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Osmotic and Activity Coefficients of Sodium Hydroxide in Water from 150 to 250 °C

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The vapor pressures of aqueous sodium hydroxide solution were measured from 150 to 250 °C in the concentration range of 0.32–3.7 *m*. The lowering of vapor pressure, ΔP, was used to calculate the osmotic and activity coefficients of NaOH by using Pitzer's equations.

Introduction

The thermodynamic properties of aqueous solutions of electrolytes have been studied extensively at room temperature (25 °C) but very little has been done at higher temperatures. Only recently has some attention been paid to the study of these solutions at temperatures above 100 °C (*1–9*). The reason is obvious: at temperatures above 100 °C, the pressure of aqueous vapor becomes greater than 1 atm and specially designed apparatus becomes necessary. Among other chemicals studied by us (*8–10*) sodium hydroxide was selected because of its industrial importance. The vapor pressure of electrolyte solutions is a single (most important) physical property, which can be used to get many other thermodynamic properties such as osmotic and activity coefficients. We have developed a special apparatus for measuring vapor pressures at elevated temperatures; details are to be found in the literature (*10*). Some work on thermodynamic properties of sodium hydroxide below 100 °C has been reported by Akerlof and Kegeles (*11*) and Haywood and Perman (*12*). Mashovets and co-workers (*13*) have reported the vapor pressures of aqueous sodium hydroxide solutions up to 350 °C in the concentration range 30–90% by weight. No data, however, are available for the range of moderate concentrations at elevated temperatures. In this paper we report the osmotic and activity coefficients of sodium hydroxide solutions in the concentration range 0.3–4 *m* at temperatures from 150 to 250 °C.

Experimental Section

The experimental procedure and design of the cell for measuring vapor pressures are given elsewhere (*10*). Special care was taken to ensure that solutions were free from any dissolved CO_2. The triple-distilled water was first boiled and then degassed 6 times by a freezing and thawing cycle under vacuum and this water was then distilled into a flask with a weighed amount of sodium hydroxide. The stock solution was kept in a dry box under inert atmosphere. The concentrations of all solutions were determined at the end of each experiment by titration.

Results and Discussion

The vapor pressure lowering, ΔP, for each concentration was determined by measuring the vapor pressure of the solution and the solvent, the same cell being used throughout. The osmotic coefficient, ϕ, is then calculated from the ΔP values by using the following equation:

$$\phi = \frac{1000}{\nu m M R T}\left[RT \ln (P^\circ/P) - \int_P^{P^\circ} \zeta \, dP - \bar{v}_1{}^\circ(\mathrm{l})\Delta P\right] \qquad (1)$$

where ν is the total number of ions resulting from the ionization of one molecule, m is the molality of the solution, M is the molecular weight of the solvent, R is the gas constant, T is the temperature on the absolute scale, and P° and P are the vapor pressures of pure solvent and of solution, respectively. The first term in the brackets gives the osmotic coefficient at low pressures, the second term is the correction for the deviation of the vapor pressure from the perfect gas law, and the last term is a close approximation for the small free energy change on compressing the solutions to the vapor pressure of pure water. Since this term is small, we have used the molar volume of pure water, $\bar{v}_1(\mathrm{l})$, the partial molar volume of water. The terms ζ, $\bar{v}_1{}^\circ$ (l), and P° were calculated from the equations of Smith, Keyes, and Gerry (*14*). The values of m, ΔP, and ϕ at various temperatures are given in Table I.

Table I. Vapor Pressures and Osmotic (ϕ) and Activity ($\gamma_\pm$) Coefficients of NaOH in Water at Various Concentrations from 150 to 250 °C

temp, °C	molality, m	ΔP, mmHg	ϕ	$\gamma_\pm$
150.0	0.3262	40.28	0.9211	0.6386
150.0	0.5402	65.56	0.9087	0.6003
150.0	0.8346	96.94	0.8738	0.5664
150.0	1.0035	114.57	0.8612	0.5519
150.0	1.4501	165.57	0.8680	0.5242
150.0	1.9998	230.47	0.8849	0.5045
150.0	2.4811	287.90	0.8991	0.4967
150.0	2.9958	351.31	0.9178	0.4964
150.0	3.7211	440.23	0.9394	0.5087
175.0	0.3262	75.52	0.8977	0.6199
175.0	0.5402	124.04	0.8960	0.5823
175.0	0.8346	184.04	0.8628	0.5493
175.0	1.0035	217.64	0.8509	0.5351
175.0	1.4510	312.64	0.8511	0.5072
175.0	1.9998	432.12	0.8645	0.4850
175.0	2.4811	539.12	0.8761	0.4730
175.0	2.9958	645.98	0.8776	0.4658
175.0	3.7211	800.00	0.8843	0.4636
200.0	0.3262	134.21	0.8843	0.5850
200.0	0.5402	218.57	0.8732	0.5426
200.0	0.8346	322.09	0.8372	0.5053
200.0	1.0035	383.49	0.8316	0.4893
200.0	1.4501	549.54	0.8310	0.4579
200.0	1.9998	751.49	0.8330	0.4332
200.0	2.4811	935.25	0.8436	0.4198
200.0	2.9958	1132.64	0.8548	0.4119
200.0	3.7211	1404.93	0.8661	0.4099
225.0	0.3262	231.37	0.8873	0.5428
225.0	0.5402	371.21	0.8635	0.4954
225.0	0.8346	547.53	0.8291	0.4539
225.0	1.0035	649.37	0.8205	0.4363
225.0	1.4510	919.93	0.8109	0.4022
225.0	1.9998	1269.53	0.8214	0.3761
225.0	2.4811	1575.81	0.8302	0.3626
225.0	2.9958	1907.93	0.8418	0.3553
225.0	3.7211	2377.61	0.8583	0.3553
250.0	0.3262	368.01	0.8504	0.5018
250.0	0.5402	587.96	0.8245	0.4534
250.0	0.8346	864.95	0.7900	0.4127
250.0	1.0035	1028.76	0.7843	0.3960
250.0	1.4510	1438.80	0.7657	0.3647
250.0	1.9998	2042.20	0.7995	0.3420
250.0	2.4811	2548.77	0.8137	0.3311
250.0	2.9958	3103.54	0.8313	0.3263
250.0	3.7211	3893.94	0.8557	0.3292

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Table II. Parameters for NaOH(aq) in Eq 2 and 4

temp, °C	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ
150.0	0.0388	0.6522	0.0039
175.0	0.0100	0.8230	0.0092
200.0	0.0029	0.9209	0.0113
225.0	0.0044	0.9459	0.0126
250.0	0.0105	0.8982	0.0144

Recently Pitzer and co-workers (*15–18*) have developed a set of equations for calculating the thermodynamic quantities. Pitzer's equation for calculating the osmotic coefficients for 1:1 electrolytes can be written as follows:

$$\phi = 1 + f^\phi + mB^\phi + m^2C^\phi \tag{2}$$

where

$$f^\phi = -A^\phi m^{1/2}/(1 + bm^{1/2})$$

$$B^\phi = \beta^{(0)} + \beta^{(1)}e^{-\alpha m^{1/2}}$$

A^ϕ is the Debye–Hückel coefficient for the osmotic coefficient and is given by

$$A^\phi = (1/3)\left(\frac{2\pi N_0\rho}{1000}\right)\left(\frac{e^2}{DkT}\right)^{3/2} \tag{3}$$

where N_0 is Avagadro's number, ρ is the density of the solvent (water in the present case) and D is the static dielectric constant of the solvent at temperature T, k is Boltzmann's constant, and e is the electronic charge.

$\beta^{(0)}$ and $\beta^{(1)}$ account for various short-range interactions between anions and cations and for cosphere overlap effects and C^ϕ accounts for triple-ion interactions and is important only at high concentrations. The parameters α and b are taken as 2 and 1.2, respectively, and are treated as temperature independent. A general least-squares program was used to obtain the values of $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ. These values are given in Table II.

Pitzer's (*15*) equation for calculating the mean ionic activity coefficient, $\gamma_\pm$, for 1:1 electrolyte can be written as follows:

$$\ln \gamma_\pm = f^{\gamma\pm} + mB^{\gamma\pm} + m^2e^{\gamma\pm} \tag{4}$$

where

$$f^{\gamma\pm} = -A^\phi\left\{\left(\frac{m^{1/2}}{1 + bm^{1/2}}\right) + (2/b)\ln(1 + bm^{1/2})\right\}$$

$$\beta^{\gamma\pm} = 2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2 m}\left\{\left(1 + \alpha m^{1/2} - \frac{\alpha^2 m}{2}\right)\right\}e^{-\alpha m^{1/2}}$$

$$C^{\gamma\pm} = {}^3\!/_2C^\phi$$

Using the values of $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ, we calculated the mean ionic activity coefficient, $\gamma_\pm$, for NaOH at various concentrations and temperatures. These results are given in Table I. The smoothed valued of m, ϕ, and $\gamma_\pm$ are given in Table III.

The osmotic coefficient of NaOH at first decreases with increase in concentration and reaches a minimum between 1 and 2 m. The minimum shifts toward higher concentration with rising temperature. Figure 1 shows the change in activity coefficient, $\gamma_\pm$, of NaOH and NaCl with concentration at various temperatures. This comparison is appropriate because cations of the two salts are common. While at 25 °C there is considerable difference in $\gamma_\pm$ values of NaOH and NaCl at each concentration, this difference decreases considerably at 250 °C. While at 25 and 250 °C the $\gamma_\pm$ values at NaOH are higher than those of NaCl at all concentrations, the trend reverses at 150 °C. At 200 °C $\gamma_\pm$'s of NaOH are higher than those of NaCl up to concentrations of 1.5 m; beyond that, the $\gamma_\pm$'s of NaCl are higher than those of NaOH. No simple explanation can be offered for this behavior at this time.

Table III. Smoothed Values of Activity Coefficients of NaOH Solutions at Various Concentrations from 150 to 250 °C

molality,	temp, °C				
m	150	175	200	225	250
0.25	0.644	0.633	0.611	0.569	0.520
0.50	0.598	0.579	0.550	0.508	0.458
0.75	0.570	0.548	0.518	0.468	0.421
1.00	0.550	0.526	0.493	0.440	0.396
1.50	0.523	0.494	0.459	0.404	0.361
2.00	0.510	0.474	0.436	0.379	0.349
2.50	0.502	0.461	0.424	0.364	0.327
3.00	0.501	0.454	0.418	0.357	0.323
3.50	0.504	0.451	0.417	0.358	0.325
4.00	0.507	0.449	0.407	0.359	0.329

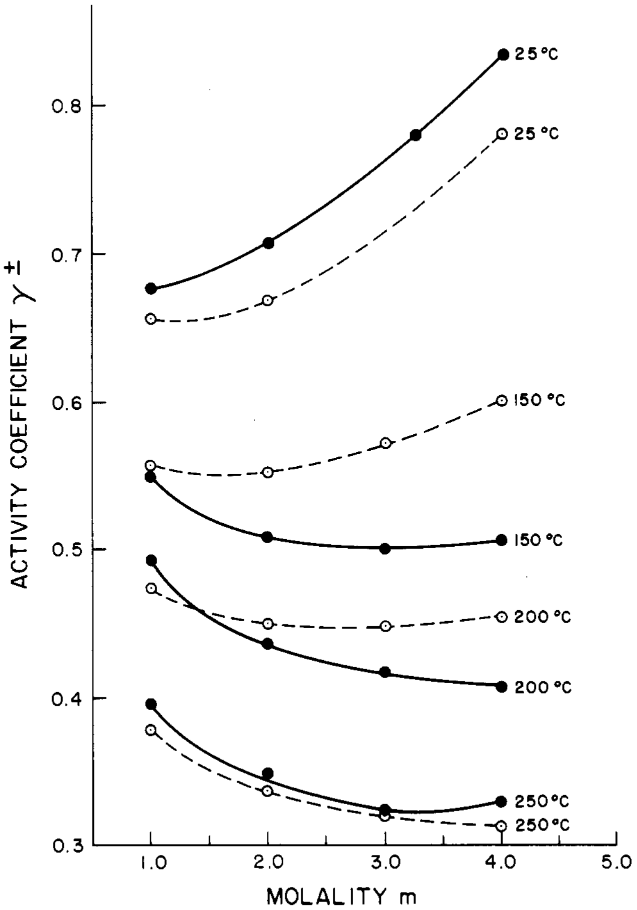

Figure 1. Activity coefficient of NaOH and NaCl in water: (●) $\gamma_\pm$ for NaOH data at 25 °C from ref *19*; other data from present work. (⊙) $\gamma_\pm$ for NaCl data at 25 °C from ref *19* and at other temperatures from ref *3* and *4*.

The values of $\beta^{(0)}$ decrease with increasing temperature, reach a minimum at 200 °C, and then commence to increase. The $\beta^{(0)}$ values for LiCl show a similar trend between 25 and 200 °C but no minimum is observed. The values of $\beta^{(0)}$ for NaCl increase with temperature and reach a maximum at about 100 °C. $\beta^{(1)}$ values of NaOH increase with temperature. A similar trend in $\beta^{(1)}$ values is observed for NaCl and LiCl. The C^ϕ values of NaOH increase with temperature while the values for NaCl and LiCl decrease.

Registry No. Sodium hydroxide, 1310-73-2.

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Conductivities of Lanthanum Chloride in Water–Dimethyl Sulfoxide Mixtures at 25 °C

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The conductivities of lanthanum chloride at various concentrations in water–dimethyl sulfoxide mixtures, varying from 10.6% to 100% dimethyl sulfoxide, have been determined. The densities, viscosities, dielectric constants, and surface tensions of the various solvents have also been determined.

Introduction

In previous papers (*1*, *2*), we have dealt with the conductivities of indium chloride in water and in water–dimethyl sulfoxide mixtures and, as a standard of comparison, the corresponding data were obtained for potassium chloride. In the present study, the work has been repeated with lanthanum chloride, $LaCl_3$, as standard of reference. Lanthanum chloride is a more suitable standard of comparison than potassium chloride, since it has the same general formula as indium chloride, is a strong electrolyte, and does not suffer from hydrolysis at low concentrations of salt as indium chloride does.

In addition to determining the conductivities of lanthanum chloride solutions, we have determined the densities, viscosities, dielectric constants, and surface tensions of water–Me_2SO mixtures and have conducted thermal analysis of the system, water–Me_2SO.

Experimental Section

Materials. Lanthanum chloride was obtained from ICN Pharmaceutical Inc. It was claimed to be 99.99% but turned out to be $LaCl_3 \cdot 7H_2O$. For measurements in anhydrous Me_2SO, it was therefore necessary for us to dehydrate it and this we did by heating at 40 °C for 4 days, with continuous evacuation. Gravimetric analysis, as silver chloride, showed 98.56% $LaCl_3$. The product, on dissolving in water, showed a slight mistiness, no doubt due to the presence of La_2O_3. This material would be inert as far as conductivity is concerned but allowance was made for its effect on concentration. For solutions in water–Me_2SO mixtures, the hydrate was used, allowance being made for the water it contained.

Table I. Dielectric Constant, Density, Viscosity, and Surface Tension of Me_2SO–Water Mixtures at 25.0 °C

$[Me_2SO]$, wt %	dielectric constant	density, g/mL	η_{rel}[a]	surface tension, dyn/cm
0	78.3	0.9970	1.000	71.97
10.59	77.6	1.010	1.246	69.8
20.00	77.0	1.024	1.543	69.4
31.14	76.8	1.041	1.985	67.5
41.59	76.0	1.057	2.597	65.4
50.00	74.9	1.069	3.164	63.4
60.30	73.2	1.085	3.828	60.0
64.02		1.088	4.050	59.2
67.57		1.091	4.158	57.5
69.11	70.3	1.092	4.185	56.8
72.00		1.094	4.144	55.3
74.21		1.095	4.078	54.4
79.88	63.6	1.098	3.799	52.0
86.70		1.099	3.243	
88.00	58.0			48.5
100	44.4	1.096	2.214	42.3

[a] Relative viscosity (H_2O = 1.000).

Characteristics of the Solvents. Ordinary distilled water was passed through an ion-exchange column, which yielded water with a specific conductivity of $k = 1.0 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$. The dimethyl sulfoxide was a Fisher Certified ACS product, kept over molecular sieves (type 44, grade 514).

Procedures. The techniques of conductivity and viscosity measurements have been described in our previous publications (for instance, ref *1*). A word should be said about the determination of the surface tension. We have used the method of Sugden (*3*). The essence of this method consists in the use of two capillaries, of different bore, side by side in the same liquid. It is then only necessary to measure the difference in height of the two columns of liquid: it is not necessary to know the position of the meniscus in the outer container; this is the major uncertainty when using only one capillary.

Dielectric constants were determined by means of a Sargent oscillometer.

For the thermal analysis of the system, water–Me_2SO, ice or liquid nitrogen was used as coolant, depending on the temperature range of investigation.

Preparation of Solutions. Water–Me_2SO mixtures from 10% to 90% Me_2SO were made up by weighing. The conductivities of very dilute solutions were determined in the Shedlovsky cell, by the addition of weighed amounts of anhydrous solute. In the

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