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THE VOLUMETRIC PROPERTIES OF VAPOR SATURATED AQUEOUS POTASSIUM HYDROXIDE SOLUTIONS
FROM 0° TO 400° AND VAPOR SATURATED AQUEOUS SODIUM HYDROXIDE SOLUTIONS FROM
0° TO 350° BASED ON A REGRESSION OF THE AVAILABLE LITERATURE DATA

by

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Pressure-volume-temperature-composition (P-V-T-X) data for brines are required to establish optimum operating conditions for the production of geothermal brine fields; to minimize scaling and corrosion; and to intelligently design turbines for production of electricity. Precise thermodynamic data derived from the volumetric properties of the brines are prerequisite for chemical and reservoir modelling of geothermal brine systems. In view of the importance of P-V-T-X data to the utilization and understanding of geothermal brine systems, a compilation of the available literature data (Potter et al., 1975) and evaluations of these data for NaCl, KCl, CaCl₂, Na₂SO₄, and K₂SO₄ have been completed (Potter and Brown, 1975, 1976a, 1976b, 1976c; Potter and Clynne, 1976).

Prior to this report, the only extensive tabulation of volumetric data for aqueous, vapor-saturated potassium and sodium hydroxide solutions was the International Critical Tables (National Research Council, 1928), in which a compilation of density values is presented for aqueous potassium hydroxide solutions for concentrations of 1 weight percent to 50 weight percent from 0°C to 100°C. There are no compilations available for potassium and sodium hydroxide solutions at pressures greater than the saturation vapor pressure (Potter, 1976). The purpose of this report is to provide an internally consistent set of density values for vapor-saturated, aqueous potassium hydroxide solutions from 0°C to 400°C and for vapor-saturated, aqueous sodium hydroxide solutions from 0°C to 350°C based on the currently available experimental data summarized by Potter et al. (1975).

The density data presented in Tables 1, 2, 4, and 5 were obtained from regression analysis of the P-V-T-X data taken from the International Critical

Tables (National Research Council, 1928) and the 43 references cited by Potter et al. (1975). The data summarized in tables 1 and 2 are for vapor-saturated potassium hydroxide solutions from 0°C to 400°C and the data in tables 4 and 5 are for vapor-saturated sodium hydroxide solutions from 0°C to 350°C. The regression was accomplished by using a linear least-squares polynomial fit method in which each data point was weighted with respect to its relative uncertainty. The uncertainties used were for the most part those assigned by the experimentalist. However, in those cases where uncertainties were not stated, an estimate was supplied on the basis of the experimental method employed in the study.

The experimental densities were fit at constant temperature as a function of composition for each solute. In most cases a simple polynomial equation relating either the density, d , and the molality, m , of the solution,

$$d = \sum_{j=1}^n B_j(t) m^j, \quad (1)$$

or the density and the square-root of the molality,

$$d = \sum_{j=1}^n C_j(t) m^{j/2}, \quad (2)$$

was used for regression purposes. However, it was found that converting the density data to apparent molal volume, ϕ_v , and then fitting this as a function of the square-root of molality resulted in a more accurate and economical (lower-order) representation of the data when very precise measurements were available. The equation used in this case is given by

$$\phi_v = \sum_{j=1}^n A_j(t) m^{j/2}. \quad (3)$$

The density can be calculated from the apparent molal volume by using the relation

$$d = \frac{1000d_o + M_2md_o}{1000 + \phi_v md_o} \quad (4)$$

where M_2 is the molecular weight of the solute and d_o is the density of water. In general the order, n , of the fitting polynomial was chosen such that the standard deviation of the resulting regression would represent the internal consistency of the data used in the fit.

Tables 3 and 6 summarize the coefficients of the equations used to generate the density tabulations given here, and may be used for interpolation to determine densities of solutions with concentrations other than those given in tables 1, 2, 4, and 5.

Because of the inadequate data base, it was not possible to generate a set of density values at pressures greater than the saturation vapor pressure for either potassium hydroxide or sodium hydroxide which would accurately represent the behavior of each solution above its saturation surface.

REFERENCES

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Table 1. Density of KOH Solutions (g/cm³).

Temp (°C)	CONCENTRATION (MOLALITY)																			
	.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0	22.5	25.0	30.0	
-40	1.0263	1.0511	1.0748	1.0974	1.1190	1.1397	1.1595	1.1786	1.1970	1.2147	1.2944	1.3623	1.4214	1.4736	1.5200	—	—	—	—	±.0002
-25	1.0214	1.0448	1.0672	1.0888	1.1095	1.1295	1.1488	1.1674	1.1854	1.2027	1.2813	1.3488	1.4074	1.4586	1.5032	—	—	—	—	±.0002
-10	1.0120	1.0348	1.0566	1.0777	1.0981	1.1177	1.1367	1.1551	1.1729	1.1901	1.2683	1.3351	1.3927	1.4434	1.4888	—	—	—	—	±.0004
0	.998	1.020	1.041	1.062	1.082	1.101	1.120	1.138	1.156	1.174	1.292	1.320	1.378	1.427	—	—	—	—	—	±.0002
25	.987	1.008	1.028	1.048	1.067	1.086	1.104	1.121	1.139	1.155	1.233	1.300	1.358	1.408	1.451	1.488	1.520	1.549	1.600	±.0002
50	.946	.967	.988	1.009	1.030	1.050	1.069	1.087	1.105	1.123	1.200	1.267	1.324	1.374	1.417	1.455	1.489	1.518	1.569	±.0002
75	.891	.917	.941	.965	.987	1.008	1.028	1.047	1.065	1.083	1.162	1.230	1.287	1.337	1.381	1.420	1.454	1.484	1.535	±.0005
100	.822	.855	.884	.910	.934	.957	.979	1.000	1.019	1.038	1.121	1.190	1.249	1.300	1.344	1.383	1.418	1.448	1.499	±.0005
150	.737	.778	.813	.844	.872	.898	.922	.944	.966	.986	1.074	1.147	1.208	1.261	1.306	1.346	1.381	1.412	1.464	±.0005
200	.644	.694	.735	.771	.802	.831	.858	.883	.907	.929	1.025	1.102	1.167	1.222	1.269	1.310	1.346	1.378	1.431	±.0005
250	—	—	—	—	—	—	—	—	—	—	—	—	1.125	1.183	1.232	1.273	1.309	1.340	1.393	±.0005

Table 2. Density of KOH Solutions (g/cm³).

emp (°C)	CONCENTRATION (WEIGHT PERCENT)																			
	1	3	5	7	9	11	13	15	20	25	30	35	40	45	50	60	70	80	90	
0	1.0095	1.0281	1.0450	1.0596	1.0711	1.0788	1.0819	1.0794	1.1954	1.2463	1.2984	1.3520	1.4075	1.4653	1.5256	--	--	--	--	±.0002
25	1.0059	1.0238	1.0419	1.0602	1.0786	1.0973	1.1161	1.1352	1.1838	1.2338	1.2853	1.3386	1.3936	1.4505	1.5085	--	--	--	--	±.0002
50	.9969	1.0144	1.0320	1.0498	1.0678	1.0860	1.1045	1.1233	1.1714	1.2211	1.2723	1.3250	1.3792	1.4353	1.4944	--	--	--	--	±.0004
75	.983	1.000	1.017	1.034	1.052	1.070	1.088	1.107	1.155	1.205	1.256	1.310	1.364	1.420	--	--	--	--	--	±.0002
100	.974	.989	1.005	1.022	1.038	1.056	1.073	1.091	1.137	1.186	1.237	1.290	1.344	1.400	1.456	1.567	--	--	--	±.0002
150	.935	.948	.964	.981	.999	1.018	1.036	1.055	1.104	1.153	1.204	1.257	1.311	1.366	1.422	1.537	1.653	1.768	--	±.0002
200	.873	.893	.914	.934	.954	.974	.994	1.014	1.064	1.115	1.166	1.220	1.274	1.330	1.387	1.503	1.620	1.730	1.850	±.0005
250	.797	.826	.851	.875	.898	.920	.942	.964	1.018	1.071	1.125	1.180	1.235	1.292	1.350	1.467	1.583	1.692	1.800	±.0005
300	.702	.742	.774	.803	.830	.856	.880	.905	.964	1.022	1.079	1.136	1.194	1.252	1.312	1.432	1.550	1.661	1.764	±.0005
350	.600	.650	.689	.723	.754	.784	.812	.839	.905	.968	1.030	1.091	1.152	1.213	1.275	1.398	1.517	1.626	1.722	±.0005
400	--	--	--	--	--	--	--	--	--	--	--	--	1.108	1.174	1.237	1.360	1.480	1.594	1.685	±.0005

Table 3. Interpolation Equation Coefficients for KOH Solutions.

The available density data for temperatures between 0° and 50°C were converted to apparent molal volumes and fit by the method of least squares to a polynomial equation of the form

$$\phi_v = \sum_{i=0}^4 A_i m^{i/2}, \text{ where } m \text{ is the molality of the solution.}$$

Density may be calculated by using the formula

$$d = (1000d_0 + M_2 m d_0) / (1000 + \phi_v m d_0),$$

where $M_2 = 56.109$ g/mole and d_0 is the density of water. The interpolation equations are valid for concentrations up to 17.8 molal (50 wt%).

Temp. (°C)	A_0	A_1	A_2	A_3	A_4	d_0 (g/cm)
0	.4093	2.7870	1.8974	-.5835	.04833	.999840
25	6.3465	-.46054	2.6470	-.67788	.05523	.997047
50	5.0719	3.47176	-.04192	.03755	-.011032	.988038

For temperatures of 75° and 100°C, the available data were fit to a 3rd-order polynomial equation. The equation for 75°C solutions is valid for concentrations from 0 to 15.3 molal (0 to 46 wt%), while the equation for 100°C solutions is valid from 0 to 31 molal (0 to 64 wt%).

	B	$10xB_1$	-10^2xB_2	10^4xB_3
75	.97508	.4584	.1321	.1836
100	.96602	.4296	.1073	.1150

For temperatures from 150° to 400°C, the available data were fit to a 5th-order polynomial equation of the form

$$d = \sum_{j=0}^5 C_j m^{j/2}$$

The range of concentrations for which these interpolation equations are valid vary, and are indicated in the table below with the coefficients:

Temp. (°C)	Range of validity (molality) (wt%)		C_0	$10xC_1$	$10xC_2$	$-10xC_3$	10^3xC_4	-10^4xC_5
150	0-108	0-86	.94076	-.4846	.9064	.1748	1.3858	.40696
200	0-158	0-90	.86476	-.09157	.7429	.1407	1.048	.2822
250	0-158	0-90	.77552	.2633	.6487	.1283	.9678	.2624
300	0-158	0-90	.660828	.76101	.51670	.11013	.8440	.2299
350	0-158	0-90	.54334	1.1571	.45238	.10623	.8417	.2338
400	0-158	0-90	-.00875	5.1638	-.75017	-.066932	-.3504	-.07993

Table 4. Density of NaOH Solutions (g/cm³).

Temp. (°C)	Concentration (Molality)																		
	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0	22.5	25.0	
0	1.0240	1.0463	1.0674	1.0875	1.1067	1.1252	1.1430	1.1601	1.1766	1.1925	1.2641	1.3243	1.3750	1.4182	1.4551	1.4870	1.5150	1.5399	±.0003
25	1.01867	1.03928	1.0591	1.0782	1.0966	1.1144	1.1316	1.1482	1.1642	1.1797	1.2499	1.3092	1.3595	1.4023	1.4389	1.4704	1.4976	1.5210	±.0003
50	1.00891	1.02873	1.0478	1.0663	1.0842	1.1015	1.1183	1.1346	1.1504	1.1656	1.2351	1.2939	1.3434	1.3850	1.4204	1.4511	1.4785	1.5039	±.0006
70	.9984	1.0181	1.0371	1.0554	1.0731	1.0902	1.1068	1.1229	1.1384	1.1535	1.2220	1.2803	1.3297	1.3718	1.4076	1.4384	1.4648	1.4879	±.0006
00	.9794	.9992	1.0182	1.0366	1.0543	1.0715	1.0881	1.1042	1.1197	1.1348	1.2032	1.2609	1.3095	1.3504	1.3854	1.4161	1.4440	1.4706	±.0006
50	.937	.958	.978	.997	1.016	1.034	1.051	1.067	1.083	1.099	1.167	1.224	1.272	1.313	1.349	1.380	1.408	1.432	±.002
00	.886	.908	.928	.949	.968	.986	1.004	1.021	1.038	1.054	1.125	1.183	1.233	1.274	1.311	1.342	1.370	1.395	±.002
50	.826	.849	.872	.893	.914	.934	.953	.971	.989	1.006	1.080	1.141	1.192	1.235	1.272	1.305	1.334	1.359	±.003
00	.751	.776	.800	.824	.846	.867	.888	.908	.927	.946	1.028	1.095	1.151	1.197	1.236	1.269	1.298	1.323	±.005
50	.639	.675	.709	.741	.771	.799	.825	.850	.873	.895	.986	1.054	1.108	1.153	1.193	1.229	1.261	1.285	±.005

Table 5. Density of NaOH Solutions (g/cm³).

Temp. (°C)	CONCENTRATION (WEIGHT PERCENT)															
	1	3	5	7	9	11	13	15	20	25	30	35	40	45	50	
0	1.0124	1.0364	1.0597	1.0828	1.1057	1.1285	1.1512	1.1738	1.2299	1.2853	1.3397	1.3925	1.4434	1.4924	1.5399	±.0003
-25	1.00813	1.03004	1.0519	1.0737	1.0956	1.1175	1.1395	1.1614	1.2163	1.2708	1.3244	1.3768	1.4274	1.4757	1.5210	±.0003
50	.99876	1.01984	1.0409	1.0620	1.0832	1.1046	1.1260	1.1476	1.2018	1.2559	1.3089	1.3602	1.4092	1.4563	1.5039	±.0006
70	.9884	1.0093	1.0302	1.0511	1.0721	1.0933	1.1145	1.1357	1.1892	1.2425	1.2952	1.3467	1.3963	1.4435	1.4879	±.0006
100	.9692	.9903	1.0113	1.0323	1.0534	1.0745	1.0957	1.1170	1.1704	1.2236	1.2757	1.3261	1.3744	1.4214	1.4707	±.0006
150	.926	.948	.971	.993	1.015	1.037	1.059	1.081	1.134	1.187	1.238	1.288	1.337	1.386	1.432	±.002
200	.875	.898	.921	.944	.967	.990	1.012	1.035	1.091	1.145	1.198	1.249	1.299	1.348	1.395	±.002
250	.814	.839	.864	.888	.913	.938	.962	.986	1.045	1.102	1.157	1.209	1.260	1.310	1.359	±.003
300	.739	.765	.792	.818	.845	.871	.898	.924	.989	1.052	1.112	1.170	1.224	1.274	1.323	±.005
350	.621	.659	.697	.734	.769	.804	.837	.869	.944	1.011	1.071	1.126	1.180	1.235	1.285	±.005

Table 6. Interpolation equation coefficients for NaOH solutions.

The available density data for temperatures between 0° and 100°C were converted to apparent molal volume and fit by the method of least squares to a polynomial equation of the form

$$\phi_v = \sum_{j=0}^n A_j m^{j/2}, \text{ where } m \text{ is the molality of the solution.}$$

Density may be calculated by using the formula

$$d = \frac{1000d_0 + M_2 m d_0}{1000 + \phi_v m d_0}, \text{ where } M_2 = 39.997 \text{ g/mole and } d_0 \text{ is the density of water}$$

The interpolation equations are valid only for concentrations less than 26 molal (51 wt%).

Temp.		COEFFICIENTS					
(°C)	n	A ₀	A ₁	A ₂	A ₃	A ₄	d ₀
0	2	-13.313	7.667	-.5232	-----	-----	.999840
25	4	-5.2618	1.982	1.2730	-.28035	.017674	.997047
50	4	-4.8480	3.7608	-.14493	.08709	-.013618	.988038
70	4	-4.4239	2.5852	.71785	-.14439	.007130	.977766
100	4	-7.5513	5.3277	-.60261	.16848	-.020118	.958357

For temperatures between 150° and 350°C, the available data were fit by the method of least squares to a polynomial equation of the form

$$d = \sum_{j=0}^4 B_j m^j.$$

The interpolation equations are valid only for concentrations less than 26 molal (51 wt%).

Temp.		COEFFICIENTS				
(°C)		B ₀	10xB ₁	-10 ² xB ₂	10 ⁴ xB ₃	-10 ⁶ xB ₄
150		.91499	.44439	.17615	.45910	.53917
200		.86315	.46138	.18182	.45662	.50933
250		.80098	.50260	.21281	.56943	.66109
300		.72533	.52969	.19847	.42286	.37630
350		.60082	.79142	.48458	1.7063	2.38441