Activity Coefficients of Sodium Bromide at High Concentrations

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The activity coefficients of sodium bromide in aqueous solutions at high concentrations were measured at 25.0° by the isopiestic method. Reference salt was calcium chloride. The experimental osmotic coefficients were fitted with a power series, and integrated to obtain the activity coefficients. In the region of overlapping concentrations, the osmotic and activity coefficients agree with published data.

ACTIVITY COEFFICIENTS of sodium bromide have been determined in dilute solutions, potentiometrically (*1*) and by the isopiestic technique at moderate concentrations (*4, 5*). Since potassium chloride was used as the reference in the latter, its limited solubility permitted measurement of the activity coefficients only up to 4*m*. The activity coefficients of sodium bromide up to its saturation point (about 9*m*) have now been obtained using calcium chloride as reference (*9*).

EXPERIMENTAL

Recrystallization of calcium chloride does not significantly reduce its alkali content (*9*). Accordingly, purification was carried out by adding a solution of ammonium carbonate to a solution of calcium chloride and washing the resulting precipitate well. The calcium carbonate formed was dissolved in hydrochloric acid, and the solution obtained was concentrated by evaporation and filtered. This stock solution was analyzed gravimetrically for chloride.

Baker analyzed sodium bromide was recrystallized from conductivity water and dried at 180°.

Equilibrations were carried out (*9*) by weighing duplicate samples of calcium chloride reference solution and solid sodium bromide in cylindrical gold cups, 25 mm. high and 30 mm. in diameter. These were placed on a silverplated copper disk, 1 cm. thick, which was then put into a vacuum desiccator. The system was evacuated repeatedly through a vessel of approximately the same volume and rocked in a bath at 25.0 ± 0.02° until equilibrium was attained.

To evaluate the precision of the technique, four samples of sodium bromide solutions were equilibrated together. The initial concentrations were 1.7616*m* in two cups and 2.3005*m* in the other two. After equilibration for only one day, the molalities were 1.7569, 1.7608, 1.8378, and 1.8435. After two days, they were 2.1686, 2.1706, 2.1711, and 2.1713, showing an average deviation of 0.009 from the mean, or 0.04%. After four days, the molalites were 2.0547, 2.0557, 2.0561, and 2.0568, showing an average deviation of 0.0006 from the mean, or 0.03%. Similar precision among the duplicate samples was obtained also for equilibrations against calcium chloride solutions. Equilibrium was reached within one day for the more concentrated solutions.

RESULTS

Osmotic coefficients of sodium bromide were calculated from the equation

$$\nu m\phi = \nu_{\mathrm{R}} m_{\mathrm{R}} \phi_{\mathrm{R}} \tag{1}$$

The osmotic coefficients of calcium chloride, ϕ_{R}, were obtained by interpolation in the tables of Robinson and Stokes (*7*, p. 463, *9*).

The experimental results are shown in Table I. The precision of the data is ± 0.1% or better.

The osmotic coefficients were fitted (*2*) to the equation:

$$\phi - 1 = -0.0490m + 0.0360m^2 - 0.0030m^3 + 6.3 \times 10^{-7}m^6 \tag{2}$$

which is valid above $m = 2$, as seen in Figure 1. The standard deviation of the calculated from the experimental results (Table I) is ±0.7%. The activity coefficients for sodium bromide were calculated by means of the equation (*7*, p. 178)

$$\ln \gamma = (\phi - 1) + \int_0^m \frac{(\phi - 1)}{m}\, dm \tag{3}$$

The part of the integral between zero and 2*m* was obtained from the data of Robinson and Stokes (*7*, p. 468), while the rest was obtained from numerical integration of Equation 2. The resulting expression for the activity coefficient is

$$\log \gamma = -0.134 - 0.0425m + 0.0234m^2 - 0.00174m^3 + 3.2 \times 10^{-7}m^6 \tag{4}$$

The curve expressing γ, calculated from Equation 4, is compared with the values published (*7*, p. 477) for $m \leq 4$ in Figure 1. The agreement is good. Values of the osmotic

Table I. Measured and Calculated Osmotic Coefficients of NaBr, 25° C.

m_{NaBr}	$m_{\mathrm{CaCl_2}}$	ϕ_{NaBr} Obs.	ϕ_{NaBr} Calcd.	m_{NaBr}	$m_{\mathrm{CaCl_2}}$	ϕ_{NaBr} Obs.	ϕ_{NaBr} Calcd.
2.800	1.626	1.086	1.077	5.952	3.043	1.377	1.379
2.907	1.674	1.090	1.086	6.117	3.108	1.389	1.390
2.924	1.683	1.092	1.087	6.227	3.159	1.403	1.397
3.684	2.056	1.170	1.157	6.238	3.146	1.390	1.404
4.286	2.319	1.216	1.215	6.982	3.446	1.450	1.461
4.591	2.463	1.250	1.249	7.662	3.719	1.506	1.513
5.152	2.688	1.289	1.305	8.907	4.194	1.596	1.610
5.355	2.779	1.312	1.318	8.910	4.220	1.613	1.611
5.634[a]	2.912	1.351	1.347			....	

[a] This equilibrium was carried out at 26° to check the temperature variability of the results. As seen from the graph, the variation is negligible.

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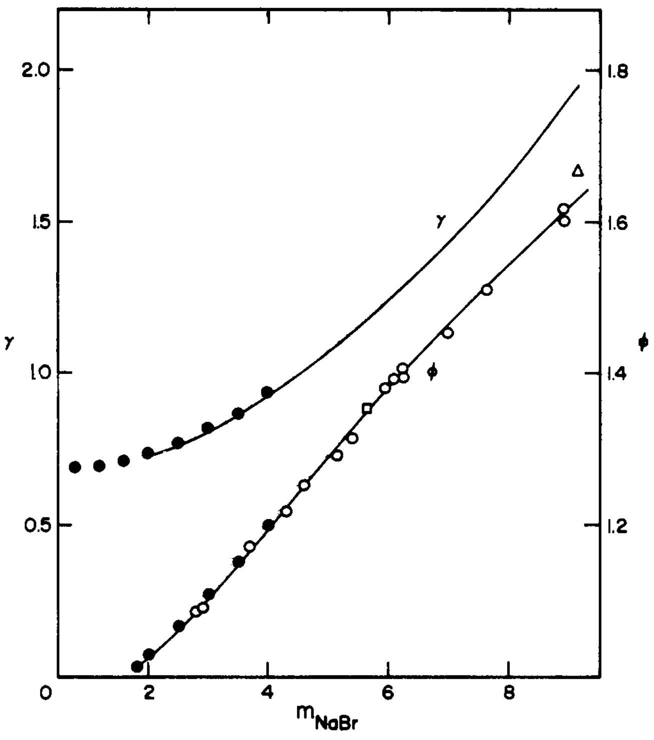

Figure 1. Activity coefficients (left hand scale) and osmotic coefficients (right hand scale) of sodium bromide solutions

○ This work
□ This work, 26° C.
△ Saturated solution data (2, 8)
● Data of Robinson and Stokes (7)

and activity coefficients for round values of m, calculated from Equations 2 and 4, are shown in Table II.

DISCUSSION

The solubility of sodium bromide in water at 25° is reported (*8*) to be 48.61 grams of NaBr in 100 grams of saturated solution (the solid phase is $NaBr \cdot 2H_2O$), which corresponds to a molality of 9.190. This value may be combined with the reported (*6*) values of the activity of water in the saturated solution, $a_W = 0.577$, to give the value for the osmotic coefficient $\phi = -\ln a_W/0.01802\ \nu m = 1.660$. The value calculated from Equation 2 is 1.639 for this molality, about 1.5% too low, which is acceptable since reported solubility is an average of values ranging about 0.8% on either side (*8*).

Table II. Osmotic and Activity Coefficients for NaBr, 25°

	ϕ		γ	
m	Ref. 7, p. 468	This work	Ref. 7, p. 477	This work
0.5	0.933	...	0.697	...
1.0	0.958	...	0.687	...
1.5	0.990	...	0.702	...
2.0	1.028	1.023	0.731	0.729
2.5	1.067	1.057	0.768	0.761
3.0	1.107	1.097	0.812	0.804
3.5	1.150	1.144	0.865	0.857
4.0	1.199	1.192	0.929	0.919
4.5	...	1.240	...	0.992
5.0	...	1.287	...	1.062
5.5	...	1.337	...	1.174
6.0	...	1.382	...	1.240
6.5	...	1.426	...	1.338
7.0	...	1.465	...	1.442
7.5	...	1.503	...	1.552
8.0	...	1.538	...	1.658
8.5	...	1.579	...	1.760
9.0	...	1.615	...	1.910

The activity coefficients of sodium bromide at high concentrations fall neatly between those of the chloride and the iodide (*3*), and are somewhat higher than those of the thiocyanate (*3*). The general conclusion is, according to Miller and Sheridan (*3*), that the behavior of sodium bromide in concentrated solutions is an extension of its behavior at low concentrations, and shows nothing unexpected.

NOMENCLATURE

a_W = activity of water, mole fraction scale
m = molality, moles per 1000 grams of water
γ = mean ionic stoichiometric activity coefficient, molal scale
ϕ = osmotic coefficient, molal scale
ν = number of ions into which an electrolyte dissociates

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Vapor-Liquid Equilibrium Data

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EXPERIMENTAL vapor-liquid equilibrium data are important for chemical engineers in considering separation factors of mixtures from an industrial and theoretical standpoint.

This paper presents equilibrium data for binary and ternary mixtures including 2-propanol, and the relation between the ternary and the binary data is analyzed thermodynamically using the Redlich-Kister equations.

EXPERIMENTAL

Binary vapor-liquid equilibrium data at 500 mm. of Hg were determined for the 2-propanol–hydrocarbon mixtures,

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