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# Phase Equilibria in Ternary Systems of Hexamethyldisiloxane–Butylamines–Water

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**Liquid–liquid phase equilibria have been studied in systems comprising hexamethyldisiloxane, water, and *n*-butylamine, isobutylamine, or *tert*-butylamine. Tie lines of two-phase conjugated systems have been determined by employing the Mertslin method, as well as partition coefficients of the amines between the aqueous and hexamethyldisiloxane phases.**

Results of our further studies have been reported on deriving some equilibrium relationships in three ternary systems comprising hexamethyldisiloxane (HMDS), water, and *n*-butyl-, isobutyl-, or *tert*-butylamine. Although HMDS has been found to be more resistant to hydrolysis (*3, 10*) than an earlier reported tetraisopropoxysilane (*6–9*), it has been, however, shown to undergo hydrolysis to some extent, especially in alkaline media. For this reason, studies on equilibrium relationships in systems involving HMDS, water, and basic components, seem to be especially useful in evaluation of the suitability of HMDS as a solvent in extraction and chromatography.

## Experimental Section

***Materials.*** HMDS was a commercial product boiling at 99.5–100.5 °C, $d^{20}{}_4$ 0.7636, $N^{20}{}_D$ 1.3774. Isomeric butylamines were also commercial products and had physical constants shown in Table I.

Table I. Physical Constants of the Amines Used

| Amine | Boiling range (°C) | $d^{20}{}_4$ | $n^{20}{}_D$ |
|---|---|---|---|
| *n*-Butyl | 77–78 | 0.7414 | 1.4009 |
| Isobutyl | 68–70 | 0.7346 | 1.3970 |
| *tert*-Butyl | 44–45 | 0.7002 | 1.3789 |

***Procedure.*** The solubility of HMDS in aqueous solutions of amines was determined by employing the Bancroft's method (*1, 2*) and that developed by Nikurashina and Mertslin (*5*). The HMDS/amine ratios used for the preparation of solutions, as well as a limiting amount of water soluble in the individual ternary systems at 20 ± 1 °C have been listed in Table II.

The results have been presented graphically in Figures 1–3 in the form of solubility curves.

Tie lines were determined by analyzing phases of the individual ternary systems over heterogeneous regions. To do this, the refraction index ($n^{20}{}_D$) of lower phases was measured. Relationships between the refraction index and amine concentration have been shown in Figures 4–6.

During determination of tie lines use was made of a characteristic property of the conjugated phases, according to which each tie line is the locus of points of a constant composition of the conjugated phases.

The concentration of components of the individual phases was read out after plotting tie lines using a graphoanalytical method developed by Nikurashin et al. (*5*). Partition coefficients of the amines between a polar and nonpolar phase were calculated based on composition of the conjugated phases.

## Results

Based on results shown in Table II, solubility curves were plotted which separate a homogeneous and a two-phase region in the ternary systems (Figures 1–3).

A relationship between the refraction index and the concentration of an amine in lower phases of heterogeneous systems is shown in Figures 4–6.

Table II. Concentration of Components Determining the Solubility Curve (weight %)

| No. | HMDS | $n$-$C_4H_9NH_2$ | $H_2O$ | HMDS | $t$-$C_4H_9NH_2$ | $H_2O$ | HMDS | $i$-$C_4H_9NH_2$ | $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.80 | 18.02 | 80.18 | 0.9 | 20.98 | 78.12 | 1.12 | 14.45 | 84.43 |
| 2 | 3.95 | 34.50 | 61.55 | 2.01 | 34.94 | 63.05 | 1.52 | 26.57 | 71.90 |
| 3 | 8.64 | 47.56 | 43.80 | 6.05 | 49.95 | 44.00 | 4.52 | 37.26 | 58.22 |
| 4 | 13.17 | 50.87 | 35.96 | 14.66 | 53.77 | 31.93 | 9.21 | 47.90 | 42.89 |
| 5 | 22.86 | 51.75 | 25.39 | 24.01 | 51.39 | 24.60 | 13.81 | 50.66 | 35.53 |
| 6 | 32.99 | 48.04 | 19.00 | 34.05 | 46.85 | 19.10 | 23.30 | 49.88 | 26.82 |
| 7 | 42.67 | 41.65 | 15.68 | 44.50 | 40.81 | 14.69 | 33.31 | 45.83 | 20.87 |
| 8 | 53.90 | 34.89 | 11.21 | 55.66 | 34.04 | 10.30 | 44.04 | 40.40 | 15.57 |
| 9 | 65.03 | 27.06 | 7.92 | 67.66 | 26.58 | 5.76 | 55.00 | 33.63 | 11.37 |
| 10 | 77.23 | 18.75 | 4.03 | 76.77 | 18.26 | 4.99 | 68.53 | 26.94 | 4.53 |
| 11 | 88.68 | 9.57 | 1.76 | 90.31 | 9.20 | 0.49 | 79.34 | 18.18 | 2.48 |
| 12 | — | — | — | — | — | — | 90.19 | 9.19 | 0.62 |

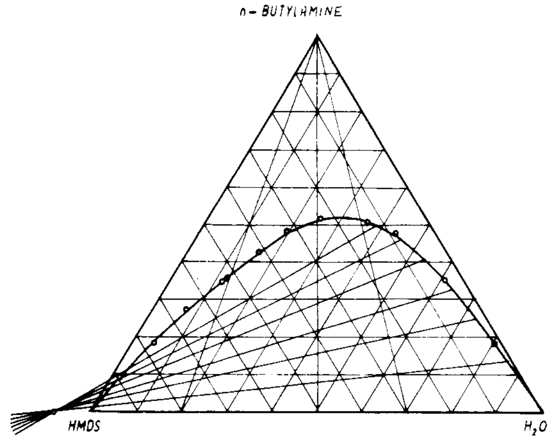

**Figure 1.** Solubility curve and tie lines in the system HMDS-*n*-butylamine-water.

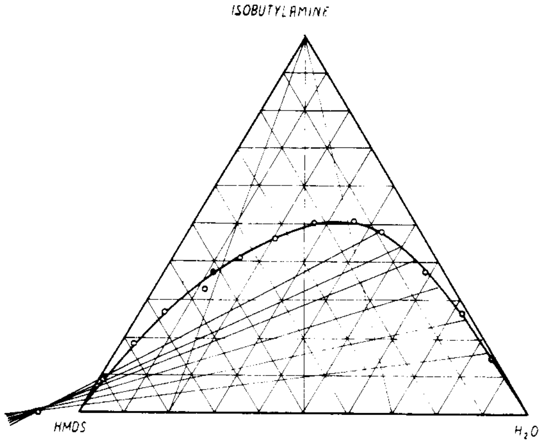

**Figure 2.** Solubility curve and tie lines in the system HMDS-isobutylamine-water.

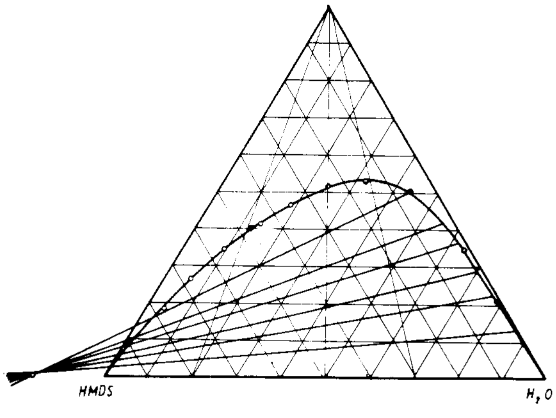

**Figure 3.** Solubility curve and tie lines in the system HMDS-*tert*-butylamine-water.

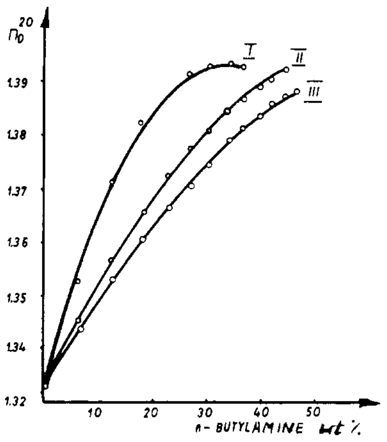

**Figure 4.** Plot of the function $n^{20}_D = f(c_{n\text{-}C_4H_9NH_2})$. Curves I, II, and III illustrate secants of the Gibbs' triangle for which the HMDS/$H_2O$ ratio is 80:20, 50:50, and 30:70, respectively.

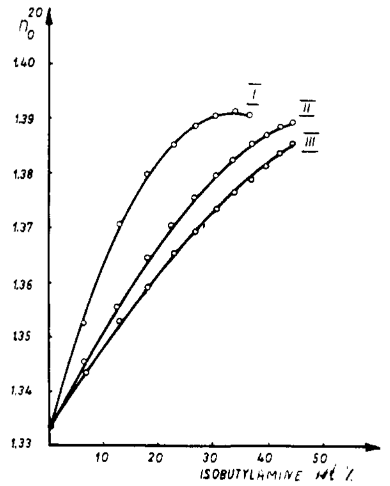

**Figure 5.** Plot of the function $n^{20}_D = f(c_{iso\text{-}C_4H_9NH_2})$. Curves I, II, and III illustrate secants of the Gibbs' triangle for which the HMDS/$H_2O$ ratio is 80:20, 50:50, and 30:70, respectively.

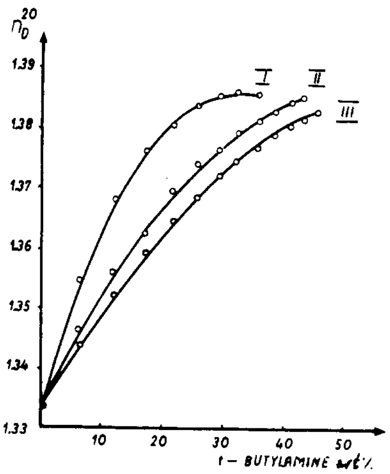

**Figure 6.** Plot of the function $n^{20}_D = f(c_{t\text{-}C_4H_9NH_2})$. Curves I, II, and III illustrate secants of the Gibbs' triangle for which the HMDS/$H_2O$ ratio is 80:20, 50:50, and 30:70, respectively.

In Tables III–V the composition of the lower and upper conjugated phases has been presented determining six tie lines of the systems studied. The composition of the conjugated phases was determined with the accuracy of ±0.1%.

Binary systems comprising HMDS and the amines, as well as the amines and water turned out to be homogeneous over the whole concentration range. On the other hand, HMDS was immiscible with water. Thus, the amines acted as homogenizing agents. The surface area of nonhomogeneity decreases in the systems studied in the following sequence: HMDS-*tert*-butylamine-$H_2O$ > HMDS-isobutylamine-$H_2O$ > HMDS-*n*-butylamine-$H_2O$. Tie lines have a constant direction, and their slope

**Table III. Composition of Conjugated Phases and Partition Coefficient of *n*-Butylamine between HMDS and Water, at 20 ± 1 °C**

| | | Phase composition (weight %) | | | Concn of the amine in the lower ($c_1$) and upper ($c_u$) phases | Partition coeff of the amine, $K$ |
|---|---|---|---|---|---|---|
| No. of phase | Phase | HMDS | $n$-$C_4H_9NH_2$ | $H_2O$ | (mol fraction) | $= c_l/c_u$ |
| 1 | Lower | 1.0 | 13.0 | 86.0 | 0.0359 | 1.20 |
| | Upper | 98.5 | 1.4 | 0.1 | 0.0300 | |
| 2 | Lower | 2.3 | 25.0 | 72.7 | 0.0779 | 1.23 |
| | Upper | 98.8 | 3.0 | 0.2 | 0.0633 | |
| 3 | Lower | 3.5 | 32.5 | 64.0 | 0.1107 | 1.35 |
| | Upper | 95.5 | 4.0 | 0.5 | 0.0815 | |
| 4 | Lower | 5.6 | 41.0 | 53.4 | 0.1578 | 1.37 |
| | Upper | 93.0 | 6.0 | 1.0 | 0.1155 | |
| 5 | Lower | 8.0 | 46.5 | 45.5 | 0.1982 | 1.36 |
| | Upper | 90.0 | 8.0 | 1.5 | 0.1458 | |
| 6 | Lower | 11.0 | 49.5 | 39.5 | 0.2306 | 1.15 |
| | Upper | 85.8 | 12.0 | 2.2 | 0.2014 | |
| | | | | | | $K_{mean} = 1.28$ |

**Table IV. Composition of Conjugated Phases and Partition Coefficient of *tert*-Butylamine between HMDS and Water, at 20 ± 1 °C**

| | | Phase composition (weight %) | | | Concn. of the amine in the lower ($c_l$) and upper ($c_u$) phase | Partition coeff of the amine, $K =$ |
|---|---|---|---|---|---|---|
| No. of phase | Phase | HMDS | $t$-$C_4H_9NH_2$ | $H_2O$ | (mol fraction) | $c_l/c_u$ |
| 1 | Lower | 0.3 | 13.2 | 86.5 | 0.0362 | 0.84 |
| | Upper | 97.9 | 2.0 | 0.1 | 0.0430 | |
| 2 | Lower | 0.7 | 22.6 | 76.7 | 0.0677 | 0.82 |
| | Upper | 95.7 | 4.0 | 0.3 | 0.0828 | |
| 3 | Lower | 1.0 | 29.0 | 70.0 | 0.926 | 0.90 |
| | Upper | 94.1 | 5.2 | 0.7 | 0.1030 | |
| 4 | Lower | 1.5 | 36.5 | 62.0 | 0.1265 | 0.84 |
| | Upper | 91.0 | 8.0 | 1.0 | 0.1508 | |
| 5 | Lower | 2.3 | 41.5 | 56.2 | 0.1534 | 0.86 |
| | upper | 88.5 | 10.0 | 1.5 | 0.1787 | |
| 6 | Lower | 6.0 | 50.0 | 44.0 | 0.2163 | 0.92 |
| | Upper | 82.0 | 15.0 | 3.0 | 0.2339 | |
| | | | | | | $K_{mean} = 0.86$ |

**Table V. Composition of Conjugated Phases and Partition Coefficient of Isobutylamine between HMDS and Water, at 20 ± 1 °C**

| | | Phase composition (weight %) | | | Concn of the amine in the lower ($c_l$) and upper ($c_u$) phases | Partition coeff of the amine, $K$ |
|---|---|---|---|---|---|---|
| No. of phase | Phase | HMDS | $i$-$C_4H_9NH_2$ | $H_2O$ | (mol fraction) | $= c_l/c_u$ |
| 1 | Lower | 0.3 | 16.0 | 83.7 | 0.0450 | 1.12 |
| | Upper | 98.0 | 1.9 | 0.1 | 0.0405 | |
| 2 | Lower | 1.5 | 25.0 | 73.5 | 0.0772 | 0.95 |
| | Upper | 96.1 | 3.8 | 0.1 | 0.0800 | |
| 3 | Lower | 3.5 | 34.0 | 62.5 | 0.1176 | 1.14 |
| | Upper | 94.8 | 5.0 | 0.2 | 0.1031 | |
| 4 | Lower | 5.0 | 40.5 | 54.5 | 0.1535 | 1.17 |
| | Upper | 93.0 | 6.5 | 0.3 | 0.1309 | |
| 5 | Lower | 7.0 | 44.0 | 49.0 | 0.1789 | 1.22 |
| | Upper | 92.0 | 7.5 | 0.5 | 0.1471 | |
| 6 | Lower | 10.0 | 48.0 | 42.0 | 0.2154 | 1.16 |
| | Upper | 89.1 | 10.0 | 0.9 | 0.1859 | |
| $K_{mean} = 1.13$ | | | | | | |

points to a better relative solubility in the system amine–water than in amine–HMDS.

The composition of mixtures at a critical point was estimated by employing the Alekseev's method, adapted to ternary systems by Krupatkin (*4*).

The critical point presents an equilibrium transition from a heterogeneous system into a homogeneous one. Its values in the systems studied were as follows: 1st system, HMDS 46.5%, *tert*-butylamine 40.5%, water 13%; 2nd system, HMDS 52%, *n*-butylamine 36.5%, water 11.5%; 3rd system, HMDS 52.5%, isobutylamine 36.5%, water 11%. Mean values of partition coefficient of *n*-butylamine, *tert*-butylamine, and isobutylamine between the aqueous and HMDS phases are 1.28, 0.84, and 1.13, respectively, at 20 ± 1 °C.

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# Direct Determination of Enthalpy of Mixing of the Binary Gaseous System $N_2$–$O_2$ by Flow Calorimetry

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**A flow calorimeter for measuring enthalpies of mixing of gases was constructed. Enthalpies of mixing for the system $N_2$–$O_2$ were measured at four temperatures (10, 25, 45, and 65 °C). For each of the four temperatures, measurements are reported at two pressures: 3.55 and 7.60 MPa (35.0 and 75.0 atm, respectively) for the 10, 45, and 65 °C isotherms, and 3.55 and 6.90 MPa (35.0 and 68.2 atm, respectively) for the 25 °C isotherm. All measurements were made in the gas phase region. The experimental results are compared with predictions using the Redlich–Kwong equation of state, with the mixing rule proposed by Chueh and Prausnitz.**

Enthalpy data for pure compounds and mixtures are frequently required for engineering design. Furthermore, enthalpies of mixing (or excess enthalpies) are particularly important on a scientific point of view: since they link directly the enthalpy of a mixture to the enthalpies of its pure components, they are useful to verify predictive methods for thermodynamic properties of mixtures originating from theories based upon assumption of intermolecular forces.

The excess enthalpy for a mixture is defined, at constant temperature and pressure as:

$$H_{T,P}^{E} = \left[ H_m - \sum_i x_i H_i \right]_{T,P} \tag{1}$$

Although many calorimetric determinations of the enthalpy of mixing of liquids have been made, very few data for gas mixtures are available in the literature. Beenakker et al. (*2, 3, 14, 25*) have studied the systems $CH_4$–$H_2$, $CH_4$–Ar, $H_2$–$N_2$, $H_2$–Ar, Ar–$N_2$, He–$CH_4$, and He–Ar. Klein (*12, 13*) investigated the system $CH_4$–$N_2$ and Hejmadi et al. (*8, 9*) obtained data for the systems $N_2$–$CO_2$, $N_2$–$C_2H_6$, and $N_2$–$O_2$. Lee and Mather (*16–18*) studied the systems $N_2$–$CO_2$ and $CH_4$–$CO_2$. Finally, Altunin et al. (*1*) studied the system $N_2$–$CO_2$. For the system $N_2$–$O_2$ only one experimental point, obtained by Hejmadi (*8*) was available in the literature prior to this investigation, at 6.90 MPa (1001 psia), 25 °C, and 0.522 mol fraction of oxygen. In our investigation, data for the $N_2$–$O_2$ system were obtained at four temperatures (10, 25, 45, and 65 °C). For each of the four temperatures, measurements are reported at two pressures, 3.55 and 7.60 MPa (35.0 and 75.0 atm, respectively), for the 10, 45, and 65 °C isotherms, and 3.55 and 6.90 MPa (35.0 and 68.2 atm, respectively) for the 25 °C isotherm, and encompassing a selected range of mole fractions of oxygen in the mixture to permit adequate construction of the entire $H^E$ isotherms from $x = 0$ to $x = 1.0$. All measurements were made in the gas phase region. For more detailed descriptions of equipment and procedures than those presented in this article the reader is referred to ref 15.

## Principle of the Experimental Determinations

A flow diagram of the enthalpy of mixing measuring facility is shown in Figure 1. The *central unit* is a *flow calorimeter*, which is specifically designed for direct determination of enthalpies of mixing for *endothermic gaseous systems*. This unit was designed and built at the Instrument Shop, Office of Research Administration of the University of Michigan, Ann Arbor, Mich. In the calorimeter, two gases at the same temperature and pressure are brought together and mixed. For the case of endothermic mixing, a temperature drop occurs. Enough electrical energy is then added to the gases so that the temperature of the effluent gas mixture is brought up to essentially the same value as that of the two incoming gases. Flow rates for each of the pure gas streams are accurately metered, so that the composition of the gas mixture is known. The mixture composition is also periodically checked by chromatographic analysis of the effluent gas mixture. The gas mixture is then discarded to the atmosphere. The enthalpy of mixing is calculated by means of an energy balance, from the knowledge of the gas flow rates and the measurements of the electrical energy input.

The system $N_2$–$O_2$, which was the object of this investigation, is actually slightly exothermic. In this case, mixing is thus accompanied by a small temperature rise, which for all our experiments never exceeded 0.1 °C. This adiabatic temperature rise was accurately measured and the enthalpy of mixing calculated by a simple energy balance. In addition to the significant practical importance of precise enthalpy values for the mixture $N_2$–$O_2$, the choice of this system, for which the values of the excess enthalpies are very small, was made to demonstrate the high precision which can be obtained with our calorimetric facility.

Our future research program envisions a systematic study of endothermic mixtures, and this is why the calorimeter is specifically designed for this type of system. The excess enthalpies for these endothermic mixtures are two orders of magnitude higher than those measured in the present work.

A description of the equipment and experimental procedure is given in the following sections.

***Calorimeter.*** The calorimeter unit is identical, except for minor design details, with that described by Hejmadi et al., and detailed drawings and description are available in ref 8 and 9. The two gases are mixed and then passed over an electrical resistance coil in the innermost of a series of concentric cylindrical shells which provide both mixing and a heat shield. The gas mixture leaving the outermost shell passes through a helical tube, which conveys it to a thermocouple well. A gold-plated heat shield surrounds the helical coil. The entire unit is enclosed within a jacketed and evacuated space. A vacuum pump (Cenco-Hyvac 7, 1725 rpm, ⅓ hp), indicated as item 19 in Figure 1, is utilized