L	latent heat of vaporization, k J mol^{-1}
P	vapor pressure, mmHg
T	temperature, K
x	mole fraction in liquid phase

Greek letters

| γ | activity coefficient |
| ρ | liquid density, g cm^{-3} |

Subscripts

| 1 | toluene |
| 2 | 1,1,2,2-tetrachloroethane |

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Acidities of Some N-Haloamides (ZCONHX) in Water and Ethanol–Water Mixtures at 25 °C

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The acidities of ten N-haloacetamides and of N-chlorourethane and N-fluorourethane in water and ethanol–water mixtures (25, 50, and 75 % by weight) were determined by potentiometric titration at 25 °C. The pK_as of N-chloroacetamide and N-chloro-α-haloacetamides in water are compared with those of the corresponding acetic acids.

Our studies on radical reactions of N-haloamides (ZCONHX) (3, 4, 8) and their electrochemical behavior (2) required a knowledge of their acidities. The pK_a values of various N-haloamides in water and ethanol–water mixtures at 25 °C are recorded in Table I; they increase as the polarity of the medium decreases as expected. Literature values of the pK_as of some carboxylic acids in water at 25 °C (6) are included for comparison purposes.

The N-chloroacetamides are less acidic than the corresponding acetic acids by about 2.5–3 pK_a units. If the substituent effects on the acidity of the N-chloroacetamides and on the acidity of the corresponding acetic acids were exactly the same, we would expect a straight line of slope unity by plotting the pK_a of ZCONHCl against the pK_a of ZCOOH. As shown in Figure 1, this is nearly the case except for N-chlorofluoroacetamide. Repeated pK_a determinations on different samples gave consistently a pK_a value of 5.74 ± 0.02. N-Chlorofluoroacetamide appears to be less acidic than N-chloroiodoacetamide (except in 50 and 75 % ethanol–water where the acidities are similar), which is quite unexpected considering the much higher electronegativity of the fluorine atom. Assuming that the correlation shown in Figure 1 would hold for Z = C$_2$H$_5$O, the pK_a of C$_2$H$_5$OCOOH would be of the order of 5.5 (as compared with 6.35 for the pK_a of aqueous carbon dioxide); it cannot be measured directly because of spontaneous decarboxylation.

Table I. pK_a Values of N-Haloamides (ZCONHX) in Water and Ethanol–Water Mixtures at 25 °C [a]

| | % ethanol–water by weight | | | | | |
| | 0% | 25% | 50% | 75% | | pK_a |
ZCONHX	pK_a	pK_a	pK_a	pK_a	ZCOOH	(water) [b]
CH$_3$CONHCl	7.22	7.72	8.11	8.89	CH$_3$COOH	4.756
ICH$_2$CONHCl	5.51	6.02	6.50	7.11	ICH$_2$COOH	3.175
BrCH$_2$CONHCl	5.36	5.78	6.24	6.90	BrCH$_2$COOH	2.90
ClCH$_2$CONHCl	5.42	5.80	6.21	6.84	ClCH$_2$COOH	2.829
FCH$_2$CONHCl	5.74	6.13	6.45	7.09	FCH$_2$COOH	2.585
Cl$_2$CHCONHCl	3.71	4.16	4.58	5.12	Cl$_2$CHCOOH	1.366
CCl$_3$CONHCl	2.91	3.37	3.70	4.22	CCl$_3$COOH	0.63
CF$_3$CONHCl	2.85	3.18	3.39	3.61	CF$_3$COOH	0.230
CH$_3$CONHBr	7.89	8.30	8.88	9.59		
ClCH$_2$CONHBr	6.20					
C$_2$H$_5$OCONHCl	8.02	8.55	9.18	10.21		
C$_2$H$_5$OCONHF	5.69	6.33	7.06	8.10		

[a] Three determinations were made for each pK_a value, the standard deviation being ±0.02 pK_a unit. [b] Taken from ref 6.

The lower acidity of N-chlorourethane as compared with N-chloroacetamide can be accounted for by the fact that the carbethoxy group is resonance stabilized to a greater extent than the acetyl group; acetates (pK_a ≃ 25) are less acidic than acetone (pK_a ≃ 20) for the same reason.

An N-chloroamide is about four to five times more acidic than the corresponding N-bromoamide and N-fluorourethane is much more acidic than N-chlorourethane in agreement with the electronegativities of the bromine, chlorine, and fluorine atoms. In basic medium, decomposition of N-fluorourethane occurs slowly but we believe the pK_a values obtained are reliable.
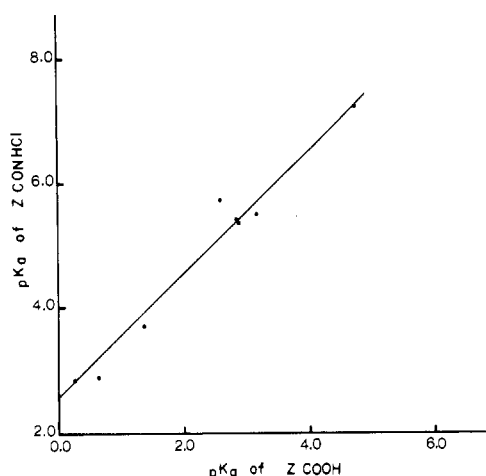
Figure 1. pK_a values of ZCONHCl vs. pK_a values of ZCOOH in water at 25 °C.

Experimental Section

The N-haloamides were prepared by the sodium hypohalite method (*1*) except for N-fluorourethane (*3*).

The potentiometric titrations were carried out on a 0.01 M solution at 25 °C using an Orion-type pH meter Model 801, a Sargent-Welch glass electrode type S-30050-15, and a saturated calomel electrode type S-30080-15. The buret, containing an NaOH 0.01 M solution, had a digital syringe, Dosimat type, Metrohm Herisan Model E 412. Before and after each titration, the electrodes were calibrated using two buffers—lithium oxalate–oxalic acid and lithium succinate–succinic acid (*5*)—prepared in the same solvent as the titrated compound. The reproducibility was of 0.02 pH unit. The pK_as of benzoic acid and p-nitrophenol determined by this method were found to be 5.68 and 7.86, respectively, in agreement with the literature values (*5, 7*).

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Densities of Dilute Aqueous Solutions of Selected Ethers†

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The densities of dilute aqueous solutions of 11 ethers [oxetane, oxepane, 1,3-dioxane, 1,3-dioxepane, 1,3,5-trioxane, 2,4,6-trimethyl-1,3,5-trioxane (paraldehyde), 2,5-dimethoxytetrahydrofuran, dimethoxymethane, diethoxymethane, 1,2-dimethoxyethane, 1,2-diethoxyethane] have been determined at 25 °C by means of a differential buoyancy technique. The solute apparent molar volumes and excess molar volumes are presented. An empirical equation is proposed to evaluate the limiting partial molar volumes of cyclic ethers with the formula $(CH_2)_n O_m$.

The volumetric properties of nonelectrolyte aqueous solutions, in conjunction with other thermodynamic properties, provide useful information about solute–water interactions (*3*). In continuation of previous studies on the volumetric behavior of ethers in water (*1*), we have determined the densities at 25 °C of dilute aqueous solutions of some cyclic monoethers (oxetane, oxepane), cyclic di- and triethers (1,3-dioxane, 1,3-dioxepane, 1,3,5-trioxane, 2,4,6-trimethyl-1,3,5-trioxane or paraldehyde, 2-5-dimethoxytetrahydrofuran), and open-chain diethers (dimethoxymethane, diethoxymethane, 1,2-dimethoxyethane, 1,2-diethoxyethane). From density data, the solute apparent molar volumes have been calculated at each concentration, and the results have been extrapolated to give the partial molar volumes at infinite dilution. These limiting quantities, in conjunction with the known molar volumes of pure liquid compounds, enabled the calculation of excess molar volumes.

Experimental Section

All chemicals were commercial products of the highest available purity. Solid 1,3,5-trioxane was sublimed under vacuum on a cold finger in a closed glass apparatus. The liquid compounds were fractionally distilled, at atmospheric pressure, after prolonged reflux over metallic sodium, using a Todd column with 30 theoretical plates. Oxepane was further rectified by a Perkin-Elmer 251 spinning band column. All the samples used in the experiments showed a GLC purity ≥99.8% and a water content less than 0.1%, as measured by a Karl Fischer reagent. In the case of 2,5-dimethoxytetrahydrofuran, the cis–trans