Thermodynamics of Solutions: Excess Volumes of Benzene, Carbon Tetrachloride, and Mesitylene Mixtures

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The excess volumes for the systems benzene–mesitylene, carbon tetrachloride–mesitylene, and benzene–carbon tetrachloride were measured at 27° and 40°C.

The thermodynamic properties of a number of binary mixtures, differing from hard sphere nature, have been investigated (*12*) by utilizing a rigid sphere model first proposed by Longuet-Higgins and Widom (5). Values of excess Gibbs energy for equimolar mixtures are usually forced to agree with experimental values at one temperature to fix necessary parameters.

In principle, the precise measurement of excess volume can provide a more direct and possibly more acceptable procedure for determining the fitting parameters involved in the hard sphere model considered. In addition, the excess volume is readily measured. From this point of view, the determination of the excess volumes for three binary mixtures was carried out. The results of the measurements for the systems benzene–mesitylene, benzene–carbon tetrachloride, and carbon tetrachloride–mesitylene at 27° and 40°C are given along with a description of a simple method for the determination of excess volumes.

Purification of Materials

Fisher reagent-grade benzene was contacted with concentrated sulfuric acid at room temperature with constant stirring until no further coloration was observed. The benzene was then washed several times with distilled water and 10% sodium carbonate solution. After drying with calcium chloride and sodium, the benzene was fractionally distilled over phosphoric acid. The middle third fraction was retained. The middle fraction was further purified by additional distillation and fractional crystallization from the liquid, a total of 23 crystallizations being required to yield material of acceptable purity (*6, 2, 10*). The percentage purity of the final product was determined by gas-chromatographic analysis. Density data are given in Table I.

Gas chromatography was used in determining purity or detection of impurity present in the sample, since it is a relatively rapid and highly efficient method of determining sample purity. Both separation and identification of spurious gas-chromatographic peaks were possible by comparison of retention values for the specific column packings and by utilizing different column stationary and supporting phases as indicated below. This was necessary to separate constant adsorption mixtures. The longer column length provided high resolution of components. Flame ionization with sensitivity of less than 5 μg, for the compounds of interest here, was used for quantitation. Quantitation was accurate to about $\pm 50\ \mu$g.

A 500-ml portion of Matheson Coleman & Bell spectrograde carbon tetrachloride was treated with sufficient water to make a 1-cm layer. To this was added 50 grams of activated charcoal. The mixture was then stirred continuously for a 24-hr period. After filtering and drying with calcium chloride, the carbon tetrachloride was shaken with a 20% chromic acid solution. The upper red layer was separated and refluxed for 4 hr over 5% $KMnO_4$ in 10% KOH and distilled. The carbon tetrachloride was then fractionally distilled over phosphoric acid, the middle third fraction being retained. Further purification consisted of 14 fractional freezings (*6, 11*).

Mesitylene proved quite difficult to purify owing to the presence of isomers. It was determined by gas-chromatographic analysis that 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, ethylbenzene, *p*-ethyltoluene, *m*-ethyltoluene, *o*-ethyltoluene, and significant nonaromatic compounds were present. Chromatographic analysis was performed by use of flame ionization and thermoconductivity detectors. Columns used were a 300-ft × $\frac{1}{16}$-in. 3% SE-30, 6-ft × $\frac{1}{4}$-in. 10% UC-W982 on 80/100 Chrom w-HP, and a 6-ft × $\frac{1}{8}$-in. 1.5% OV-17 on 100/120 HP Chromosorb G. All columns were stainless steel.

Matheson Coleman & Bell practical-grade mesitylene was distilled over KOH pellets. After drying, the mesitylene was fractionally distilled with a column of 40-plate efficiency. Additional distillations were carried out over phosphoric acid. The middle third fraction was retained. A total of 41 fractional freezings was necessary to obtain the desired purity (3, 9).

Apparatus

Densities of pure carbon tetrachloride, benzene, and mesitylene and of mixtures of carbon tetrachloride–benzene, carbon tetrachloride–mesitylene, and benzene–mesitylene were measured at 27° and 40°C in a pycnometer of conventional design similar to that used by Mathot and Desmyter (7), of 53-cc capacity by use of a Mettler H-5 balance. The measurements were used to calculate the volume change on mixing of the three mixtures.

The dual-stem borosilicate glass pycnometer used to determine density and volume change was constructed from a 50-ml sealed, round-bottom flask, to which two portions of a 0.2-ml pipet were attached. The capillaries were 8½ cm × 1 mm and 9 cm × 1 mm, respectively, and topped with caps to prevent sample evaporation. The pipet scale served to obviate tedious adjustments of volume by bringing menisci exactly to some particular mark.

Experimental Procedure

The pycnometer stems were calibrated and all readings corrected back to an arbitrary mark on the stems, conveniently made by a steel edge. Readings of the levels in the capillaries were made to ±0.01 mm with a Gaerthner Scientific Corp. cathetometer fitted with a close-up lens, which was not calibrated.

Water used to calibrate the pycnometer was obtained by distillation from alkaline permanganate solution in an all pyrex-conditioned system followed by transfer through a deionizing column. The procedure was performed several times. The standard water had a specific conductance in the neighborhood of 10×10^{-9}.

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Table I. Densities and Percentage Purities

Substance	Exptl, g cm^{-3}		Lit, g cm^{-3}		Purity, mol %
	$d_{27°C}$	$d_{40°C}$	$d_{27°C}$	$d_{40°C}$	
Benzene	0.8713_4	0.8573_3	0.87158 (*15*)	0.85771 (*15*)	99.987 ± 0.005
Carbon tetrachloride	1.5804_7	1.5551_5	1.5804 (*16*)	1.5552 (*16*)	99.979 ± 0.005
1,3,5-Trimethylbenzene (mesitylene)	0.8584_7	0.8473_3	0.85948 (*15*)	0.84882 (*15*)	99.411 ± 0.005

Table II. Excess Volume of Mixing for Carbon Tetrachloride-Benzene

T, °C	x_{CCl_4}	V^E, cm^3 mol^{-1}	V^E (*14*), cm^3 mol^{-1}
27	0.1610	0.013	
	0.2497	0.015	
	0.2740	0.014	
	0.4180	0.012	
	0.4981	0.011	
	0.5400	0.014	
	0.7771	0.017	
	0.9110	0.015	
40	0.1609	0.033	0.028
	0.2498	0.037	0.034
	0.2739	0.038	0.035
	0.4180	0.040	0.039
	0.4981	0.040	0.039
	0.7772	0.039	0.036
	0.9110	0.032	0.021
	Duplicate determinations		
27	0.5011	0.011	
30	0.5011	0.019	
40	0.5011	0.041	

Table III. Excess Volume of Mixing for Carbon Tetrachloride-Mesitylene

T, °C	x_{CCl_4}	V^E, cm^3 mol^{-1}
27	0.2531	−0.410
	0.3781	−0.298
	0.5000	−0.186
	0.6593	+0.147
	0.7451	+0.152
	0.8906	+0.075
40	0.2532	−0.030
	0.3781	−0.021
	0.5000	+0.073
	0.6592	+0.346
	0.7451	+0.367
	0.8907	+0.269

Calibration was conducted after every pair of measurements with the water described, freed of air. A reproducibility of ±0.001 cc at 27° and 40°C was attained. The density of water at 27°C was taken as 0.9965160 g/cc and 40°C as 0.9922191 g/cc (*15*). A buoyancy correction is necessary when calibrating with water, and the typical correction was applied.

Temperature control was maintained by an insulated conventional thermostat. A Fisher proportional temperature control unit capable of ±0.01°C regulation was utilized in conjunction with a jet-type stirrer to obtain a temperature variation of ±0.001°C at 27°C and ±0.004°C at 40°C. A Hewlett-Packard quartz temperature probe was used to measure the temperature. The probe was calibrated according to the manufacturers specifications. Hysteresis and ambient temperature effects were negligible. Linearity, stability, and calibration allowed an absolute accuracy in temperature measurement of ±0.01°C at both temperatures.

Manipulation

The pycnometer was initially cleaned with hot cleaning solution, distilled water, and alcohol and allowed to age before using. Thereafter, no heat was applied for either cleaning or drying. The latter was accomplished by rinsing with redistilled alcohol and attaching one capillary to a dry nitrogen line for purging.

In carrying out a measurement, the pycnometer was weighed prior to filling and immediately afterward. By direct insertion through one stem, a syringe was used to fill the pycnometer. At 40°C it became necessary to withdraw the pycnometer from the thermostat and reweigh, because of sample loss on expansion and readjustment of the liquid level in the capillary to obtain readings within a convenient range. In this case, a clean, damp, chamois cloth was utilized for wiping. It was necessary to wipe the pycnometer to prevent adsorption of moisture by the glass. Prior to weighing, the pycnometer was allowed to remain in the balance case for 45 min to reach equilibrium and reduce the possibility of convection currents.

The density of a pure component could be determined from a knowledge of sample weight and volume, whereas the excess volume of mixing was determined from a knowledge of the pure liquid density and mixture density.

In calculating the composition of mixtures from weights and components, no correction was made for air buoyancy since such correction would not significantly affect values obtained for the weight fractions of components.

Densities will vary with the amount of dissolved air. It was assumed that the amount of air dissolved did not change upon making the solutions and that this air caused the same effect on the pure components as the solutions.

In making the solutions, corrections were not made for the displacement of vapor of the first component on addition of the second and for density of the vapor in the space above the liquid. These corrections were assumed unnecessary, since the more volatile component was added first. Mixtures of known compositions were made up directly in the balance case, in 100-ml flasks.

Experimental Results

Duplicate densities agreed to ±0.5 × 10^{-4} g cm^{-3}. An analysis of experimental uncertainties led to the conclusion that the excess volume of mixing was measured to ±0.009 cm^3 mol^{-1}.

Density data of the pure components are indicated in Table I. The excess volume of mixing data for the three mixtures is given in Tables II–IV. Experimental values

Table IV. Excess Volume of Mixing for Benzene–Mesitylene

T, °C	$x_{C_6H_6}$	V^E, cm^3 mol^{-1}
27	0.1251	−0.189
	0.2103	−0.221
	0.2461	−0.239
	0.3781	+0.026
	0.5000	+0.319
	0.6377	+0.325
	0.7518	+0.323
	0.9261	+0.163
40	0.1250	−0.078
	0.2103	+0.055
	0.2462	+0.193
	0.3781	+0.378
	0.5000	+0.448
	0.6377	+0.441
	0.7518	+0.419
	0.9261	+0.258

previously obtained for the system benzene–carbon tetrachloride are also indicated in Table II.

The change in sign of V^E for the carbon tetrachloride–mesitylene mixture can be attributed to weak complex formation. Spectroscopic evidence (*8, 1*) indicates a 1:1 complex of carbon tetrachloride–benzene. The complex interaction increases with increasing number of methyl groups on the benzene ring and is considerably greater for the carbon tetrachloride–mesitylene mixture than the corresponding benzene system (*12*). This is to be expected since the CCl_4 is acting as an electron acceptor, and the presence of methyl groups tends to enhance the electron-donating ability of the substituted benzene. Goates et al. (*4*) suggested pi-bonding between the benzene ring and the empty 3d level of the chloride atom. This specific interaction causes a contraction in volume. An increase in the concentration of carbon tetrachloride tends to decrease complex formation (*13*). A more favorable packing arrangement or possibly enhanced unlike interaction also causes the excess volume sign change for the benzene–mesitylene mixture.

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Heats of Mixing of Tri-*n*-dodecylamine with *n*-Octane, Benzene, or Chlorobenzene

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Excess enthalpies of mixing of binary systems of tri-*n*-dodecylamine and *n*-octane, benzene, and chlorobenzene are determined at 303.15K with a solution calorimeter. In all systems the endothermic heats of mixing are not symmetric on the mole fraction scale but are nearly so on the volume fraction scale. The heats of mixing, H^E in equimolar mixtures 64.44, 1120, and 767.0 J/mol, respectively, are essentially due to the large differences in the type of molecular interactions. Exothermic contributions from possible π-bondings with the aromatic hydrocarbons are small.

Tri-*n*-dodecylamine (trilauryl) dissolved in nonpolar or slightly polar, water-immiscible organic solvents is used as the organic phase in solvent extraction processes. In the frame of a long-term program designed to provide thermochemical data by direct calorimetric measurements pertinent to the chemistry of liquid-liquid extraction processes, we now report the heat of mixing of this amine with representatives of normal aliphatic, aromatic, and substituted aromatic hydrocarbons, all commonly used as diluents in solvent extraction processes (*4*).

Experimental

Materials. The amine, a Schuchardt product, was of the highest purity commercially available and was purified by fractional distillation under reduced pressure. The fraction used gave a single peak when gas chromatographed on a 1.5-m long column of SE30 (15%) at 300°C. The estimated purity was 99.9%. The density of the purified product was d_4^{25} = 0.8217, as compared to 0.8219 given in the literature (*2*).

Benzene, analytical-grade Mallinckrodt product, and *n*-octane, analytical-grade Fluka product, were dried

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