

Registry No. Ethanol, 64-17-5.

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Protonation Constants of Mono-, Di-, and Triethanolamine. Influence of the Ionic Composition of the Medium

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The ionization constants in aqueous solution of mono-, di-, and triethanolamine were determined potentiometrically at 25 °C for ionic strengths ranging from 0.05 to 1.5 M, the inert electrolyte being KCl, KBr, or KNO₃. A linear relationship was found to hold between pK and $I^{1/2}$. The thermodynamical constants have been calculated.

Introduction

The properties of alkanolamines, including their important capacity for removing acidic components from natural and refinery gases, depend among other factors on their basic nature. Although values have been published for the ionization constants of alkanolamines at various temperatures and in various solvents (1-5), we are aware of no systematic study of the effect of the ionic composition of the medium. To fill this gap the present article describes a study of the influence of the nature and concentration of the inert electrolyte upon the ionization constants of protonated monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA), i.e., upon the constants corresponding to the process $AH^+ \rightleftharpoons A + H^+$. The corresponding thermodynamical constants have also been calculated.

Experimental Section

All the chemical products employed were Merck p.a. The ionization constants of protonated MEA, DEA, and TEA were determined by titrating aqueous solutions of the alkanolamines with hydrochloric acid at various ionic strengths (0.05, 0.10, 0.25, 0.50, 1.00, and 1.50 M) and with various inert electrolytes (KCl, KBr, and KNO₃). The thermostated titration cell had inlets for the microburet, a current of nitrogen, a thermometer, and an electrode. pH was measured with a Beckman 4500 pH-meter accurate to 0.001 pH unit and Radiometer GK2401C electrode. The pH-meter was calibrated before each titration by using Beckman buffer solutions of pH 7 and 10. The titration curves from which the protonation constants of the alkanolamines are calculated lie within this pH range. The temperature

Table I. Ionization Constants of Protonated MEA, DEA, and TEA at $T = 25^\circ\text{C}$

I/M	pK_{exptl}		
	KBr	KCl	KNO ₃
Monoethanolamine			
1.50	9.86 ± 0.01	9.87 ± 0.01	9.83 ± 0.01
1.00	9.81 ± 0.01	9.81 ± 0.01	9.79 ± 0.01
0.50	9.75 ± 0.01	9.74 ± 0.01	9.74 ± 0.01
0.25	9.72 ± 0.01	9.70 ± 0.01	9.69 ± 0.01
0.10	9.64 ± 0.01	9.67 ± 0.01	9.65 ± 0.01
0.05	9.65 ± 0.02	9.65 ± 0.01	9.60 ± 0.01
0.00 ^a	9.58 ± 0.02	9.60 ± 0.01	9.59 ± 0.02
Diethanolamine			
1.50	9.37 ± 0.01	9.40 ± 0.01	9.33 ± 0.01
1.00	9.31 ± 0.01	9.33 ± 0.01	9.27 ± 0.01
0.50	9.19 ± 0.01	9.23 ± 0.01	9.18 ± 0.01
0.25	9.11 ± 0.01	9.15 ± 0.01	9.12 ± 0.01
0.10	9.05 ± 0.01	9.10 ± 0.01	9.06 ± 0.01
0.05	9.02 ± 0.01	9.02 ± 0.01	9.02 ± 0.01
0.00 ^a	8.96 ± 0.03	8.97 ± 0.02	8.96 ± 0.01
Triethanolamine			
1.50	8.31 ± 0.01	8.27 ± 0.01	8.19 ± 0.01
1.00	8.18 ± 0.01	8.21 ± 0.01	8.13 ± 0.01
0.50	8.04 ± 0.01	8.10 ± 0.01	8.05 ± 0.01
0.25	7.99 ± 0.01	8.00 ± 0.01	8.02 ± 0.01
0.10	7.93 ± 0.01	7.96 ± 0.01	7.96 ± 0.01
0.05	7.89 ± 0.01	7.96 ± 0.01	7.92 ± 0.01
0.00 ^a	7.80 ± 0.02	7.86 ± 0.02	7.87 ± 0.01

^a Extrapolated value.

of all experiments was maintained at $25 \pm 0.1^\circ\text{C}$ by water flow from a thermostat.

Results and Discussion

The pK was calculated by using the equation

$$pK_{\text{exptl}} = \text{pH} - \log \left[\frac{B_0}{c_0 V + [(K_w)(10^{\text{pH}}) - 10^{-\text{pH}}](V_0 + V)} - 1 \right] \quad (1)$$

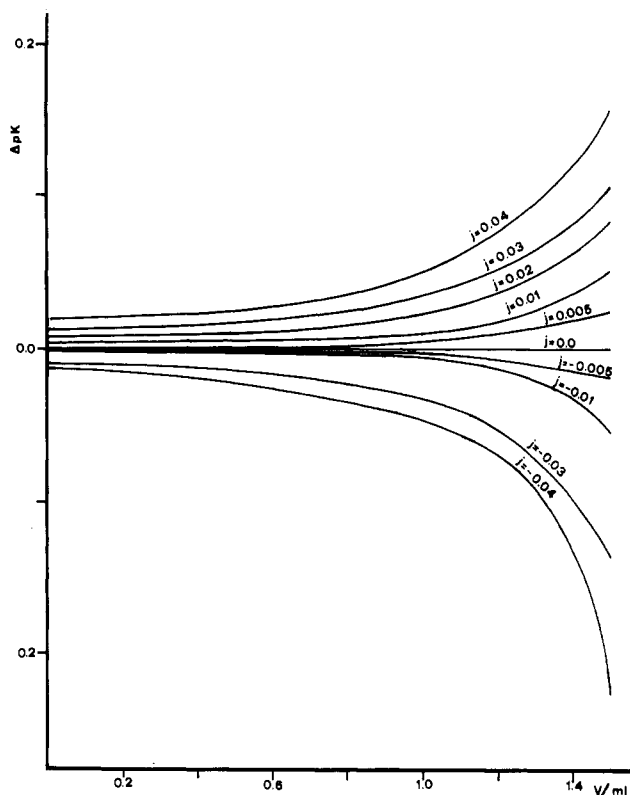


Figure 1. Influence of the error j in the initial concentration of TEA upon the value of the ionization pK of $TEAH^+$.

Table II. Thermodynamic Ionization Constants of Protonated MEA, DEA, and TEA

	pK	
	a	b
MEA	9.59 ± 0.01	9.53 ± 0.02
DEA	8.96 ± 0.01	8.96 ± 0.01
TEA	7.84 ± 0.04	7.86 ± 0.01

^a Extrapolated value. ^b Value calculated as in ref 6.

where K_{exptl} is a mixed equilibrium constant, V the volume of HCl added, V_0 the initial volume of the solution, c_0 the concentration of the HCl, and B_0 the number of moles of alka-

nomine initially present. This equation is deduced as in ref 6 from the conservation of matter together with the conditions of equilibrium and electroneutrality that hold for the aqueous solution. To see how any errors in the determination of the initial concentration of alkanolamine might affect the pK value calculated, eq 1 was analyzed by replacing B_0 by $(1-j)B_0$, j being a hypothetical proportional error which was varied between 1% and 4%. Figure 1 shows the result of this analysis for a typical titration. As can be seen, for $j \neq 0$ the pK diverges increasingly from the correct value as the titration proceeds. To reduce this error to a minimum the calculation of pK_{exptl} was based on the least affected period of titration, besides which the value of B_0 itself was optimized by means of the Davies, Swann, and Campey algorithm (7), the optimal value being taken as that for which the possible errors in pK_{exptl} would be least. In no case was the error j found to be greater than 2%, which is in accord with the precision of the volumetric apparatus used.

Table I shows the optimized values of the ionization pK 's of the protonated alkanolamines for the various inert electrolytes and ionic strengths employed. The basicity of the alkanolamine may be observed to fall as the number of substituent alcohol groups rises. The effect of the nature of the inert electrolyte is minimal. The graphs of pK against $I^{1/2}$ are straight lines which allow the extrapolated value of the thermodynamic constant to be obtained. These values are shown in Table II together with those that we have obtained using the experimental procedure described by Albert and Serjeant (6). The agreement between the two is quite acceptable.

Registry No. MEA, 141-43-5; DEA, 111-42-2; TEA, 102-71-6.

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Viscosities, Densities, and Refractive Indexes of Mixtures of Methyl Isobutyl Ketone-Isobutyl Alcohol

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Viscosities, densities, and refractive indexes were determined for methyl isobutyl ketone-isobutyl alcohol mixtures at 20, 25, 30, and 35 °C and at atmospheric pressure. These properties were correlated with the composition and temperature of mixtures through empirical relations. The calculated values were in agreement with the experimental data in the temperature range of the measurements.

Viscosity, density, and refractive index data of binary liquid mixtures are frequently used in chemical engineering work; therefore, an attempt was made to correlate these properties by single equations wherein the effects of temperature and

composition are involved, thereby allowing interpolation of the data.

Materials. Methyl isobutyl ketone (AR, Merck) was distilled, refluxed, and fractionated. The fraction boiling between 115 and 116 °C was collected and used in the experiments. Isobutyl alcohol (AR, Merck) was used without further purification and drying (7). The physical properties of the substances used are compared with corresponding data reported in the literature in Table I.

Experimental Section

Solutions of different composition of the methyl isobutyl ketone-isobutyl alcohol system were prepared by weight in a