splined-fit values probably provide the more reliable Gautreaux–Coates values for these two systems.

The magnitudes of the γ_2^∞ values obtained from the three methods fall in the following order: Barker, Mixon et al., Gautreaux–Coates. The Barker values are related to the G^E correlation constants obtained from a fit of the data points across the entire composition range; hence, the Barker method is often insensitive to any unusual behavior in the P vs. x_1 curves near the end points such as that shown at high x_1 values in Figures 1 and 2. The splined-fit values used by the Mixon et al. method and the Gautreaux–Coates equations are, of course, much more sensitive to the shape of the experimental P curve at the end points. However, the sensitivity often is moderated for the Mixon et al. method by the way that that finite-difference method "reaches" the $x_1 = 0.0$ and 1.0 values. The $G^E = 0$ value at $x_1 = 0$ and at 1.0 plus the two adjacent G^E values at each end are fitted to quadratic equations and the slopes at $x_1 = 0.0$ and 1.0 are obtained from those equations. The slopes sometimes differ appreciably from those given by the splined fits. When that happens, the γ_i^∞ values from the Mixon et al. method are usually lower than those obtained from the Gautreaux–Coates using the splined-fit slopes; i.e., the use of the G^E fits near the end points appears to moderate the values of γ_i^∞ obtained.

It is believed that the Mixon et al. results at high x_1 values are more reliable than the Barker results. Also, any designer using the data should be aware of the relatively high probability that the γ_2^∞ values may be considerably higher than those provided by the Mixon et al. method.

Registry No. Acetone, 67-64-1; isopropylbenzene, 98-82-8; isopropenylbenzene, 98-83-9.

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Heat Capacity of Aqueous Methyldiethanolamine Solutions

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Measurements of the heat capacity of aqueous solutions of methyldiethanolamine (MDEA) containing 23 and 50 wt % amine were made at temperatures of 25, 50, and 75 °C.

Aqueous solutions of methyldiethanolamine (MDEA) are finding increasing use for the selective removal of H_2S from gas mixtures containing hydrogen sulfide and carbon dioxide (*1*). Methyldiethanolamine is a tertiary amine which does not form a carbamate and the rate of reaction with carbon dioxide is slow relative to that with hydrogen sulfide. Little information on the thermophysical properties of MDEA solutions is available. Experimental data for the solubility of H_2S and CO_2 in MDEA solutions have recently been obtained in this laboratory (*2*). There is a need for enthalpies of MDEA solutions for the design of the heat-exchange equipment used in gas treating processes.

Experimental Section

The calorimeter originally devised for the measurement of the enthalpy of solution of CO_2 in alkanolamine solutions (*3*) was used in this work. It consisted of a 1.5-L stainless-steel Dewar closed by a flange sealed by an O-ring. Suspended from the lid were two thermistors, a 240-Ω heater and a cooling coil. The liquid in the calorimeter was stirred with a magnetic stirrer driven by a permanent magnet mounted underneath the Dewar. The calorimeter was immersed in a thermostated oil bath. The temperature of the oil bath was measured by a platinum resistance thermometer calibrated on IPTS-68. The difference in temperature between the calorimeter contents and the oil bath was detected by a set of four Conax TH14 thermistors connected in a differential mode. The thermistors were calibrated by using distilled water with heat capacities taken from Perry (*4*). The methyldiethanolamine was obtained from Aldrich Chemical Co. and had a purity of 97%. The solutions were prepared by weight with distilled water. About 1 L of solution was charged to the calorimeter and allowed to reach the bath temperature. The mass was determined by difference. Electrical energy was added by using a dc power supply in an amount sufficient to cause about a 3 °C temperature rise in 5–6 min. The electrical energy input was determined by using standard resistors and an electrical timer. Cooling water was then circulated through the cooling coil in order to return the contents of the calorimeter to the initial temperature and the experiment was repeated. Four determinations of the heat capacity were made at each temperature for each solution.

Table I. Heat Capacities of MDEA Solutions

	C_p, kJ/(kg °C)	
T, °C	23 wt %	50 wt %
25.0	3.735 ± 0.032	3.380 ± 0.007
50.0	3.773 ± 0.026	3.428 ± 0.013
75.0	3.794 ± 0.014	3.527 ± 0.006

Results and Discussion

The heat capacities were determined at atmospheric pressure for solutions containing 23 and 50 wt % MDEA at temperatures of 25, 50, and 75 °C. The mean values of the heat capacity and the standard deviations of the four determinations are presented in Table I. The data were fitted by least

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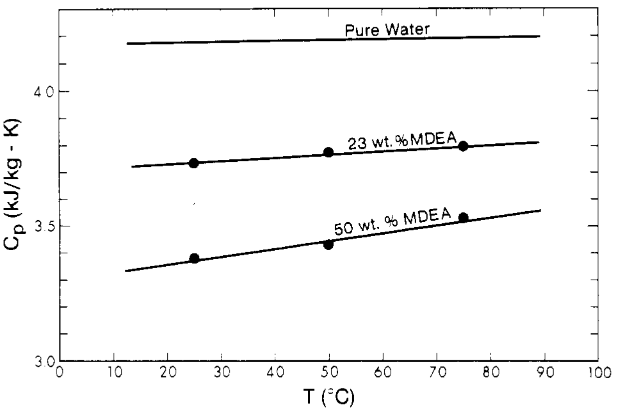

Figure 1. Effect of temperature on the heat capacity of MDEA solutions.

squares, with all points weighted equally. A linear dependence of heat capacity on temperature was found to reproduce the results within the precision of the data and gave the following equations:

23 wt % MDEA solution

$$C_p = 3.7085 + 0.00117t$$

50 wt % MDEA solution

$$C_p = 3.2975 + 0.00295t$$

(t in °C, C_p in kJ/(kg °C)).

These equations are plotted in Figure 1, together with the experimental data and the literature values for pure water. The heat capacities of MDEA solutions are almost the same as those of diethanolamine (DEA) solutions (*5*) at the same temperatures.

Registry No. Methyldiethanolamine, 105-59-9.

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Solution Thermodynamics of Some Slightly Soluble Hydrocarbons in Water

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This paper summarizes a series of measurements of the solubilities of 14 hydrocarbons in water at temperatures ranging from 275 to 304 K using a generator-column-high-pressure liquid-chromatographic method. The compounds investigated were benzo[*a*]pyrene, benz[*a*]anthracene, anthracene, hexylbenzene, benzene, chrysene, pyrene, triphenylene, fluoranthene, 1-methylphenanthrene, 2-methylanthracene, phenanthrene, fluorene, and naphthalene. We have calculated values of $\Delta G°$, $\Delta H°$, and $\Delta C_p°$ at 298.15 K for the processes compound(liquid or solid) = compound(aqueous) using the model of Clarke and Glew. We have also calculated these same thermodynamic parameters from the information available on these compounds in the literature.

Introduction

For the past few years, this laboratory has been systematically measuring the aqueous solubilities and octanol-water partition coefficients of organic compounds (*1-4*) using a "generator" or "dynamic-coupled-column" liquid-chromatographic method. Because of the environmental importance of polycyclic aromatic hydrocarbons, we wish to summarize the solubility data on 14 of these compounds. Also, while we have already reported measurements on 12 of these compounds, the calculations of the thermodynamic parameters and a comparison with the existing literature data have not been done with an adequate thermodynamic model. The Gibbs energy changes ($\Delta G°$), the enthalpy changes ($\Delta H°$), and the heat capacity changes ($\Delta C_p°$) have been determined from the solubility measurements at different temperatures and compared with values calculated from measurements in the literature.

These measurements are also of interest for a variety of reasons: (1) since many of these compounds are carcinogenic, there is a need to know the degree to which they can enter the environment; (2) the thermodynamic information is of fundamental importance in understanding hydrophobic interactions and in calculating the transfer properties of solutes between various solvents (*5*); and (3) direct calorimetric measurements cannot presently yield meaningful values for substances having very low solubilities. The direct calorimetric measurement is also complicated (*6*) by the volatility problem which exists for many of these compounds.

Experimental Section

The experimental procedures have been described in detail elsewhere (*3*, *4*). All chemicals were obtained from commercial sources and were found to be at least 99 mol % pure by using chromatographic procedures.

Results and Discussion

The experimental results are summarized in Table I. For each compound, the experimentally determined solubilities as a function of temperature are reported. The molar masses used to calculate the mole fraction solubilities are given in