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# Dissociation Constants of Diethanolamine and Diisopropanolamine in an Aqueous 1.00 M Potassium Chloride Solution

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**The dissociation constants of diethanolamine (DEA) and diisopropanolamine (DIPA) have been determined potentiometrically in an aqueous potassium chloride solution (1.00 M) at 293, 303, 313, and 323 K. Their dissociation constants were shown to be identical, within experimental error, and can be expressed at zero ionic strength ($I = 0$) by the equation $\log K_{I=0} = (-1.82 \times 10^3)/T - 4.10 + (4.44 \times 10^{-3})T$.**

## Introduction

Alkanolamines are frequently used to remove acidic components (e.g., $H_2S$ and $CO_2$) from natural and refinery gases. The most important alkanolamines for this operation are monoethanolamine (MEA), diethanolamine (DEA), and diisopropanolamine (DIPA) (*3*), and they are usually employed in aqueous solution. For some applications, however, a combined solvent is more efficient (e.g., water and sulfolane in the "Sulfinol" process (*2*)).

The capabilities of the various amines in the absorption of acidic gases depend on, among other factors, their dissociation constants. The dissociation constant of DIPA has been reported only once, but this value (p$K$ = 9.5 at 298 K (*6*)) differs considerably more from those of DEA (p$K$ = 8.88 at 298 K (*4*)) and isopropanolethanolamine (IPEA, p$K$ = 8.81 at 298 K (*4*)) than can be expected on basis of the closely resembling molecular structures. The reported dissociation constant of the secondary amine DIPA is even very similar to that recorded for MEA, a primary amine (p$K$ = 9.498 at 298 K (*4*)).

Therefore the main aim of the present investigation was to provide reliable dissociation constants for DIPA at several temperatures (293, 303, 313, and 323 K). Further, as commercial grade DIPA contains small amounts of monoisopropanolamine (MIPA), the dissociation constants obtained for both commercial grade and pure DIPA were compared.

## Experimental Section

***Chemicals.*** Aqueous hydrochloric acid and sodium hydroxide solutions were prepared from Merck Titrisol ampules and potassium chloride (Merck analytical-grade reagent). Carbon dioxide-free double-distilled water was used throughout.

Table I. Dissociation Constants for DEA and Commercial-Grade DIPA in 1.00 M Potassium Chloride Solution[a]

| | $10^9 K$, mol/L | | | |
|---|---|---|---|---|
| $T$, K | 293 | 303 | 313 | 323 |
| DIPA commercial grade | 0.512 | 0.914 | 1.62 | 3.01 |
| | 0.534 | 0.915 | 1.63 | 2.79 |
| DEA | 0.527 | 0.957 | 1.67 | 2.94 |
| | 0.538 | 0.951 | 1.59 | 2.88 |

[a] $K = m_{H^+} m_{Am} / m_{AmH^+}$; $m_i$ = concentration of component i.

The amines were analyzed by gas chromatography (*5*): DEA (UCB) was 98.5% pure on a water-free basis and pure DIPA (99.9%) was obtained by vacuum distillation of commercial-grade (BASF) DIPA (99.0%).

***Procedure.*** The dissociation constants were determined at constant ionic strength in aqueous 1.00 M potassium chloride solutions, at least in duplicate, as follows. Samples of the aqueous amine solutions (±0.1 M, 4 and 6 mL) were blanketed with nitrogen, acidified with an excess of aqueous hydrochloric acid (0.1000 M, 8 mL) to prevent absorption of carbon dioxide, and finally diluted to 50 mL with potassium chloride (1.00 M).

The protonated amine, acting as a weak acid, and the excess of hydrochloric acid were titrated in a thermostatically controlled vessel with an aqueous sodium hydroxide solution (0.1000 M). The titration was followed potentiometrically by using a Knick industrial pH meter (type DIN) and a Schott combined glass-calomel electrode (type N) with a platinum-wire diaphragm. The method used for calibration of the electrode is identical with that used by Bos (*1*).

The data from the titration curve were used to calculate the excess of hydrochloric acid, the amount of protonated amine, and the dissociation constant of the amine by means of the multiparameter curve-fitting procedure described by Bos (*1*). The sum of excess hydrochloric acid and the amount of protonated amine was found to be within 1% of the total quantity of hydrochloric acid initially added.

## Results and Discussion

Two series of experiments were performed. In the first series the dissociation constants of DEA and commercial-grade DIPA were compared at 293, 303, 313, and 323 K (Table I). From these results it can be concluded that at 1.00 M ionic

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Table II. Dissociation Constants for Commercial-Grade and Pure DIPA in 1.00 M Potassium Chloride Solution[a]

| | $10^9K$, mol/L | | | |
|---|---|---|---|---|
| $T$, K | 293 | 303 | 313 | 323 |
| DIPA commercial grade | 0.456 | 0.846 | 1.47 | 2.35 |
| | 0.453 | 0.838 | 1.42 | 2.28 |
| | 0.454 | | 1.40 | 2.34 |
| DIPA pure | 0.480 | 0.851 | 1.42 | 2.34 |
| | 0.450 | 0.841 | 1.42 | 2.43 |
| | 0.451 | | | 2.62 |
| | | | | 2.35 |

[a] See footnote of Table I.

strength the dissociation constants of DIPA and DEA are essentially equal. The deviations of the dissociation constants of DEA and DIPA, due to nonideality of the solutions, will also be essentially the same because of the structural similarity of the molecules.

Therefore it can be concluded that, at zero ionic strength, the dissociation constants of DIPA are given by the equation which describes the dissociation constants of DEA (*4*):

$$\log K_{I=0} = (-1.82 \times 10^3)/T - 4.10 + (4.44 \times 10^{-3})T$$

The second series of experiments gives the dissociation constants for commercial-grade and pure DIPA at 293, 303, 313, and 323 K (Table II). These results show that the presence of small amounts of MIPA have no effect on the dissociation constant of DIPA.

The standard deviation of the results is 5% of the $K$ values (0.02 p$K$ units) for each of both series of experiments (Tables I and II). The larger difference (10-20% in $K$ values, 0.04-0.08 p$K$ units) between the results for commercial-grade DIPA shown in Tables I and II is due to the separate calibration procedures of the electrode since for each of these series new calibration solutions were prepared. The estimated accuracy for our calibration solutions for pH > 10 is ±0.05 pH unit.

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# Vapor-Pressure Measurements of 1-Methylnaphthalene, 2-Methylnaphthalene, and 9,10-Dihydrophenanthrene at Elevated Temperatures

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**Vapor pressures of three polynuclear aromatic compounds were measured over the following elevated temperature ranges: (1) 1-methylnaphthalene, 424.43-593.38 K; (2) 2-methylnaphthalene, 424.41-638.93 K; and (3) 9,10-dihydrophenanthrene, 437.28-552.61 K. The measurements were carried out with a high-temperature static apparatus. The experimental vapor-pressure data have been fitted to Chebyshev polynomials. The values of $dp/dT$ over the temperatures investigated for 1-methylnaphthalene and 2-methylnaphthalene are reported.**

## Introduction

In a previous paper (*1*) we reported the vapor pressures of three polynuclear aromatic compounds, diphenylmethane, thianaphthene, and bicyclohexyl. In this work we continue the measurements of vapor pressures of compounds which appear in oils associated with the liquefaction of coal. We report the vapor pressures of 1-methylnaphthalene, 2-methylnaphthalene, and 9,10-dihydrophenanthrene over a wide range of temperatures up to their respective conditions of measurable initial thermal decomposition.

No experimental vapor-pressure values are reported in the literature in the range of the present investigation for 9,10-dihydrophenanthrene. The data of Camin and Rossini (*2*) for 1-methylnaphthalene and 2-methylnaphthalene cover the temperature range up to their boiling points.

## Materials

The samples of 1-methylnaphthalene, 2-methylnaphthalene, and 9,10-dihydrophenanthrene were purchased from Aldrich Chemical Co. with reported purities of 97, 99, and 97%, respectively. 1-Methylnaphthalene was purified in a low temperature zone refiner (for substances with melting points above room temperature); 32 and 48 passes were made, respectively. The purities were checked by the freezing-point method of Rossini et al. (*3*), and the results were as follows: 1-methylnaphthalene, 99.95%; 2-methylnaphthalene, 99.98%; and 9,10-dihydrophenanthrene, 99.95%.

## Apparatus and Procedure

The measurements of vapor pressures were carried out with a high-temperature static apparatus described elsewhere (*1*, *4*). Some modifications were made to the apparatus to control the sublimation of the bath fluid. Monsanto Therminol 88 was replaced by a commercial mixture of inorganic salts (Draw Temp 275 manufactured by E. F. Houghton Co.).

The temperature near the equilibrium cell was measured in IPTS-68 with an accuracy of ±0.01 K by means of a Leeds and Northrup platinum resistance thermometer with a calibration traceable to the National Bureau of Standards and checked in

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