The changes in V_m^E with increasing number of methyl groups in the hydrocarbon parallel those observed in mixtures with the hexanes. Although the *n*-pentane mixture has been studied at a higher temperature than the other two systems, its characteristics would not be expected to change appreciably in 5 °C (*1*).

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Osmotic and Activity Coefficients of Lithium Chlorate and Lithium Bromate

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Osmotic and activity coefficients are reported for solutions of lithium chlorate and lithium bromate. It is demonstrated that the coefficients of the lithium, sodium, and potassium chlorates, bromates, and iodates have the expected relationship one to another.

The osmotic and activity coefficients of many of the simple uni-univalent electrolytes are available in the literature. Some of the electrolytes have not been studied, however, because of lack of a direct use for the data or because of the difficulties in handling. We had had occasion to measure the coefficients for the lithium (*1*), sodium (*2*), and potassium (*1*) iodates. Data for the sodium and potassium chlorates and bromates are available (*3*) elsewhere in the literature. It seemed that the completion of the families by measurement of the coefficients of the lithium chlorate and bromate would be of interest in that a quantitative pattern could be established for the variation of the coefficients with ion size and polarizability.

Method

Lithium chlorate and bromate may be purchased from Pfaltz and Bauer but the purity of the product is not specified. Lithium chlorate is particularly difficult to purify and handle as the solid because of its deliquescent nature. It was decided to obtain solutions of the lithium salts rather than to attempt to weigh accurate amounts of the solids. Consequently, solutions of reagent grade sodium salts were passed through a cation-exchange column which had been converted to the lithium form. The concentrations of the effluent solutions were determined by passing measured quantities through a second ion-exchange column in the acid form and subsequent titration. This method has been used to determine molecular weights of salts which agree with the calculated formula weight within 0.1% (*4*). It is believed that the error in the osmotic coefficients caused by the uncertainty in the solution concentration does not exceed 0.2%.

The isopiestic equilibration of solutions of these salts and solutions of sodium chloride was performed in the usual manner. 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
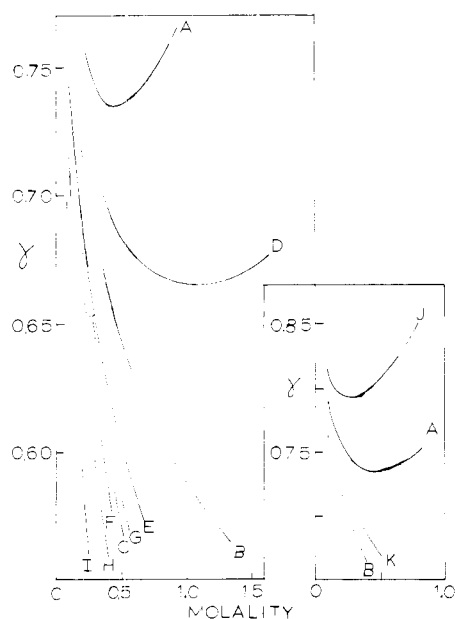
Table I. Molalities of Isopiestic Solutions

NaCl	LiClO₃	LiBrO₃
0.2782	0.2719	0.2779
0.5335	0.5111	0.5319
0.819	0.769	0.815
1.011	0.931	1.002
1.221	1.114	1.209
1.475	1.329	1.456
1.817	1.612	1.785
2.195	1.925	2.155
2.455	2.141	2.412
3.207	2.753	3.144
3.591	3.057	3.519
4.022	3.414	3.945
4.486	3.797	4.398
5.022	4.226	4.925

Table II. Osmotic and Activity Coefficients at 25 °C

m	LiClO₃ ϕ	LiClO₃ γ	LiBrO₃ ϕ	LiBrO₃ γ
0.1	0.939	0.790	0.932	0.778
0.2	0.941	0.758	0.926	0.735
0.3	0.945	0.742	0.924	0.711
0.4	0.951	0.735	0.922	0.694
0.5	0.961	0.736	0.924	0.684
0.6	0.971	0.739	0.927	0.677
0.7	0.983	0.745	0.930	0.672
0.8	0.994	0.752	0.934	0.668
0.9	1.008	0.762	0.938	0.666
1.0	1.020	0.772	0.943	0.666
1.2	1.044	0.796	0.953	0.666
1.4	1.069	0.825	0.964	0.669
1.6	1.094	0.855	0.976	0.675
1.8	1.112	0.886	0.990	0.683
2.0	1.142	0.921	1.003	0.691
2.5	1.203	1.018	1.035	0.718
3.0	1.267	1.130	1.070	0.749
3.5	1.326	1.254	1.107	0.788
4.0	1.384	1.394	1.144	0.832
4.2	1.408	1.454		
4.5			1.183	0.883
5.0			1.223	0.938

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 from different experiments.

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

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 tetraalkyl-ammonium (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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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

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-tetramethylguanidium 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