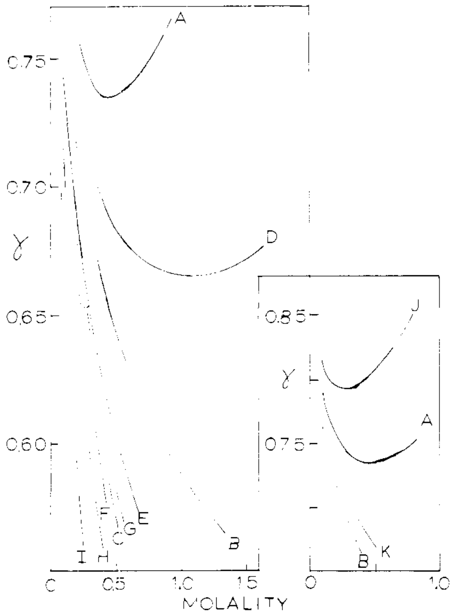

**Figure 1.** Activity coefficients of electrolytes at 25 °C: (A) $LiClO_3$, (B) $NaClO_3$, (C) $KClO_3$, (D) $LiBrO_3$, (E) $NaBrO_3$, (F) $KBrO_3$, (G) $LiIO_3$, (H) $NaIO_3$, (I) $KIO_3$, (J) $LiClO_4$, (K) $NaClO_4$.

## Results and Discussion

The primary data are presented in Table I. The activity and osmotic coefficients at rounded concentrations are reported in Table II. Osmotic coefficients were calculated from the equation

$$\phi = (m_{ref}/m)\phi_{ref}$$

Activity coefficients were calculated from the relationship (*5*)

$$\ln \gamma = \ln \gamma_{ref} + \ln \frac{m_{ref}}{m} + 2\int_0^{m_{ref}} \left(\frac{m_{ref}}{m} - 1\right) d \ln (m\gamma)_{ref}^{1/2}$$

It is demonstrated in Figure 1 that the activity coefficients of the lithium, sodium, and potassium chlorates, bromates, and iodates have a relationship to one another which would be expected. Furthermore, the lithium and sodium chlorates and perchlorates (*6*) exhibit the expected pattern. The large values of the activity coefficients of $LiClO_3$ and especially of $LiClO_4$ are suggestive of the behavior of the cesium (*7*) and tetraalkylammonium (*8*) fluorides. These large values of the activity coefficients are characteristic of 1:1 electrolytes in which the cation and anion differ greatly in size.

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# Osmotic and Activity Coefficients of Some Tetramethylguanidinium Salts at 298.15 K

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**Osmotic and activity coefficients are reported for tetramethylguanidinium bromide and chloride. The coefficients of these salts are similar to the corresponding tetramethylammonium salts. It appears that cation–anion association through hydrogen bonding does not play as great a role as is the case of guanidinium chloride or fluoride.**

We have recently published (*1*, *2*) osmotic and activity coefficients of several guanidinium salts because we felt that a knowledge of the colligative properties of these salts was essential to a complete understanding of their effectiveness as protein denaturants. It was observed (*2*) that the guanidinium ion was very effective in hydrogen bonding to acceptors including counterions of appreciable charge density. The spectroscopic studies of this phenomenon were hindered, however, because of the complexity of the spectrum containing three $-NH_2$ groups. It has been reported (*3*) that 1,1,3,3-tetramethylguanidinium salts (TMGu) are also denaturants but not nearly as effective as the parent guanidinium salts. They should be preferable for spectroscopic studies in the N–H stretching region since they possess only one $-NH_2$ group. The colligative property data reported herewith are the initial results obtained from investigations of this family of salts.

## Method

The free base 1,1,3,3-tetramethylguanidine as received from Pfaltz and Bauer was exactly neutralized with chemically pure grade hydrochloric or hydrobromic acid. The resultant salt solutions were evaporated to dryness under vacuum with temperatures never exceeding 313 K. The dried salts were then recrystallized three times from methanol–acetone mixtures and again dried in the same manner. The molecular weights of the salts as determined by passing solutions through ion-exchange columns in the hydrogen form and titration of the eluent led to

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Table I. Experimental Results: Molalities of Isopiestic Solutions at $T$ = 298.15 K

| NaCl | TMGuCl | TMGuBr | NaCl | TMGuCl | TMGuBr |
|---|---|---|---|---|---|
| 0.591 | 0.621 | 0.672 | 3.039 | 3.322 | 4.113 |
| 0.707 | 0.747 | 0.819 | 3.481 | 3.834 | 4.766 |
| 0.863 | 0.917 | 1.018 | 3.703 | 4.056 | 5.003 |
| 1.055 | 1.129 | 1.272 | 4.091 | 4.497 | 5.675 |
| 1.309 | 1.411 | 1.626 | 4.433 | 4.876 | 6.178 |
| 1.594 | 1.726 | 2.017 | 4.912 | 5.419 | 6.920 |
| 1.903 | 2.066 | 2.454 | 5.365 | 5.939 | 7.610 |
| 2.186 | 2.381 | 2.861 | 5.519 | 6.123 | 7.872 |
| 2.436 | 2.665 | 3.234 | 6.103 | 6.775 | 8.640 |
| 2.797 | 3.065 | 3.759 | | | |

a value agreeing with that calculated for each anhydrous salt within 0.1%.

The isopiestic equilibrations of solutions of the salts reported here and solutions of sodium chloride were performed in the usual manner except that glass dishes were used as a precautionary measure instead of the usual platinum-clad silver dishes. This was done since guanidinium bromide had been found to slowly air oxidize with the rate of decomposition being accelerated in metal dishes. No decomposition was experienced with these salts and equilibrium measurements after different time intervals were in perfect agreement (0.1%). The evacuation of the isopiestic vessel to approximately the vapor pressure of the solutions leaves very little air in any case. Heat transfer was rapid since the thin flat-bottom dishes were in good thermal contact with a silver-plated copper block. It was established that equilibrium was reached when the concentrations of identical samples were within 0.1% agreement, with one sample losing weight and the other gaining weight to attain equilibrium. The equilibration time varied from 24 h for the most concentrated solutions to about 10 days for the most dilute. An additional check on the accuracy of the data is the coincidence of molality ratio curves for different series of experimental equilibrations.

## Results and Discussion

The primary results of the isopiestic equilibrations are presented in Table I. The osmotic and activity coefficients at rounded concentrations are given in Table II. Osmotic coefficients were calculated from the relationship

$$\phi = (m_{\mathrm{ref}}/m)\phi_{\mathrm{ref}}$$

Activity coefficients were calculated from the equation (*4*)

$$\ln \gamma = \ln \gamma_{\mathrm{ref}} + \ln (m_{\mathrm{ref}}/m) + 2\int_0^{m_{\mathrm{ref}}} \{(m_{\mathrm{ref}}/m) - 1\} \mathrm{d} \ln (m_{\mathrm{ref}}\gamma_{\mathrm{ref}})^{1/2}$$

The values of the osmotic and activity coefficients of sodium chloride, the reference salt, are those of Robinson and Stokes (*5*).

Table II. Osmotic and Activity Coefficients at 298.15 K

| molality, | TMGuCl | | TMGuBr | |
|---|---|---|---|---|
| $m$ | $\phi$ | $\gamma$ | $\phi$ | $\gamma$ |
| 0.1 | 0.923 | 0.764 | 0.909 | 0.741 |
| 0.2 | 0.907 | 0.708 | 0.882 | 0.669 |
| 0.3 | 0.898 | 0.674 | 0.860 | 0.622 |
| 0.4 | 0.889 | 0.648 | 0.843 | 0.584 |
| 0.5 | 0.884 | 0.629 | 0.828 | 0.557 |
| 0.6 | 0.880 | 0.614 | 0.817 | 0.533 |
| 0.7 | 0.878 | 0.601 | 0.809 | 0.514 |
| 0.8 | 0.876 | 0.590 | 0.800 | 0.498 |
| 0.9 | 0.875 | 0.580 | 0.794 | 0.483 |
| 1.0 | 0.874 | 0.573 | 0.789 | 0.470 |
| 1.2 | 0.876 | 0.561 | 0.780 | 0.448 |
| 1.4 | 0.879 | 0.552 | 0.772 | 0.429 |
| 1.6 | 0.883 | 0.546 | 0.765 | 0.413 |
| 1.8 | 0.889 | 0.542 | 0.760 | 0.400 |
| 2.0 | 0.895 | 0.539 | 0.758 | 0.389 |
| 2.5 | 0.916 | 0.539 | 0.758 | 0.369 |
| 3.0 | 0.940 | 0.545 | 0.760 | 0.353 |
| 3.5 | 0.966 | 0.554 | 0.765 | 0.343 |
| 4.0 | 0.994 | 0.569 | 0.774 | 0.336 |
| 4.5 | 1.022 | 0.584 | 0.784 | 0.330 |
| 5.0 | 1.050 | 0.604 | 0.795 | 0.326 |
| 5.5 | 1.077 | 0.624 | 0.807 | 0.324 |
| 6.0 | 1.104 | 0.647 | 0.819 | 0.323 |
| 6.5 | 1.133 | 0.672 | 0.831 | 0.322 |
| 7.0 | | | 0.843 | 0.322 |
| 7.5 | | | 0.855 | 0.323 |
| 8.0 | | | 0.870 | 0.324 |
| 8.5 | | | 0.892 | 0.329 |

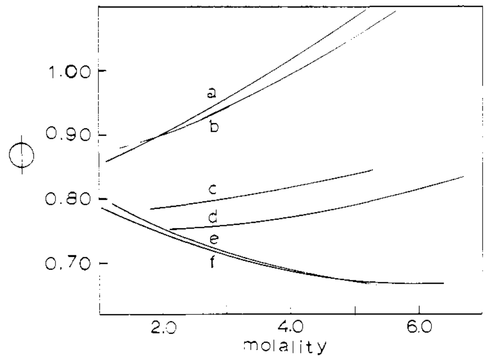

**Figure 1.** Osmotic coefficients of tetramethylammonium, tetramethylguanidinium, and guanidinium salts: (a) tetramethylammonium chloride, (b) tetramethylguanidinium chloride, (c) tetramethylammonium bromide, (d) tetramethylguanidinium bromide, (e) guanidinium bromide, (f) guanidinium chloride.

The concentration dependence of the osmotic coefficients of six salts containing large cations is plotted in Figure 1. It may be noted that the behavior of the tetramethylguanidinium salts is more nearly like that of the tetramethylammonium salts (*6*) than that of the corresponding guanidinium salts. This behavior would lead one to suspect "solvent-assisted ion pairing" for both of the tetramethyl-substituted cations and their counterions. The osmotic coefficients of the bromides are lower than those of the chloride salts as would be expected.

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