Table III. Acid Dissociation Constants (p*K*a) of Heterocyclic N-Oxides Conjugate Acids at 25° ± 1°C

Base	$[B]^{\circ}_{tot}$, *M*	p*K*a Found	p*K*a Reported	*P*
PO	0.04	0.55 ± 0.01	0.79[a], 0.56[b]	2.4×10^{-3}
2MPO	0.04	1.10 ± 0.02	1.02[c]	14.3×10^{-3}
3MPO	0.04	1.00 ± 0.01	1.08[a]	6.7×10^{-3}
4MPO	0.04	1.32 ± 0.02	1.29[a]	3.3×10^{-3}
2,6DMPO	0.008	1.41 ± 0.01	1.44[c]	100.0×10^{-3}

[a] Ref. 5. [b] Ref. 6. [c] Ref. 4.

that the average distribution ratios ($\bar{D}$) given in Table I may be equated to the thermodynamic partition coefficients (*P*).

The p*K*a values of the pyridine N-oxides thus obtained are compared in Table II with the reported values.

The results obtained show that the p*K*a values of the pyridine N-oxides follow the same order as those of the corresponding pyridines—i.e., PO < 3MPO < 2MPO < 4MPO < 2,6DMPO.

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Enthalpy and Entropy of Dilution of Tetraethanolammonium Bromide

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The excess enthalpy of aqueous solutions of tetraethanolammonium bromide has been measured from 0.025–3.0*m* at 25°C. The excess entropy has been calculated from the enthalpy and Gibbs free energy. Unlike tetrapropylammonium bromide, tetraethanolammonium bromide has low values of excess enthalpy and entropy.

A large body of evidence has accumulated indicating that the interaction of the surface of a molecule with a solvent has a profound influence on the thermodynamic and kinetic properties of solutions *(4–6, 17–19)*. In spite of a large amount of work in the area, we still cannot predict the way in which a change in the surface properties of a molecule affects its solution properties. Recent advances in statistical mechanics allow the calculation of the properties of a solution up to moderate concentrations ($\sim 1m$) from a knowledge of the law of force between two solute molecules in an infinitely dilute solution *(8)*.

Recently, Ramanathan and Friedman *(15)* have reversed this procedure to find out what laws of force are needed to explain experimental data. In this way, quantitative information on the way solute solvation influences the attractive and repulsive forces between solutes is derived. Measurements on tetraethanolammonium bromide [tetrakis(2-hydroxyethyl)ammonium bromide] are of particular interest because previous results on the free energy *(19)*, volumes *(19)*, conductance *(6)*, viscosity *(5)*, partial molal heat capacity *(19)*, volume of mixing with other electrolytes *(18)*, salting out coefficients *(17)*, and heats of transfer *(19)* have indicated that the substitution of a terminal hydroxy group for a terminal methyl group in the tetrapropylammonium ion results in a drastic change of properties. The present data show how this change in the surface of the molecule affects the enthalpy and entropy of aqueous solutions.

Experimental

Since the experimental details have been described *(3)*, only a brief description is given here.

The tetraethanolammonium bromide was prepared by the method of Wen and Saito *(19)* as modified by Evans et al. *(6)*. A mixture of 248 grams of triethanolamine (1.6 moles), 100 grams of 2-bromoethanol (0.8 mole), and 300 ml of methanol was refluxed for 24 hr. After titration with concentrated aqueous hydrobromic acid to pH 3, the mixture was cooled and the triethanolamine hydrobromide removed by filtration. The filtrate was evaporated. The resulting oil was cooled slowly with occasional stirring until it crystallized and the crystals of tetraethanolammonium bromide were removed by filtration.

A saturated solution of tetraethanolammonium bromide in methanol was cooled to −20°C, and the much less soluble crystals of the hydrobromide were filtered off. This was done two times. The filtrate was evaporated to dryness.

The tetraethanolammonium bromide was first precipitated three times from warm methanol by adding fourfold excess of ethanol and cooling. Then the sample was recrystallized four times from ethanol. Since tetraethanolammonium bromide is hygroscopic, all recrystallizations were performed in a dry box. The crystals were dried in an Abderhalden drying pistol at 56°C for 24 hr.

The solutions of tetraethanolammonium bromide were prepared in a dry box. Each sample was weighed out separately and used the same day. There was no appreciable weight gain of the solid tetraethanolammonium bromide in the dry box.

Analysis

The tetraethanolammonium bromide sample was analyzed for bromide and triethanolamine hydrobromide. The bromide ion was determined gravimetrically by precipitation as AgBr. The results were 29.10 and 29.09% bromide. The calculated value was 29.15% bromide.

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A pH titration of an approximately 0.1-gram sample of tetraethanolammonium bromide in 2 ml of water *vs.* standardized 0.1*N* NaOH was used to determine triethanolamine hydrobromide. The NaOH decomposes the tetraethanolammonium bromide, so the titration must be performed as quickly as possible. A blank run and a standardization using 6 meq of triethanolamine hydrobromide were also run. The results indicated there was 1.5 mole % triethanolamine hydrobromide present as an impurity. The initial pH of the tetraethanolammonium bromide sample in 2 ml of water was about pH 6.5, indicating that there were only trace amounts of triethanolamine present. [The pK_a of triethanolamine is 7.77 *(1).*]

One calorimeter was a 250-ml Dewar flask containing a 200-rpm propeller stirrer, a 2000-ohm thermistor, a heater, and a glass ampoule for the sample. The heat of breaking the ampoule was 0.02 ± 0.01 calorie. The details of the calorimeter and the method of operation have been described *(2, 20).* The calorimeter has been checked repeatedly *(2, 20)* by other workers who measured the heat of neutralization of solid tris(hydroxymethyl)-aminomethane.

The heats of dilution of the low concentration solutions were measured with a LKB 10700 flow microreaction calorimeter (LKB-Produckter AB, S-161 25 Bromma 1, Sweden). This instrument is very similar to that described by Monk and Wadso *(13).* The calorimeter consists of a flow reaction cell surrounded by thermopiles attached to an aluminum heat sink.

Results and Discussion

The results of the measurement with the flow reaction calorimeter are given in Table I. These low concentration ϕ_L values were extrapolated using an extended Debye-Hückel equation *(9, 10).* In this program, the following equations are used to find ϕ_L:

$$\Delta\phi_L = \phi_L(m_f) - \phi_L(m_i) \tag{1}$$

where

$$\phi_L = 707\, m^{1/2}\,[1/(1 + m^{1/2}) - \sigma(m^{1/2})/3] + Bm + Cm^{3/2} \tag{2}$$

also

$$\sigma(y) = 3/y^3\,[(1 + y) - 1/(1 + y) - 2 \ln (1 + y)] \tag{3}$$

707 is the Debye-Hückel slope, m is the molality, and constants B and C were obtained by a least-squares procedure from the low concentration heats of dilution data.

The values of constants B and C were −1830 and 1184, respectively. The ϕ_L values for the dilution of 0.025 molal tetraethanolammonium bromide in Table I were discarded because the least-squares procedure gives a very large error ($2\sigma = -33.0$ cal/mol) when this value is included. Without this point there is a very good fit ($2\sigma = \pm 1.4$ cal/mol). A comparison of a graph of the data with graphs of other salts shows that the curve does not resemble the ϕ_L curves of the other salts if this point is included. Without this point, the curves are similar and a graphical extrapolation gives the same result as the computer fit (±2 cal/mol).

The results of the runs with the 250-ml Dewar calorimeter are given in Table II. The values of ϕ_L final were calculated from a plot of ϕ_L *vs.* molality, using the ϕ_L values obtained from the least-squares fit of the low concentration data.

Since there was approximately 1.5 mole % triethanolamine hydrobromide impurity, a correction should be made for the heat of dilution of this salt. Some rough measurements *(3)* of the heat of dilution of triethanolamine hydrobromide indicate that the values of ϕ_L in Table II should be raised by 4 ± 4 calories per mole. This correction was not applied because it is less than the estimated over-all accuracy of the results (about ±10 cal/mole).

The values of ϕ_L for tetraethanolammonium bromide are very negative and in the same region as salts that are known to be strong structure breakers. For instance, at 3m the values of ϕ_L in cal/mol are: Et_4NBr, −902 *(11)*; $(EtOH)_4NBr$, −1054; Me_4NBr, −1080 *(11)*; $NaClO_3$, −866 *(14)*; and KNO_3, −1586 *(14).* In addition, it is clear that tetraethanolammonium bromide is quite different in behavior from its analog, tetrapropylammonium bromide [ϕ_L of Pr_4NBr = 1480 *(11)* at 3m]. This reinforces the results of previous measurements of other properties of tetraethanolammonium salts *(4–6, 17–18).* The hydrophobic hydration of the tetrapropylammonium ion has been destroyed by a substitution of hydroxy groups for terminal methyl groups.

In aqueous solutions a consideration of the excess entropies is often more useful than a consideration of excess enthalpies *(7).* The values of TS^{ex} for a variety of salts were calculated from the equation:

$$TS^{ex} = \phi_L - \nu RT[\ln \gamma + (1 - \phi)]$$

where T is the absolute temperature, S^{ex} the excess (nonideal) relative entropy, ν the number of ions per mole

Table I. Heats of Dilution of $(EtOH)_4NBr$ at 25°C

m_i, mol kg^{-1}	m_f, mol kg^{-1}	n^a, µmol sec^{-1}	q^b, µcal sec^{-1}	$\Delta\phi_L{}^c$(exptl), cal mol^{-1}	$\Delta\phi_L{}^d$(calcd), cal mol^{-1}
0.2004	0.0986	0.578	−45.2	78.2	78.2
0.1994	0.0968	0.575	−45.2	78.6	78.8
0.0999	0.0489	0.293	−11.2	38.1	37.5
0.1004	0.0498	0.294	−11.1	37.6	37.4
0.0500	0.0251	0.151	−1.9	12.3	13.4
0.0500	0.0251	0.151	−2.0	13.6	13.4
0.0250	0.01259	0.0761	1.3	−16.9	1.5
0.0250	0.01259	0.0761	1.3	−16.9	1.5

[a] Flow rate, µmol/sec. [b] Heat flow, µcal/sec. [c] Experimental value for change in apparent heat content on dilution, cal/mol. [d] Value for change in ϕ_L on dilution calculated from Equations 1 and 2 with constants $B = -1830$, $C = 1184$ evaluated by least-squares procedure.

Table II. Heats of Dilutions of $(EtOH)_4NBr$ at 25°C

m_i, mol kg^{-1}	m_f, mol kg^{-1}	n, mol	q, cal	$\Delta\phi_L{}^a$, cal mol^{-1}	$\phi_L(m_f)$,^{b} cal mol^{-1}	$\phi_L(m_i)^c$, cal mol^{-1}	TS^{ex}, cal mol^{-1}
3.000	0.0272	0.00685	−7.35	1077	25	−1052	
3.000	0.0249	0.00628	−6.77	1081	26	−1055	
					$\phi_L(m_i)$	= −1054	40
2.000	0.0234	0.00593	−5.16	874	26	−848	
2.000	0.0179	0.00451	−3.90	869	27	−842	
					$\phi_L(m_i)$	= −845	116
1.000	0.0160	0.00408	−2.23	5.74	27	−547	
1.000	0.00923	0.00233	−1.31	5.71	27	−544	
					$\phi_L(m_i)$	= −546	191

[a] Change in apparent molal heat content on dilution. [b] Apparent molal heat content at final concentration, m_f. [c] Apparent molal heat content at initial concentration, m_i. Estimated accuracy is about ±10 cal/mol. Major source of error is probably impurities in salt.

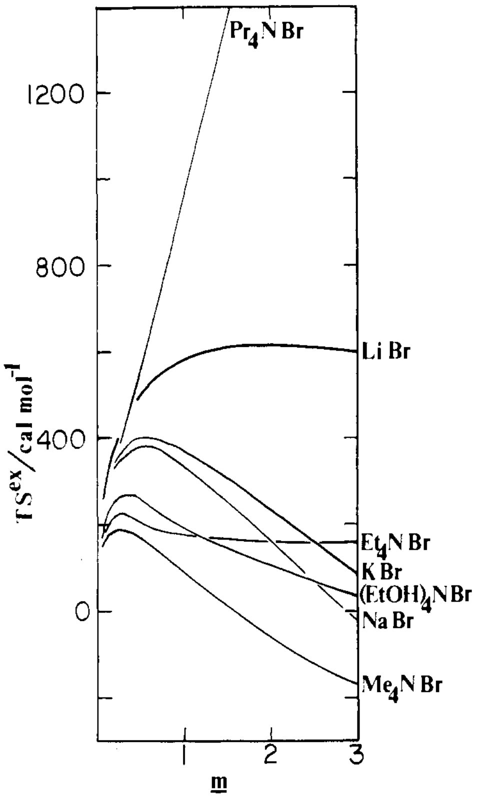

Figure 1. Values of TS^{ex} plotted against molality for various salts

of salt, γ the mean molal activity coefficient, and ϕ the osmotic coefficient. For tetraethanolammonium bromide, values of TS^{ex} were calculated using the results of this work and the activity and osmotic coefficient measurements of Wen and Saito *(19)*. The excess entropies for the other salts shown in Figure 1 were calculated from literature values *(11, 12, 14, 16)*.

An examination of Figure 1 shows that at low concentrations the excess entropy of tetraethanolammonium bromide starts out low and then curves upward compared to the alkali metal halides. The curve for tetraethylammonium bromide behaves in the same manner, but the shift is more pronounced. This effect at high concentration is probably due to the large size of the ions which is expected to dominate their behavior at the concentration increases. A more detailed interpretation of these results is best left until the results of statistical mechanical calculations are available.

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