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Vapor Pressure Measurements with a Nonisothermal Static Method between 293.15 and 363.15 K for Electrolyte Solutions. Application to the H_2O + NaCl System

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We present new measurements of the osmotic coefficients of the binary system H_2O + NaCl for temperatures from 293.15 to 363.15 K and for salt molalities from 1 to 5.5 mol·kg^{-1} of water. Osmotic coefficients were deduced from vapor pressure measurements using a new nonisothermal static apparatus which is also described. Our experimental results were fitted using Apelblat's correlation and are in very good agreement with those presented in the literature, especially with reference to the data from Clarke.

Introduction

Thermodynamic properties of aqueous solutions of strong electrolytes at high temperature are of considerable importance for many processes in the chemical industry. Liquid−vapor equilibrium measurements constitute a major method for determining these properties. However, with few exceptions, the available experimental data are limited to temperatures close to the ambient temperature.

A nonisothermal static apparatus allowing the measurements of vapor pressures has been constructed. The main advantage of this apparatus is its capability to measure accurate values of vapor pressures in a wide temperature range from room temperature to 363.15 K.

The apparatus was tested using the H_2O + NaCl reference system. Results obtained in this temperature range can be extrapolated to higher temperature using the method proposed by Apelblat (1993). Moreover, a classical electrolyte thermodynamic model, such as proposed by Pitzer (1979), can be used to calculate thermodynamic properties of the solutions.

Experimental Apparatus and Procedures

The experimental apparatus shown in Figure 1 is based on a nonisothermal static method, including a measurement set (A), and a device (B) to prepare solutions and control their composition. The cell is made of stainless steel. Two cryostat thermostats (Julabo), controlled by a IBM-PC compatible computer, are used to regulate the temperature T_1 of the lower part of the cell and the temperature T_2 of the top of the cell. We have fixed $T_2 = T_1 + 2$ K (±0.1 K), to avoid vapor phase condensation. The stability of the thermal regulations is ±0.02 K.

The design of the apparatus ensures that the amount of vapor contained in the dead volume of the cell (15 cm^3) can be neglected with respect to the total amount of the liquid solution (150 cm^3). Consequently, the composition of the liquid, stirred by a magnetic bar, can be considered as constant during the measurements.

Two calibrated platinum thermometers (Pt 100) connected to a digital multimeter (AOIP, PN 5207) are set in the liquid, near the surface, spaced out in the vertical plane 2 mm apart. Each of the platinum thermometers gives a measurement with a precision of ±0.01 K. The equilibrium at the surface is supposed to be obtained when the difference between the temperatures of two thermometers is less than ±0.02 K. The equilibrium temperature, *T*, is given by the thermometer which is nearest to the surface, with a maximum uncertainty of ±0.02 K.

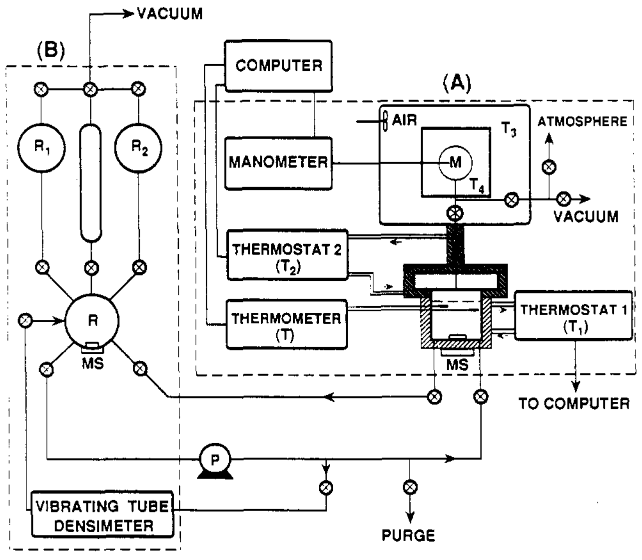

Figure 1. Experimental apparatus: T = temperature of the solution; T_1 = temperature of the thermostat 1 fluid; T_2 = temperature of the thermostat 2 fluid with $T_2 = T_1 + 2$ K; T_3 = temperature of the air thermostat, $T_3 = 380 \pm 0.1$ K; T_4 = temperature of the pressure jauge, $T_4 = 403.15 \pm 0.1$ K; MS = magnetic stirrer; P = pump; R = mixing flask; R_1, R_2 = storage flasks; ⊗ = valve.

The pressure is measured with a 0−1000 Torr absolute manometer (MKS, Baratron, high accuracy, type 315 B) calibrated by linearization between zero (high vacuum) and atmospheric pressure. The accuracy is 0.1% of the reading. The pressure gauge is placed in an aluminum thermostated jacket to ensure good thermal stability of the sensor $T_4 = (403.15 \pm 0.1)$ K. Moreover, this part of the device is placed in a temperature-controlled enclosure, kept at $T_3 = (383.15 \pm 0.1)$ K to avoid condensation in the tubes.

Aqueous solutions of electrolytes are prepared in the flask R by mixing a concentrated solution (flask R_1) with distilled pure water (flask R_2). Liquids were previously

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degassed with the method proposed by Van Ness and Abbot (1978).

The composition of the mixture is calculated from the density measured with a temperature-controlled vibrating tube densimeter (ANTON PAAR, type DMA45), calibrated with standard solutions. The accuracy of the composition is ±0.001 mol·kg^{-1}.

Mass transfer from the flask R to the measurement cell is accomplished using a pump (P). Before each experiment, the cell is degassed in order to eliminate any trace of air that may cause corrosion of steel. A solution of known composition is introduced into the cell, and the total pressure is measured at different temperatures. The temperature equilibrium time is 30 min at each temperature.

Measurements of vapor pressures of pure water were made to test the apparatus. The agreement between our experimental values and those reported by Haar et al. (1984) in the *NBS/NRC Steam Tables* is better than 0.1%.

With the present apparatus, measurements are performed as a function of temperature on a constant liquid composition and not as a function of composition at constant temperature as is the case with the majority of static installations described in the literature.

Theory

The H_2O + NaCl system has been studied at nine compositions corresponding to molalities between 1 and 5.5 mol·kg^{-1} of water. The salt is not volatile, so the total measured pressure at equilibrium P is the vapor pressure of water. It has been measured at temperatures T between 293.15 and 363.15 K.

The equilibrium relationship between the two phases is given by

$$f_w(1,T,P,m) = f^*_w(\text{vap},T,P) \tag{1}$$

in which $f_w(1,T,P,m)$ is the fugacity of the water in the liquid solution of molality m and $f^*_w(\text{vap},T,P)$ is the fugacity of pure water in the vapor phase.

Moreover, we can define the activity of water with respect to pure water by

$$a_w = f_w(1,T,P,m)/f^*_w(1,T,P) \tag{2}$$

where $f^*_w(1,T,P)$ is the fugacity of pure liquid water, which can be expressed with the following relation:

$$f^*_w(1,T,P) = f^*_w(1,T,P^s_w)\exp[(V^*_w/RT)(P - P^s_w)] \tag{3}$$

in which V^*_w is the molar volume of pure liquid water and P^s_w is the saturated vapor pressure of water at the temperature T.

Consequently, the activity of water is given by

$$a_w = \frac{\varphi^*_w(\text{vap},T,P)}{\varphi^*_w(\text{vap},T,P^s_w)}\left(\frac{P}{P^s_w}\right)\exp\left[\frac{V^*_w}{RT}(P^s_w - P)\right] \tag{4}$$

in which $\varphi^*_w(\text{vap},T,P)$ and $\varphi^*_w(\text{vap},T,P^*_w)$ are the fugacity coefficients of pure water at temperature T under pressures P and P^s_w. In this pressure range, they can be calculated with the Virial equation of state:

$$\frac{PV^*_w}{RT} = 1 + \frac{B_2(T)}{RT}P + \frac{B_3(T)}{RT}P^2 + ... \tag{5}$$

Under the experimental pressure conditions, contributions

Table 1. Measured Vapor Pressure of Water, *P*, at the Equilibrium Temperature, *T*, Calculated Values of the Activity of Water in the Liquid Phase, a_w, and the Osmotic Coefficient, ϕ, at Different Molalities *m*

T/K	P/Pa	a_w	ϕ	T/K	P/Pa	a_w	ϕ
m = 5.423 mol·kg^{-1}							
294.48	1989	0.7845	1.242	323.40	9793	0.7848	1.241
299.21	2642	0.7840	1.246	328.35	12470	0.7854	1.237
304.04	3497	0.7839	1.246	333.27	15732	0.7865	1.229
308.87	4584	0.7840	1.246	343.05	24398	0.7875	1.223
313.68	5944	0.7840	1.246	352.87	36877	0.7891	1.212
318.55	7653	0.7841	1.245	362.64	54249	0.7909	1.201
m = 4.608 mol·kg^{-1}							
294.51	2089	0.8224	1.178	328.45	13116	0.8221	1.180
299.28	2784	0.8224	1.177	333.32	16505	0.8229	1.174
304.06	3674	0.8226	1.176	338.18	20585	0.8229	1.174
308.94	4824	0.8218	1.182	343.14	25625	0.8237	1.168
313.74	6251	0.8219	1.181	348.01	31531	0.8239	1.167
318.60	8054	0.8218	1.182	352.92	38650	0.8251	1.158
323.49	10302	0.8218	1.182	362.81	57062	0.8263	1.149
m = 4.086 mol·kg^{-1}							
294.42	2138	0.8465	1.132	333.28	16932	0.8456	1.139
299.30	2872	0.8474	1.125	338.25	21225	0.8457	1.138
304.10	3793	0.8472	1.126	343.09	26265	0.8459	1.136
308.94	4966	0.8461	1.135	348.07	32477	0.8464	1.133
313.81	6455	0.8455	1.140	352.94	39717	0.8470	1.128
318.67	8315	0.8454	1.140	357.81	48263	0.8476	1.123
323.54	10623	0.8452	1.142	362.79	58555	0.8483	1.118
328.41	13466	0.8454	1.141	367.93	70967	0.8482	1.118
m = 3.655 mol·kg^{-1}							
294.48	2193	0.8649	1.102	333.33	17332	0.8635	1.114
299.19	2912	0.8648	1.103	338.25	21678	0.8636	1.113
304.07	3862	0.8641	1.109	343.08	26811	0.8638	1.111
309.06	5110	0.8649	1.102	352.98	40623	0.8648	1.103
313.78	6586	0.8639	1.111	357.93	49516	0.8654	1.098
318.64	8482	0.8636	1.114	362.87	59955	0.8657	1.095
323.54	10852	0.8635	1.115	368.00	72674	0.8661	1.091
328.46	13799	0.8642	1.108				
m = 3.141 mol·kg^{-1}							
294.41	2240	0.8871	1.058	323.45	11082	0.8855	1.075
299.16	2981	0.8875	1.055	328.33	14066	0.8864	1.066
303.97	3942	0.8871	1.059	333.30	17759	0.8858	1.071
308.89	5188	0.8861	1.068	343.10	27531	0.8861	1.068
313.64	6705	0.8860	1.070	352.92	41557	0.8867	1.063
318.63	8693	0.8854	1.075	362.75	61182	0.8872	1.057
m = 2.617 mol·kg^{-1}							
294.39	2292	0.9087	1.015	333.27	18172	0.9076	1.028
299.18	3053	0.9072	1.032	338.21	22731	0.9070	1.035
303.97	4032	0.9072	1.033	343.08	28158	0.9069	1.036
308.88	5308	0.9071	1.034	347.97	34690	0.9074	1.031
313.74	6902	0.9072	1.032	352.93	42557	0.9074	1.031
318.62	8901	0.9070	1.035	357.77	51636	0.9076	1.028
323.48	11367	0.9069	1.036	362.81	62768	0.9080	1.023
328.39	14439	0.9072	1.033	368.07	76447	0.9083	1.020
m = 2.200 mol·kg^{-1}							
294.43	2341	0.9261	0.969	333.22	18478	0.9250	0.984
299.2	3116	0.9248	0.986	338.15	23105	0.9243	0.993
304.00	4116	0.9244	0.991	343.03	28651	0.9247	0.988
308.83	5390	0.9237	1.002	347.97	35344	0.9244	0.992
313.67	7001	0.9235	1.004	352.87	43263	0.9246	0.990
318.55	9037	0.9244	0.992	357.75	52582	0.9248	0.986
323.38	11526	0.9241	0.996	362.71	63688	0.9247	0.988
328.32	14665	0.9244	0.992	368.04	77794	0.9251	0.983
m = 1.671 mol·kg^{-1}							
294.34	2380	0.9465	0.914	333.23	18865	0.9438	0.961
299.11	3169	0.9456	0.929	338.16	23598	0.9435	0.965
304.01	4205	0.9438	0.961	343.02	29238	0.9439	0.959
308.84	5510	0.9437	0.962	348.00	36144	0.9439	0.958
313.67	7153	0.9435	0.965	352.92	44263	0.9439	0.959
318.52	9218	0.9441	0.956	357.87	53942	0.9441	0.956
323.39	11778	0.9437	0.962	362.71	65035	0.9439	0.958
328.32	14985	0.9445	0.948	367.99	79287	0.9443	0.951
m = 1.245 mol·kg^{-1}							
294.46	2428	0.9585	0.946	333.26	19185	0.9584	0.947
299.24	3237	0.9586	0.944	338.12	23945	0.9589	0.935
304.03	4276	0.9585	0.946	343.07	29771	0.9590	0.934
308.84	5594	0.9581	0.955	347.95	36650	0.9590	0.933
313.74	7291	0.9582	0.952	352.89	44916	0.9589	0.936
318.55	9377	0.9588	0.937	357.87	54809	0.9591	0.931
323.47	12007	0.9583	0.951	362.75	66155	0.9586	0.943
328.37	15239	0.9582	0.953	367.98	80567	0.9596	0.919

Table 2. Calculated *A*, *B*, and *C* Parameters, According to Apelblat's Expression at Different Molalities *m*

m/(mol·kg^{-1})	A	B	C
5.423	98.96	−8050.39	−11.97
4.608	105.75	−8338.04	−13.07
4.086	109.09	−8497.47	−13.61
3.655	100.41	−8165.25	−12.25
3.141	102.88	−8275.61	−12.67
2.617	99.68	−8157.83	−12.19
2.200	99.95	−8180.12	−12.26
1.671	124.10	−9162.72	−16.14
1.245	95.37	−7998.20	−11.64

Table 3. Comparison between Experimental Osmotic Coefficient Values, ϕ, and Those Proposed by Clarke, ϕ_{ref}, and the Corresponding Deviations in Osmotic Coefficient and Vapor Pressure at Different Molalities *m*

$$\Delta\phi = |\phi_{ref} - \phi| \text{ and } \frac{\Delta P}{P} = \frac{(P_{ref} - P)}{P} = \frac{\nu M_w}{1000} m \Delta\phi$$

Where M_w Is the Molar Mass of Water, 18.0153 g, and ν the Number of Ions Generated on Complete Dissociation, ν = 2 for NaCl

T/K	ϕ	ϕ_{ref}	$\Delta\phi$	100($\Delta P/P$)
		m = 1.2 mol·kg^{-1}		
298.15	0.9391	0.9457	0.0066	0.029
323.15	0.9389	0.9530	0.0141	0.061
343.15	0.9320	0.9523	0.0203	0.088
363.15	0.9213	0.9476	0.0263	0.114
		m = 1.5 mol·kg^{-1}		
298.15	0.9551	0.9598	0.0047	0.025
323.15	0.9584	0.9690	0.0106	0.057
343.15	0.9532	0.9686	0.0154	0.083
363.15	0.9432	0.9637	0.0205	0.111
		m = 2 mol·kg^{-1}		
298.15	0.9837	0.9866	0.0029	0.021
323.15	0.9916	0.9977	0.0061	0.044
343.15	0.9884	0.9977	0.0093	0.067
363.15	0.9789	0.9921	0.0132	0.095
		m = 3 mol·kg^{-1}		
298.15	1.0486	1.0485	0.0001	0.001
323.15	1.0605	1.0607	0.0002	0.002
343.15	1.0583	1.0596	0.0013	0.014
363.15	1.0478	1.0517	0.0039	0.042
		m = 4 mol·kg^{-1}		
298.15	1.1237	1.1177	0.0060	0.086
323.15	1.1328	1.1275	0.0053	0.076
343.15	1.1276	1.1233	0.0043	0.062
363.15	1.1133	1.1115	0.0018	0.026
		m = 5 mol·kg^{-1}		
298.15	1.2090	1.1916	0.0174	0.313
323.15	1.2085	1.1957	0.0128	0.231
343.15	1.1963	1.1862	0.0101	0.182
363.15	1.1754	1.1690	0.0064	0.115

of the third and higher virial coefficients can be neglected.

In this case, we have:

$$\ln[\varphi_w^{*}(T,P)] = (B_2/RT)P \qquad (6)$$

From expressions 4 and 6, the following equation can be written:

$$\ln a_w = \ln\left(\frac{P}{P_w^s}\right) + \frac{(P - P_w^s)}{RT}(B_2(T) - V_w^{*}) = \ln\left(\frac{P}{P_w^s}\right) + \delta \qquad (7)$$

The corrective term, δ, on the right hand side of eq 7 represents the Poynting correction and the deviation from the ideal gas behavior. Its value is very small and does not exceed 0.2% of the P/P_w^s approximation. However, it is on the same order of magnitude as our experimental accuracy and consequently must be taken into account in the calculations.

The molar volume of pure liquid water, V_w^{*}, is known with high precision (Kell, 1975), and $B_2(T)$ has been calculated with the equation proposed by Le Fevre et al. (1975).

The osmotic coefficient, ϕ, defined on the molality scale is given by

$$\phi = (1000/\nu M_w m) \ln a_w \qquad (8)$$

where M_w is the molar mass of water (M_w = 18.015 34 g) and ν is the number of ions generated on complete dissociation (ν = 2 for NaCl). For each composition, experimental results were regressed using the empirical relation given by Apelblat (1993). This expression can be extrapolated to high temperature with a good precision for nondilute solution:

$$\ln \Delta P = A + \frac{B}{T} + C\left(\ln T - \frac{T}{2T_C}\right) \qquad \text{(constant composition)} \quad (9)$$

where $\Delta P = P_w^s - P$, T_C is the critical temperature of pure water (T_C = 647.14 K), T is the absolute temperature in kelvin, and A, B, and C are adjustable parameters.

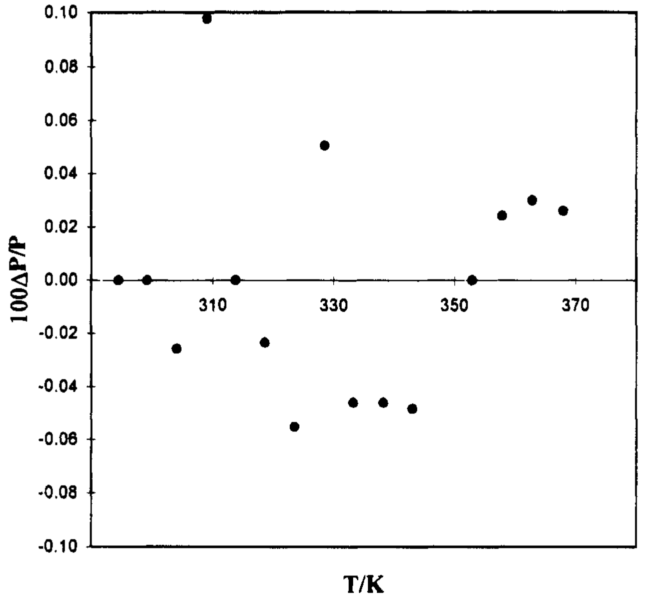

Figure 2. Relative deviation between experimental vapor pressures and values calculated using Apelblat's expression: ΔP = P(Apelblat) − P at m = 3.655 mol·kg^{-1}.

Results

We have reported in Table 1 our isocomposition experimental vapor pressures P, corresponding values of activity a_w, and osmotic coefficient ϕ. The vapor pressures of pure water used in the calculation of a_w are those reported by Haar et al. (1984) in the *NBS/NRC Steam Tables*.

We have used Apelblat's relation to generate values of the activity and osmotic coefficient at temperatures between 293.15 and 363.15 K. For each composition, the A, B, and C parameters of eq 9 have been reported in Table 2. The relative deviations between experimental vapor pressures and values calculated with this relationship are very low (≤0.1%) as is illustrated in Figure 2 for m = 3.655 mol·kg^{-1}.

Discussion

Our experimental osmotic coefficients, according to Apelblat's expression, determined at T = 298.15 K, are in very good agreement with values proposed by Pearce and Nelson (1932) and Pepela and Dunlop (1972) as is illustrated in

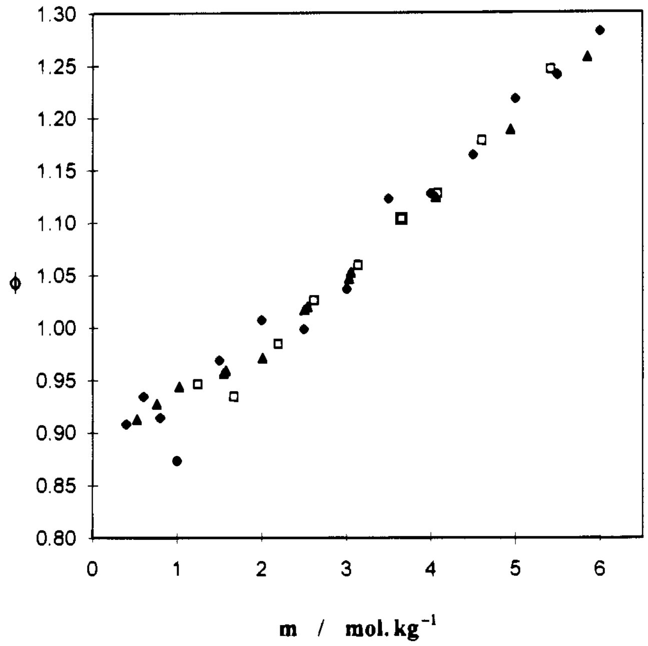

Figure 3. Comparison between our experimental osmotic coefficients and the data in the literature at $T = 298.15$ K: (◆) Pearce and Nelson (1932), (□) this work, (▲) Pepela and Dunlop (1972).

Figure 3. The corresponding agreement is 1.9% and 1.2%, respectively.

A more detailed comparison of our results can be made using the experimental values of the osmotic coefficient proposed by the compilation of Clarke and Glew (1985). It must be noted that the values chosen by Clarke are in very good agreement with results proposed in the compilation by Pitzer et al. (1984).

At each temperature, our experimental values were systematically regressed using a polynomial expression in molality, in order to obtain the osmotic coefficient over the large molality range $1.2 \leq m \leq 5.5$. Results have been reported in Table 3, together with the osmotic coefficient proposed by Clarke, ϕ_{ref}, and corresponding deviations in osmotic coefficient and vapor pressure, $\Delta\phi$ and $\Delta P/P$.

According to the expression

$$\Delta\phi \cong \frac{1000}{\nu M_w}\frac{1}{m}\frac{\Delta P}{P} \qquad (10)$$

a very small deviation in vapor pressure can lead to an important deviation, $\Delta\phi$, when the molality m tends to zero. We can observe in Table 3 that important absolute deviations in osmotic coefficient, $\Delta\phi = |\phi_{\text{ref}} - \phi|$, are obtained in the case of low molalities, $m = 1.2$ mol·kg^{-1} and $m = 1.5$ mol·kg^{-1}. However, this discrepancy is not significant, because it corresponds to a very small relative deviation in vapor pressure, $\Delta P/P$ (with $\Delta P = P_{\text{ref}} - P$). For higher concentrations, our values are systematically higher than those proposed by Clarke, but the deviations $\Delta\phi$ are very low.

Conclusion

The empirical treatment of the experimental results allos the quality of measurements obtained with our apparatus to be ensured. Its original design leads to a rapid data acquisition of the osmotic coefficient representation of the solution at all compositions higher than $m = 1$ mol·kg^{-1} between 293.15 and 363.15 K. Moreover, we have measured the dissolution enthalpy of NaCl in water versus the composition and the temperature. The values obtained, combined with the liquid–vapor equilibrium measurements of the present work, allow a complete thermodynamical treatment of the H_2O + NaCl system with Pitzer's model which will be published soon.

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