fect of $MgSO_4$ solutions can be estimated with the aid of literature data which rate the relative influence of the two individual salts on polyethylene oxide solution properties in general (*1*). The drag reduction efficiency of the anionic PAM is much less affected by increases in salt concentration than is PEO. As a matter of fact, the data suggest that the PAM sample will continue to function quite efficiently long after the drag reducing activity of the PEO sample has ceased (about 0.9*M* in $MgSO_4$). However, as already pointed out, the progressive decreases in drag reduction efficiency in the case of the commercial PAM's cannot be correlated with polymer intrinsic viscosity in the same solutions as was the case with PEO. No useful explanation for the dissimilar behavior observed with polyelectrolytes as compared with nonionic polymers can be easily offered at the present time.

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# Osmotic and Activity Coefficients of Solutions of $(NH_4)_2B_{10}H_{10}$, $Na_2B_{12}H_{12}$ in $H_2O$, and of Four Tetraalkylammonium Halides in $H_2O$ and in $D_2O$ at 25°C

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**Osmotic and activity coefficients of aqueous $(NH_4)_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$ solutions were measured at 25°C by the isopiestic comparison method and differed considerably for the two borates. In addition, the osmotic and activity coefficients of the $D_2O$ solutions of $(CH_3)_4NBr$, $(C_4H_9)_4NBr$, $(CH_3)_4NF$, and $(C_4H_9)_4NF$ were determined at 25°C and compared with the corresponding values of the $H_2O$ solutions to see the solvent isotope effect.**

Stability of the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ ions toward heat, acids, and bases, as well as oxidizing agents, is well documented (*4*, *6*). Alkali metal and ammonium salts of these anions are soluble in water and form stable aqueous solutions. In spite of many similarities in behaviors of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, they are not chemically equivalent (*7*). Inasmuch as two salts, $(NH_4)_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$, were made available to us, we determined the osmotic and activity coefficients of the aqueous solutions at 25°C. Interactions between water and the cage anions (bicapped square antiprism and icosahedron) (*2*, *20*) are of particular interest to us.

In a separate study, we have measured the osmotic and activity coefficients of the $D_2O$ solutions of $(CH_3)_4NBr$, $(C_4H_9)_4NBr$, $(CH_3)_4NF$, and $(C_4H_9)_4NF$. They are compared with the corresponding values of the $H_2O$ solutions to see the solvent isotope effect, if any.

## Experimental

***Materials and analyses.*** Ammonium decahydrodecaborate, $(NH_4)_2B_{10}H_{10}$, and the hydrate of sodium dodecahydrododecaborate, $Na_2B_{12}H_{12}$, were kindly supplied to us by H. L. Friedman of the State University of New York at Stony Brook who obtained the compounds from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co. These salts were used without further purification except drying. $(NH_4)_2B_{10}H_{10}$ was dried at 50°C in vacuo for 16 hr to a constant weight (density: 0.9862 g/cc). The anion content was determined gravimetrically using $AgNO_3$ as the precipitant, indicating 99.44 ± 0.43% purity. The hydrate of $Na_2B_{12}H_{12}$ was dried at 110°C to a constant weight; gravimetric analysis indicated the anion content to be 91.65 ± 0.63% (density: 1.1765 g/cc).

The $D_2O$ purchased from Matheson Coleman & Bell was used without further purification. The mole percent of $D_2O$ was checked by the density measurement by means of the following relation:

$$\text{mol \% } D_2O = \frac{924.64\ \Delta d}{1 - 0.0328\ \Delta d}$$

where $\Delta d$ is the measured density minus that of $H_2O$. Our result indicated that the heavy water used contained 99.72% $D_2O$.

$(CH_3)_4NBr$ and $(C_4H_9)_4NBr$ were obtained from Eastman Kodak Co. and recrystallized before use. $(C_4H_9)_4NF$ solutions were prepared by the following methods. The $H_2O$ and $D_2O$ hydrates of $(C_4H_9)_4NF$ were made by the double metatheses of $BaF_2$, $Ag_2SO_4$, and $(C_4H_9)_4NI$ in $H_2O$ or $D_2O$ (*12*). The resultant AgI, $BaSO_4$, and excess $BaF_2$ were removed by filtration and clear $(C_4H_9)_4NF$ solutions of about 1*M* concentration were cooled to 5°C to produce the crystalline hydrates. These hydrates were purified by recrystallization from $H_2O$ or $D_2O$. The melting point of $(C_4H_9)_4NF\cdot32.8H_2O$ is 25°C, whereas the melting point of $(C_4H_9)_4NF\cdot32.8D_2O$ is 30-30.5°C.

For the $H_2O$ solution, $(C_4H_9)_4NF$ was also prepared by the titration of $(C_4H_9)_4NOH$ with the HF solution to a pH of 8. The hydrates prepared were dissolved in $H_2O$ or $D_2O$ to make stock solutions. The stock solution was analyzed for both cat-

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ion and anion. The $(C_4H_9)_4N^+$ ion was analyzed by the gravimetric method with $NaB(C_6H_5)_4$ as precipitant, whereas $F^-$ ion was subjected to the gravimetric analysis with $CaCl_2$ as the precipitating agent. The analyses of the cation and anion agreed with each other to within 1%. $(CH_3)_4NF$ was prepared and analyzed by the same method used for $(C_4H_9)_4NF$, but $(CH_3)_4NF$ formed only low hydrates (mp of $H_2O$ hydrate: 45.5°C). $D_2O$ solutions of $(CH_3)_4NF$ were prepared by the metathesis reaction. The fluorides prepared by the double metathesis method and by the hydroxide-to-fluoride titration method gave identical isopiestic results.

***Apparatus and procedure.*** The isopiestic apparatus used in this work was similar to that employed by Owen and Cooke (*14*). It consisted mainly of gold-plated silver or gold dishes, copper block, glass desiccators, and rocking mechanisms (*1*). The temperatures of the water baths were controlled to 25° ± 0.005°C, and the pressure in the desiccators was reduced in stages to 25 torr. The equilibrium was assumed to be established when the concentrations of a pair of solutions in the duplicate dishes differed by less than 0.1% for reference and sample solutions. Attention was given to correction for the loss of weight owing to the evaporation of water between the time of opening the desiccator and weighing the dish. All weights of salts and solutions were reduced to those in vacuo.

## Results

***Solutions of $(NH_4)_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$.*** Osmotic coefficients of these borates in $H_2O$ were measured by the isopiestic comparison method with KCl solutions as the reference. The measured molalities of isopiestic solutions at 25°C are given in Table I. From these and the osmotic coefficients of KCl solutions listed in the book of Robinson and Stokes (*17*), the osmotic and activity coefficients of the two borates were calculated by the standard method (*18*) and are summarized in Table II. The data are believed to be reliable to within 0.5%.

***Solutions of tetraalkylammonium salts.*** The molality $m$ is used to indicate that $m$ moles of solute are dissolved in 1000 grams of solvent. For the light and heavy water as solvent, the aquamolality $m'$ is used to signify that $m'$ moles of salt are dissolved in 55.51 moles of solvent. In $H_2O$ solutions, $m$ and $m'$ are identical, whereas in $D_2O$ solutions they are related by $m' = 1.11147m$. The osmotic coefficients of the reference KCl in $D_2O$ solutions were taken from the work of Kerwin (*5*).

The data for the four tetraalkylammonium salts in $H_2O$ solutions at 25°C are listed in Table III. The values of $(CH_3)_4NBr$ are those of Levien (*9*), and $(C_4H_9)_4NBr$ are those of unpublished values by Saito and Wen, believed to be slightly better than those published by Lindenbaum and Boyd (*11*), though not as accurate as the emf data obtained by Ku (*8*). For self-consistency we use our own values of $(C_4H_9)_4NBr$ for $H_2O$–$D_2O$ comparison. The aquamolalities of isopiestic $D_2O$ solutions for the four salts are tabulated in Table IV, and the osmotic and activity coefficients are listed in Table V.

## Discussion

***Solutions of $(NH_4)_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$.*** As shown in Figure 1, where the mean molal activity coefficients $\gamma_\pm$ are plotted against the molality $m$, $\gamma_\pm$ for $(NH_4)_2B_{10}H_{10}$ decrease

Table I. Isopiestic Molalities of $(NH_4)_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$ in $H_2O$ at 25°C

| KCl | $(NH_4)_2B_{10}H_{10}$ | KCl | $Na_2B_{12}H_{12}$ |
|---|---|---|---|
| 0.1411[a] | 0.1070 | 0.1405 | 0.0972 |
| 0.2101 | 0.1602 | 0.3011 | 0.197 |
| 0.3141 | 0.2375 | 0.4704 | 0.293 |
| 0.4712 | 0.3560 | 0.4899 | 0.305 |
| 0.6751 | 0.5084 | 0.7218 | 0.425 |
| 1.004 | 0.7546 | 1.205 | 0.648 |
| 1.311 | 0.9816 | 1.623 | 0.817 |
| 1.561 | 1.166 | 2.099 | 0.995 |
| 1.773 | 1.320 | 2.684 | 1.197 |
| 2.383 | 1.779 | 3.230 | 1.376 |
| 2.968 | 2.235 | 3.267 | 1.384 |
| 3.711 | 2.840 | 4.019 | 1.617 |
| 4.294 | 3.342 | 4.406 | 1.729 |
| 4.805 | 3.806 | | |

[a] Unit: moles of solute per kg of solvent.

Table II. Osmotic and Activity Coefficients of $(NH_4)_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$ in $H_2O$ Solutions at 25°C

| | $(NH_4)_2B_{10}H_{10}$ | | $Na_2B_{12}H_{12}$ | |
|---|---|---|---|---|
| $m$ | $\phi$ | $\gamma_\pm$ | $\phi$ | $\gamma_\pm$ |
| 0.1 | 0.809 | 0.458 | 0.887 | 0.544 |
| 0.2 | 0.798 | 0.398 | 0.926 | 0.533 |
| 0.3 | 0.795 | 0.365 | 0.964 | 0.535 |
| 0.4 | 0.794 | 0.344 | 1.01 | 0.553 |
| 0.5 | 0.793 | 0.328 | 1.05 | 0.581 |
| 0.6 | 0.794 | 0.316 | 1.09 | 0.616 |
| 0.7 | 0.795 | 0.306 | 1.14 | 0.657 |
| 0.8 | 0.797 | 0.298 | 1.19 | 0.706 |
| 0.9 | 0.799 | 0.292 | 1.24 | 0.760 |
| 1.0 | 0.802 | 0.286 | 1.29 | 0.821 |
| 1.2 | 0.808 | 0.278 | 1.39 | 0.968 |
| 1.4 | 0.814 | 0.272 | 1.49 | 1.14 |
| 1.6 | 0.819 | 0.266 | 1.59 | 1.35 |
| 1.8 | 0.823 | 0.262 | | |
| 2.0 | 0.826 | 0.257 | | |
| 2.5 | 0.831 | 0.250 | | |
| 3.0 | 0.833 | 0.243 | | |
| 3.5 | 0.834 | 0.236 | | |

Table III. Osmotic and Activity Coefficients of $(CH_3)_4NBr$, $(C_4H_9)_4NBr$, $(CH_3)_4NF$, and $(C_4H_9)_4NF$ in $H_2O$ at 25°C

| | $(CH_3)_4NBr$[a] | | $(C_4H_9)_4NBr$ | | $(CH_3)_4NF$ | | $(C_4H_9)_4NF$ | |
|---|---|---|---|---|---|---|---|---|
| $m$ | $\phi$ | $\gamma_\pm$ | $\phi$ | $\gamma_\pm$ | $\phi$ | $\gamma_\pm$ | $\phi$ | $\gamma_\pm$ |
| 0.1 | 0.898 | 0.720 | 0.876 | 0.684 | 0.945 | 0.795 | 1.004 | 0.904 |
| 0.2 | 0.869 | 0.645 | 0.832 | 0.600 | 0.957 | 0.776 | 1.045 | 0.955 |
| 0.3 | 0.850 | 0.598 | 0.800 | 0.539 | 0.974 | 0.778 | 1.089 | 1.025 |
| 0.4 | 0.836 | 0.564 | 0.777 | 0.493 | 0.992 | 0.787 | 1.138 | 1.115 |
| 0.5 | 0.825 | 0.538 | 0.759 | 0.460 | 1.012 | 0.802 | 1.189 | 1.220 |
| 0.6 | 0.818 | 0.516 | 0.746 | 0.434 | 1.034 | 0.823 | 1.243 | 1.336 |
| 0.7 | 0.811 | 0.497 | 0.736 | 0.415 | 1.055 | 0.846 | 1.297 | 1.468 |
| 0.8 | 0.805 | 0.483 | 0.727 | 0.400 | 1.075 | 0.873 | 1.350 | 1.618 |
| 0.9 | 0.801 | 0.469 | 0.720 | 0.387 | 1.096 | 0.902 | 1.404 | 1.785 |
| 1.0 | 0.798 | 0.458 | 0.713 | 0.374 | 1.120 | 0.931 | 1.458 | 1.940 |
| 1.2 | | | 0.698 | 0.350 | 1.166 | 0.998 | 1.562 | 2.409 |
| 1.4 | | | 0.682 | 0.326 | 1.215 | 1.077 | 1.660 | 2.895 |
| 1.5 | 0.788 | 0.417 | | | | | | |
| 1.6 | | | 0.664 | 0.304 | 1.262 | 1.171 | 1.778 | 3 .595 |
| 1.8 | | | 0.648 | 0.287 | 1.312 | 1.276 | | |
| 2.0 | 0.788 | 0.392 | 0.632 | 0.275 | 1.363 | 1.385 | | |
| 2.5 | 0.793 | 0.376 | 0.596 | 0.243 | 1.489 | 1.728 | | |
| 3.0 | 0.802 | 0.364 | | | 1.617 | 2.170 | | |

[a] Ref. *9*.

slowly with concentration, whereas $\gamma_\pm$ for $Na_2B_{12}H_{12}$ increase rapidly with the increase of $m$. It is unfortunate that we could not study two borates with an identical cation (either both sodium salts or both ammonium salts). However, the concentration dependence of the activity coefficients of the two borates studied is so widely different that the large difference cannot be attributed entirely to the difference in cations. This large difference in $\gamma_\pm$ for the two salts is very likely due to the different ways in which the two borate anions interact with solvent water.

We suggest that $B_{10}H_{10}^{2-}$ ions are hydrogen bonded strongly to water; in contrast, $B_{12}H_{12}^{2-}$ ions are very weakly hydrogen bonded to water, if at all. Water molecules are considered to hydrogen bond at the two apical positions of the $B_{10}H_{10}^{2-}$ cage. This suggestion is not unreasonable in view of the extensive work done on borates by Muetterties and his coworkers (*7*,

Table IV. Isopiestic Aquamolalities of Four Tetraalkylammonium Salts in $D_2O$ at 25°C

| KCl | $(CH_3)_4NBr$ | KCl | $(C_4H_9)_4NBr$ | KCl | $(CH_3)_4NF$ | KCl | $(C_4H_9)_4NF$ |
|---|---|---|---|---|---|---|---|
| 0.1078[a] | 0.1123 | 0.1108 | 0.1171 | 0.1198 | 0.1164 | 0.1251 | 0.1146 |
| 0.1834 | 0.1935 | 0.1142 | 0.1212 | 0.2393 | 0.2289 | 0.1957 | 0.1740 |
| 0.2339 | 0.2489 | 0.1799 | 0.1962 | 0.3651 | 0.3408 | 0.2631 | 0.2273 |
| 0.2897 | 0.3105 | 0.1873 | 0.2051 | 0.4848 | 0.4420 | 0.3836 | 0.3157 |
| 0.3587 | 0.3886 | 0.2961 | 0.3370 | 0.7713 | 0.6677 | 0.5312 | 0.4157 |
| 0.4612 | 0.5052 | 0.3074 | 0.3510 | 1.1013 | 0.9072 | 0.6698 | 0.5026 |
| 0.5306 | 0.5861 | 0.4888 | 0.5795 | 1.4869 | 1.1657 | 0.8809 | 0.6239 |
| 0.5498 | 0.6086 | 0.5117 | 0.6091 | 2.0084 | 1.4876 | 1.0486 | 0.7139 |
| 0.5772 | 0.6404 | 0.5357 | 0.6403 | 2.6634 | 1.8606 | 1.2156 | 0.8004 |
| 0.7968 | 0.8981 | 0.8317 | 1.0383 | 3.4268 | 2.2651 | 1.4532 | 0.9158 |
| 0.8168 | 0.9220 | 0.8644 | 1.0856 | 4.2622 | 2.6782 | 1.4769 | 0.9271 |
| 0.8404 | 0.9498 | 0.9053 | 1.1449 | | | 1.6456 | 1.0052 |
| 1.0073 | 1.1499 | 1.1543 | 1.5335 | | | 2.0288 | 1.1759 |
| 1.0347 | 1.1818 | 1.2009 | 1.6131 | | | 2.1330 | 1.2208 |
| 1.0594 | 1.2124 | 1.2442 | 1.6897 | | | 2.2842 | 1.2856 |
| 1.1040 | 1.2654 | 1.4487 | 2.0757 | | | 2.3546 | 1.3157 |
| 1.1260 | 1.2919 | 1.4767 | 2.1338 | | | | |
| 1.1546 | 1.3263 | 1.5054 | 2.1946 | | | | |
| 1.5306 | 1.7732 | 1.6611 | 2.5421 | | | | |
| 1.5981 | 1.8546 | 1.7058 | 2.6486 | | | | |
| 1.6369 | 1.9015 | 1.7379 | 2.7283 | | | | |
| 1.7196 | 1.9990 | | | | | | |
| 1.7555 | 2.0425 | | | | | | |
| 1.8093 | 2.1062 | | | | | | |
| 1.9952 | 2.3297 | | | | | | |
| 2.0420 | 2.3860 | | | | | | |
| 2.1010 | 2.4508 | | | | | | |
| 2.3079 | 2.6978 | | | | | | |
| 2.3877 | 2.7913 | | | | | | |
| 2.4521 | 2.8669 | | | | | | |

[a] Unit: moles of salt per 55.51 moles of solvent.

Table V. Osmotic and Activity Coefficients of $(CH_3)_4NBr$, $(C_4H_9)_4NBr$, $(CH_3)_4NF$, and $(C_4H_9)_4NF$ in $D_2O$ at 25°C

| | $(CH_3)_4NBr$ | | $(C_4H_9)_4NBr$ | | $(CH_3)_4NF$ | | $(C_4H_9)_4NF$ | |
|---|---|---|---|---|---|---|---|---|
| $m'$ | $\phi$ | $\gamma_\pm$ | $\phi$ | $\gamma_\pm$ | $\phi$ | $\gamma_\pm$ | $\phi$ | $\gamma_\pm$ |
| 0.1 | 0.894 | 0.714 | 0.884 | 0.707 | 0.922 | 0.790 | 1.002 | 0.912 |
| 0.2 | 0.865 | 0.635 | 0.837 | 0.606 | 0.929 | 0.766 | 1.038 | 0.956 |
| 0.3 | 0.847 | 0.588 | 0.804 | 0.548 | 0.960 | 0.760 | 1.088 | 1.032 |
| 0.4 | 0.833 | 0.554 | 0.784 | 0.505 | 0.978 | 0.767 | 1.140 | 1.120 |
| 0.5 | 0.822 | 0.527 | 0.769 | 0.472 | 1.000 | 0.781 | 1.196 | 1.230 |
| 0.6 | 0.812 | 0.505 | 0.756 | 0.446 | 1.022 | 0.799 | 1.253 | 1.356 |
| 0.7 | 0.806 | 0.487 | 0.746 | 0.425 | 1.044 | 0.821 | 1.311 | 1.498 |
| 0.8 | 0.800 | 0.471 | 0.737 | 0.407 | 1.066 | 0.847 | 1.368 | 1.656 |
| 0.9 | 0.796 | 0.459 | 0.729 | 0.391 | 1.089 | 0.876 | 1.423 | 1.834 |
| 1.0 | 0.791 | 0.447 | 0.721 | 0.377 | 1.112 | 0.906 | 1.482 | 2.040 |
| 1.2 | 0.785 | 0.427 | 0.704 | 0.353 | 1.160 | 0.972 | 1.588 | 2.504 |
| 1.4 | 0.781 | 0.414 | 0.688 | 0.332 | 1.210 | 1.052 | | |
| 1.6 | 0.779 | 0.402 | 0.671 | 0.312 | 1.261 | 1.143 | | |
| 1.8 | 0.779 | 0.394 | 0.653 | 0.294 | 1.311 | 1.246 | | |
| 2.0 | 0.780 | 0.385 | 0.636 | 0.278 | 1.365 | 1.360 | | |
| 2.5 | 0.783 | 0.368 | 0.595 | 0.246 | 1.500 | 1.710 | | |

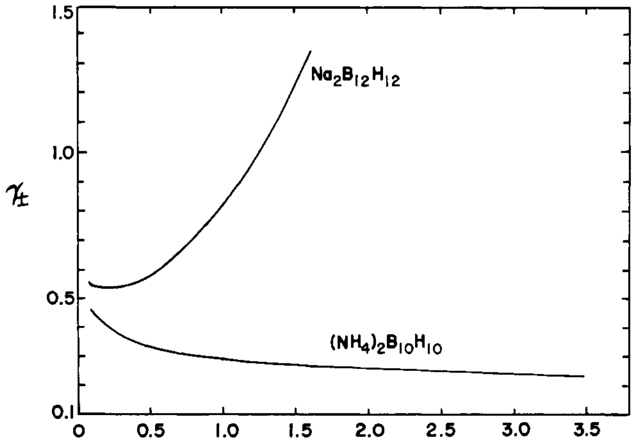

**Figure 1.** Mean molal activity coefficients $\gamma_\pm$ of $(NH_4)_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$ in $H_2O$ at various molal concentrations $m$ at 25°C

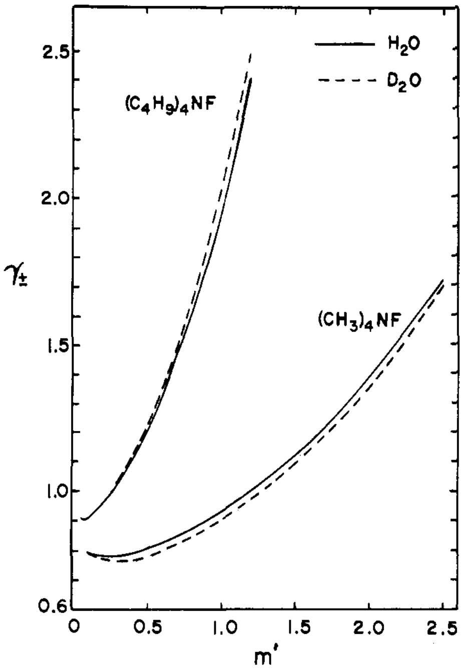

**Figure 2.** Mean molal activity coefficients $\gamma_\pm$ of $(CH_3)_4NF$ and $(C_4H_9)_4NF$ in $H_2O$ and in $D_2O$ at various aquamolal concentrations $m'$ at 25°C

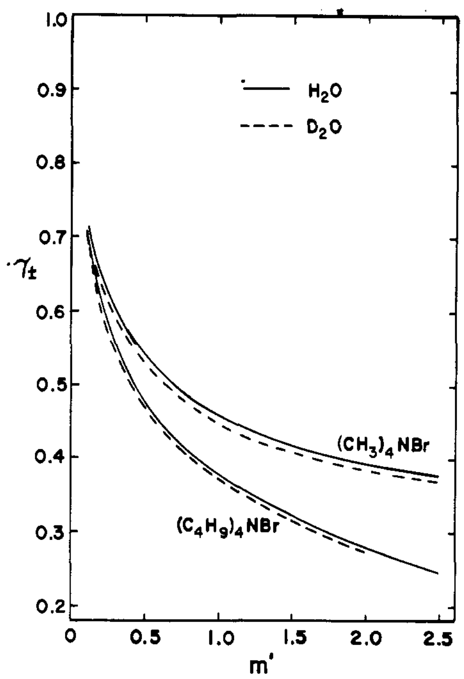

**Figure 3.** Mean molal activity coefficients $\gamma_\pm$ of $(CH_3)_4NBr$ and $(C_4H_9)_4NBr$ in $H_2O$ and in $D_2O$ at various aquamolal concentrations $m'$ at 25°C

*13*). Large univalent cations yield relatively water-insoluble salts of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, but in general, the salts of $B_{10}H_{10}^{2-}$ are more water soluble than their $B_{12}H_{12}^{2-}$ counterparts. A striking example is cited for the triethylammonium salts. The $B_{10}H_{10}^{2-}$ salt is highly water soluble, whereas the $B_{12}H_{12}^{2-}$ salt is very insoluble (*13*).

Spectroscopic data of Muetterties suggest a significant and localized (symmetry loss) interaction between cation and anion. This effect is said to be more notable in $B_{10}H_{10}^{2-}$ than in $B_{12}H_{12}^{2-}$ and is consistent with the general finding that $B_{10}H_{10}^{2-}$ is more susceptible to electrophilic attack (*13*). In $D_2O$ solutions containing DCl, H-D exchange is reported to take place converting some B-H of the anions to B-D. The relative rates of deuteration are reported as $B_{12}H_{12}^{2-}$ = 1, equatorial $B_{10}H_{10}^{2-}$ = 68, and apical $B_{10}H_{10}^{2-}$ = 330 (*13*).

It seems, therefore, highly probable that $B_{10}H_{10}^{2-}$ ions would hydrogen bond to water; in contrast, the hydrogen bonding of water to $B_{12}H_{12}^{2-}$ will be much less, if any. If the "hydrated" $B_{10}H_{10}^{2-}$ ion and "hydrated" $NH_4^+$ ion are structurally compatible, there will be structural salting-in leading to low values of $\gamma_\pm$. The effect will be over and above that owing to the charge-charge interactions. In contrast, if the less hydrated or "hydrophobic" $B_{12}H_{12}^{2-}$ ion and the "hydrated" $Na^+$ ion are structurally incompatible, there will be structural salting-out (over and above usual charge-charge interactions) leading to high values of $\gamma_\pm$. The latter situation is somewhat similar to those of tetraalkylammonium fluorides in water (*19*).

***Solutions of tetraalkylammonium halides.*** As shown in Tables III and V as well as in Figures 2 and 3, the decreasing order of the $\gamma_\pm$ found for tetraalkylammonium halides at constant aquamolality is

$$(C_4H_9)_4NF > (CH_3)_4NF > (CH_3)_4NBr > (C_4H_9)_4NBr$$

in $H_2O$ as well as in $D_2O$. In $D_2O$ solutions, $\gamma_\pm$ values for $(C_4H_9)_4NF$ are greater than that in $H_2O$ solutions, whereas for the other three salts studied, $\gamma_\pm$ values in $D_2O$ are lower than the corresponding values in $H_2O$. Similar to some other thermodynamic properties, the effect in $H_2O$ seems to be magnified slightly when the solvent is $D_2O$ (*10, 15*). Whether these observations are the manifestation of the greater structuredness of $D_2O$, or are owing to more crowded energy levels of $D_2O$ molecules over those of $H_2O$ molecules, is currently under debate and still unsettled at this moment (*3, 16*). It is hoped that our data will be useful for testing concepts and theories for the solvent isotope effects.

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