J. Chem. Eng. Data **1980**, *25*, 331-332

Table V. Results of Data Reduction[a]

	348.1 K	358.1 K	368.3 K
abs max ΔP, kPa	0.053	0.067	0.053
RMS ΔP, kPa	0.039	0.037	0.038
ΔP bias, kPa	+0.0067	+0.0030	−0.0015
abs max Δy_1	0.005	0.004	0.005
RMS Δy_1	0.0031	0.0019	0.0025
Δy_1 bias	+0.0011	+0.0002	+0.0008

[a] Δ = calculated value − experimental value.

φ_i, φ_i^s fugacity coefficient of component *i* in the vapor mixture and as pure, saturated vapor

Subscripts

1	*n*-heptane
2	*o*-xylene

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Vapor Pressures of Aqueous Solutions of (Ag,Tl,Na)NO_3 at 98.5 °C

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Vapor pressures of aqueous solutions of the liquid melt (Ag,Tl,Na)NO_3 at 98.5 °C and Ag/Tl = 1.06 have been measured in the water-poor region by the static technique. The mole fraction of $NaNO_3$ in the melt was 0.025, 0.050, 0.075, and 0.101. The data was fitted to a form of the BET equation adapted to concentrated aqueous solutions, and BET parameters were deduced. These allowed the calculation of Henry's constant for water dissolved in the melt, and, by use of a simple previously verified additivity rule, parameters for the pure third salt ($NaNO_3$) were extracted.

Introduction

There are relatively few thermodynamic data for electrolyte solutions in the water-poor region of concentration. Solubility limits contribute to this lack. These data however are needed for suggesting and testing theories of concentrated electrolyte solutions, of which there are few which are successful. Not long ago we measured the vapor pressures of the system (Ag,Tl)NO_3 + H_2O, which is liquid over the complete water concentration range below 100 °C (*1a*). Later we studied the systems (Ag,Tl,M)NO_3 + H_2O at the same temperature, where M = Cd (*1b,c*), Ca (*1d*), or Cs (*1e*). In all cases the water activity data could be represented by a modified BET equation, and the BET constants varied linearly with the third cation concentration in the melt. Henry's constants for water dissolved in molten salt were also deduced.

In the present paper we report vapor pressure data for aqueous solutions of (Ag,Tl,Na)NO_3 under experimental conditions uniform with our previous work.

Experimental Section

Vapor pressures were measured by the static method, the details of which were given previously (*1a*). The preparation of the salt mixture has also been given (*1e*). The Ag/Tl ratio was fixed at 1.06, and $NaNO_3$ (Anachemia Reagent, used without further purification) was added to the melt to give $NaNO_3$ melt mole percentages of 2.5, 5.0, 7.5, and 10.1, indicated by $S_{2.5}$, S_5, $S_{7.5}$, and $S_{10.1}$ (*1b*). S_0 represents the system with no $NaNO_3$ added.

The data were treated as before (*1a*), the fugacity *f* of water being calculated from the pressure *p* by means of the second virial coefficient at 98.5 °C; the water activity is then $a_w = f/f_0$, where f_0 is the fugacity of pure water at the temperature in question. Water activity and mole fraction x_w in the solution are related to the water activity coefficient γ_w by $a_w = x_w\gamma_w$.

Results and Discussion

The data for the four systems $S_{2.5}$–$S_{10.1}$ are given in Table I as x_w, p, f, a_w, and γ_w. As before, the data can be represented satisfactorily by an adapted BET adsorption isotherm (*2*) in the form

$$a_w(1 - x_w)/x_w(1 - a_w) = 1/cr + (c - 1)a_w/cr \qquad (1)$$

where *c* and *r* are the BET constants. In this model water is considered to occupy sites provided by the molten salt. The mole ratio of adsorption sites to salt is *r*, and *c* is the Boltzmann factor $\exp(-\Delta E/RT)$, where $\Delta E = E_{ads} - E_L$ is the difference between the energy of adsorption of water by a bare site and the energy of condensation of water into pure water (or onto a sorbed water molecule).

The data plotted according to eq 1 appear in Figure 1; the coefficients of correlation for these straight lines are respectively 0.9998, 0.9994, 0.9986, and 0.9992 for $S_{2.5}$, S_5, $S_{7.5}$, and $S_{10.1}$. As indicated previously (*1a*, *3*), the BET intercept $1/cr = \gamma_w^\infty$, the activity coefficient of water at infinite dilution in molten salt; from this can be calculated Henry's law constants K_H through eq 2. The BET parameters and derived quantities for the

$$f = f_0\gamma_w^\infty x_w = K_H x_w \qquad (2)$$

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Table I. Vapor Pressures and Derived Quantities for the System $(Ag,Tl,Na)NO_3 + H_2O$ at Ag/Tl = 1.06 and 98.5 °C

	x_w	P, torr	f, torr	a_w	γ_w
$S_{2.5}$	0.1192	111.6	111.4	0.1569	1.316
	0.1798	169.9	169.3	0.2385	1.326
	0.2059	194.5	193.7	0.2729	1.325
	0.2373	224.5	223.5	0.3148	1.327
	0.2531	238.9	237.8	0.3349	1.323
	0.2702	255.5	254.2	0.3581	1.325
	0.3189	300.4	298.6	0.4206	1.319
	0.3674	342.9	340.6	0.4798	1.306
	0.4154	382.9	380.0	0.5354	1.289
	0.4556	415.4	412.0	0.5803	1.274
	0.4959	446.8	442.8	0.6238	1.258
	0.5643	495.6	490.7	0.6913	1.225
S_5	0.1513	135.6	135.2	0.1905	1.259
	0.2063	186.1	185.4	0.2611	1.266
	0.2187	197.6	196.8	0.2772	1.267
	0.2463	222.9	221.9	0.3125	1.269
	0.2910	262.6	261.2	0.3680	1.265
	0.3317	299.2	297.4	0.4190	1.263
	0.3402	306.5	304.6	0.4291	1.261
	0.3609	324.0	321.9	0.4535	1.257
	0.3990	356.5	354.0	0.4986	1.250
	0.4365	388.1	385.1	0.5425	1.243
	0.5167	450.1	446.1	0.6284	1.216
	0.5368	464.9	469.7	0.6489	1.209
	0.5979	508.1	503.0	0.7085	1.185
$S_{7.5}$	0.1421	121.2	120.9	0.1703	1.198
	0.1991	171.4	170.8	0.2406	1.208
	0.2551	221.3	220.3	0.3104	1.217
	0.2869	248.8	247.6	0.3488	1.216
	0.3349	290.6	288.9	0.4070	1.215
	0.3423	297.2	295.4	0.4161	1.216
	0.3698	322.6	320.5	0.4515	1.221
	0.4048	351.4	348.9	0.4916	1.214
	0.4238	366.5	363.8	0.5125	1.209
	0.4581	393.2	390.1	0.5496	1.200
	0.4614	395.7	392.6	0.5531	1.199
	0.4950	423.5	419.9	0.5916	1.195
	0.5422	458.5	454.3	0.6400	1.180
	0.6029	500.8	495.8	0.6985	1.159
$S_{10.1}$	0.2247	186.6	185.9	0.2619	1.166
	0.2645	220.7	219.7	0.3095	1.170
	0.2847	237.6	236.5	0.3331	1.170
	0.3480	293.0	291.3	0.4103	1.179
	0.3705	310.9	309.0	0.4353	1.175
	0.3883	325.9	323.8	0.4561	1.175
	0.4266	358.1	355.5	0.5009	1.174
	0.4828	402.1	398.9	0.5619	1.164
	0.5307	439.2	435.3	0.6132	1.155
	0.5555	457.5	453.3	0.6386	1.150
	0.5882	482.1	477.5	0.6726	1.143

Table II. BET Parameters and Derived Quantities for the Title System

	$1/cr = \gamma_w^\infty$	$(c-1)/cr$	r	c	$-\Delta E$, kJ mol^{-1}	K_H, atm
S_0[a]	1.34	0.722	0.486	1.54	1.33	1.25
$S_{2.5}$	1.27	0.665	0.517	1.52	1.30	1.18
S_5	1.20	0.608	0.553	1.51	1.27	1.12
$S_{7.5}$	1.14	0.557	0.589	1.49	1.23	1.07
$S_{10.1}$	1.09	0.516	0.624	1.48	1.20	1.02

[a] Reference *1b*.

present systems are presented in Table II.

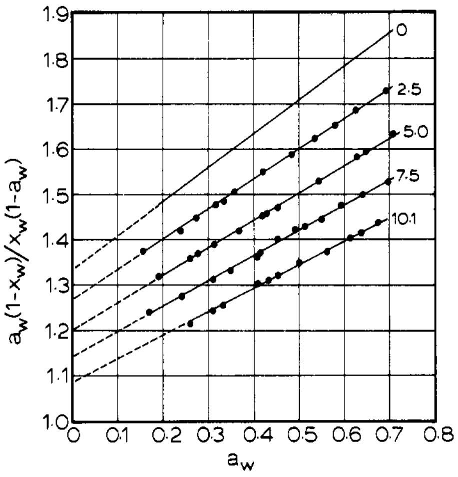

Figure 1. Adapted BET isotherms for the title system. The curves are labeled according to the mole percentage of $NaNO_3$ in the melt. Curve for zero sodium content taken from ref *1b*.

Table III. BET Parameters for Water Dissolved in Single Molten Salts

	temp, °C	r	$-\Delta E$, kJ mol^{-1}	$-r\Delta E$, kJ mol^{-1}	γ_w^∞	ref
$CsNO_3$	98.5	0.81	−1.45	−1.17	1.97	*1e*
$TlNO_3$	111	0.26	0.62	0.16	3.15	*1f*
$AgNO_3$	111	0.75	1.47	1.10	0.83	*1f*
$NaNO_3$	98.5	1.86	0.90	1.67	0.40	this work
$Cd(NO_3)_2$	98.5	3.67	3.97	14.6	0.08	*1b,c*
$Ca(NO_3)_2$	98.5	3.53	4.39	15.5	0.07	*1d*[a]

[a] Note the following corrections in this reference: (1) p 623, eq 6: read kcal mol^{-1} instead of kJ mol^{-1}; (2) p 624, Table III: read 4.39 instead of 4.60 in last column.

The parameters r and $r\Delta E$ have been found (*1b*) to be linear in the mole fraction of the third cation in the melt. In the present instance this linearity can be represented by eq 3 and 4. On

$$r = 1.38X_{Na} + 0.484 \tag{3}$$

$$-r\Delta E = 1.02X_{Na} + 0.644 \text{ kJ mol}^{-1} \tag{4}$$

the assumption (*1b*) that the $(Ag,Tl)NO_3$ and $NaNO_3$ in the melt contribute to r and $r\Delta E$ in a simple additive manner, it is possible to extract BET parameters for the third salt in the mixture. The results for $NaNO_3$ appear in Table III, together with those for previously investigated systems. It is to be noted that, in contrast to ordinary practice (*4*), the present technique enables the deduction of Henry's law constants (i.e., solubilities) for water dissolved in single supercooled molten salts, i.e., as if the salts were liquid at the temperature of study.

The experimental precision in the pressures reported in Table I is one part per thousand or less (*1a*). The experimental uncertainties in the other quantities in Tables I and II are indicated by the number of significant figures used in reporting the results, i.e., the last digit is uncertain.

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