# Transport, Thermodynamic, and Volumetric Properties of a New Bridging Salt–Water System: [TlNO₃–CsNO₃–Cd(NO₃)₂]–H₂O

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**Abstract:** Until now, few salt–water systems have been investigated regarding the electrical conductance, the viscosity, the surface tension, the water vapor pressure, and the molar volume as functions of the temperature and the water concentration, from pure fused salts to dilute aqueous solutions. These systems referred to as *bridging systems* are of considerable interest because they allow one to establish a link between the two research fields: fused salts and dilute aqueous solutions. In this paper, we report the results on the measurements of the above-mentioned properties of a new bridging system whose salt composition is $0.467TlNO_3$–$0.214CsNO_3$–$0.319Cd(NO_3)_2$. The results are discussed in terms of the BET model, the transition-state theory, and the hole and liquid quasi-lattice concepts. A remarkable feature of the equations used in the discussion lies in the fact that they can be applied over a large water concentration range, using few empirical parameters, in some cases only one. The empirical parameters are examined in relation to the nature of the ions and the effect of the temperature. Correlations that appear chemically significant are noted and discussed.

## 1. Introduction

Now and then, it has been suggested that more progress in the understanding of concentrated aqueous solutions could come from the consideration of solutions obtained by adding water to fused salts rather than concentrating dilute aqueous solutions. From this point of view, electrolyte systems which can be investigated in the liquid phase from pure fused salt to dilute aqueous solutions are of considerable importance.

In earlier publications,[1–3] some transport and thermodynamic properties of fused nitrate–water systems were studied as functions of the water mole fraction, over nearly the whole concentration range. These systems referred to as *bridging systems* are of considerable interest because they allow one to establish a link between the two research fields: fused salts and dilute aqueous solutions. Until now, few of them have been investigated regarding the following fundamental properties: the electrical conductance, the viscosity, the surface tension, the water vapor pressure, and the molar volume. These systems were obtained by addition of water to nitrate mixtures having the following fixed compositions, in mole fraction: $0.515AgNO_3$–$0.485TlNO_3$ and $0.464AgNO_3$–$0.436TlNO_3$–$0.100M(NO_3)_n$, with M = Cs, Cd, and Ca. These molten salts mixtures were chosen because, around 373 K, they are liquid and completely miscible with water, so that the establishment of an experimental link between molten salts and aqueous solutions is facilitated.

Recently,[4] preliminary results were obtained on the viscosity and the electrical conductance of a new bridging salt–water system

whose salt composition is $0.467TlNO_3$–$0.214CsNO_3$–$0.319Cd(NO_3)_2$. According to Protsenko and Rubleva,[5] this salt composition is that of a eutectic mixture whose freezing point is 357 K. In the present paper, we report the results of an investigation of the surface tension and the water vapor pressure of this system, together with the effect of the temperature on the electrical conductance, the viscosity, and the molar volume, from pure salt to pure water or dilute aqueous solutions, between 360 and 400 K.

Given the nature of the methodological approach adopted in this study, the discussion of the experimental results will be made using concepts which have been successfully applied to molten salts.[6–8]

## 2. Experimental Procedures and Results

The viscosities $\eta$ were measured with an Ostwald–Ubbelohde viscometer, the densities $\rho$, by pycnometry, the specific electrical conductances $\chi$, with a digital conductance meter YSI Model 32, the surface tensions $\sigma$, by the capillary rise method, and the water vapor pressures $p$, with a dew-point apparatus. The technical details and the measurement procedures are given in preceding papers.[1,4,9–12] The experimental values of these properties are

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**Table I.** The Density $\rho$, Molar Volume $V$, and Excess Molar Volume $V^{ex}$ of the $TlNO_3$–$CsNO_3$–$Cd(NO_3)_2$–$H_2O$ System, as Functions of Composition and Temperature[a]

| $x_w$ | $x_1$ | $x_2$ | $x_3$ | $\rho \times 10^{-3}$ (kg m$^{-3}$) | $V \times 10^6$ (m$^3$ mol$^{-1}$) | $V^{ex} \times 10^6$ (m$^3$ mol$^{-1}$) |
|---|---|---|---|---|---|---|
| | | | | $T = 368.2$ K | | |
| 0 | 0.467 | 0.214 | 0.319 | 3.960 | 60.99 | 0 |
| 0.198 | 0.375 | 0.172 | 0.256 | 3.796 | 51.97 | −0.65 |
| 0.490 | 0.238 | 0.109 | 0.163 | 3.381 | 39.04 | −1.24 |
| 0.630 | 0.173 | 0.079 | 0.118 | 3.053 | 32.99 | −1.37 |
| 0.784 | 0.101 | 0.046 | 0.069 | 2.491 | 26.64 | −1.23 |
| 0.814 | 0.087 | 0.040 | 0.059 | 2.342 | 25.44 | −1.15 |
| 0.936 | 0.030 | 0.014 | 0.020 | 1.547 | 20.89 | −0.54 |
| 1 | 0 | 0 | 0 | 0.962 | 18.73 | 0 |
| | | | | $T = 376.2$ K | | |
| 0 | 0.467 | 0.214 | 0.319 | 3.950 | 61.15 | 0 |
| 0.200 | 0.374 | 0.171 | 0.255 | 3.779 | 52.08 | −0.61 |
| 0.400 | 0.280 | 0.128 | 0.191 | 3.530 | 43.09 | −1.14 |
| 0.630 | 0.173 | 0.079 | 0.118 | 3.044 | 33.09 | −1.40 |
| 0.707 | 0.137 | 0.063 | 0.093 | 2.787 | 29.96 | −1.28 |
| 0.845 | 0.072 | 0.033 | 0.049 | 2.151 | 24.48 | −0.92 |
| 0.900 | 0.047 | 0.021 | 0.032 | 1.808 | 22.33 | −0.74 |
| 1 | 0 | 0 | 0 | 0.956 | 18.84 | 0 |
| | | | | $T = 383.2$ K | | |
| 0 | 0.467 | 0.214 | 0.319 | 3.936 | 61.35 | 0 |
| 0.151 | 0.396 | 0.182 | 0.271 | 3.817 | 54.43 | −0.52 |
| 0.300 | 0.327 | 0.150 | 0.223 | 3.655 | 47.74 | −0.89 |
| 0.430 | 0.266 | 0.122 | 0.182 | 3.470 | 41.91 | −1.20 |
| 0.576 | 0.198 | 0.091 | 0.135 | 3.171 | 35.57 | −1.35 |
| 0.725 | 0.128 | 0.059 | 0.088 | 2.707 | 29.36 | −1.25 |
| 0.829 | 0.080 | 0.037 | 0.055 | 2.235 | 25.16 | −1.03 |
| 1 | 0 | 0 | 0 | 0.951 | 18.94 | 0 |

$^a$ $x_w$, $x_1$, $x_2$ and $x_3$ are the mole fractions respectively of $H_2O$, $TlNO_3$, $CsNO_3$, and $Cd(NO_3)_2$.

given in Tables I–V, as functions of the temperature and the composition of the system $TlNO_3$–$CsNO_3$–$Cd(NO_3)_2$–$H_2O$, in which the mole ratios $TlNO_3$/$CsNO_3$ and $TlNO_3$/$Cd(NO_3)_2$ are respectively fixed at 2.18 and 1.46.

In Table I are also included the values of the molar volume $V$ and the excess molar volume $V^{ex}$. The molar volume $V$ of a solution is related to its density $\rho$ by

$$V = \frac{x_s \sum_i X_i M_i + x_w M_w}{\rho} \qquad (1)$$

where $M_i$ is the molecular weight of the salt $i$, $M_w$, the water molecular weight, $X_i$, the mole fraction of the salt $i$ in the anhydrous salt system, $x_s$, the salt mole fraction in the salt–water system, and $x_w$, the water mole fraction.

The excess molar volume $V^{ex}$ is defined by

$$V^{ex} = V - V^{id} \qquad (2)$$

where $V^{id}$ is the ideal molar volume calculated by the expression

$$V^{id} = x_s V_s + x_w V_w \qquad (3)$$

in which $V_s$ and $V_w$ are respectively the molar volume of the anhydrous salt mixture and the pure water.

Together with the values of the specific electrical conductance $\chi$, those of the equivalent electrical conductance $\Lambda$ are given in Table III. The values of $\Lambda$ were obtained from $\chi$ and $V$ by the equation

$$\Lambda = \frac{\chi V}{x_s \sum_i X_i n_{ei}} \qquad (4)$$

where $n_{ei}$ is the electrochemical valency of the salt i.

In addition to the values of the water vapor pressure $p$, Table V includes those of the fugacity $f_w$, the activity $a_w$, and the activity

**Table II.** The Viscosity $\eta$ of the $TlNO_3$–$CsNO_3$–$Cd(NO_3)_2$–$H_2O$ System, as Function of Composition and Temperature[a]

| $T$ (K) | $\eta \times 10^3$ (kg m$^{-1}$ s$^{-1}$) | $T$ (K) | $\eta \times 10^3$ (kg m$^{-1}$ s$^{-1}$) |
|---|---|---|---|
| $x_w = 0$; $x_1 = 0.467$; $x_2 = 0.214$; $x_3 = 0.319$ | | $x_w = 0.100$; $x_1 = 0.420$; $x_2 = 0.193$; $x_3 = 0.287$ | |
| 368.9 | 286 | 369.6 | 143.2 |
| 373.6 | 213 | 372.6 | 123.0 |
| 377.9 | 166.2 | 375.7 | 104.7 |
| 383.2 | 127.7 | 378.9 | 90.60 |
| 387.6 | 103.6 | 382.6 | 77.38 |
| 392.5 | 84.27 | 383.2 | 75.76 |
| 396.5 | 71.65 | 385.2 | 69.24 |
| 399.6 | 64.02 | 388.8 | 60.15 |
| 402.8 | 56.73 | 393.0 | 52.10 |
| $x_w = 0.200$; $x_1 = 0.374$; $x_2 = 0.171$; $x_3 = 0.255$ | | $x_w = 0.300$; $x_1 = 0.327$; $x_2 = 0.150$; $x_3 = 0.223$ | |
| 369.3 | 78.35 | 368.3 | 45.18 |
| 371.7 | 70.58 | 371.4 | 40.39 |
| 374.4 | 63.12 | 374.4 | 36.40 |
| 376.8 | 57.05 | 377.5 | 33.02 |
| 380.6 | 49.97 | 380.1 | 30.51 |
| 383.2 | 45.57 | 382.1 | 28.91 |
| 385.7 | 42.00 | 383.6 | 27.67 |
| 388.7 | 38.18 | 386.3 | 25.62 |
| 391.3 | 35.31 | 388.4 | 24.24 |
| $x_w = 0.403$; $x_1 = 0.279$; $x_2 = 0.128$ $x_3 = 0.190$ | | $x_w = 0.500$; $x_1 = 0.233$; $x_2 = 0.107$ $x_3 = 0.160$ | |
| 366.6 | 26.27 | 366.3 | 14.53 |
| 369.9 | 23.79 | 368.5 | 13.90 |
| 372.3 | 21.99 | 371.8 | 12.98 |
| 374.5 | 20.77 | 374.4 | 12.38 |
| 376.5 | 19.79 | 377.5 | 11.57 |
| 379.7 | 18.34 | 379.6 | 11.10 |
| 381.9 | 17.45 | 381.7 | 10.67 |
| 383.6 | 16.76 | 384.3 | 10.17 |
| 385.6 | 16.13 | 386.3 | 9.75 |
| $x_w = 0.630$; $x_1 = 0.173$; $x_2 = 0.079$; $x_3 = 0.118$ | | $x_w = 0.700$; $x_1 = 0.140$; $x_2 = 0.064$; $x_3 = 0.096$ | |
| 366.1 | 6.40 | 365.2 | 3.84 |
| 368.0 | 6.17 | 367.7 | 3.67 |
| 369.8 | 5.93 | 369.8 | 3.51 |
| 372.4 | 5.66 | 372.4 | 3.42 |
| 374.5 | 5.49 | 375.2 | 3.29 |
| 376.8 | 5.30 | 377.4 | 3.20 |
| 379.4 | 5.10 | 380.8 | 3.06 |
| 381.4 | 4.96 | 382.9 | 2.96 |
| 384.3 | 4.75 | 384.9 | 2.88 |
| $x_w = 0.800$; $x_1 = 0.093$; $x_2 = 0.043$; $x_3 = 0.064$ | | $x_w = 0.900$; $x_1 = 0.047$; $x_2 = 0.021$; $x_3 = 0.032$ | |
| 363.5 | 1.76 | 354.8 | 0.82 |
| 365.1 | 1.74 | 357.1 | 0.80 |
| 367.8 | 1.67 | 359.2 | 0.78 |
| 370.0 | 1.64 | 362.4 | 0.75 |
| 371.7 | 1.60 | 365.7 | 0.73 |
| 373.9 | 1.58 | 368.7 | 0.70 |
| 376.5 | 1.52 | 371.7 | 0.68 |
| 379.4 | 1.48 | 373.5 | 0.67 |
| 381.9 | 1.46 | 375.6 | 0.66 |

$^a$ $x_w$, $x_1$, $x_2$, and $x_3$ are the mole fractions respectively of $H_2O$, $TlNO_3$, $CsNO_3$, and $Cd(NO_3)_2$.

coefficient $\gamma_w$ of water calculated by means of the equations

$$a_w = f_w/f_w^0 \qquad (5)$$

$$f_w = p \exp(Bp/RT) \qquad (6)$$

$$\gamma_w = a_w/x_w \qquad (7)$$

where $f_w^0$ is the fugacity of pure water, $R$, the gas constant and $T$, the Kelvin temperature. $B$, the second virial coefficient of water, is given by

**Table III.** The Specific Electrical Conductance $\chi$ and Equivalent Electrical Conductance $\Lambda$ of the $TlNO_3$–$CsNO_3$–$Cd(NO_3)_2$–$H_2O$ System, as Functions of Composition and Temperature[a]

| $T$ (K) | $\chi$ ($\Omega^{-1}\ m^{-1}$) | $\Lambda \times 10^4$ ($\Omega^{-1}\ m^2$ equiv$^{-1}$) | $T$ (K) | $\chi$ ($\Omega^{-1}\ m^{-1}$) | $\Lambda \times 10^4$ ($\Omega^{-1}\ m^2$ equiv$^{-1}$) |
|---|---|---|---|---|---|
| $x_w = 0$; $x_1 = 0.467$; $x_2 = 0.214$; $x_3 = 0.319$ | | | $x_w = 0.100$; $x_1 = 0.420$; $x_2 = 0.193$; $x_3 = 0.287$ | | |
| 367.6 | 0.91 | 0.42 | 366.8 | 1.49 | 0.71 |
| 372.5 | 1.18 | 0.55 | 371.7 | 1.86 | 0.88 |
| 377.6 | 1.52 | 0.71 | 375.2 | 2.15 | 1.03 |
| 382.3 | 1.89 | 0.88 | 378.2 | 2.43 | 1.16 |
| 388.5 | 2.36 | 1.10 | 382.6 | 2.83 | 1.36 |
| 393.4 | 2.81 | 1.31 | 386.5 | 3.24 | 1.55 |
| 398.6 | 3.35 | 1.57 | 390.9 | 3.73 | 1.79 |
| 402.3 | 3.75 | 1.76 | 393.8 | 4.08 | 1.96 |
| | | | 396.7 | 4.47 | 2.15 |
| $x_w = 0.200$; $x_1 = 0.374$; $x_2 = 0.171$; $x_3 = 0.255$ | | | $x_w = 0.300$; $x_1 = 0.327$; $x_2 = 0.150$; $x_3 = 0.223$ | | |
| 368.6 | 2.61 | 1.29 | 367.7 | 3.95 | 2.03 |
| 371.7 | 2.93 | 1.44 | 371.0 | 4.38 | 2.25 |
| 374.9 | 3.28 | 1.62 | 374.1 | 4.80 | 2.47 |
| 377.4 | 3.57 | 1.76 | 376.7 | 5.19 | 2.68 |
| 380.7 | 3.92 | 1.94 | 379.3 | 5.51 | 2.84 |
| 382.8 | 4.17 | 2.06 | 382.4 | 5.97 | 3.08 |
| 385.5 | 4.52 | 2.24 | 384.7 | 6.32 | 3.27 |
| 388.8 | 4.94 | 2.45 | 387.6 | 6.78 | 3.51 |
| 391.3 | 5.30 | 2.63 | 390.2 | 7.17 | 3.71 |
| $x_w = 0.403$; $x_1 = 0.279$; $x_2 = 0.128$; $x_3 = 0.190$ | | | $x_w = 0.500$; $x_1 = 0.233$; $x_2 = 0.107$; $x_3 = 0.160$ | | |
| 366.1 | 5.86 | 3.18 | 364.7 | 8.15 | 4.76 |
| 370.0 | 6.50 | 3.53 | 367.5 | 8.90 | 5.20 |
| 372.3 | 6.88 | 3.75 | 370.8 | 9.57 | 5.60 |
| 375.4 | 7.41 | 4.04 | 373.8 | 10.20 | 5.98 |
| 378.3 | 7.91 | 4.32 | 376.9 | 10.80 | 6.35 |
| 381.2 | 8.37 | 4.57 | 379.5 | 11.26 | 6.62 |
| 383.7 | 8.83 | 4.83 | 382.4 | 11.90 | 7.01 |
| 386.1 | 9.25 | 5.07 | 385.5 | 12.57 | 7.41 |
| 387.3 | 9.46 | 5.19 | | | |
| $x_w = 0.630$; $x_1 = 0.173$; $x_2 = 0.079$; $x_3 = 0.118$ | | | $x_w = 0.700$; $x_1 = 0.140$; $x_2 = 0.064$; $x_3 = 0.096$ | | |
| 364.9 | 14.40 | 9.72 | 363.8 | 18.99 | 14.41 |
| 367.1 | 15.04 | 10.16 | 365.6 | 19.59 | 14.88 |
| 369.9 | 15.78 | 10.68 | 368.0 | 20.37 | 15.49 |
| 372.1 | 16.34 | 11.07 | 370.7 | 21.22 | 16.16 |
| 374.3 | 16.94 | 11.49 | 372.6 | 21.76 | 16.60 |
| 376.3 | 17.47 | 11.86 | 375.8 | 22.61 | 17.28 |
| 379.4 | 18.07 | 12.28 | 378.2 | 23.17 | 17.74 |
| 381.8 | 18.67 | 12.71 | 381.0 | 23.90 | 18.32 |
| 384.4 | 19.31 | 13.16 | 384.4 | 24.71 | 18.98 |
| 386.3 | 19.77 | 13.48 | | | |
| $x_w = 0.800$; $x_1 = 0.093$; $x_2 = 0.043$; $x_3 = 0.064$ | | | $x_w = 0.900$; $x_1 = 0.047$; $x_2 = 0.021$; $x_3 = 0.032$ | | |
| 361.9 | 27.75 | 27.42 | 353.9 | 33.29 | 55.51 |
| 363.7 | 28.35 | 28.04 | 355.5 | 33.78 | 56.40 |
| 365.6 | 28.77 | 28.49 | 357.4 | 34.42 | 57.53 |
| 368.0 | 29.48 | 29.22 | 360.4 | 35.26 | 59.07 |
| 370.6 | 30.22 | 30.00 | 363.3 | 36.22 | 60.79 |
| 373.5 | 31.06 | 30.89 | 366.5 | 37.17 | 62.53 |
| 376.5 | 31.98 | 31.85 | 371.0 | 38.55 | 65.04 |
| 379.8 | 32.83 | 32.75 | 373.4 | 39.18 | 66.22 |
| 382.7 | 33.61 | 33.57 | 377.7 | 40.38 | 68.45 |

[a] $x_w$, $x_1$, $x_2$ and $x_3$ are the mole fractions respectively of $H_2O$, $TlNO_3$, $CsNO_3$, and $Cd(NO_3)_2$.

$$B\ (cm^3\ mol^{-1}) = -7669 + 33.6T - 0.038T^2 \qquad (8)$$

This equation used by Sacchetto and Kodejš[13] was derived by fitting the values of $B$ reported by O'Connell and Prausnitz[14] over the temperature range 323–423 K.

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**Table IV.** The Surface Tension of the $TlNO_3$–$CsNO_3$–$Cd(NO_3)_2$–$H_2O$ System, as Function of Composition and Temperature[a]

| $T$ (K) | $\sigma \times 10^3$ (N m$^{-1}$) | $T$ (K) | $\sigma \times 10^3$ (N m$^{-1}$) |
|---|---|---|---|
| $x_w = 0$; $x_1 = 0.467$; $x_2 = 0.214$; $x_3 = 0.319$ | | $x_w = 0.102$; $x_1 = 0.420$; $x_2 = 0.192$; $x_3 = 0.286$ | |
| 365.3 | 110.9 | 364.7 | 109.6 |
| 368.3 | 110.5 | 368.8 | 109.0 |
| 373.2 | 109.8 | 373.4 | 108.5 |
| 378.3 | 109.3 | 378.3 | 107.9 |
| 383.2 | 108.6 | 383.2 | 107.4 |
| 388.2 | 108.0 | 387.7 | 106.8 |
| 391.4 | 107.7 | 391.0 | 106.4 |
| 395.6 | 107.1 | 393.2 | 106.1 |
| 399.0 | 106.6 | 396.5 | 105.7 |
| 403.6 | 106.0 | 398.6 | 105.3 |
| $x_w = 0.200$; $x_1 = 0.374$; $x_2 = 0.171$; $x_3 = 0.255$ | | $x_w = 0.300$; $x_1 = 0.327$; $x_2 = 0.150$; $x_3 = 0.223$ | |
| 358.7 | 109.5 | 362.0 | 106.9 |
| 362.9 | 109.1 | 363.7 | 106.6 |
| 365.2 | 108.7 | 366.5 | 106.1 |
| 369.4 | 108.1 | 369.6 | 105.6 |
| 373.5 | 107.6 | 372.2 | 105.2 |
| 377.7 | 107.1 | 375.4 | 104.6 |
| 380.4 | 106.6 | 379.5 | 103.9 |
| 383.2 | 106.2 | 382.2 | 103.4 |
| 387.2 | 105.7 | 387.6 | 102.6 |
| 393.2 | 104.9 | 391.4 | 102.0 |
| $x_w = 0.401$; $x_1 = 0.280$; $x_2 = 0.128$; $x_3 = 0.191$ | | $x_w = 0.502$; $x_1 = 0.232$; $x_2 = 0.107$; $x_3 = 0.159$ | |
| 362.6 | 103.0 | 360.7 | 99.3 |
| 365.9 | 102.4 | 364.7 | 98.7 |
| 369.3 | 101.9 | 368.2 | 98.3 |
| 373.4 | 101.2 | 372.6 | 97.7 |
| 376.9 | 100.7 | 376.8 | 97.1 |
| 380.4 | 100.2 | 380.5 | 96.6 |
| 383.2 | 99.8 | 383.3 | 96.2 |
| 387.5 | 99.1 | 387.4 | 95.6 |
| 390.3 | 98.6 | | |
| 393.4 | 98.2 | | |
| $x_w = 0.600$; $x_1 = 0.187$; $x_2 = 0.085$; $x_3 = 0.128$ | | $x_w = 0.700$; $x_1 = 0.140$; $x_2 = 0.064$; $x_3 = 0.096$ | |
| 360.8 | 94.2 | 358.8 | 84.5 |
| 362.6 | 93.9 | 361.5 | 84.0 |
| 365.5 | 93.5 | 363.2 | 83.7 |
| 368.4 | 93.1 | 365.3 | 83.4 |
| 371.6 | 92.6 | 368.4 | 82.9 |
| 374.2 | 92.2 | 371.5 | 82.4 |
| 377.5 | 91.7 | 374.7 | 81.9 |
| 380.4 | 91.2 | 377.6 | 81.4 |
| 383.2 | 90.8 | 380.4 | 81.0 |
| 386.4 | 90.4 | 383.2 | 80.6 |
| $x_w = 0.800$; $x_1 = 0.093$; $x_2 = 0.043$; $x_3 = 0.064$ | | $x_w = 0.900$; $x_1 = 0.047$; $x_2 = 0.021$; $x_3 = 0.032$ | |
| 355.7 | 77.7 | 356.9 | 71.2 |
| 358.4 | 77.3 | 358.7 | 70.8 |
| 363.6 | 76.5 | 361.8 | 70.3 |
| 366.4 | 76.1 | 363.7 | 69.9 |
| 369.9 | 75.6 | 366.4 | 69.4 |
| 373.5 | 75.1 | 369.4 | 68.9 |
| 376.7 | 74.6 | 372.5 | 68.4 |
| 379.4 | 74.1 | 375.6 | 67.8 |
| 383.2 | 73.6 | 377.3 | 67.5 |

[a] $x_w$, $x_1$, $x_2$ and $x_3$ are the mole fractions respectively of $H_2O$, $TlNO_3$, $CsNO_3$, and $Cd(NO_3)_2$.

For pure water, the values of the density, viscosity, surface tension, and vapor pressure were taken from different sources.[15–17]

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(17) Dorsey, N. E. *Properties of Ordinary Water-Substance*; Reinhold: New York, 1940.

**Table V.**  The Water Vapor Pressure $p$, Water Fugacity $f_w$, Water Activity $a_w$, and Water Activity Coefficient $\gamma_w$ of the $TlNO_3$–$CsNO_3$–$Cd(NO_3)_2$–$H_2O$ System, as Functions of Composition and Temperature[a]

| $x_w$ | $x_1$ | $x_2$ | $x_3$ | $T$ (K) | $p$ (kPa) | $f_w$ (kPa) | $a_w$ | $\gamma_w$ |
|---|---|---|---|---|---|---|---|---|
| 0.232 | 0.359 | 0.164 | 0.245 | 361.3 | 8.2 | 8.2 | 0.127 | 0.546 |
| | | | | 370.4 | 11.8 | 11.8 | 0.130 | 0.561 |
| | | | | 377.9 | 16.0 | 16.0 | 0.135 | 0.583 |
| | | | | 387.0 | 22.5 | 22.4 | 0.141 | 0.606 |
| 0.307 | 0.324 | 0.148 | 0.221 | 364.7 | 11.4 | 11.4 | 0.155 | 0.505 |
| | | | | 370.5 | 14.5 | 14.5 | 0.159 | 0.519 |
| | | | | 378.0 | 18.9 | 18.9 | 0.159 | 0.519 |
| | | | | 386.5 | 25.1 | 25.0 | 0.159 | 0.518 |
| 0.367 | 0.296 | 0.135 | 0.202 | 368.6 | 15.4 | 15.4 | 0.181 | 0.493 |
| | | | | 371.1 | 17.0 | 17.0 | 0.183 | 0.497 |
| | | | | 378.4 | 21.9 | 21.8 | 0.182 | 0.497 |
| | | | | 386.6 | 28.3 | 28.2 | 0.179 | 0.487 |
| 0.453 | 0.255 | 0.117 | 0.175 | 370.7 | 27.2 | 27.1 | 0.296 | 0.653 |
| | | | | 378.3 | 35.9 | 35.7 | 0.299 | 0.660 |
| | | | | 386.8 | 48.3 | 48.0 | 0.302 | 0.667 |
| 0.499 | 0.234 | 0.107 | 0.160 | 369.9 | 28.3 | 28.2 | 0.317 | 0.636 |
| | | | | 377.8 | 37.8 | 37.6 | 0.320 | 0.642 |
| | | | | 386.2 | 51.1 | 50.8 | 0.326 | 0.654 |
| 0.604 | 0.185 | 0.085 | 0.126 | 370.6 | 39.1 | 38.9 | 0.422 | 0.698 |
| | | | | 378.1 | 51.5 | 51.2 | 0.422 | 0.699 |
| | | | | 387.0 | 66.9 | 66.4 | 0.417 | 0.690 |
| 0.611 | 0.182 | 0.083 | 0.124 | 370.6 | 41.0 | 40.8 | 0.446 | 0.731 |
| | | | | 378.1 | 53.0 | 52.6 | 0.443 | 0.725 |
| | | | | 387.0 | 72.4 | 71.8 | 0.450 | 0.736 |
| 0.654 | 0.162 | 0.074 | 0.110 | 364.8 | 36.5 | 36.3 | 0.492 | 0.752 |
| | | | | 370.6 | 45.5 | 45.2 | 0.495 | 0.757 |
| | | | | 378.2 | 60.2 | 59.7 | 0.501 | 0.766 |
| | | | | 386.3 | 78.9 | 78.2 | 0.501 | 0.765 |
| 0.699 | 0.141 | 0.064 | 0.096 | 362.7 | 41.4 | 41.1 | 0.604 | 0.864 |
| | | | | 371.2 | 57.1 | 56.6 | 0.608 | 0.870 |
| | | | | 379.0 | 73.1 | 72.4 | 0.592 | 0.847 |
| 0.746 | 0.119 | 0.054 | 0.081 | 362.2 | 42.7 | 42.4 | 0.635 | 0.851 |
| | | | | 371.0 | 59.3 | 58.8 | 0.635 | 0.851 |
| | | | | 378.7 | 76.9 | 76.2 | 0.629 | 0.843 |
| 0.799 | 0.094 | 0.043 | 0.064 | 362.5 | 48.4 | 48.0 | 0.710 | 0.888 |
| | | | | 371.3 | 68.2 | 67.6 | 0.723 | 0.904 |
| | | | | 378.9 | 88.3 | 87.3 | 0.715 | 0.895 |
| 0.800 | 0.093 | 0.043 | 0.064 | 362.7 | 49.3 | 48.9 | 0.718 | 0.897 |
| | | | | 371.1 | 66.8 | 66.2 | 0.713 | 0.892 |
| | | | | 378.3 | 85.5 | 84.6 | 0.707 | 0.884 |
| 0.851 | 0.070 | 0.032 | 0.047 | 362.5 | 55.2 | 54.7 | 0.808 | 0.949 |
| | | | | 371.3 | 75.1 | 74.3 | 0.796 | 0.935 |
| | | | | 375.4 | 85.5 | 84.5 | 0.782 | 0.919 |
| 0.903 | 0.045 | 0.021 | 0.031 | 361.8 | 56.9 | 56.4 | 0.856 | 0.948 |
| | | | | 371.2 | 81.0 | 80.1 | 0.859 | 0.952 |
| | | | | 379.0 | 105.9 | 104.5 | 0.854 | 0.946 |

[a] $x_w$, $x_1$, $x_2$ and $x_3$ are the mole fractions respectively of $H_2O$, $TlNO_3$, $CsNO_3$, and $Cd(NO_3)_2$.

## 3. Discussion

### 3.1. The Viscosity and the Equivalent Electrical Conductance.
Previous investigations[2,18–21] on molten salts and very ionic aqueous solutions have shown that approaches based on the absolute reaction rate theory[22,23] and the quantum concept of hole[2,8] can be fruitful as far as transport properties are concerned, although other theories are used when cooperative phenomena have to be considered in liquids of relatively high viscosity.[24]

The Eyring equation[23] may be written in the form:

$$\eta = \frac{h}{v} \exp\left(\frac{\Delta G_\eta^*}{RT}\right) \tag{9}$$

where $h$ is the Planck constant, $v$, the volume of a hole considered

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(24) Spiro, M.; King, F. In *Ionic Liquids*; Inman, D., Lovering, D., Eds.; Plenum Press: New York, 1981; Chapter 5.

to be close to that of a particle,[2,23] and $\Delta G_\eta^*$, the molar free energy of activation for the viscous flow.

In the case of a salt–water system, $v$ is obviously an average parameter, like $\Delta G_\eta^*$, which depends on the nature of the flow units originating from the salt and the water. Species involved in the viscous flow mechanisms are not known and one might suppose the existence of ion pairs, complex ion clusters, etc. At first sight, two relatively simple situations are worth examining in order to estimate the extent to which $\Delta G_\eta^*$ may be subject to an error due to the uncertainty attached to $v$.

Assuming the flow units to be the water molecules and the salt entities ($Tl^+$, $NO_3^-$), ($Cs^+$, $NO_3^-$), and ($Cd^{2+}$, $2\ NO_3^-$), $v$ is expressed by

$$v = V/N_A \tag{10}$$

where $N_A$ is the Avogadro constant.

If the flow units are the water molecules and the ions $Tl^+$, $Cs^+$, $Cd^{2+}$, and $NO_3^-$, $v$ is expressed by

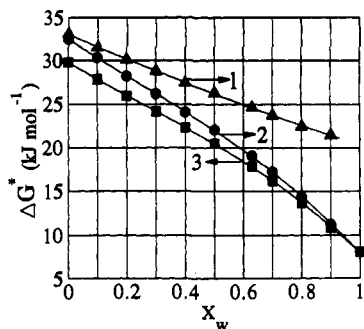$$v = \frac{V}{N_A[x_s \sum_i X_i(\nu_{i-} + \nu_{i+}) + x_w]} \tag{11}$$

**Figure 1.** The free energy of activation for the viscosity $\Delta G_\eta^*$ and the free energy of activation for the equivalent electrical conductance $\Delta G_\Lambda^*$ as functions of the water mole fraction $x_w$, for the $TlNO_3$–$CsNO_3$–Cd-$(NO_3)_2$–$H_2O$ system, at 372 K: (1) $\Delta G_\Lambda^*$; (2) $\Delta G_\eta^*$ with $v$ given by eq 10; (3) $\Delta G_\eta^*$ with $v$ given by eq 11.

where $v_{i+}$ and $v_{i-}$ are the number of cations and anions produced by the dissociation of 1 mole of the electrolyte $i$.

In Figure 1, $\Delta G_\eta^*$ is plotted against $x_w$, at 372 K, using values of $v$ given by eq 10 (curve 2) and eq 11 (curve 3). For the anhydrous molten salt, the two alternatives in the evaluation of $v$ lead to a difference in $\Delta G_\eta^*$ of less than 10%, and, in both cases, $\Delta G_\eta^*$ is a linear function of $x_w$ between 0 and $\sim 0.5$.

Application of the absolute reaction rate theory to the equivalent electrical conductance requires, in principle, knowledge of one-half the migration distance $d_i$, across the potential barriers, of any electrical charge carrier and its free energy of activation $\Delta G_{\Lambda i}^*$. Since these parameters are not known, the following extension of an equation proposed by Stearn and Eyring[25] was suggested[8] in order to provide an average value of the free energy of activation $\Delta G_\Lambda^*$ characteristic of an electrolyte solution:

$$\Lambda = AV^{2/3}\left(\frac{1}{1 - B_D}\right)B_d^{2/3}B_z \exp\left(-\frac{\Delta G_\Lambda^*}{RT}\right) \quad (12)$$

$$A = \frac{8}{3}\left(\frac{3}{4\pi}\right)^{2/3}\frac{F^2}{hN_A^{5/3}} \quad (13)$$

$$B_D = x_s\frac{V_s(D_s - 1)}{V(D_s + 2)} + x_w\frac{V_w(D_w - 1)}{V(D_w + 2)} \quad (14)$$

$$B_d = \frac{1}{x_s\sum_i X_i(v_{i-} + v_{i+}) + x_w} \quad (15)$$

$$B_z = \frac{\sum_i X_i n_{ei}}{\sum_i X_i(v_{i-} + v_{i+})} \quad (16)$$

where $F$ is the Faraday constant, and $D_s$ and $D_w$ are the dielectric constants of the pure salt and the pure water. For the pure water, the values of $D_w$ were estimated from its known values between 0 and 100 °C.[15] For the salt mixture, the average value 2 was assigned to $D_s$, since for several nitrates the values of $D_s$ are about 1.5–2.5.[26]

It is observed in Figure 1 that $\Delta G_\Lambda^*$, at a given temperature, is a quasi-linear function of $x_w$ over the very large concentration range $x_w = 0$–$\sim 0.9$.

From $\Delta G^*$, follow the entropy of activation $\Delta S^*$ and the enthalpy of activation $\Delta H^*$ by means of the equations:

$$\Delta S^* = -\delta \Delta G^*/\delta T \quad (17)$$
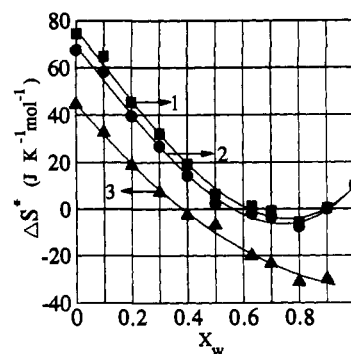
$$\Delta H^* = \Delta G^* + T\Delta S^* \quad (18)$$

(25) Stearn, A. E.; Eyring, H. *J. Chem. Phys.* **1937**, *5*, 113–124.
(26) Janz, G. J. *Molten Salts Handbook*; Academic Press: New York, 1967.



**Figure 2.** The entropy of activation for the viscosity $\Delta S_\eta^*$ and the entropy of activation for the equivalent electrical conductance $\Delta S_\Lambda^*$ as functions of the water mole fraction $x_w$, for the $TlNO_3$–$CsNO_3$–Cd(NO_3)_2$–$H_2O$ system: (1) $\Delta S_\eta^*$ with $v$ given by eq 11; (2) $\Delta S_\eta^*$ with $v$ given by eq 10; (3) $\Delta S_\Lambda^*$.
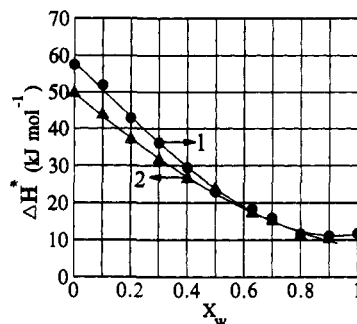


**Figure 3.** The enthalpy of activation for the viscosity $\Delta H_\eta^*$ and the enthalpy of activation for the equivalent electrical conductance $\Delta H_\Lambda^*$ as functions of the water mole fraction $x_w$, for the $TlNO_3$–$CsNO_3$–Cd-$(NO_3)_2$–$H_2O$ system: (1) $\Delta H_\eta^*$; (2) $\Delta H_\Lambda^*$.

In Figures 2 and 3, the average values of $\Delta S_\eta^*$, $\Delta S_\Lambda^*$, $\Delta H_\eta^*$, and $\Delta H_\Lambda^*$ valid over the explored temperature ranges are plotted against $x_w$.

Hole theories predict that $\Delta H_\eta^*$ of molten salt mixtures should increase with the component freezing points.[27,28] This effect is observed, for example, when salts such as $Cd(NO_3)_2$ and $CsNO_3$ are added to the $AgNO_3$–$TlNO_3$ mixture.[28] For the $AgNO_3$–$TlNO_3$ and the $TlNO_3$–$CsNO_3$–Cd(NO_3)_2$ mixtures, the values of $\Delta H_\eta^*$ are 29 and 58 kJ mol$^{-1}$, respectively, the latter value presumably due to the high $CsNO_3$ and $Cd(NO_3)_2$ concentrations.

Supercooling of the anhydrous $TlNO_3$–$CsNO_3$–Cd(NO_3)_2$ system occurs sometimes, casting doubts on the reported freezing point.[5] In this kind of electrolyte having a quasi-lattice structure, there is alternation of monovalent cations and divalent cations for electrostatic reason. This alternate distribution has to be broken up in order that a pure component might crystallize.[29] Supercooling could be a consequence of the inaptitude of certain sort of particles for passing over high potential barriers arising in such structural rearrangement.[29–31] Since the existence of these barriers should be reflected in $\Delta H_\eta^*$, high values of this parameter may be exhibited by ionic mixtures having a great tendency to supercool.

In contrast to the $AgNO_3$–$TlNO_3$–$H_2O$ system for which $\Delta H_\eta^*$ and $\Delta H_\Lambda^*$ are close to one another over the whole water concentration range,[32] for the $TlNO_3$–$CsNO_3$–Cd(NO_3)_2$–$H_2O$ system these parameters have the same order of magnitude only

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*Properties of a New Bridging Salt–Water System*

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**Table VI.** The Apparent Fluidity of Pure Water, $\phi'_w$, and the Apparent Equivalent Electric Conductance of the Salt at Infinite Dilution, $\Lambda'_\infty$ of the $TlNO_3$–$CsNO_3$–$Cd(NO_3)_2$–$H_2O$ System, Compared to the Fluidity of the Pure Water, $\phi_w$, the Fluidity of the Pure Salt, $\phi_s$, and the Equivalent Electric Conductance of the Pure Salt $\Lambda_s$, as Functions of Temperature

| $T$ (K) | $\phi_w$ ($kg^{-1}$ m s) | $\phi_s$ ($kg^{-1}$ m s) | $\phi'_w$ ($kg^{-1}$ m s) | $\Lambda_s \times 10^4$ ($\Omega^{-1}$ $m^2$ equiv$^{-1}$) | $\Lambda'_\infty \times 10^4$ ($\Omega^{-1}$ $m^2$ equiv$^{-1}$) |
|---|---|---|---|---|---|
| 365 | 4010 | 3.03 | 1490 | 0.40 | 62.6 |
| 372 | 4323 | 4.28 | 1380 | 0.53 | 61.1 |
| 380 | 4720 | 6.46 | 1270 | 0.76 | 59.4 |
| 388 | 5123 | 9.46 | 1170 | 1.05 | 57.9 |

in the case of the water-rich solutions. At low values of $x_w$, their difference increases, reaching a maximum for the anhydrous molten salt. Most striking is the manner in which $\Delta H^*$ and $\Delta S^*$ combine to bring about the shapes of $\Delta G^*$, especially in the case of $\Delta G_\Lambda^*$. Although both functions $\Delta S_\Lambda^*$ and $\Delta H_\Lambda^*$ have a pronounced curvature over the interval $x_w = 0$–0.9, they compensate one another, yielding an almost straight line to represent $\Delta G_\Lambda^*$. This is also observed with $\Delta H_\eta^*$ and $\Delta S_\eta^*$, but in a narrower range, $x_w = 0$–0.5. Curiously enough, concerning the anhydrous salt, $\Delta G_\Lambda^*$ is close to $\Delta G_\eta^*$ if the viscous flow units are assumed to be the entities ($Tl^+$, $NO_3^-$), ($Cs^+$, $NO_3^-$), and ($Cd^{2+}$, $2NO_3^-$), even though the enthalpy and entropy contributions are different for the two transport properties.

Over the range $x_w = 0$–~0.5, the fact that $\Delta G^*$ is a linear function of $x_w$ may be a fundamental reason why the following equations, each of them containing only one adjustable parameter, $\phi_w'$ and $\Lambda_\infty'$, are found to hold:[10]

$$\phi = (\phi_s)^{x_s}(\phi_w')^{x_w} \quad (19)$$

$$\Lambda = (\Lambda_s)^{x_s}(\Lambda_\infty')^{x_w} \quad (20)$$

where, in eq 19, $\phi$ is the fluidity of the solution, i.e., the reciprocal of its viscosity, and $\phi_s$ is the experimental fluidity of the pure salt. $\phi_w'$, called the apparent fluidity of the pure water, plays formally a role analogous to that of $\phi_s$. The parameter $\phi_w'$ is a characteristic of the water dissolved in the molten salt, considered as a fluid distinguishable from pure water. In eq 20, $\Lambda$ is the equivalent electrical conductance of the solution, and $\Lambda_s$ is the experimental equivalent electrical conductance of the pure salt. $\Lambda_\infty'$, called the apparent equivalent electrical conductance of the salt at infinite dilution, represents the equivalent electrical conductance at infinite dilution the salt would exhibit if the properties of pure water were the same as those of the water dissolved in the salt whose fluidity is $\phi_w'$.

The values of $\phi_w'$ and $\Lambda_\infty'$ at various temperatures are listed in Table VI, together with those of $\phi_s$, $\Lambda_s$, and the fluidity of the pure water, $\phi_w$. As may be seen in this table, the influence of the temperature on the apparent parameters $\phi_w'$ and $\Lambda_\infty'$ is opposite to that on $\phi_w$, $\phi_s$, and $\Lambda_s$. A peculiar feature to notice is the similarity between the behavior of the water dissolved in the salt and that of gaseous substances. Although the order of magnitude of $\phi_w'$ is that of a condensed phase, this parameter decreases as the temperature increases like the water vapor fluidity.[15,21]

**3.2. The Water Activity.** In a recent study, Trudelle-Abraham[3] drew the conclusion that the approach based on the BET model[33] adapted to electrolyte solutions[34] is most relevant to express the relationship between the activity and the concentration of water in very ionic solutions. For instance, contrary to the Pitzer equation,[35] based on regular solution theories, the Stokes and Robinson equation[34] is compatible with the possible

coexistence of negative and positive deviations of the water activity with respect to the Raoult law, for a given salt–water system.[3,36,37]

Taking into account the modification introduced into the BET model by Anderson,[38] the Stokes and Robinson equation is written[34]

$$\frac{a_w(1 - x_w)}{x_w(1 - ba_w)} = \frac{1}{bcr} + \frac{c - 1}{cr}a_w \quad (21)$$

in which $b$, $c$, and $r$ are constants.

The constants $b$ and $c$ are expressed by:

$$b = \exp[-(E_b - E_L)/RT] \quad (22)$$

$$c = \exp[-(E - E_b)/RT] \quad (23)$$

in which $E$ is the molar binding energy of water on sites close to the ions, usually considered to be cations, $E_b$, is the molar binding energy of water in multilayer hydration sphere of the ions where the nearest neighbors are only water molecules, and $E_L$ is the molar binding energy of water in pure water (heat of liquefaction).

The constant $r$ is given by:

$$r = N_{si}/N_A \quad (24)$$

where $N_{si}$ is the number of available sites with the binding energy $E$ for the water molecules, per mole of salt.

The values of $b$, $c$, $r$, ($E_b - E_L$), and ($E - E_b$), at different temperatures, obtained by nonlinear least-squares fitting of eq 21 to the experimental data, using Marquardt method, are listed in Table VII. As an illustration, the curve calculated by means of eq 21, at 372 K, is compared with the experimental data in Figure 4. It is seen that the agreement is good over the large water mole fraction range $x_w = \sim 0.2$–0.9.

We may observe in Table VII that $E_b$ is very close to $E_L$, so that the BET constants $c$ and $r$ are sufficient to compute the water activity, as was done with other highly ionic melts.[3,39]

It is interesting to notice that the order of magnitude of the BET constant $r$ could have been predicted from the results obtained with other nitrate–water systems containing $Tl^+$, $Cs^+$, and $Cd^{2+}$ ions. Using values attributed to single salts by an extrapolation procedure previously used,[3] i.e., $r = 0.3$, 0.8, and 3.7 respectively for $TlNO_3$, $CsNO_3$, and $Cd(NO_3)_2$, at 372 K, one obtains for the present study $r = (0.467 \times 0.3) + (0.214 \times 0.8) + (0.319 \times 3.7) = 1.5$, to be compared with $r = 1.4$.

Although eq 21 was developed from simplifying assumptions, it provides a convenient method for the determination of the Henry law constant $K_H$ for the dissolution of water in molten salts.[3,39,40] This constant is related to $f_w^0$ and the water activity coefficient at infinite dilution in the salt $\gamma_w^\infty$ by the equation

$$K_H = f_w^0 \gamma_w^\infty \quad (25)$$

The activity coefficient $\gamma_w^\infty$ is obtained from the BET constants by

$$\gamma_w^\infty = 1/bcr \quad (26)$$

Values of $\gamma_w^\infty$ and $K_H$ are listed in Table VII as functions of the temperature.

Comparison of the $TlNO_3$–$CsNO_3$–$Cd(NO_3)_2$–$H_2O$ system with the $AgNO_3$–$TlNO_3$–$H_2O$ system previously studied[3] clearly illustrates the influence of the hydrating power of the cations on the Henry law constant.[40,41] For example, at 372 K, $K_H = 31$ kPa

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**Table VII.** The BET Constants $c$, $r$, and $b$ in Eq 21, $(E - E_b)$ in Eq 22, $(E_b - E_L)$ in Eq 23, Activity Coefficient of Water at Infinite Dilution in the Salt $\gamma_w^\infty$, and the Henry Law Constant $K_H$ of the $TINO_3$–$CsNO_3$–$Cd(NO_3)_2$–$H_2O$ System, as Functions of Temperature

| $T$ (K) | $r$ | $c$ | $b$ | $(E - E_b)$ (kJ mol⁻¹) | $(E_b - E_L)$ (kJ mol⁻¹) | $\gamma_w^\infty$ | $K_H$ (kPa) |
|---|---|---|---|---|---|---|---|
| 365 | 1.35 | 2.38 | 0.994 | −2.63 | 0.02 | 0.314 | 23.6 |
| 372 | 1.38 | 2.25 | 0.994 | −2.51 | 0.02 | 0.324 | 31.2 |
| 380 | 1.41 | 2.12 | 0.995 | −2.37 | 0.02 | 0.336 | 43.3 |
| 388 | 1.43 | 2.03 | 0.995 | −2.28 | 0.02 | 0.345 | 58.1 |
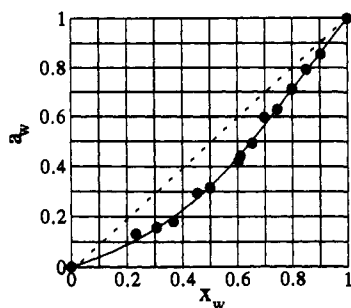


**Figure 4.** The water activity $a_w$ calculated by means of eq 21 as a function of the water mole fraction $x_w$, for the $TINO_3$–$CsNO_3$–$Cd(NO_3)_2$–$H_2O$ system, at 372 K.
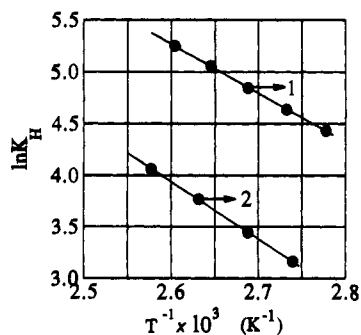


**Figure 5.** The logarithm of the Henry law constant $\ln K_H$ as a function of the reciprocal of the temperature $T^{-1}$: (1) $0.515AgNO_3$–$0.485TINO_3$ + $H_2O$; (2) $0.467TINO_3$–$0.214CsNO_3$–$0.319Cd(NO_3)_2$ + $H_2O$.

for the system containing the strongly hydrated $Cd^{2+}$ ions at high concentration, whereas the system which contains the relatively weakly hydrated $Ag^+$ and $Tl^+$ ions has the much higher $K_H = 127$ kPa.

The molar enthalpy of vaporization of water at infinite dilution in the molten salt $\Delta H_v^\infty$, valid over given temperature ranges, may be calculated by the equation

$$\frac{d \ln K_H}{d(1/T)} = -\frac{\Delta H_v^\infty}{R} \tag{27}$$

In Figure 5, $\ln K_H$ is shown plotted against $T^{-1}$ for the two systems $TINO_3$–$CsNO_3$–$Cd(NO_3)_2$–$H_2O$ and $AgNO_3$–$TINO_3$–$H_2O$,[3,42] whose $\Delta H_v^\infty$ values are 46 and 39 kJ mol⁻¹, respectively. It is seen that the aptitude of the $Cd^{2+}$ ions to lower the tendency of water to escape from the molten salts is also apparent in $\Delta H_v^\infty$.

**3.3. The Volumetric Properties.** The BET theory adapted to electrolyte solutions has also proved to be fruitful in the case of volumetric studies. Over the range $x_w = 0$–$\sim 0.5$, the following equation based on this model was proposed by Abraham,[43] relating the excess molar volume $V^{ex}$ to the water activity $a_w$:

$$V^{ex} = x_w(1 - a_w)(V_w^\infty - V_w + A_V x_w) \tag{28}$$

where $V_w^\infty$ is the apparent molar volume of water at infinite dilution in the molten salt, and $A_v$ is an empirical parameter

(42) Abraham, M.-C.; Abraham, M.; Sangster, J. M. *Can. J. Chem.* **1980**, *58*, 1480–1483.

(43) Abraham, M. *J. Chim. Phys.* **1984**, *81*, 207–212.
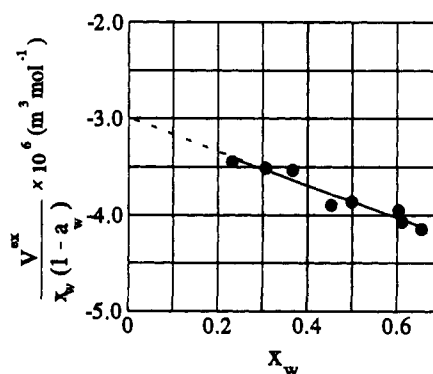


**Figure 6.** The expression $V^{ex}/[x_w(1 - a_w)]$ as a function of the water mole fraction $x_w$, for the $TINO_3$–$CsNO_3$–$Cd(NO_3)_2$–$H_2O$ system, at 376 K.

**Table VIII** The Parameters $A_v$ and $(V_w^\infty - V_w)$ in Eq 28 and the Apparent Molar Volume of Water at Infinite Dilution in the Molten Salt $V_w^\infty$

| salt composition | $T$ (K) | $A_v \times 10^6$ (m³ mol⁻¹) | $(V_w^\infty - V_w) \times 10^6$ (m³ mol⁻¹) | $V_w^\infty \times 10^6$ (m³ mol⁻¹) |
|---|---|---|---|---|
| $0.467TINO_3$–$0.214CsNO_3$–$0.319Cd(NO_3)_2$ | 368 | −2.2 | −2.8 | 15.9 |
| | 376 | −1.7 | −3.0 | 15.8 |
| | 383 | −1.4 | −3.2 | 15.7 |
| $0.515AgNO_3$–$0.485TINO_3$ | 353 | −6.3 | −0.7 | 17.9 |
| | 363 | −6.2 | −0.8 | 17.9 |
| | 372 | −6.6 | −0.7 | 18.0 |
| $0.464AgNO_3$–$0.436TINO_3$–$0.100CsNO_3$ | 372 | −5.0 | −1.1 | 17.7 |
| $0.464AgNO_3$–$0.436TINO_3$–$0.100Cd(NO_3)_2$ | 372 | −2.7 | −2.3 | 16.5 |

independent of $x_w$. Values of $A_v$ and $(V_w^\infty - V_w)$ were discussed in terms of a competition between two mechanisms of water insertion in the salt on the basis of quasi-lattice and hole theories: an s-mechanism, whereby water molecules are substituted for ions followed by the introduction of holes, and an i-mechanism, whereby available interstices or empty sites are filled by water molecules. This approach lead to the following relations:

$$A_v = (\partial P_{i\text{-}m}/\partial x_w)(V_{i\text{-}m}^\infty - V_{s\text{-}m}^\infty) \tag{29}$$

$$V_w^\infty = P_{s\text{-}m}^\infty V_{s\text{-}m}^\infty + P_{i\text{-}m}^\infty V_{i\text{-}m}^\infty \tag{30}$$

$P_{i\text{-}m}$ is the probability of occurrence of the i-mechanism assumed to be a linear function of $x_w$ in the validity range of the BET model, as suggested by the experimental data. $P_{i\text{-}m}^\infty$ and $P_{s\text{-}m}^\infty$ are the probabilities of occurrence of the i-mechanism and the s-mechanism, respectively, at infinite dilution in the molten salt. $V_{i\text{-}m}^\infty$ and $V_{s\text{-}m}^\infty$ are the apparent molar volumes of water at infinite dilution in the molten salt introduced respectively by the i-mechanism and the s-mechanism. Since the s-mechanism induces a dilation effect and the i-mechanism, a contraction effect:

$$V_{i\text{-}m}^\infty - V_{s\text{-}m}^\infty < 0 \tag{31}$$

Equation 28 is found to be valid also for the $TINO_3$–$CsNO_3$–$Cd(NO_3)_2$–$H_2O$ system, as shown in Figure 6, where the expression $V^{ex}/[x_w(1 - a_w)]$ is plotted against $x_w$, at 376 K. Table VIII gives the values of $A_v$, $(V_w^\infty - V_w)$, and $V_w^\infty$ for the studied

**Table IX.** The Surface Enthalpy $H_\sigma$ and Surface Entropy $S_\sigma$, per Unit Area, of the $TlNO_3$–$CsNO_3$–$Cd(NO_3)_2$–$H_2O$ System, as Functions of Composition[a]

| $x_w$ | $x_1$ | $x_2$ | $x_3$ | $H_\sigma \times 10^3$ (N m$^{-1}$) | $S_\sigma \times 10^6$ (N m$^{-1}$ K$^{-1}$) | correl coeff of eq 32 |
|---|---|---|---|---|---|---|
| 0 | 0.467 | 0.214 | 0.319 | 156.9 | 126.0 | 0.9994 |
| 0.102 | 0.420 | 0.192 | 0.286 | 154.3 | 122.6 | 0.9991 |
| 0.200 | 0.374 | 0.171 | 0.255 | 158.3 | 135.9 | 0.9993 |
| 0.300 | 0.327 | 0.150 | 0.223 | 167.6 | 167.8 | 0.9997 |
| 0.401 | 0.280 | 0.128 | 0.191 | 159.1 | 154.8 | 0.9997 |
| 0.502 | 0.232 | 0.107 | 0.159 | 148.8 | 137.3 | 0.9997 |
| 0.600 | 0.187 | 0.085 | 0.128 | 148.4 | 150.3 | 0.9997 |
| 0.700 | 0.140 | 0.064 | 0.096 | 141.6 | 159.4 | 0.9997 |
| 0.800 | 0.093 | 0.043 | 0.064 | 130.8 | 149.2 | 0.9997 |
| 0.900 | 0.047 | 0.021 | 0.032 | 135.1 | 179.2 | 0.9997 |
| 1 | 0 | 0 | 0 | 125.4 | 178.0 | |

[a] $x_w$, $x_1$, $x_2$ and $x_3$ are the mole fractions respectively of $H_2O$, $TlNO_3$, $CsNO_3$, and $Cd(NO_3)_2$.
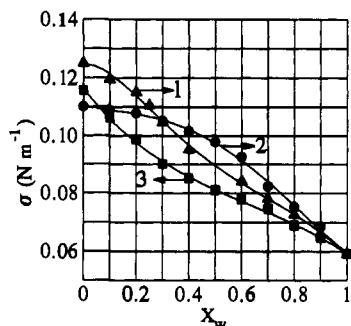


**Figure 7.** The surface tension $\sigma$ as a function of the water mole fraction $x_w$, at 372 K: (1) $0.464AgNO_3$–$0.436TlNO_3$–$0.100Cd(NO_3)_2$ + $H_2O$; (2) $0.467TlNO_3$–$0.214CsNO_3$–$0.319Cd(NO_3)_2$ + $H_2O$; (3) $0.515AgNO_3$–$0.485TlNO_3$ + $H_2O$.

system and other salt–water systems.[3,43] It can be seen that the $TlNO_3$–$CsNO_3$–$Cd(NO_3)_2$–$H_2O$ system has the highest value of $A_v$ and the smallest value of $V_w^\infty$ as a consequence of the presence, at a high concentration, of the $Cd^{2+}$ cation. In effect, the values of $V_w^\infty$ represent in a significant manner the enhanced electrostriction effects due to the presence of $Cd^{2+}$. Moreover, the values of $A_v$ may be interpreted in terms of structural perturbations of the molten salt quasi-lattice by water. For a given molten salt system, as water is dissolved in the salt, hydrogen bonds and cation–water dipole bonds, which have a more directional character than highly ionic bonds, will impose structure with larger free volume, whence, an increase of $P_{i-m}$ with $x_w$, a positive value of $(\partial P_{i-m}/\partial x_w)$ and a negative value of $A_v$. This parameter is less negative in the case of melts containing $Cd^{2+}$ because water is then less likely to perturb the salt quasi-lattice and to create free volume, due to the strong interactions of $Cd^{2+}$ with $NO_3^-$.

**3.4. The Surface Phase.** At a fixed water mole fraction, the surface tension $\sigma$ may be expressed as function of the temperature $T$ by

$$\sigma = H_\sigma - S_\sigma T \tag{32}$$

where $H_\sigma$ is the surface enthalpy and $S_\sigma$, the surface entropy, per unit area.

Over the explored temperature ranges, $H_\sigma$ and $S_\sigma$ are independent of $T$, as for other nitrate–water systems.[1] Their values are listed in Table IX as functions of the composition. Equation 32 allows one to calculate $\sigma$ at a fixed temperature, for each composition.

Figure 7 summarizes the surface tensions of the studied system and two other systems[1] for comparison, as a function of the water mole fraction, at a given temperature, 372 K. Over the whole concentration range, the curve $\sigma = f(x_w)$ of the $TlNO_3$–$CsNO_3$–$Cd(NO_3)_2$–$H_2O$ system is concave to the abscissa in opposition to the $AgNO_3$–$TlNO_3$–$H_2O$ system, whose curve is convex to the abscissa. More than likely, this striking difference is due to the presence at high concentration of the divalent cation $Cd^{2+}$, having a strong hydrating power. In effect, upon addition of $Cd^{2+}$ at 10

mol % to the $AgNO_3$–$TlNO_3$–$H_2O$ system, its curve is distorted, exhibiting a change from convex to concave for very dilute solutions of water in the salt.

From the surface tension and water activity data, an estimation of the surface water mole fraction can be made by application of the Guggenheim and Adam method[44,45] as follows.

The Gibbs adsorption formula is written

$$\Gamma_{w(s)} = -\frac{1}{kT}\frac{d\sigma}{d \ln a_w} \tag{33}$$

where $k$ is the Boltzmann constant and $\Gamma_{w(s)}$, 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, $\Gamma_w$, and the number of salt entities ($M^{z+}$, $zNO_3^-$), $\Gamma_s$, per unit area, by

$$\Gamma_{w(s)} = \Gamma_w - \Gamma_s\frac{x_w}{1-x_w} \tag{34}$$

With the assumption of a liquid quasi-lattice having a monolayer surface phase[45], $\Gamma_w$ and $\Gamma_s$ are related to the water molecular area $A_w$ and to the salt entity area $A_s$ by the equation

$$\Gamma_s A_s + \Gamma_w A_w = 1 \tag{35}$$

The water mole fraction in the surface phase $x_w'$ is then obtained by

$$x_w' = \Gamma_w/(\Gamma_w + \Gamma_s) \tag{36}$$

$A_w$ and $A_s$ were calculated by the equations[1]

$$A_w = \pi r_w^2 \tag{37}$$

$$A_s = \pi \sum_i X_i(r_{i+}^2 + z_{i+}r_-^2) \tag{38}$$

in which $r_w$ is the water radius,[46] $r_-$, the $NO_3^-$ radius,[47] $r_{i+}$, the cation $i$ radius,[15] and $z_{i+}$, the cation $i$ valency.

The water mole fraction in the surface phase $x_w'$ is shown plotted against the water mole fraction in the bulk phase $x_w$, at 372 K, in Figure 8, for the studied system and three other systems which do not contain $Cd^{2+}$ at high concentration. It is seen that the values of $x_w'$ for the $TlNO_3$–$CsNO_3$–$Cd(NO_3)_2$–$H_2O$ system are sensitively lower than for the other systems, reflecting the tendency of the $Cd^{2+}$ cations to attract water molecules.

In studies on the surface tension and the viscosity of molten carbonates,[19] molten nitrates, and aqueous solutions of nitrates,[1] the free energy of activation of the viscous flow in eq 9 was compared to the free energy of hole formation as expressed in the

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

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

(46) Marcus, Y. *J. Soln. Chem.* **1983**, *12*, 271–275.

(47) Waddington, T. C. In *Advances in Inorganic Chemistry and Radiochemistry*; Emeleus, H. J., Sharpe, A. G., Eds.; Academic Press: New York, 1959, Vol. I; p 180.
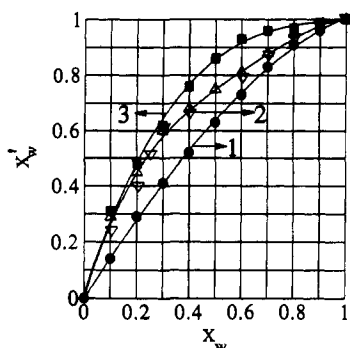
**Figure 8.** The water mole fraction in the surface phase $x_w'$ as a function of the water mole fraction in the bulk phase $x_w$, at 372 K: (1) 0.467TlNO$_3$–0.214CsNO$_3$–0.319Cd(NO$_3$)$_2$ + H$_2$O; (2) ($\nabla$) 0.464AgNO$_3$–0.436Tl-NO$_3$–0.100Cd(NO$_3$)$_2$ + H$_2$O and ($\Delta$) 0.515AgNO$_3$–0.485TlNO$_3$ + H$_2$O; (3) 0.464AgNO$_3$–0.436TlNO$_3$–0.100CsNO$_3$ + H$_2$O.

Fürth[48] theory of liquids. For the studied system, average values of the free energy of hole formation $\overline{\Delta G_\sigma}$ were calculated by an equation previously proposed for salt–water systems:[1]

$$\overline{\Delta G_\sigma} = 4\pi\sigma N_A \frac{x_s[\sum_i X_i(r_{i+}^2 + z_{i+}r_-^2)] + x_w r_w^2}{x_s[\sum_i X_i(1 + z_{i+})] + x_w} \tag{39}$$

Concerning $\Delta G_\eta^*$, the values of $v$ in eq 9 can be calculated using either the expressions 10 or 11, or by the simplified procedure based on the particles radii:

$$v = \frac{4}{3}\pi \frac{x_s[\sum_i X_i(r_{i+}^3 + z_{i+}r_-^3)] + x_w r_w^3}{x_s[\sum_i X_i(1 + z_{i+})] + x_w} \tag{40}$$

In Figure 9, $\overline{\Delta G_\sigma}$ and $\Delta G_\eta^*$ are plotted against $x_w$ at 372 K. Over the large concentration range $x_w = \sim 0.4$–1, and especially when $v$ is evaluated by eq 11, $\overline{\Delta G_\sigma}$ and $\Delta G_\eta^*$ have, roughly, the same order of magnitude. Yet, for the dilute solutions of water in the molten salt, the difference between $\overline{\Delta G_\sigma}$ and $\Delta G_\eta^*$ is greater, contrary to what was observed with other nitrate–water systems.[1] This behavior could presumably be attributed to the high degree of quasi-crystalline character of this ternary molten salt mixture containing a great amount of Cd$^{2+}$ cations, and all the more pronounced as the temperature is relatively low. As a matter of fact, an important effect of substituting divalent for

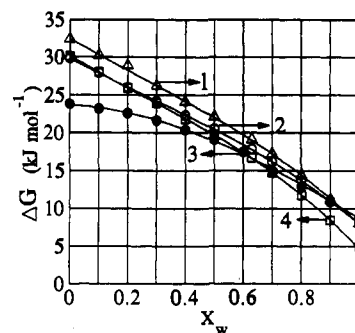(48) Fürth, R. *Proc. R. Soc. Camb. Phil. Soc.* **1941**, *27*, 252–275.



**Figure 9.** The free energy of hole formation $\overline{\Delta G_\sigma}$ and the free energy of activation for the viscosity $\Delta G_\eta^*$ as functions of the water mole fraction $x_w$, for the TlNO$_3$–CsNO$_3$–Cd(NO$_3$)$_2$–H$_2$O system, at 372 K: (1) $\Delta G_\eta^*$ with $v$ given by eq 10; (2) $\Delta G_\eta^*$ with $v$ given by eq 11; (3) $\overline{\Delta G_\sigma}$; (4) $\Delta G_\eta^*$ with $v$ given by eq 40.

monovalent cations is to intensify the cationic electrical field and to strengthen the structure of the liquid quasi-lattice which will become more crystal-like, particularly near the pure fused salt.[21] In this case, the vacancy model could perhaps be more appropriate to represent the physical reality of the liquid than the hole model on which eq 39 is based.[28]

## 4. Conclusion

Other approaches than those used in the discussion may be applied to the study of the thermodynamic, transport, and volumetric properties of highly ionic liquids. However, the new bridging salt–water system investigated in the present work again draws attention to the relevance of the BET model, the transition-state theory, and the hole and liquid quasi-lattice concepts to ionic liquids, from pure fused salts to dilute aqueous solutions. A remarkable feature of this study is the use of equations which are valid over large water concentration range, using few empirical parameters, in some cases only one. In effect, over the water concentration range $x_w = 0$–$\sim 0.5$, with regard to the fluidity and the equivalent electrical conductance, only one empirical parameter is needed to represent the experimental data in a satisfactory manner. In the same range, the excess molar volumes can be related to the water activity by means of an equation based on the BET model which contains two empirical parameters. It must also be pointed out that the equation based on the BET model which represents the water activity as a function of the water mole fraction can be applied over an unusually large water concentration range, up to $x_w = \sim 0.9$. And, moreover, the empirical parameters appear to be chemically significant as to the influence of the nature of the ions and the effect of the temperature.