microscopy was performed on an Olympus B-2 microscope equipped with a Thomas (Philadelphia, PA) hot stage and an Omega microprocessor controller and digital reporting thermocouple. Mixtures of the disklike molecules were prepared by freeze-drying benzene solutions of the two components.

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Supplementary Material Available: ^{1}H NMR spectra, IR spectra, and combustion analysis data for all new compounds (12 pages). Ordering information is given on any current masthead page.

Surface Tension of Liquids from Molten Nitrate Mixtures to Water

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Abstract: For a long time, progress in the studies of molten salt chemistry and aqueous solution chemistry was made almost independently. Recently, salt–water systems were investigated from molten salts to water, to bridge the gap between these two fields of research, particularly concerning thermodynamic and transport properties. Another property of considerable importance to arriving at structural information on salt–water systems is the surface tension which has never been studied over the whole concentration range. Therefore, as a new step, this paper reports the results on surface tension measurements of some $AgNO_3$–$TlNO_3$–H_2O and $AgNO_3$–$TlNO_3$–$M(NO_3)_n$–H_2O systems with M = Cs, Cd, and Ca, with regard to the influence of both the water mole fraction and the temperature. By applying the Guggenheim and Adam method and the Butler equation, reasonable orders of magnitude for the values of the water mole fraction, activity, and activity coefficient in the surface phase were obtained. Moreover, it was found that the free energy of hole formation in the Fürth theory of liquids is close to the free energy of activation for the viscous flow in the Eyring equation. This result suggests that holes may be considered as fundamental structural entities in the chemistry of all solutions from molten salts to water.

1. Introduction

Compared to dilute aqueous electrolyte solutions, there is a lack of information concerning electrolyte solutions in which water plays the role of the solute, instead of the solvent. This type of solution covers a large concentration range, from the fused salts themselves to the aqueous solutions where the water mole fraction is about 0.5. In addition to technical reasons,[1-3] another one of scientific nature has attracted attention to this kind of solution. It is the suggestion,[2,4-10] made now and then, that more progress in the understanding of very concentrated aqueous solutions could come from the consideration of solutions obtained by adding water to fused salts rather than concentrating dilute aqueous solutions. As a matter of fact, this approach has proved to be fruitful in the studies of the water vapor pressure, the viscosity, and the electrical conductance of salt–water systems, over large concentration ranges.[10-15] Some of these systems have been investigated over the whole concentration range, from fused salts to water, to bridge the gap between molten salt chemistry and aqueous solution chemistry, the studies of which have advanced almost independently for a long time.

A property of considerable importance to arriving at structural information on salt–water systems is the surface tension which has never been studied over the whole concentration range. Therefore, as a new step, investigations on the surface tension of nitrate–water systems were made with regard to the influence of both the water concentration and the temperature. In the present paper, we report the results obtained in the study of electrolyte–water systems obtained by addition of water to molten salt mixtures having fixed compositions, so that they can be considered as two-component systems, i.e. salt and water. These systems are the following: $[0.515AgNO_3–0.485TlNO_3] + H_2O$ and $[0.464AgNO_3–0.436TlNO_3–0.100M(NO_3)_n] + H_2O$, with M = Cs, Cd, and Ca. The anhydrous salt system $0.515AgNO_3–0.485TlNO_3$ is a eutectic mixture whose freezing point is 83 °C.[16] This mixture is convenient to establish an experimental link between molten salts and aqueous solutions, since below 100 °C it is completely miscible with water. Furthermore, around 100 °C this eutectic mixture can be doped with other nitrates, e.g. $CsNO_3$, $Cd(NO_3)_2$, and $Ca(NO_3)_2$, at mole fractions up to 0.100. The cations contained in these melts have different hydrating powers which were found to be reflected by thermodynamic and transport properties.[2,12,14] One is then induced to examine whether the surface tension also reflects the cation hydrating power.

The water vapor pressures of these systems have been previously measured,[17-20] so that a basis exists to facilitate the exploitation

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Table I. The Density ρ and the Molar Volume V of the $AgNO_3$–$TlNO_3$–$CsNO_3$–H_2O System as Functions of the Composition at Two Temperatures[a]

x_w	x_1	x_2	x_3	10^6V, $m^3\ mol^{-1}$	$10^{-3}\rho$, $kg\ m^{-3}$
			T = 353 K		
0	0.464	0.436	0.100	47.47	4.519
0.150	0.394	0.371	0.085	42.95	4.308
0.272	0.337	0.318	0.073	39.28	4.100
0.416	0.271	0.255	0.058	34.93	3.801
0.540	0.213	0.201	0.046	31.25	3.469
0.651	0.162	0.152	0.035	28.01	3.091
0.750	0.116	0.109	0.025	25.19	2.665
0.869	0.061	0.057	0.013	21.86	2.002
0.925	0.035	0.032	0.008	21.37	1.533
1[b]	0	0	0	18.538	0.9718
			T = 363 K		
0	0.464	0.436	0.100	47.65	4.502
0.175	0.382	0.366	0.083	42.34	4.254
0.272	0.337	0.318	0.073	39.43	4.085
0.405	0.276	0.260	0.059	35.38	3.814
0.500	0.232	0.218	0.050	32.54	3.573
0.540	0.213	0.201	0.046	31.37	3.455
0.631	0.171	0.161	0.037	28.72	3.152
0.696	0.141	0.133	0.030	26.82	2.899
0.837	0.076	0.071	0.016	22.86	2.189
0.877	0.057	0.054	0.012	21.73	1.941
0.943	0.026	0.025	0.006	20.04	1.458
1[b]	0	0	0	18.662	0.9653

[a] x_w, x_1, x_2, and x_3 are the mole fractions of H_2O, $AgNO_3$, $TlNO_3$, and $CsNO_3$, respectively. [b] Reference 25.

of the surface tension data in connection with the thermodynamics of the surface phase. The viscosities have also been measured,[13,15,21] allowing a comparison of the free energy of hole formation in the Fürth theory of liquids[22] to the free energy of activation of the viscous flow in the Eyring equation.[23]

2. Experimental Procedures and Results

The classical capillary rise method was employed with a cell analogous to that of Campbell and Williams.[24] A cathetometer M-912 from Gaertner Scientific Corporation, which permits position readings to be made to 0.01 mm, was used to measure the capillary rise. The precision bore capillary tubings, made of borosilicate glass, were from Lab-Crest Scientific Glass Company and were 30 cm in length. Two groups of tubings were selected by determination of their inside diameter with known values of water surface tension between 50 and 90 °C.[25] In one group, the inside diameter was 0.0208 cm and in the other 0.0294 cm. These values were in accordance with the dimensional tolerances indicated by the supplier: 0.0201 ± 0.0008 and 0.0300 ± 0.0008 cm. Measurements on carbon tetrachloride and benzene between 50 and 70 °C, made with these selected tubings, gave results with less than 1% deviation from known values.[26] The cell was mounted in a thermostated bath, using a system of alignment previously devised for viscosity measurements,[21] and the salt-water mixtures were prepared following a procedure described in the same study. The heights to which the liquids rose in the capillaries were between 4 and 8 cm. The reproducibility of the surface tension determinations was better than 1%. The limits of the temperature ranges were chosen as to avoid water evaporation and salt crystallization. The densities required to calculate the values of the surface tension from the capillary rise measurements were obtained by interpolation of data given elsewhere[13,15,21] and in Table I. The values of the surface tension σ are listed in Tables II–V.

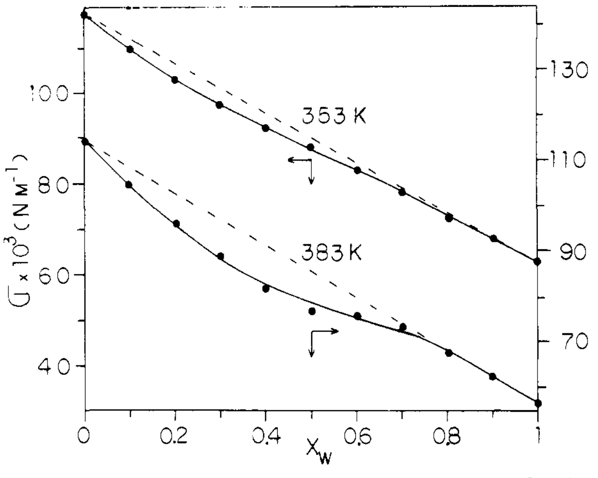

Figure 1. Surface tension σ as a function of the water mole fraction x_w for the $AgNO_3$–$TlNO_3$–H_2O system, at two temperatures.

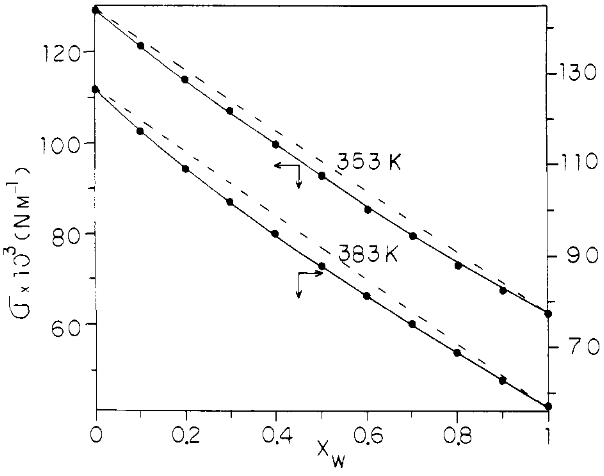

Figure 2. Surface tension σ as a function of the water mole fraction x_w for the $AgNO_3$–$TlNO_3$–$CsNO_3$–H_2O system, at two temperatures.

3. Discussion

1. Temperature Dependence of Surface Tension. At a fixed water mole fraction x_w, the following linear function of the temperature fits the experimental data

$$\sigma = -mT + b \tag{1}$$

The parameters m and b are given in Table VI, together with their uncertainties and the correlation coefficients.

Since the surface tension σ is the surface free energy per unit area, the surface entropy S_σ and the surface enthalpy H_σ, per unit area, are expressed by the equations:

$$S_\sigma = -\mathrm{d}\sigma/\mathrm{d}T \tag{2}$$

and

$$H_\sigma = \sigma - T\,\mathrm{d}\sigma/\mathrm{d}T \tag{3}$$

where T is the temperature in Kelvin.

Thus, H_σ and S_σ, respectively represented by b and m in eq 1, appear independent of the temperature. The constancy of H_σ and S_σ with respect to temperature variation was observed for various pure molten salts, molten salt mixtures, etc.[24,27] The values of H_σ for the anhydrous mixtures in Table VI are close to those of pure nitrates and nitrate mixtures obtained by Bloom, Davis, and James[27] at much higher temperatures.

These above-mentioned authors[27] supposed that a correlation exists between the ionic, or covalent, character of a liquid substance

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Table II. The Surface Tension σ of the $AgNO_3$–$TlNO_3$–H_2O System in Contact with Air as a Function of the Composition and the Temperature T[a]

T, K	$10^3\sigma$, N m^{-1}	T, K	$10^3\sigma$, N m^{-1}	T, K	$10^3\sigma$, N m^{-1}
$x_w = 0; x_1 = 0.515; x_2 = 0.485$					
359.3	116.9	370.2	115.9	383.4	114.7
363.5	116.5	373.3	115.6	388.6	114.2
366.9	116.2	378.5	115.1	392.3	113.7
$x_w = 0.100; x_1 = 0.463; x_2 = 0.436$					
357.8	108.5	368.5	106.7	380.4	104.7
360.6	108.0	372.2	106.1	383.9	104.4
363.3	107.5	376.1	105.6	385.4	104.2
$x_w = 0.203; x_1 = 0.410; x_2 = 0.387$					
349.7	103.7	362.0	101.1	376.6	97.7
353.9	102.9	365.5	100.2	379.7	96.9
357.6	102.1	369.8	99.2	382.4	96.4
		373.3	98.4		
$x_w = 0.300; x_1 = 0.361; x_2 = 0.339$					
348.8	98.7	357.9	96.1	373.3	91.5
351.9	97.8	360.8	95.2	377.6	90.6
354.7	96.8	364.2	94.1	382.5	89.1
		368.5	92.9		
$x_w = 0.400; x_1 = 0.309; x_2 = 0.291$					
348.8	93.6	359.7	90.1	371.7	85.1
351.9	92.7	363.5	87.8	375.7	84.0
355.8	91.1	367.6	86.0	379.5	82.4
$x_w = 0.500; x_1 = 0.258; x_2 = 0.242$					
348.4	89.6	357.5	87.2	370.5	81.7
351.4	88.9	360.6	85.5	374.7	80.1
354.5	88.0	363.4	84.1	379.5	78.2
		366.6	82.7		
$x_w = 0.600; x_1 = 0.206; x_2 = 0.194$					
348.6	83.7	357.5	81.6	371.7	78.2
351.6	83.2	360.7	80.7	375.2	77.1
354.6	82.5	363.4	80.2	379.0	76.0
		366.5	79.5		
$x_w = 0.700; x_1 = 0.155; x_2 = 0.145$					
348.7	78.6	357.4	77.0	369.6	75.2
351.5	78.0	360.4	76.6	373.2	74.5
354.4	77.5	363.3	76.2	375.9	74.1
		366.5	75.7		
$x_w = 0.800; x_1 = 0.103; x_2 = 0.097$					
348.7	73.4	356.5	71.9	367.6	70.0
351.8	72.9	359.5	71.2	370.7	69.3
353.9	72.3	361.4	71.0	373.3	68.9
		363.3	70.7		
$x_w = 0.900; x_1 = 0.052; x_2 = 0.048$					
348.4	69.0	356.4	67.6	366.7	65.8
350.9	68.4	359.6	67.1	369.4	65.2
353.5	67.9	361.8	66.6	371.7	64.6
		363.3	66.4		

[a] x_w, x_1, and x_2 are the mole fractions of H_2O, $AgNO_3$, and $TlNO_3$, respectively.

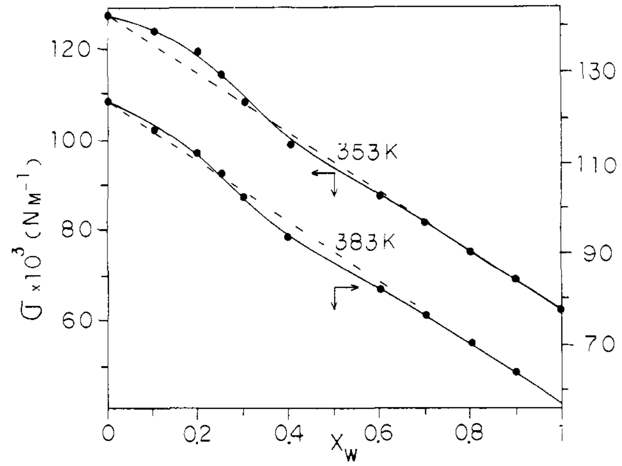

Figure 3. Surface tension σ as a function of the water mole fraction x_w for the $AgNO_3$–$TlNO_3$–$Cd(NO_3)_2$–H_2O system, at two temperatures.

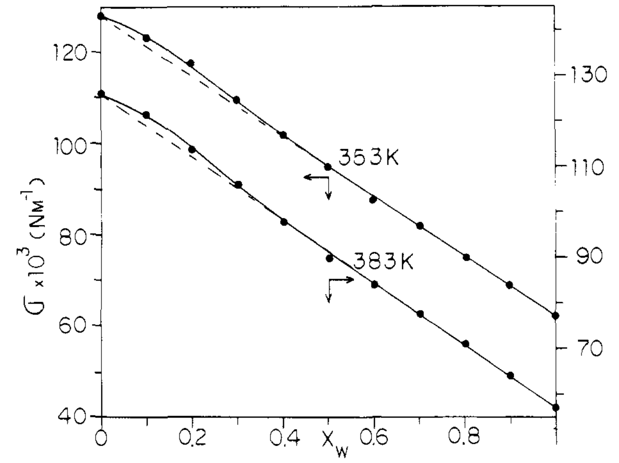

Figure 4. Surface tension σ as a function of the water mole fraction x_w for the $AgNO_3$–$TlNO_3$–$Ca(NO_3)_2$–H_2O system, at two temperatures.

and the magnitude of H_σ. Such a correlation is not confirmed by the data of Table VI. As a matter of fact, the order of magnitude of H_σ is the same for the pure water and for the highly ionic nitrate mixtures. It may especially be noticed that the value of H_σ for H_2O is only ~15% lower than that for the anhydrous $(Ag,Tl)NO_3$ system. However, the difference between the values of their electrical conductance is considerable: 11.3 Ω^{-1} m^{-1} for the $(Ag,Tl)NO_3$ system[13] and 1.2×10^{-4} Ω^{-1} m^{-1} for H_2O,[28] at 372 K.

2. Surface Tension Isotherms. Equation 1 allows an estimation of the values of σ, at a fixed temperature, from pure salt to pure water, and in Figures 1–4 plots of σ vs x_w are given for the studied nitrate–water systems, at two temperatures.

An approximate linear relationship is observed between σ and x_w, over the range x_w = ~0.6–1. It has been known for a long time that σ is often a linear function of the amount of salt in dilute aqueous solutions, at ordinary temperature,[29] and in this connection the equation proposed by Buliginsky[30] must be recalled:

$$\sigma = \sigma_w[m_w + L_m(1 - m_w)] \qquad (4)$$

m_w and $(1 - m_w)$ are the water and salt contents and L_m is a constant depending on the salt. The linear character of the empirical function found in the case of the nitrate–water systems suggests eq 4 with the mole fraction chosen as the concentration parameter:

$$\sigma = \sigma_w[x_w + L(1 - x_w)] \qquad (5)$$

L is the constant on the mole fraction scale.

It is interesting to note that the equation known as the simple mixture law may be seen as a special case of eq 5 in which the parameter L takes on a value depending only upon the pure components.

In effect, if the following expression is attributed to L

$$L_0 = \sigma_s/\sigma_w \qquad (6)$$

then eq 5 becomes the simple mixture equation

$$\sigma = \sigma_w x_w + \sigma_s x_s \qquad (7)$$

Further, the comparison of L with L_0 provides a convenient manner to express the extent to which σ departs from the simple mixture law. This can be done by formulating the relative deviation of L with respect to L_0, i.e. $(L - L_0)/L_0$ (%). Table VII gives the values of L, L_0, and the relative deviation of L, at three temperatures.

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Table III. The Surface Tension σ of the $AgNO_3$–$TlNO_3$–$CsNO_3$–H_2O System in Contact with Air as a Function of the Composition and the Temperature T^a

T, K	$10^3\sigma$, N m^{-1}	T, K	$10^3\sigma$, N m^{-1}	T, K	$10^3\sigma$, N m^{-1}
$x_w = 0$; $x_1 = 0.464$; $x_2 = 0.436$; $x_3 = 0.100$					
363.3	128.8	373.5	127.8	385.2	126.8
366.4	128.4	378.2	127.4	389.7	126.4
370.3	128.1	381.6	127.2	393.0	126.1
$x_w = 0.100$; $x_1 = 0.417$; $x_2 = 0.393$; $x_3 = 0.090$					
352.1	121.7	360.8	120.5	375.2	118.8
354.9	121.3	364.2	120.1	378.5	118.4
357.6	121.0	368.4	119.6	381.3	118.1
		371.7	119.2		
$x_w = 0.200$; $x_1 = 0.731$; $x_2 = 0.349$; $x_3 = 0.080$					
354.0	114.4	362.6	113.0	375.2	110.6
357.0	114.0	365.2	112.5	379.3	109.9
359.4	113.6	368.7	111.9	381.4	109.5
		371.7	111.2		
$x_w = 0.300$; $x_1 = 0.324$; $x_2 = 0.306$; $x_3 = 0.070$					
350.3	108.0	359.8	106.5	371.7	104.5
353.0	107.6	362.6	106.0	375.4	103.6
356.7	106.9	365.5	105.6	378.3	102.9
		368.2	105.1		
$x_w = 0.400$; $x_1 = 0.278$; $x_2 = 0.262$; $x_3 = 0.060$					
349.6	99.9	357.7	98.8	371.7	96.9
351.9	99.6	360.3	98.4	375.5	96.4
354.8	99.2	363.4	97.9	378.6	96.0
		367.6	97.4		
$x_w = 0.500$; $x_1 = 0.232$; $x_2 = 0.218$; $x_3 = 0.050$					
349.4	93.4	359.5	91.7	371.7	89.8
353.3	92.7	362.6	91.3	374.9	89.4
356.4	92.2	365.3	90.9	376.4	89.2
		368.5	90.3		
$x_w = 0.600$; $x_1 = 0.185$; $x_2 = 0.175$; $x_3 = 0.040$					
349.4	85.7	358.8	84.6	371.7	83.0
352.7	85.3	361.8	84.1	374.3	82.6
355.5	85.0	364.5	83.8	376.6	82.4
		367.9	83.4		
$x_w = 0.700$; $x_1 = 0.139$; $x_2 = 0.131$; $x_3 = 0.030$					
349.7	80.1	357.4	78.8	368.5	77.2
351.6	79.8	360.2	78.4	371.7	76.7
354.3	79.4	363.4	78.0	374.4	76.3
		366.6	77.5		
$x_w = 0.800$; $x_1 = 0.093$; $x_2 = 0.087$; $x_3 = 0.020$					
348.6	73.3	356.5	72.2	369.1	70.8
350.4	73.0	359.2	71.9	371.7	70.4
353.3	72.6	362.5	71.5	374.6	70.0
		365.5	71.2		
$x_w = 0.900$; $x_1 = 0.046$; $x_2 = 0.044$; $x_3 = 0.010$					
348.4	67.9	355.5	67.0	365.4	65.5
351.5	67.6	357.5	66.7	368.8	65.1
353.4	67.3	359.3	66.4	371.7	64.7
		362.2	66.0		

[a] x_w, x_1, x_2, and x_3 are the mole fractions of H_2O, $AgNO_3$, $TlNO_3$, and $CsNO_3$, respectively.

Table IV. The Surface Tension σ of the $AgNO_3$–$TlNO_3$–$Cd(NO_3)_2$–H_2O System in Contact with Air as a Function of the Composition and the Temperature T^a

T, K	$10^3\sigma$, N m^{-1}	T, K	$10^3\sigma$, N m^{-1}	T, K	$10^3\sigma$, N m^{-1}
$x_w = 0$; $x_1 = 0.464$; $x_2 = 0.436$; $x_3 = 0.100$					
361.9	126.3	376.8	124.3	387.3	122.8
367.0	125.6	380.9	123.8	390.2	122.4
372.0	124.9	383.9	123.3	393.4	122.1
$x_w = 0.100$; $x_1 = 0.417$; $x_2 = 0.393$; $x_3 = 0.090$					
359.3	122.4	370.3	119.7	379.8	117.6
363.4	121.4	373.3	119.0	382.3	117.0
367.0	120.6	376.3	118.4	384.2	116.6
$x_w = 0.201$; $x_1 = 0.730$; $x_2 = 0.349$; $x_3 = 0.080$					
353.1	119.5	363.2	117.2	376.7	113.9
357.4	118.5	367.3	116.3	380.4	113.0
360.6	117.8	370.9	115.5	383.2	112.3
		373.7	114.8		
$x_w = 0.250$; $x_1 = 0.348$; $x_2 = 0.327$; $x_3 = 0.075$					
352.0	114.9	363.2	112.4	378.3	109.3
355.5	114.2	367.3	111.5	381.4	108.6
359.4	113.3	371.5	110.6	383.5	108.2
		375.8	109.7		
$x_w = 0.300$; $x_1 = 0.324$; $x_2 = 0.306$; $x_3 = 0.070$					
349.4	108.2	361.3	106.3	376.5	104.0
353.7	107.6	365.2	105.9	379.2	103.4
357.5	107.0	369.8	105.1	382.4	103.0
		373.2	104.5		
$x_w = 0.400$; $x_1 = 0.278$; $x_2 = 0.262$; $x_3 = 0.060$					
348.7	99.4	357.6	97.8	371.4	95.2
351.5	98.8	360.2	97.3	375.8	94.5
354.9	98.4	363.3	96.7	380.5	93.7
		367.4	95.9		
$x_w = 0.600$; $x_1 = 0.185$; $x_2 = 0.175$; $x_3 = 0.040$					
348.8	88.2	359.6	86.3	372.6	83.9
352.0	87.6	363.2	85.6	376.3	83.2
355.4	87.0	366.5	85.0	378.4	82.9
		369.9	84.3		
$x_w = 0.700$; $x_1 = 0.139$; $x_2 = 0.131$; $x_3 = 0.030$					
348.9	82.0	357.6	80.4	369.3	78.6
351.5	81.6	360.7	80.0	372.4	78.1
354.6	81.0	363.2	79.4	375.6	77.5
		366.4	79.0		
$x_w = 0.800$; $x_1 = 0.093$; $x_2 = 0.087$; $x_3 = 0.020$					
348.7	76.5	355.9	75.3	367.7	73.4
351.7	76.0	358.6	75.0	370.3	72.9
353.8	75.7	361.3	74.5	373.8	72.4
		364.6	74.0		
$x_w = 0.900$; $x_1 = 0.046$; $x_2 = 0.044$; $x_3 = 0.010$					
348.7	70.3	356.5	68.9	366.4	67.2
351.6	69.7	358.6	68.5	369.3	66.7
353.3	69.4	361.7	68.0	371.4	66.3
		363.4	67.7		

[a] x_w, x_1, x_2, and x_3 are the mole fractions of H_2O, $AgNO_3$, $TlNO_3$, and $Cd(NO_3)_2$, respectively.

The deviation percentage decreases sensitively when the divalent cations Cd^{2+} and Ca^{2+} are substituted for the monovalent cations Ag^+, Tl^+, and Cs^+. Moreover, beyond the validity range of eq 5, the systems containing the divalent cations exhibit positive deviations from the simple mixture law, contrary to the other systems which exhibit negative deviations over the whole concentration range, as can be seen in Figures 1–4.

A remarkable result is that the (Ag,Tl,Cd)NO_3–H_2O and (Ag,Tl,Ca)NO_3–H_2O systems, made of a salt mixture and water whose surface tensions σ_s and σ_w are very far apart, have surface tension values close to those predicted by the simple mixture law (eq 7), the positive or negative deviations being always less than ~5% for the system containing Cd^{2+} and ~3% for the system containing Ca^{2+}. This original behavior could perhaps be accounted for by the hypothesis of a competition between two opposite tendencies: that of the Cd^{2+} and Ca^{2+} cations promoting positive deviations and that of the Ag^+, Tl^+, and Cs^+ cations promoting negative deviations, in correlation, at least partially, with the strong hydrating power of Cd^{2+} and Ca^{2+} compared to Ag^+, Tl^+, and Cs^+. In this connection, it must be noted that the hydrating power of the cations was also set forth in the discussion of the water activity in these nitrate–water melts, with regard to positive and negative deviations from the Raoult law.[17,18]

3. Water Mole Fraction, Activity, and Activity Coefficient in the Surface Phase. The estimation of the surface water mole fraction was made by application of the Guggenheim and Adam method[31,32] as follows.

The Gibbs adsorption formula is written

$$\Gamma_{w(s)} = -\frac{1}{kT}\frac{d\sigma}{d\ln a_w} \qquad (8)$$

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(31) Guggenheim, E. A.; Adam, N. K. *Proc. R. Soc.* **1933**, *A139*, 218–236.

(32) Guggenheim, E. A. *Mixtures*; Clarendon Press: Oxford, 1952; pp 169–172.

Table V. Surface Tension σ of the $AgNO_3$–$TlNO_3$–$Ca(NO_3)_2$–H_2O System in Contact with Air as a Function of the Composition and the Temperature T[a]

T, K	$10^3\sigma$, N m^{-1}	T, K	$10^3\sigma$, N m^{-1}	T, K	$10^3\sigma$, N m^{-1}
$x_w = 0$; $x_1 = 0.464$; $x_2 = 0.436$; $x_3 = 0.100$					
363.2	127.1	279.2	126.0	387.7	125.4
367.3	126.9	383.3	125.7	391.9	125.2
375.5	126.2			393.9	125.1
$x_w = 0.100$; $x_1 = 0.417$; $x_2 = 0.393$; $x_3 = 0.090$					
355.8	123.2	367.4	122.3	381.5	121.3
359.3	123.0	372.0	122.0	384.3	121.1
363.2	122.7	375.6	121.8	386.4	120.9
		378.9	121.5		
$x_w = 0.200$; $x_1 = 0.371$; $x_2 = 0.349$; $x_3 = 0.080$					
357.7	117.0	367.6	115.7	376.5	114.4
360.4	116.6	370.4	115.2	379.2	114.0
363.2	116.2	373.7	114.8	383.2	113.4
$x_w = 0.301$; $x_1 = 0.324$; $x_2 = 0.305$; $x_3 = 0.070$					
356.7	109.1	367.4	108.0	378.4	106.8
359.3	108.8	371.7	107.5	381.2	106.6
363.2	108.4	375.6	107.1	383.3	106.3
$x_w = 0.400$; $x_1 = 0.278$; $x_2 = 0.262$; $x_3 = 0.060$					
349.6	102.2	359.8	101.0	373.3	99.3
353.9	101.7	363.2	100.6	376.9	98.8
356.5	101.4	366.4	100.2	379.4	98.4
		369.6	99.7		
$x_w = 0.500$; $x_1 = 0.232$; $x_2 = 0.218$; $x_3 = 0.050$					
350.1	95.0	360.9	93.2	366.5	92.0
353.4	94.3	363.3	92.8	370.4	91.5
356.7	93.9			373.3	90.9
$x_w = 0.600$; $x_1 = 0.185$; $x_2 = 0.175$; $x_3 = 0.040$					
349.3	88.0	357.5	86.8	370.0	85.3
351.6	87.7	360.5	86.5	372.8	84.9
354.2	87.2	363.3	86.1	376.4	84.4
		367.0	85.7		
$x_w = 0.700$; $x_1 = 0.139$; $x_2 = 0.131$; $x_3 = 0.030$					
351.5	81.8	360.5	80.5	372.8	78.8
354.8	81.3	363.3	80.2	375.4	78.5
357.8	80.8	366.5	79.8	376.7	78.3
		369.6	79.3		
$x_w = 0.800$; $x_1 = 0.093$; $x_2 = 0.087$; $x_3 = 0.020$					
348.8	75.7	357.5	74.6	369.6	72.9
351.4	75.3	360.6	74.1	372.8	72.4
354.6	74.9	363.2	73.7	375.4	72.2
		366.4	73.3		
$x_w = 0.900$; $x_1 = 0.046$; $x_2 = 0.044$; $x_3 = 0.010$					
348.9	69.8	357.5	68.3	365.9	67.0
351.8	69.3	360.1	67.9	367.2	66.8
354.6	68.8	363.3	67.4	368.9	66.5

[a] x_w, x_1, x_2, and x_3 are the mole fractions of H_2O, $AgNO_3$, $TlNO_3$ and $Ca(NO_3)_2$ respectively.

Table VI. Values of the Parameters m and b of Equation 1, Their Uncertainties Δm and Δb, and the Correlation Coefficient r

x_w	$10^6 m$, N m^{-1} K^{-1}	$10^6\Delta m$, N m^{-1} K^{-1}	$10^3 b$, N m^{-1}	$10^3\Delta b$, N m^{-1}	r
$AgNO_3$–$TlNO_3$–H_2O					
0	94.6	1.5	150.9	0.6	0.9991
0.100	156.4	3.4	164.4	1.3	0.9984
0.203	228.2	2.1	183.6	0.8	0.9997
0.300	289.0	3.7	197.6	1.3	0.9993
0.400	371.9	12.7	223.4	4.6	0.9959
0.500	380.5	11.0	222.6	4.0	0.9967
0.600	253.7	4.7	172.3	1.7	0.9986
0.700	160.7	2.7	134.5	1.0	0.9989
0.800	182.1	3.9	136.8	1.4	0.9982
0.900	178.7	5.3	131.2	1.9	0.9965
1	178.0		125.4		
$AgNO_3$–$TlNO_3$–$CsNO_3$–H_2O					
0	88.2	1.7	160.8	0.6	0.9988
0.100	123.1	1.5	165.0	0.6	0.9994
0.200	183.1	2.4	179.3	0.9	0.9993
0.300	177.1	5.4	170.2	2.0	0.9963
0.400	135.3	1.7	147.2	0.6	0.9994
0.500	155.1	2.1	147.5	0.8	0.9993
0.600	123.3	1.7	128.8	0.6	0.9992
0.700	153.1	1.7	133.6	0.6	0.9995
0.800	122.3	2.0	115.8	0.7	0.9989
0.900	141.7	2.1	117.3	0.8	0.9991
$AgNO_3$–$TlNO_3$–$Cd(NO_3)_2$–H_2O					
0	135.4	1.7	175.3	0.7	0.9994
0.100	232.8	2.4	206.0	0.9	0.9996
0.201	238.7	3.4	203.9	1.2	0.9992
0.250	214.1	2.3	190.2	0.8	0.9995
0.300	159.2	2.5	163.9	0.9	0.9990
0.400	181.2	2.5	162.6	0.9	0.9993
0.600	180.8	1.4	151.3	0.5	0.9998
0.700	167.2	3.1	140.3	1.1	0.9986
0.800	164.2	2.4	133.8	0.9	0.9991
0.900	172.6	1.5	130.4	0.5	0.9997
$AgNO_3$–$TlNO_3$–$Ca(NO_3)_2$–H_2O					
0	67.2	2.0	151.5	0.8	0.9972
0.100	75.1	1.1	149.9	0.4	0.9991
0.200	139.6	1.7	166.9	0.6	0.9995
0.301	104.0	1.2	146.2	0.4	0.9995
0.400	126.9	1.8	146.6	0.7	0.9992
0.500	174.5	4.6	156.1	1.7	0.9979
0.600	129.6	2.2	133.2	0.8	0.9988
0.700	136.7	2.2	129.8	0.8	0.9990
0.800	133.9	2.0	122.4	0.7	0.9991
0.900	163.2	1.7	126.7	0.6	0.9996

Table VII. Values of L of Equation 5 and L_0 of Equation 6 at Different Temperatures

salt system	T, K	L_0	L	$100 \times [(L - L_0)/L_0]$
$AgNO_3$–$TlNO_3$	353	1.88	1.80	−4.2
	372	1.95	1.80	−7.7
	383	2.02	1.84	−8.9
$AgNO_3$–$TlNO_3$–$CsNO_3$	353	2.07	1.92	−7.2
	372	2.16	2.00	−7.4
	383	2.23	2.08	−6.7
$AgNO_3$–$TlNO_3$–$Cd(NO_3)_2$	353	2.03	1.98	−2.5
	372	2.11	2.05	−2.8
	383	2.17	2.10	−3.2
$AgNO_3$–$TlNO_3$–$Ca(NO_3)_2$	353	2.04	2.00	−2.0
	372	2.14	2.10	−1.9
	383	2.21	2.19	−1.0

where k is the Boltzmann constant, a_w is the water activity in the bulk phase, and $\Gamma_{w(s)}$ is the Gibbs parameter which measures the adsorption of water per unit area, relative to the salt.

$\Gamma_{w(s)}$ is related to the number of water molecules, Γ_w, and the number of salt entities (M^{z+},zNO_3^-), Γ_s, per unit area, by

$$\Gamma_{w(s)} = \Gamma_w - \Gamma_s \frac{x_w}{1 - x_w} \qquad (9)$$

With the assumption of a monolayer surface phase, Γ_w and Γ_s are related to the water molecular area A_w and to the salt entity area A_s by the equation

$$\Gamma_s A_s + \Gamma_w A_w = 1 \qquad (10)$$

Finally, the water mole fraction in the surface phase x_w' is given by

$$x_w' = \frac{\Gamma_w}{\Gamma_w + \Gamma_s} \qquad (11)$$

The values of a_w have already been determined at 372 K by water vapor pressure measurements, except for the (Ag,Tl,Cs)-NO_3–H_2O system, over the concentration range x_w = ~0.6–1, in which case they were computed with the help of a regular solution equation.[2,11]

Generally, only rough values of the molecular areas can be introduced into the equations of the surface phase thermodynamics, and they are considered as independent of the composition.

Table VIII. The Water Mole Fraction x_w' in the Surface Phase of the System $AgNO_3$–$TlNO_3$–H_2O at 372 K[a]

x_w	a_w	$\Gamma_{w(s)}$	Γ_s	Γ_w	x_w'
0	0	0	58×10^{17}	0	0
0.100	0.138	16×10^{17}	51×10^{17}	21×10^{17}	0.29
0.203	0.277	26×10^{17}	45×10^{17}	38×10^{17}	0.45
0.300	0.413	41×10^{17}	38×10^{17}	57×10^{17}	0.60
0.400	0.535	50×10^{17}	33×10^{17}	72×10^{17}	0.68
0.500	0.643	56×10^{17}	29×10^{17}	85×10^{17}	0.75
0.600	0.737	66×10^{17}	23×10^{17}	10×10^{18}	0.81
0.700	0.804	84×10^{17}	16×10^{17}	12×10^{18}	0.88
0.800	0.854	12×10^{18}	70×10^{16}	15×10^{18}	0.95
0.900	0.908	14×10^{18}	25×10^{16}	16×10^{18}	0.98
1	1	16×10^{18}	0	16×10^{18}	1

[a] $\Gamma_{w(s)}$, Γ_s, and Γ_w are given in m^{-2}.

Table IX. The Water Mole Fraction x_w' in the Surface Phase of the System $AgNO_3$–$TlNO_3$–$CsNO_3$–H_2O at 372 K[a]

x_w	a_w	$\Gamma_{w(s)}$	Γ_s	Γ_w	x_w'
0	0	0	57×10^{17}	0	0
0.100	0.144	17×10^{17}	50×10^{17}	23×10^{17}	0.31
0.200	0.283	29×10^{17}	44×10^{17}	40×10^{17}	0.48
0.300	0.414	45×10^{17}	37×10^{17}	60×10^{17}	0.62
0.400	0.532	69×10^{17}	27×10^{17}	87×10^{17}	0.76
0.500	0.636	94×10^{17}	18×10^{17}	11×10^{18}	0.86
0.600	0.722	12×10^{18}	98×10^{16}	14×10^{18}	0.93
0.700	0.789	13×10^{18}	66×10^{16}	15×10^{18}	0.96
0.800	0.838	14×10^{18}	39×10^{16}	15×10^{18}	0.97
0.900	0.888	15×10^{18}	20×10^{16}	16×10^{18}	0.99
1	1	16×10^{18}	0	16×10^{18}	1

[a] $\Gamma_{w(s)}$, Γ_s, and Γ_w are given in m^{-2}.

Table X. The Water Mole Fraction x_w' in the Surface Phase of the System $AgNO_3$–$TlNO_3$–$Cd(NO_3)_2$–H_2O at 372 K[a]

x_w	a_w	$\Gamma_{w(s)}$	Γ_s	Γ_w	x_w'
0	0	0	56×10^{17}	0	0
0.100	0.062	10×10^{17}	51×10^{17}	16×10^{17}	0.24
0.201	0.138	19×10^{17}	46×10^{17}	30×10^{17}	0.40
0.250	0.180	30×10^{17}	41×10^{17}	43×10^{17}	0.51
0.300	0.234	42×10^{17}	36×10^{17}	57×10^{17}	0.61
0.400	0.345	44×10^{17}	33×10^{17}	66×10^{17}	0.66
0.600	0.591	55×10^{17}	25×10^{17}	92×10^{17}	0.79
0.700	0.709	72×10^{17}	18×10^{17}	11×10^{18}	0.87
0.800	0.807	98×10^{17}	95×10^{16}	14×10^{18}	0.93
0.900	0.894	12×10^{18}	41×10^{16}	15×10^{18}	0.97
1	1	15×10^{18}	0	16×10^{18}	1

[a] $\Gamma_{w(s)}$, Γ_s, and Γ_w are given in m^{-2}.

Table XI. The Water Mole Fraction x_w' in the Surface Phase of the System $AgNO_3$–$TlNO_3$–$Ca(NO_3)_2$–H_2O at 372 K[a]

x_w	a_w	$\Gamma_{w(s)}$	Γ_s	Γ_w	x_w'
0	0	0	56×10^{17}	0	0
0.100	0.061	12×10^{17}	50×10^{17}	17×10^{17}	0.26
0.200	0.137	23×10^{17}	44×10^{17}	34×10^{17}	0.44
0.301	0.232	30×10^{17}	40×10^{17}	47×10^{17}	0.54
0.400	0.344	46×10^{17}	33×10^{17}	69×10^{17}	0.68
0.500	0.468	49×10^{17}	29×10^{17}	78×10^{17}	0.73
0.600	0.593	69×10^{17}	21×10^{17}	10×10^{18}	0.83
0.700	0.712	77×10^{17}	17×10^{17}	12×10^{18}	0.87
0.800	0.808	10×10^{18}	91×10^{16}	14×10^{18}	0.94
0.900	0.890	12×10^{18}	35×10^{16}	15×10^{18}	0.98
1	1	15×10^{18}	0	16×10^{18}	1

[a] $\Gamma_{w(s)}$, Γ_s, and Γ_w are given in m^{-2}.

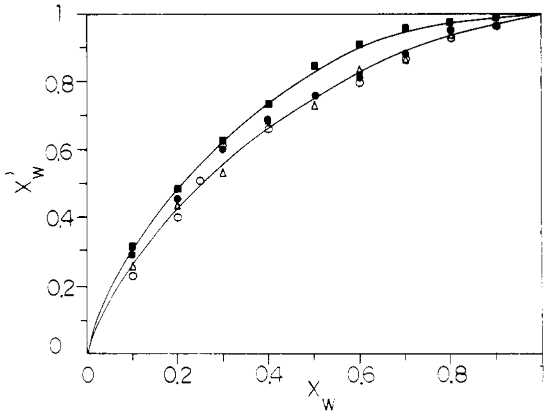

Figure 5. The water mole fraction in the surface phase x_w' as a function of the water mole fraction in the bulk phase x_w, at 372 K: (●) $AgNO_3$–$TlNO_3$–H_2O; (■) $AgNO_3$–$TlNO_3$–$CsNO_3$–H_2O; (○) $AgNO_3$–$TlNO_3$–$Cd(NO_3)_2$–H_2O; and (△) $AgNO_3$–$TlNO_3$–$Ca(NO_3)_2$–H_2O.

Boardman, Palmer, and Heymann,[33] in a study of the surface tension of binary halide and nitrate mixtures, Nissen and van Domelan,[34] in the calculation of isothermal surface tension curves of molten salt mixtures by regular solution theories, and Goldsack and Sarvas,[35] in the derivation of surface tension equations for organic systems, took values of molecular areas deduced from molar volumes by simple equations. Concerning the nitrate–water systems, we found that volumetric methods of estimation of A_s and A_w could yield negative values of the surface mole fractions as calculated by means of eqs 8–11. Thus, for the $(Ag,Tl)NO_3$–H_2O and $(Ag,Tl,Cs)NO_3$–H_2O systems, the values of x_w' are negative in the case of the solutions rich in water ($x_w >$ ~0.6–0.7), probably due to an overestimation of the water surface particle by these volumetric methods. Yet, positive and reasonable values of the surface water mole fraction were obtained over the whole concentration range, using a method of evaluation based on the particle radii.

The particle area of water was calculated with the equation

$$A_w = \pi r_w^2 \tag{12}$$

The water particle radius r_w, confirmed by Marcus[36] to be 1.39 Å in aqueous solutions, gives 6.1 Å^2 for the value of A_w.

To take into account the presence of various ions in an anhydrous salt mixture, average values of the salt entity area were calculated by

$$A_s = \pi \sum_i X_i (r_{i+}^2 + z_{i+} r_-^2) \tag{13}$$

where X_i is the mole fraction of the salt i in the anhydrous salt mixture, r_{i+} is its cation radius, z_{i+} is its cation valency, and r_- is the NO_3^- radius. The classical Pauling cationic radii[25] and the NO_3^- radius proposed by Waddington[37] are, in Å, the following: Ag^+, 1.26; Tl^+, 1.47; Cs^+, 1.67; Cd^{2+}, 0.97; Ca^{2+}, 0.99; NO_3^-, 1.89.

From these radii, the values of A_s are 17.1 Å^2 for $(Ag,Tl)NO_3$, 17.4 Å^2 for $(Ag,Tl,Cs)NO_3$, and 17.9 Å^2 for $(Ag,Tl,Cd)NO_3$ and $(Ag,Tl,Ca)NO_3$.

Tables VIII–XI contain all the data used to calculate x_w' at 372 K, and the curves $x_w' = f(x_w)$ are shown in Figure 5.

It may be observed that the curves $x_w' = f(x_w)$ are of the same shape for the four systems and indicate a steady enrichment of water in the surface phase as x_w is increased, over the whole concentration range. In the case of the solutions of water in the salt, i.e., x_w = 0 to ~0.5, this enrichment is rapid. What is somewhat unexpected is the fact that the values of x_w' of the systems containing Cd^{2+} and Ca^{2+} are close to those of the other systems, especially the $(Ag,Tl)NO_3$–H_2O system.

If the relatively strong hydrating power of the cations Cd^{2+} and Ca^{2+} is not reflected by the concentration in the surface as it is

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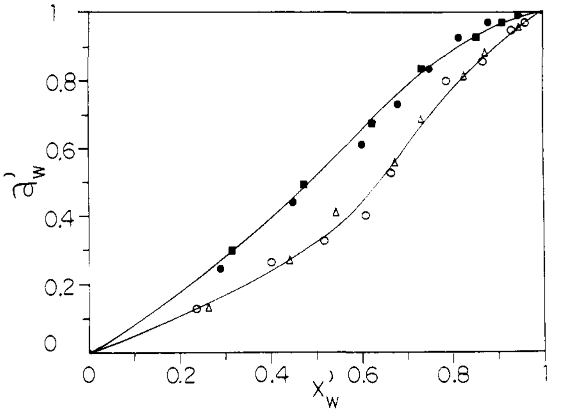

Figure 6. The water activity in the surface phase a_w' as a function of the water mole fraction in the surface phase x_w', at 372 K: (●) $AgNO_3$–$TlNO_3$–H_2O; (■) $AgNO_3$–$TlNO_3$–$CsNO_3$–H_2O; (○) $AgNO_3$–$TlNO_3$–$Cd(NO_3)_2$–H_2O; and (△) $AgNO_3$–$TlNO_3$–$Ca(NO_3)_2$–H_2O.

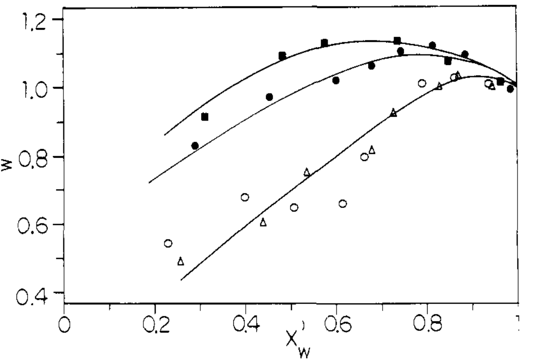

Figure 7. The water activity coefficient in the surface phase γ_w' as a function of the water mole fraction in the surface phase x_w', at 372 K: (●) $AgNO_3$–$TlNO_3$–H_2O; (■) $AgNO_3$–$TlNO_3$–$CsNO_3$–H_2O; (○) $AgNO_3$–$TlNO_3$–$Cd(NO_3)_2$–H_2O; and (△) $AgNO_3$–$TlNO_3$–$Ca(NO_3)_2$–H_2O.

by the curves $\sigma = f(x_w)$, then it should be reflected by the water activity and/or activity coefficient in the surface.

Computation of the water activity in the surface phase, a_w', from the water activity in the bulk phase, a_w, was performed by means of the Butler equation[38] written in the form

$$a_w' = a_w \exp\left[\frac{A_w(\sigma - \sigma_w)}{kT}\right] \tag{14}$$

The related water activity coefficient in the surface phase γ_w' was obtained from its definition

$$\gamma_w' = a_w'/x_w' \tag{15}$$

The parameters a_w' and γ_w' are plotted against x_w' in Figures 6 and 7. It is seen that the addition of Cs^+ to the $(Ag,Tl)NO_3$ system does not change practically the position of the curve $a_w' = f(x_w')$. On the contrary, the addition of Cd^{2+} and Ca^{2+} sensitively lowers the position of the curve, both cations having the same effect. This influence of the nature of the cations is similar to what is observed for the water activity in the bulk phase, listed in Tables VIII–XI. It is noticed that when the water is the solute, i.e. $x_w = 0$ to ~0.5, the relative positions of the curves $\gamma_w' = f(x_w')$ are in correlation with the hydrating power of the cations contained in these mixtures, Cd^{2+} and Ca^{2+} having the strongest hydrating power and Cs^+ the weakest one.[14,17,19]

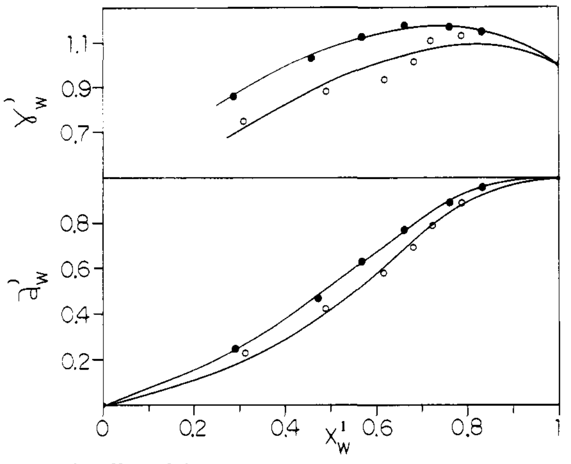

Figure 8. The effect of the temperature on the water activity a_w' and the water activity coefficient γ_w' in the surface phase for the $AgNO_3$–$TlNO_3$–H_2O system: (●) 360 and (○) 384 K.

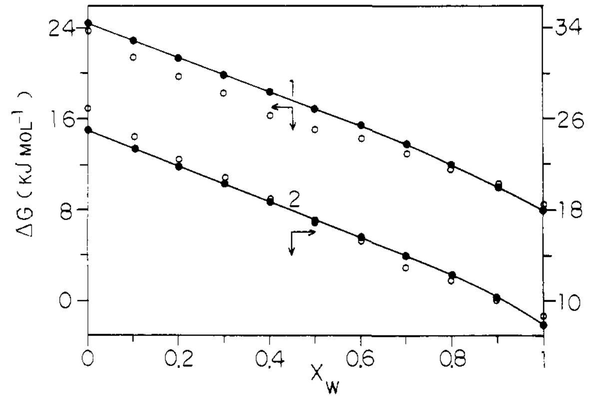

Figure 9. The free energy of hole formation $\overline{\Delta G_\sigma}$ and the free energy of activation of the viscosity ΔG_η^* as functions of the water mole fraction x_w, at 372 K: (1) $AgNO_3$–$TlNO_3$–H_2O and (2) $AgNO_3$–$TlNO_3$–$CsNO_3$–H_2O; (●) ΔG_η^* and (○) $\overline{\Delta G_\sigma}$.

The $(Ag,Tl)NO_3$–H_2O system is the only one for which water vapor pressure data are available at other temperatures than 372 K,[20] allowing testing of the influence of the temperature on a_w' and γ_w'. Figure 8 shows that a temperature increase lowers the values of the water activity and activity coefficient in the surface phase. A similar temperature effect was observed on the water activity and activity coefficient in the bulk phase.[20]

4. Surface Tension and Hole Theory. The Fürth hole theory of liquids[22] makes use of the following equation expressing the molar free energy of hole formation ΔG_σ

$$\Delta G_\sigma = 4\pi r^2 \sigma N_A \tag{16}$$

where r is the radius of a hole and N_A is the Avogadro constant.

Equation 16 has played an important role in the discussion of molten salt properties and the development of their theories.[39–44] In these approaches it has frequently been concluded, or assumed, that a hole size is comparable to that of an ion. In this respect, Janz and Saegusa,[41] in a study on the viscosity on molten carbonates, compared the free energy and enthalpy of hole formation to the free energy and enthalpy of activation of viscous flow in the Eyring equation[23]

$$\eta = \frac{hN_A}{V} \exp\left(\frac{\Delta G_\eta^*}{RT}\right) \tag{17}$$

in which η is the viscosity coefficient, ΔG_η^* is the molar free energy

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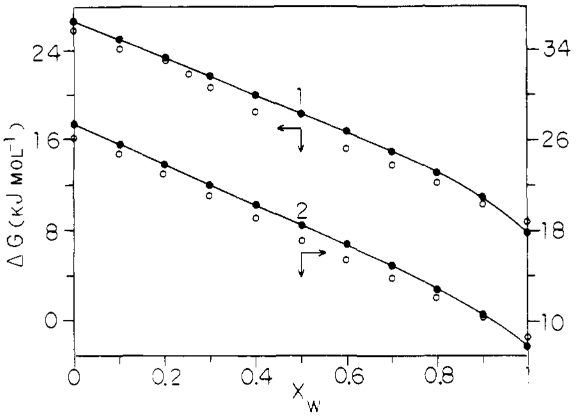

Figure 10. The free energy of hole formation $\overline{\Delta G_\sigma}$ and the free energy of activation of the viscosity ΔG_η^* as functions of the water mole fraction x_w, at 372 K: (1) $AgNO_3$-$TlNO_3$-$Cd(NO_3)_2$-H_2O and (2) $AgNO_3$-$TlNO_3$-$Ca(NO_3)_2$-H_2O; (●) ΔG_η^* and (○) $\overline{\Delta G_\sigma}$.

of activation of viscous flow, V is the molar volume, R is the gas constant, and h is the Planck constant.

For the salt-water systems of this study, over the whole concentration range, average values of ΔG_σ were calculated taking into account all the species in the solutions:

$$\overline{\Delta G_\sigma} = 4\pi\sigma N_A \overline{r_i^2} \qquad (18)$$

The parameter $\overline{r_i^2}$ is the weight average of the squared particle radii given by

$$\overline{r_i^2} = \frac{x_s[\sum_i X_i(r_{i+}^2 + z_{i+}r_-^2)] + x_w r_w^2}{x_s[\sum_i X_i(1 + z_{i+})] + x_w} \qquad (19)$$

The values of $\overline{\Delta G_\sigma}$ obtained from eq 18 and those of ΔG_η^* in eq 17 determined in previous investigations,[13,15] for the nitrate-water systems at 372 K, are plotted against x_w in Figures 9 and 10. It can be seen that $\overline{\Delta G_\sigma}$ is close to ΔG_η^*. These results lend support to the assumption that hole formation is an essential step of the viscous flow mechanisms not only in certain types of molten salts but in dilute aqueous solutions and water as well, above ordinary temperatures.

Contrary to $\overline{\Delta G_\sigma}$ and ΔG_η^*, the entropy of hole formation and that of activation in viscous flow cannot be compared to one another, since the particle radii provide approximate evaluations of hole sizes and their variation with the temperature is not known.

4. Conclusion

This study showed that the application of the Guggenheim and Adam method and the Butler equation yield reasonable orders of magnitude of the water mole fraction, activity, and activity coefficient in the surface phase of some nitrate-water melts, over the whole concentration range from fused salts to water. The correlation between the water activity, or activity coefficient, in the surface phase and the hydrating power of the cations predispose to consider the monolayer surface phase as a convenient model. Besides, it was found that the free energy of hole formation in the Fürth theory of liquids is close to the free energy of activation for the viscous flow in the Eyring equation. This result tends to confirm that holes may be considered as fundamental structural entities in the chemistry of all solutions from molten salts to water.

Sequential Bond Energies of $Fe(CO)_x^+$ (x = 1-5): Systematic Effects on Collision-Induced Dissociation Measurements

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Abstract: Collision-induced dissociation (CID) of $Fe(CO)_x^+$ (x = 1-5) is studied by using guided ion beam mass spectrometry. A flow tube source is used to produce thermalized iron carbonyl ions. We discuss in detail our threshold modeling procedures and several possible sources of systematic error that can affect accurate determination of bond energies from CID threshold measurements. Careful analysis of CID thresholds provides the following 0 K bond dissociation energies: $D°[(CO)_4Fe^+$-$CO]$ = 1.16 ± 0.04 eV (26.8 ± 0.9 kcal/mol); $D°[(CO)_3Fe^+$-$CO]$ = 1.07 ± 0.07 eV (24.7 ± 1.4 kcal/mol); $D°[(CO)_2Fe^+$-$CO]$ = 0.69 ± 0.05 eV (15.9 ± 1.2 kcal/mol); and $D°[(CO)Fe^+$-$CO]$ = 1.61 ± 0.15 eV (36.1 ± 1.8 kcal/mol). We also measure $D°[Fe^+$-$CO]$ = 1.59 ± 0.08 eV (36.6 ± 1.8 kcal/mol), but this dissociation may correspond to production of excited $Fe^+(^4F)$, in which case the $D°[Fe^+$-$CO]$ for dissociation to $Fe^+(^6D)$ is 1.36 ± 0.08 eV (31.3 ± 1.8 kcal/mol). The sum of the five bond energies, 6.12 ± 0.09 eV (140.1 ± 3.1 kcal/mol), is in excellent agreement with literature thermochemistry, and the individual bond strengths are in reasonable accord with prior measurements and theoretical calculations.

Introduction

In the century since the first synthesis of $Fe(CO)_5$,[1] iron carbonyl and its derivatives have found myriad uses as reagents for chemical synthesis.[2] Besides numerous reactivity studies, a considerable amount of experimental[3-7] and theoretical[8-11] effort has gone into elucidating the fundamental physical properties of these species. A similarly large research effort has been devoted to iron carbonyl ions. While these ions (especially the anions) are known and have been studied in solution,[12] most of the work concerning them has been done in the gas phase. The gas phase is an ideal arena for detailed study of these highly reactive species. Solvation effects are absent, and the coordinatively and electronically unsaturated ions can be isolated and their reactivity observed.

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