Molecular Weights and Conductivities of Diphenylphosphinic Acid, Diphenylphosphinic Anhydride, and Acetic Diphenylphosphinic Anhydride in Dimethyl Sulfoxide

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Molecular weights and conductivities of diphenylphosphinic acid and acetic diphenylphosphinic anhydride were determined in dimethyl sulfoxide; the data were found consistent with solutions of monomeric nonelectrolytes. The results obtained for diphenylphosphinic anhydride suggested a reaction between solute and solvent.

Because of the slight solubility of diphenylphosphinic acid in water, other nonreactive polar solvents were sought for contemplated studies of diphenylphosphinic acid solutions. One solvent studied, acetic anhydride, reacted with diphenylphosphinic acid with the formation of acetic diphenylphosphinic anhydride and diphenylphosphinic anhydride (*11*). Although extremely hygroscopic, dimethyl sulfoxide (DMSO) is reported to be a useful solvent for cryoscopic molecular weight (*1, 4, 8, 13*) and conductivity (*7, 13*) investigations. Consequently, DMSO was investigated as a solvent for diphenylphosphinic acid and the two anhydrides, and the results of molecular weight determinations and conductivities are reported herein.

EXPERIMENTAL

Molecular weights were determined by use of the standard Beckman freezing-point apparatus and procedure. A constant temperature bath set at 13.5°C (±0.1°C) was convenient to maintain a temperature approximately 5° below the freezing point of the DMSO. A slow stream of nitrogen, a gas only slightly soluble in DMSO (*3*), was first passed through a column of molecular sieve and then used to blanket the solutions to prevent absorption of moisture. The cryoscopic constant used in this report, 4.2 ± 0.1° C/molar, was determined by the freezing-point depression of DMSO solutions of naphthalene and benzoic acid. Values of 4.4 ± 0.5°C/molal (*1, 4, 8*) and 4.09°C/molal (*13*) have been reported. The precision of the molecular weight determinations was about 5%.

Conductivity measurements were made using three-piece cells described by Crockford and Nowell (*2*). The DMSO solutions were prepared and the cells filled and stoppered within a drybox. An Industrial Instruments, Inc., Model 16B-1 conductivity bridge was used to measure the solution resistances at 1000 Hz. Measurements were made after the solutions were brought to equilibrium temperatures of a constant-temperature bath set at 25.00 ± 0.06°C.

National Bureau of Standards–certified samples of benzoic acid and naphthalene were used as reference materials for the conductivity and molecular weight determinations. Diphenylphosphinic acid (mp 195–6°C), diphenylphosphinic anhydride (mp 148.0–8.5°C), and acetic diphenylphosphinic anhydride (mp 89.5–91.0°C) were prepared according to the methods of Venezky and Poranski (*11*).

Baker Analyzed Reagent DMSO was redistilled under reduced pressure and the fraction boiling between 64° and 77°C at 5 to 8 torr was collected directly over Linde 3A Molecular Sieve and stored in a stoppered wash bottle. When needed, the reagent was dispensed by applying dry nitrogen to the mouthpiece of the bottle. Proton magnetic resonance (pmr) and infrared spectral data of the purified DMSO indicated that hydroxyl-containing compounds were absent or below the limits of detection.

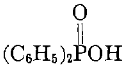
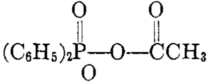
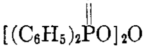
RESULTS AND DISCUSSION

Diphenylphosphinic acid has been reported to form dimers in naphthalene solutions (*5*) and to form species averaging slightly greater than dimeric form in benzene solutions (*8*). Although the degree of association in polar solvents has not yet been reported, the resemblance of phosphinic acids to monocarboxylic acids would suggest monomeric species associated with polar solvents such as water [ϵ = 80.4 at 20°C (*12*)] or DMSO [ϵ = 48.9 at 20°C (*3*)].

The values of the molar conductivities (Table I), corrected for the solvent, indicate that diphenylphosphinic acid and the anhydrides act as nonelectrolytes and are very slightly, if at all, ionized in DMSO (*7, 13*). The molecular weights of diphenylphosphinic acid (theory, 218; found 210 ± 10) and acetic diphenylphosphinic anhydride (theory, 260; found 260 ± 10) are in agreement with the monomeric theoretical values. However, the determined molecular weight of diphenylphosphinic anhydride (theory 418; found 350 ± 20) is 16% lower than the theoretical molecular weight and is attributed to the reaction between solute and solvent (*9*).

Pmr data (*10*) suggests that a strong hydrogen bond exists between DMSO and diphenylphosphinic acid. Consequently, the acid, in monomeric form and without detectable ionization,

Table I. Conductivities in DMSO

Compound	Molarity, × 10³	Specific conductivity, × 10⁶, ohm⁻¹ cm⁻¹	Molar conductivity, × 10⁴, ohm⁻¹ cm² mole⁻¹	Cell constant, cm⁻¹
DMSO	...	0.259	...	...
Naphthalene	10.4	1.53	1.47	0.2943
Benzoic acid	1.18	1.46	12.4	0.3658
 $(C_6H_5)_2P(=O)OH$	4.20	2.27	5.40	0.2943
 $(C_6H_5)_2P(=O)—O—C(=O)CH_3$	2.46	1.68	6.83	0.3658
 $[(C_6H_5)_2P(=O)O]_2O$	1.27	0.414	3.26	0.2943

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must exist as a complex with solvent molecules in DMSO solutions.

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Thermodynamic Properties of Binary Liquid Mixtures Containing Aromatic and Saturated Hydrocarbons

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Total vapor pressure data were obtained for nine binary systems in the temperature range 10–80°C. These data were reduced to obtain excess Gibbs energies.

The properties of liquid hydrocarbon mixtures have been studied by many investigators. Mixtures of saturated hydrocarbons show little deviation from ideal behavior, but solutions of saturated hydrocarbons with aromatics show appreciable nonideality; they often contain azeotropes.

Vapor-liquid equilibrium data are plentiful for mixtures of aromatics with saturated hydrocarbons; however, few of these data are for mixtures of aromatics with branched, saturated hydrocarbons or for mixtures with aromatics containing more than seven carbon atoms. For rational design of distillation equipment and for a fundamental understanding of the effect of molecular structure on thermodynamic properties, we require vapor-liquid equilibrium data for mixtures of aromatics with branched paraffins as well as for mixtures with aromatic molecules containing eight or nine carbon atoms.

In this work we report new vapor-liquid equilibrium data for nine binary systems: 2,2-dimethylbutane–benzene; 2,3-dimethylbutane–benzene; 2-methylpentane–benzene; 3-methylhexane–benzene; 3-methylpentane–toluene; methylcyclohexane–ethylbenzene; *n*-heptane–isopropylbenzene; 2,2,4-trimethylpentane–ethylbenzene; and 3-methylhexane–*n*-propylbenzene. The data are reduced to yield thermodynamic excess functions.

EXPERIMENTAL

Total vapor pressures were measured at constant temperature. A schematic diagram of the apparatus is shown in Figure 1; a detailed description of the apparatus is given by Hermsen (*4*), and modifications are described by Harris (*3*). Advantages and disadvantages of a constant-temperature apparatus are discussed by Scatchard (*8*).

The components used were of the highest purity commercially available. Benzene, toluene, *n*-heptane, 2,2,4-trimethylpentane, and methylcyclohexane from Matheson, Coleman and Bell were more than 99.9% pure. Ethylbenzene, isopropylbenzene, 2-methylpentane, and 3-methylpentane from Phillips Petroleum Co. were also more than 99.9% pure. These hydrocarbons were dried over Linde molecular sieves and used without further purification. 2,2-Dimethylbutane, 2,3-dimethylbutane, and 3-methylhexane from Matheson, Coleman and Bell, along with *n*-propylbenzene from Aldrich Chemical Co. were better than 97% pure. They were further purified by distilling at high reflux in a 10-plate Oldershaw column; the beginning and end fractions were eliminated. All components used showed negligible impurities when analyzed by gas-solid chromatography. This analysis indicates that the impurities probably consist of isomers of the main constituent. Such isomers have a negligible effect on the results reported here.

The components were sealed in separate vacuum stills for degassing. In the measurement of vapor pressures, the prob-

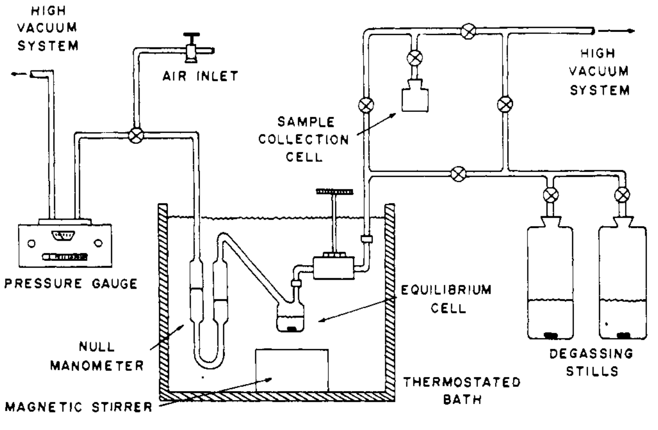

Figure 1. Total pressure apparatus

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