	0.592	0.947	0.903
3.5	0.586	0.588	0.591	0.956	0.887
4.0	0.587	0.589	0.592	0.963	0.870
4.5	0.589	0.588	0.593	0.969	0.855
5.0	0.591		0.595	0.975	0.839
5.5	0.592		0.597	0.980	0.824
6.0	0.594		0.598	0.985	0.808
6.5	0.595		0.598	0.988	0.793
7.0	0.596		0.600	0.991	0.779
7.5	0.596		0.601	0.994	0.765

[a] γ_B evaluated by Method 1, relative to NH_4Cl. Integral taken as 0.0090 m for all concentrations up to 1.5 m. [b] γ_B evaluated by Method 2, relative to KCl. [c] Results of Shul'ts and Simanova (*6*), relative to NaCl. [d] Smooth values from experiment for concentrations greater than 0.3 m. Below this concentration, values are obtained from the plot of $\phi_{NH_4Br} - \phi_{NH_4Cl}$ against m.

was solved graphically. Values of γ_B obtained from the above equation are presented in Table II. In general, they are 0.85% lower than those given by Shul'ts and Simanova (*6*) which is within the uncertainty inherent in integration of an equation of the form of Equation 1. We are unaware that this equation has been widely used, but its applicability to other salt pairs is noteworthy.

The second method consisted of evaluating Equation 2 (*5*)

$$\ln \gamma_B = \ln \gamma_K + \ln R + 2 \int_0^{a_K{}^{1/2}} (R - 1)(a_K)^{-1/2} da_K{}^{1/2} \tag{2}$$

where the subscript K refers to the standard KCl. R is the isopiestic ratio; $m_K = Rm_B$. The evaluation was performed by comparison with data for KCl (*5*) because the lowest concentrations were studied with this standard. These γ_B values thus do not incorporate the average obtained from consideration of both standard salts and do not extend to the highest concentrations reached. Smooth values of $(R - 1)$ were read from a graph, and the integral was evaluated by graphical integration. The results are compared with those of Method 1 and those of Shul'ts and Simanova in Table II. Smoothed values of the osmotic coefficients and the activity of water obtained from $-55.51 \ln a_W = -2 m\phi$ are included; the latter values are consistent with those tabulated by Kirgintsev and Luk'yanov (*3*). The agreement between activity coefficients computed by the two methods (one or better in the last figure) suggests that most of the difference between our data and those of Shul'ts and Simanova is real and larger than the experimental error estimated at 0.2%.

As for the respective salts of Li, Na, and K, the activity coefficients of NH_4Br are seen to be higher than those of the chloride. Comparison of γ_B with values for tetraalkylammonium bromides (*4*) reveals that below 1.5 m the activity coefficients decrease in the order $NH_4^+ > (CH_3)_4N^+ > (C_2H_5)_4N^+ > (C_3H_7)_4N^+ > (C_4H_9)_4N^+$, but above 1.5 m the curves for the latter four salts intersect and show no rational pattern.

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Heats of Formation of Solid Indium–Lead Alloys

HONG-IL YOON and RALPH HULTGREN[1]
Department of Materials Science and Engineering and Inorganic Materials Research Division,
Lawrence Berkeley Laboratory, University of California, Berkeley, Calif. 94720

Indium and lead form wide-ranging solid solutions in one another, with a single intermediate phase, β, as shown in Figure 1 (*1*). The crystal structures of all three solid phases are based on the face-centered cubic structure of Pb, but for In the c-axis is elongated about 7.6%, and for β, c is shortened by about 7%, making the two latter phases face-centered tetragonal (*6*).

The thermodynamic properties of the liquid phase are reasonably well established, but solid heats of formation have been determined only by a quantitative differential thermal analysis method (*2*) which does not have high precision. It was therefore decided to measure heats of formation by liquid tin solution calorimetry.

EXPERIMENTAL

The tin, lead, and indium used were all reported to be 99.999% pure. Nine 12-gram samples of indium–lead alloys were

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[1] To whom correspondence should be addressed.