

**Figure 5.** Titration of the aqueous phase after extraction with 0.17 N (2.2 wt %) tributylamine in chloroform.

indicates an advantage for higher molecular weight amines. Along this line, the water-soluble base in TOPO solvent mixtures, noted in Experimental Procedure, should be explored and identified as TOPO itself, an impurity in the TOPO and/or a complex of TOPO and acetic acid.

**Formic Acid vs. Acetic Acid.** Tables IX and X compare the extractions of formic acid and acetic acid with various phosphoryl and amine solvents. In all cases the formic acid is more ef-

fectively extracted. The results for the amines agree with other authors (5, 6), who have found that these solvents extract stronger acids more effectively.

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## Infrared Spectroscopic Determination of the Liquid-Vapor Equilibrium in the Ternary System Hexamethyldisiloxane-Chloroform-Carbon Disulfide

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The liquid-vapor equilibrium has been determined in the ternary system hexamethyldisiloxane (HMDS)- $\text{CHCl}_3$ - $\text{CS}_2$  by employing the ebulliometric method under isobaric conditions at an atmospheric pressure of 758 mmHg. The infrared spectroscopic technique has been used for determination of the composition of the liquid and vapor phases. Analytical bands for HMDS,  $\text{CS}_2$ , and  $\text{CHCl}_3$  were 2900, 2160, and 3010  $\text{cm}^{-1}$ , respectively. The system has been found to form one phase and to be zeotropic.

#### Introduction

Studies on liquid-vapor equilibria are important in purification and separation processes in industry. Notwithstanding a large number of publications confined to phase equilibria, experimental data concerning equilibrium parameters ( $x$ ,  $y$ ,  $p$ ,  $T$ ) in binary, ternary, and multicomponent systems are still unsatisfactory to meet commercial needs for high-purity products (4).

The primary objective of this work was to determine the liquid-vapor equilibrium in the ternary system hexamethyldisiloxane (HMDS)- $\text{CHCl}_3$ - $\text{CS}_2$  under isobaric conditions at an atmospheric pressure of 758 mmHg.

HMDS,  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ , is a hydrophobic liquid that provides an excellent solvent for nonpolar compounds. For this reason, and owing to low cost of its manufacture, HMDS is likely to find a wide application (2). However, prior to employing the solvent in industrial processes, its thermodynamic parameters should be determined including liquid-vapor phase equilibria under

isothermic and isobaric conditions.

This work provides a continuation of our studies on the liquid-liquid and liquid-vapor equilibria in binary and ternary systems comprising HMDS (8-10). These studies may reveal certain hitherto unknown features of HMDS associated with a specific structure of its molecule in which two trimethylsilyl groups are linked through an oxygen atom.

The IR spectroscopy has been used in this work as a rapid and relatively accurate technique for the determination of components of the system.

Quantitative IR spectroscopic determinations have been used by many authors in various branches of chemistry (1, 6, 7, 11, 13), but not in studies of phase equilibria.

Analytical utilization of the IR spectroscopy has been found to be possible when a system meets the following requirements: (i) bands due to characteristic modes of individual components do not overlap; (ii) absorption bands should be strong and well developed, (iii) the system should obey the Beer-Lambert law over a definite concentration range.

The system studied in this work has been found to meet all the aforementioned criteria.

It is worth noting that by employing the Fourier transform IR spectroscopic technique, determinations of high accuracy and sensitivity can be accomplished (5).

#### Experimental Section

All compounds used were of analytical reagent grade purity. They were purified before use by fractional distillation.

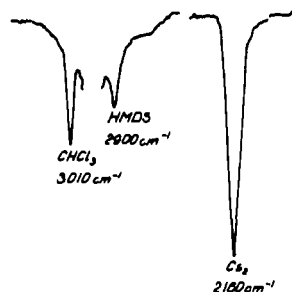


Figure 1. Selected analytical IR bands.

Solutions for determinations were prepared after Litvinov (3). The components of the system considered formed one liquid phase over the whole concentration range.

A dependence between the boiling point and composition was determined ebulliometrically by using a modified Swietoslowski ebulliometer (12) adapted for withdrawing aliquots of conjugate phases. The aliquots were analyzed for the three components by IR spectroscopy.

A comparative quantitative evaluation of the mixture was also made consisting of the spectroscopic assay of  $\text{CS}_2$  and a measurement of the refractive index of the mixture. Refractive index was measured on a Carl-Zeiss refractometer with an accuracy of  $\pm 0.0002$ .

The IR measurements were carried out on a Perkin-Elmer Model 257 spectrophotometer using a 0.1-mm NaCl cuvet, a "slow" sweeping rate, and a "normal" slit width.

Prior to carrying out quantitative measurements, spectra of individual components were recorded to choose bands of the components suitable for quantization (7, 11). The selected bands were those at 2900, 3010, and 2160  $\text{cm}^{-1}$  for HMDS,  $\text{CHCl}_3$ , and  $\text{CS}_2$ , respectively (Figure 1).

In mixtures of various composition neither shifts of the bands nor their overlapping was observed. For quantitative measurements, three series of standard mixtures were taken, each containing the three components, in which the content of one of the components was varied within the mole fraction range 0.1–1.0. With each standard mixture five independent measurements were run. The absorbance was determined by the baseline technique. The mean values were then utilized for constructing three calibration graphs (absorbance vs. composition) for HMDS,  $\text{CHCl}_3$ , and  $\text{CS}_2$ . After collecting samples of condensates and liquid phases, the content of individual components was taken from the calibration graphs. The temperature was measured by means of a mercury thermometer with the accuracy of  $\pm 0.1^\circ\text{C}$ .

## Results and Conclusions

The liquid-vapor equilibrium of the system  $\text{HMDS-CS}_2\text{-CHCl}_3$ , was determined under isobaric conditions by employing a dynamic method with a full analysis of composition of the boiling liquid and of vapor being in equilibrium with the liquid.

The composition of the liquid and vapor phases under isobaric conditions at an atmospheric pressure of 758 mmHg is shown in a triangular diagram (Figure 2). Arrows indicate the composition of the vapor being in equilibrium with the liquid. A circle on an arrow indicates the composition of the liquid and that of the vapor is shown by the end of the arrow.

In Table I results of ebulliometric measurements are shown including the composition of the liquid and vapor and temperatures of the liquid-vapor equilibrium in the  $\text{HMDS-CHCl}_3\text{-CS}_2$  systems.

The IR spectrophotometry turned out to be a rapid and accurate technique for the determination of the composition of both phases.

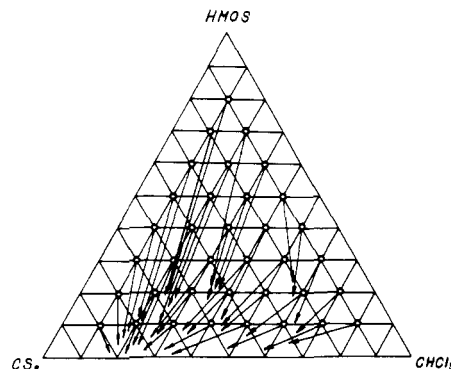


Figure 2. Composition of the liquid and vapor phases in equilibrium under isobaric conditions at an atmospheric pressure of 758 mmHg.

Table I. Liquid-Vapor Equilibrium in the System  $\text{HMDS-CHCl}_3\text{-CS}_2$

Soln no.	Liquid			Temp, °C	Vapor		
	HMDS	$\text{CHCl}_3$	$\text{CS}_2$		HMDS	$\text{CHCl}_3$	$\text{CS}_2$
1	0.1	0.8	0.1	57.1	0.04	0.62	0.34
2	0.1	0.7	0.2	54.2	0.03	0.55	0.42
3	0.1	0.6	0.3	51.6	0.03	0.46	0.51
4	0.1	0.5	0.4	49.7	0.03	0.34	0.63
5	0.1	0.4	0.5	48.2	0.03	0.31	0.66
6	0.1	0.3	0.6	47.2	0.02	0.25	0.37
7	0.1	0.2	0.7	46.4	0.02	0.21	0.77
8	0.1	0.1	0.8	46.2	0.02	0.18	0.80
9	0.2	0.7	0.1	57.2	0.09	0.67	0.24
10	0.2	0.6	0.2	52.7	0.08	0.50	0.42
11	0.2	0.5	0.3	51.2	0.07	0.44	0.49
12	0.2	0.4	0.4	49.1	0.06	0.34	0.60
13	0.2	0.3	0.5	47.8	0.06	0.27	0.67
14	0.2	0.2	0.6	46.9	0.03	0.22	0.75
15	0.2	0.1	0.7	46.3	0.03	0.18	0.79
16	0.3	0.6	0.1	56.1	0.10	0.63	0.27
17	0.3	0.5	0.2	54.0	0.09	0.44	0.47
18	0.3	0.4	0.3	50.3	0.08	0.34	0.58
19	0.3	0.3	0.4	49.0	0.05	0.25	0.70
20	0.3	0.2	0.5	47.3	0.02	0.23	0.75
21	0.3	0.1	0.6	46.9	0.02	0.19	0.79
22	0.4	0.5	0.1	57.0	0.17	0.56	0.27
23	0.4	0.4	0.2	52.8	0.11	0.42	0.47
24	0.4	0.3	0.3	50.4	0.09	0.33	0.58
25	0.4	0.2	0.4	48.2	0.09	0.26	0.65
26	0.4	0.1	0.5	46.6	0.08	0.18	0.74
27	0.5	0.4	0.1	56.5	0.20	0.56	0.24
28	0.5	0.3	0.2	53.2	0.17	0.36	0.47
29	0.5	0.2	0.3	50.1	0.15	0.27	0.58
30	0.5	0.1	0.4	48.2	0.11	0.19	0.70
31	0.6	0.3	0.1	56.8	0.19	0.39	0.42
32	0.6	0.2	0.2	52.6	0.18	0.26	0.44
33	0.6	0.1	0.3	49.7	0.09	0.21	0.70
34	0.7	0.2	0.1	57.2	0.20	0.34	0.46
35	0.7	0.1	0.2	52.2	0.18	0.23	0.59
36	0.8	0.1	0.1	58.1	0.20	0.23	0.57

The  $\text{HMDS-CS}_2\text{-CHCl}_3$  system was found to be zeotropic over the whole concentration range of the components.

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## Thermodynamic Evidence for Complex Formation between Tetrahydrofuran and Aromatic Hydrocarbons

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The excess enthalpies and excess volumes of mixtures of tetrahydrofuran with benzene, toluene, and xylenes were measured at 298.15 K as a function of composition.  $H^E$  and  $V^E$  values have been found to be negative for these systems. These results are consistent with complex formation between the unlike molecules and provide further evidence for electron donor capacity of ethers with aromatic hydrocarbons.

### Introduction

The existence of specific interactions in binary liquid mixtures containing ethers as one of the components has been established (2, 7, 13, 14, 18) from thermodynamic measurements. The electron donor capacity of ethers is well known (2, 3, 5, 6, 8, 9, 15) and it has been pointed out that in tetrahydrofuran and benzene systems such interactions may involve a charge-transfer type of mechanism (2) between the lone pair of electrons on the oxygen atom of tetrahydrofuran and benzene. As part of an investigation of the thermodynamic properties of such systems we have measured  $H^E$  and  $V^E$  of tetrahydrofuran with benzene, toluene, and xylenes to further support the presence of such interactions between tetrahydrofuran and aromatic hydrocarbons.

### Experimental Section

The materials were purified, and their purity was checked as described earlier (11, 12). Excess volumes were measured dilatometrically (17) as a function of composition. The dilatometer was similar to that used by Brown and Smith (4) but with slight modifications. Our dilatometer dispensed with the use of a hypodermic syringe. This improvement eliminates completely the vapor phase, which otherwise had been a potential source of error.

Excess enthalpies were measured in a calorimeter designed in our laboratory (16) (Figure 1). It consists of a double-walled glass mixing vessel having B-7 and B-12 standard joints at its ends. The liquid components of the binary mixture were kept separated with mercury taking care to avoid any vapor space in the two chambers of the calorimeter. The capillary tube, fused to the middle of the mixing vessel, was partly filled with mercury in order to avoid the liquids coming in direct contact with the atmosphere. This capillary provides an air space which, while remaining out of contact with the liquids, ensures that the volume change on mixing causes no change of pressure in the calorimeter. The calorimeter heater of constantan wire was wound around a very thin glass tube fused with a B-12 standard joint. A thermistor is passed through the glass tube to record the change in temperature. The empty space between the ther-

Table I. Excess Volumes of Mixtures Containing Tetrahydrofuran at 298.15 K

Mole fraction $x_1$	$V^E$ , cm <sup>3</sup> mol <sup>-1</sup>	Mole fraction $x_1$	$V^E$ , cm <sup>3</sup> mol <sup>-1</sup>
Tetrahydrofuran (1) + Benzene (2)			
0.0704	-0.055	0.5509	-0.213
0.1946	-0.140	0.6155	-0.204
0.3481	-0.198	0.6991	-0.184
0.4349	-0.212	0.7957	-0.148
0.4953	-0.216	0.8890	-0.089
Tetrahydrofuran (1) + Toluene (2)			
0.1625	-0.195	0.5088	-0.344
0.2048	-0.228	0.5610	-0.345
0.2664	-0.272	0.6851	-0.325
0.3594	-0.316	0.7885	-0.268
0.4108	-0.331	0.8501	-0.220
		0.9399	-0.123
Tetrahydrofuran (1) + <i>o</i> -Xylene (2)			
0.1725	-0.149	0.5120	-0.288
0.2786	-0.215	0.6352	-0.280
0.3250	-0.238	0.6996	-0.258
0.4011	-0.265	0.7601	-0.225
0.4519	-0.279	0.8969	-0.123
Tetrahydrofuran (1) + <i>m</i> -Xylene (2)			
0.1751	-0.129	0.4632	-0.232
0.2508	-0.172	0.5506	-0.233
0.3056	-0.193	0.6779	-0.214
0.3286	-0.202	0.8166	-0.157
0.3901	-0.221	0.9011	-0.099
Tetrahydrofuran (1) + <i>p</i> -Xylene (2)			
0.1101	-0.131	0.5099	-0.347
0.2250	-0.238	0.5842	-0.344
0.2831	-0.276	0.6345	-0.334
0.3628	-0.318	0.8167	-0.233
0.4384	-0.339	0.8950	-0.136

mistor and glass tube was filled with mercury to ensure good thermal contact.

The loaded calorimeter was clamped in a water thermostat which in turn was placed in another water thermostat, the temperature of which was controlled to better than  $\pm 0.01$  K. The contents were allowed to attain equilibrium. The outer jacket was then evacuated. Liquid components were mixed by repeatedly tilting the glass vessel, and current was passed through the calorimeter heater for compensation (in the case of endothermic mixing). Readings of the galvanometer spot were taken continuously. Again at a particular time, current was passed through the heater and readings of the galvanometer spot were taken. The heat of mixing was then calculated using the relationship

$$H^E(\text{J mol}^{-1}) = (C^2 R t_1 + C^2 R t_2 (\Delta h_1 / \Delta h_2)) / (n_1 + n_2) \quad (1)$$

where  $C$  is the current in amperes,  $R$  is the resistance of