J. Chem. Eng. Data 1980, 25, 227-230

Liquid-Liquid Equilibria for Benzene-*n*-Heptane Systems with Triethylene Glycol, Tetraethylene Glycol, and Sulfolane Containing Water at Elevated Temperatures

Bachan S. Rawat* and Guru Prasad

Indian Institute of Petroleum, Dehra Dun, India

Liquid-liquid equilibria for the benzene-heptane system have been determined with three industrial solvents, triethylene glycol, tetraethylene glycol, and sulfolane, at elevated temperatures. The solvents are employed in the petroleum industry for extraction of aromatics at elevated temperatures where the literature data are scarce. Also, the solubilities of solvents in heptane at several temperatures have been determined in order to cross-check their equilibrium solubilities in the hydrocarbon phase reported in the literature.

In the petrochemical industry, aromatics like benzene and toluene are extracted from re-formed naphthas and pyrolysis gasolines with solvents like triethylene glycol (TEG), tetraethylene glycol (tetra), and sulfolane at temperatures ranging generally from 100 to 150 °C (superatmospheric pressures), depending upon the type of the solvent and the feed stock.

The generation of liquid-liquid equilibrium (LLE) data is therefore essential at about the same temperatures at which the actual operations are to be carried out in the industry in order to design the extractor part of the solvent extraction processes. Such data on hydrocarbon-solvent systems are also useful in better understanding of the molecular processes in nonideal solutions.

Ternary LLE data for a number of solvents and hydrocarbon systems at different temperatures were compiled earlier (*1*). The LLE data are mostly available at temperatures ranging from 25 to 50 °C. For sulfolane, TEG, and tetra, which are used in the industry, LLE data are scarcely available in the literature. Although some LLE data or equilibrium diagrams for some hydrocarbons and these solvent systems are reported (*2-4*) in the literature at elevated temperatures (100-150 °C), the equilibrium data/diagrams show that the solvent concentrations in the hydrocarbon phase (raffinate phase compositions of the equilibrium diagram) as reported in the literature (*2-4*) are not consistent. In the present study therefore, LLE for benzene-heptane and these three solvents separately have been determined at approximately the same temperatures at which these solvents are used in the industry and the solvent contents of the equilibrated raffinate phases thus determined have been cross-checked by determining the solubilities of the solvents in *n*-heptane at different temperatures.

Experimental Section

Chemicals. Sulfolane and benzene were obtained from Phillips Petroleum Co., heptane was obtained from Prolabo, Rhone-PoulenC, France, and TEG and tetra were obtained from Aldrich Chemical Co. All three solvents were further purified by distilling them in an Oldershaw column under reduced pressure. A heart cut, discarding the first 10% distillate and the last 10% residue, was collected for use. Hydrocarbons were dried over 5-Å molecular sieves before use.

The physical properties like density, refractive index, and boiling point were measured for all these chemicals which corresponded to minimum 99.9% purity.

Determination of Liquid-Liquid Equilibria. The liquid-liquid equilibrium batch runs were carried out in a metallic pressure still (Figure 1) at different temperatures. The still has the provisions of two sight glasses for seeing the interphase level, jackets for circulation of thermostatic liquid, a thermometer pocket, and a screw tube for introduction of solvent and hydrocarbon feed.

The solvent and hydrocarbon feed of known weight and composition were taken in the still, and the charging tube was then pluged with a nut wrapped by Teflon tape. The still was then brought to the required temperature by circulating the heating oil through Teflon tubings. The temperature was maintained within ±1 °C. The contents, were mixed for about 20 min by placing the still horizontally on a shaker, To ensure good mixing the still was given about 200 shakes/min. The exploratory runs carried out earlier showed that 10 min of mixing was sufficient to attain equilibrium.

After the contents were mixed, the still was placed back vertically. The phases were then allowed to settle till both phases became transparent. The phases were then separated through the needle valve (Figure 1) and the cooled condenser (at ~5 °C). A few cubic centimeters of the first and last portions of each phase were discarded in order to avoid any possible overlapping of the phases and also to discard the initial dead volume between the needle valve and the bottom-outlet of the mixer-settler. The raffinate phase, after the first few cubic centimeters were discarded, was collected through another condenser in order to avoid any carry over of the solvent phase to it.

The representative equilibrium phases thus collected were analyzed by a standardized method described elsewhere (*5*).

Solubility of Solvents in Heptane. As very small amounts of solvents are miscible in heptane, the titration method gave erroneous results due to the settling of the solvent droplets at the bottom which do not come in contact of the bulk heptane even on thorough shaking for sufficient time. Sufficient heptane (about 100 g) and a small known quantity of the solvent were therefore placed into a conical flask having the provision of a stopper with thermometer. The thermometer extended up to the bottom of the flask. The contents were heated over hot water with constant shaking till all the solvent droplets dissolved. The contents were then slowly cooled. The temperature at which the turbidity appeared was recorded, and the solubility of the solvent in heptane at that temperature was calculated from the known quantities of heptane and solvent taken. The process was repeated by adding more solvent.

The solubilities at elevated temperatures (>70 °C) were determined in sealed Pyrex glass tubes as per the procedure described elsewhere (*10*).

Results and Discussion

Liquid-liquid equilibrium data for benzene-heptane model hydrocarbon mixture with sulfolane, TEG, and tetra are presented in Tables I and II and Figures 2-4 at different temperatures. The solvents are employed in the industry in the presence of

0021-9568/80/1725-0227$01.00/0

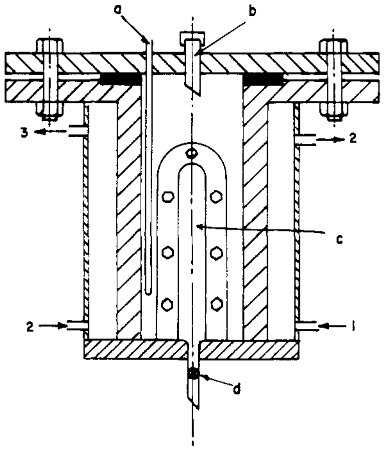

Figure 1. Sketch of liquid-liquid equilibrium still used in the study: (a) thermometer pocket; (b) screw charging tube; (c) sight glasses; (d) needle valve.

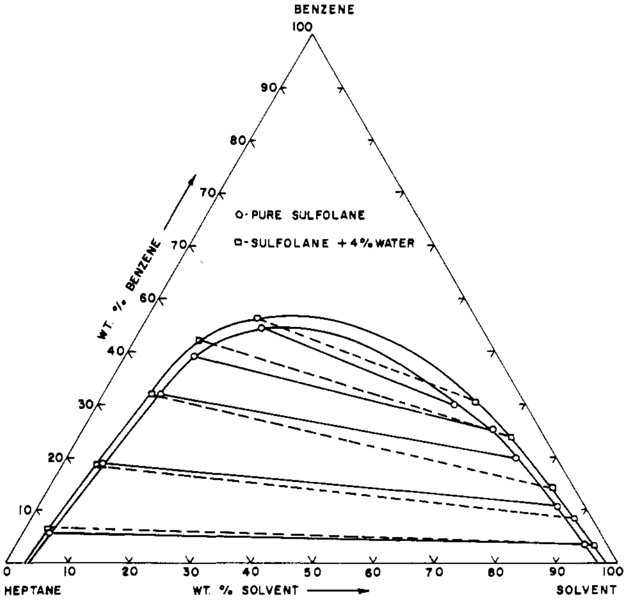

Figure 2. Liquid-liquid equilibrium for benzene-heptane-sulfolane system at 110 °C.

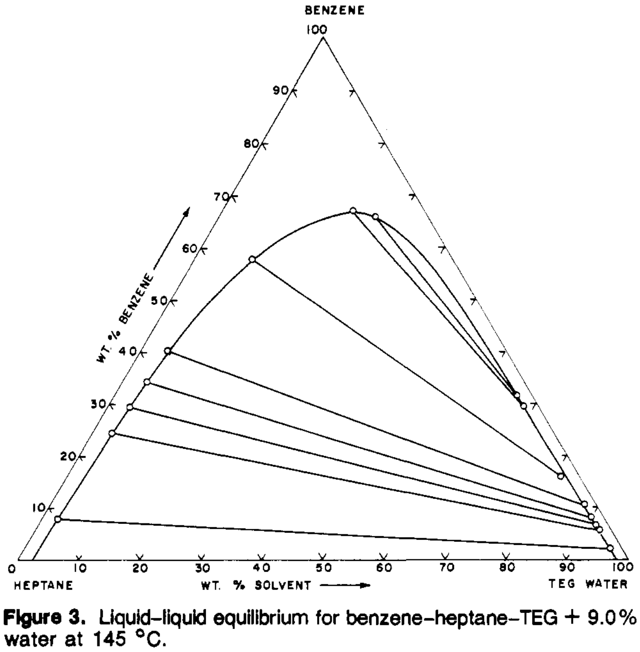

Figure 3. Liquid-liquid equilibrium for benzene-heptane-TEG + 9.0% water at 145 °C.

Table I. Liquid-Liquid Equilibrium Data (Wt %) for Benzene-Heptane-Solvent Systems

extract phase			raffinate phase		
benzene	heptane	solvent	benzene	heptane	solvent
Sulfolane (Pure), 110 °C					
3.5	3.4	93.1	5.8	90.2	4.0
10.8	4.2	85.0	18.8	75.0	6.2
20.0	6.4	73.6	32.0	58.8	9.2
26.1	8.7	65.2	39.0	50.0	11.0
30.0	11.4	58.6	39.8	40.8	19.4
Sulfolane + 4% Water, 110 °C					
3.2	2.2	94.6	6.4	90.2	3.4
8.2	3.1	88.7	18.8	75.9	5.3
14.2	3.7	82.1	32.0	60.5	7.5
23.8	5.5	70.7	42.1	47.5	10.4
30.5	7.8	61.7	45.9	36.0	18.1

Table II. Liquid-Liquid Equilibrium Data (Wt %) for Benzene-Heptane-Solvent Systems

extract phase			raffinate phase		
benzene	heptane	solvent	benzene	heptane	solvent
Triethylene Glycol + 5% Water, 121.5 °C					
2.2	1.9	95.9	8.5	90.0	1.5
6.3	1.8	91.9	24.2	73.2	2.6
11.6	2.2	86.2	41.8	55.0	3.2
17.9	2.1	80.0	58.1	35.0	6.9
35.7	3.2	61.1	60.8	9.3	29.9
Triethylene Glycol + 9% Water, 145 °C					
10.5	1.9	87.6	40.4	55.4	4.2
8.1	2.1	89.8	34.5	61.7	3.8
6.8	1.7	91.5	29.5	67.0	3.5
2.1	1.7	96.2	7.9	89.6	2.5
5.7	1.6	92.7	24.8	72.1	3.0
15.8	3.2	81.0	58.1	32.7	9.2
29.7	1.9	68.4	67.3	10.9	21.8
31.6	2.3	66.1	65.6	8.8	25.6
Tetraethylene Glycol + 5% Water, 120 °C					
2.5	1.9	95.6	7.0	89.7	3.3
7.2	2.3	90.5	24.3	71.6	4.0
12.7	2.3	85.0	41.0	54.3	4.7
20.7	3.1	76.2	55.5	34.9	9.6
26.6	3.6	69.8	60.3	24.4	15.3
35.2	4.8	60.0	55.9	14.2	29.9

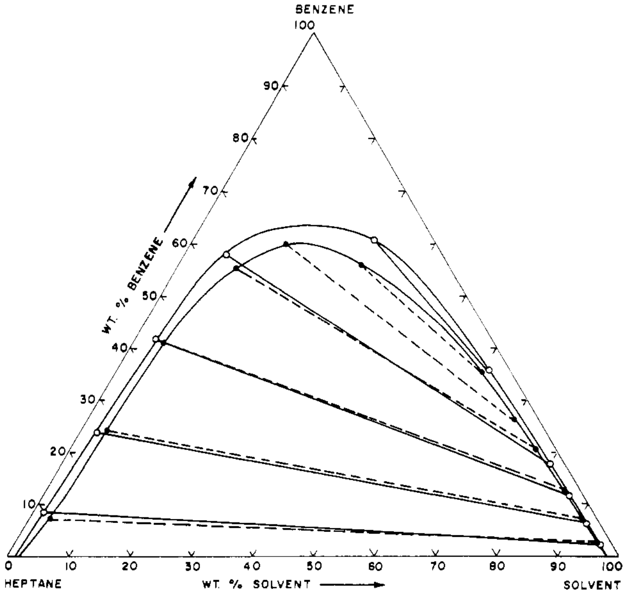

Figure 4. Liquid-liquid equilibria for benzene-heptane-solvent systems: (O) triethylene glycol + 5% water, 121.5 °C; (●) tetraethylene glycol + 5% water, 120 °C.

Table III. Liquid-Liquid Equilibrium Data/Diagrams for Hydrocarbon-Solvent Systems

no.	hydrocarbon system	wt % water	temp, °C	lit.
		Sulofane		
1	benzene-heptane	0.0	25	5
2	benzene-heptane	5.2, 10.2	25	6
3	toluene-heptane	0.0	25, 40, 50, 75, 100	2, 5, 7, 8
4	cyclohexane-benzene	0.0	25, 50, 75, 100	2
5	hexane-benzene	0.0	25, 50, 75, 100	2
6	1-hexene-benzene	0.0	25, 50, 75, 100	2
		Triethylene Glycol		
7	benzene-heptane	0.0	25	9
8	benzene-heptane	5, 7.7, 13.0	121, 149	3, 4
9	ethylbenzene-heptane	0.0	25	9
		Tetraethylene Glycol		
10	benzene-heptane	3.9	100	4
11	benzene-heptane	0.0	25	9
12	ethylbenzene-heptane	0.0	25	9

water which is used as an antisolvent. The LLE was, therefore, determined with solvents containing water in such concentrations that they represented the best industrial conditions. To our knowledge, the data on benzene-heptane-sulfolane and with sulfolane containing water have not been reported in the literature at elevated temperatures. Similarly, very small amounts of data or equilibrium diagrams are reported with TEG or tetra. The data (or equilibrium diagrams) available with these three solvents are given in Table III. If we look into the data/diagrams reported on these solvents in the literature (Table III), we find some discrepancy in the solvent concentrations of hydrocarbon phase (raffinate phases). For example, the hydrocarbon solubility in glycols or the solubility of glycols in hydrocarbons generally increases (*9*) in the order ethylene glycol (EG) diethylene glycol (DEG), TEG, and tetra. However, the concentrations of DEG and tetra in the hydrocarbon phases as shown (*4*, *10*) in the equilibrium diagrams are just the reverse whereas the solubility of TEG is indicated almost equal to that of tetra. Even in presence of water, the solvent concentrations in hydrocarbon phase will increase in the order DEG, TEG, and tetra. This is because almost all the water goes with the solvent phase (*6*). The distribution of water does not take place in the same ratio in which it is taken initially with the solvent (*6*). The solvent in the raffinate phase is therefore almost waterfree (*6*) and its concentration in raffinate phase will therefore correspond to that of pure solvent particularly in the lower region of the diagrams (Figures 2-4), that is, the top region of the extractor where aromatics are in very low concentrations. Thus, the raffinate hydrocarbons in this region will almost represent pure heptane. The model mixture of benzene-heptane was chosen because it represents the re-formed naphtha which is the feedstock for aromatics.

The equilibrium solubilities of solvents in heptane were therefore determined accurately, and the data are presented in Table IV and Figure 5.

The solubilities of sulfolane in heptane are reported (*2*) at four temperatures. However, these data (Figure 5) show a linear relationship between temperature and solubilities which generally is a curve.

The higher solubilities of tetra as compared to TEG can also be seen from Figure 4 and Tables II and IV. Tetra has therefore higher capacity for aromatics compared to TEG. It is for this reason that the use of tetra is recommended in Udex process for higher recovery of aromatics at lower solvent to feed ratios and temperatures. The experimental LLE data for all the systems studied show, on empirical basis, a reasonable internal con-

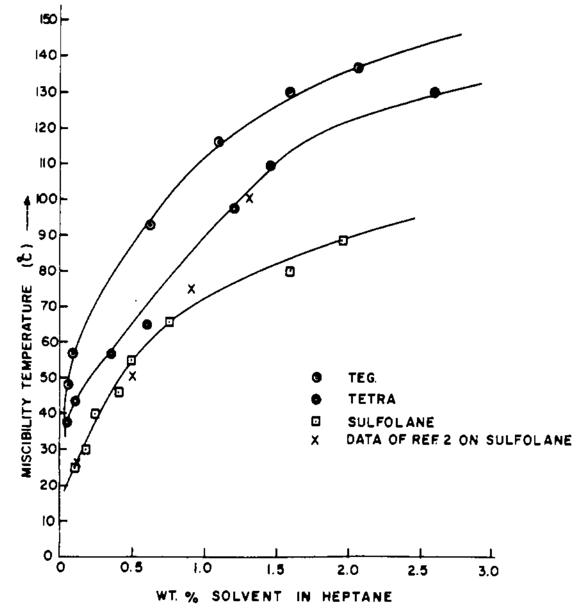

Figure 5. Solubilities of solvents in heptane at different temperatures.

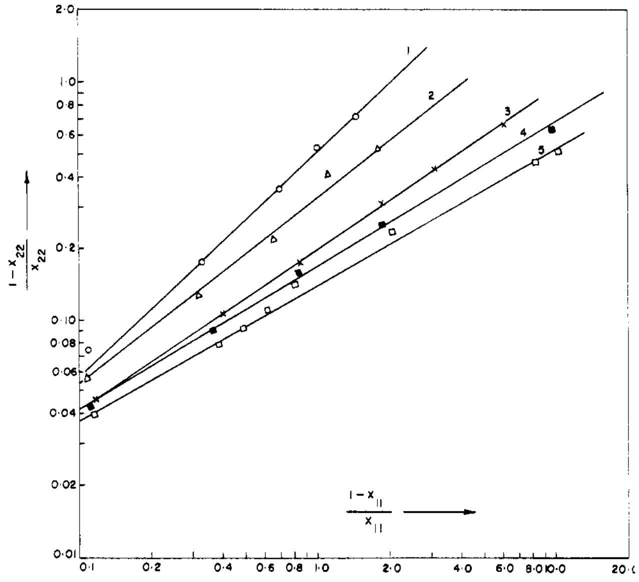

Figure 6. Othmer–Tobias correlation for benzene–heptane–solvent systems: (1) pure sulfolane, 110 °C; (2) sulfolane + 4% water, 110 °C; (3) tetraethylene glycol + 5% water, 120 °C; (4) TEG + 5% water 121.5 °C; (5) TEG + 9% water, 145 °C.

Table IV. Solubilities of Different Solvents in Heptane

wt % solvent in heptane	temp, °C	wt % solvent in heptane	temp, °C
	1. Tetraethylene Glycol		
0.08	38.0	1.20	97–98
0.11	44.0	1.4	109–110
0.35	57.0	2.6	129–130
0.60	65–66		
	2. Triethylene Glycol		
0.06	48.0	1.10	116–117
0.08	57.0	1.66	129–130
0.65	93–94	2.07	136–137
	Sulfolane		
0.10	25.0	0.49	55.0
0.17	30.0	0.76	66.0
0.23	40.0	1.60	79–80
0.41	46.0	1.94	88–89

sistency as indicated in Figure 6 by the Othmer-Tobias coordinate (*11*).

Acknowledgment

The authors wish to express their sincere thanks to Dr. I. B. Gulati, Director, for the encouragement from time to time.

Glossary

X	liquid-phase composition, weight fraction

Subscripts

1	*n*-heptane
2	solvent
3	benzene
11	composition (weight fraction) of component 1 in phase 1 (*n*-heptane-rich phase)
22	composition (weight fraction) of component 2 in phase 2 (solvent-rich phase)

Literature Cited

(1) Rawat, B. S., Gulati, I. B., *J. Sci. Ind. Res.*, **35**, 383 (1976).
(2) De Fre, R. M., Verhoeye, L. A., *J. Appl. Chem. Biotechnol.*, **26**, 469 (1976).
(3) Graham, H. L., *J. Chem. Eng. Data*, **7**, 214 (1962).
(4) Somekh, G. S., Friedlander, B. I., *Adv. Chem. Ser.*, **No. 97**, 228 (1970).
(5) Rawat, B. S., Gulati, I. B., *J. Appl. Chem. Biotechnol.*, **26**, 425 (1976).
(6) Hartwig, G. M., Hood, G. C., Maycock, R. L., *J. Phys. Chem.*, **59**, 52 (1955).
(7) Feldman, J., *Adv. Chem. Ser.*, **No. 97**, 242 (1970).
(8) Tripathi, R. P., Raja Ram, A., Rao, P. B., *J. Chem. Eng. Data*, **20**, 261 (1975).
(9) Somekh, G. S., *Hydrocarbon Process. Pet. Refiner*, **42**, 161 (1963).
(10) Johnson, G. C., Francis, A. W., *Ind. Eng. Chem.*, **46**, 1662 (1954).
(11) Othmer, D. F., Tobias, P. E., *Ind. Eng. Chem.*, **34**, 690 (1942).

Received for review August 20, 1979. Accepted March 28, 1980.

Liquid-Vapor Equilibria in Binary Systems of Hexamethyldisiloxane-1-Butanol, -2-Butanol, and -2-Methyl-1-propanol

Aleksander Radecki* and Barbara Kaczmarek

Department of Physical Chemistry, Institute of Chemistry and Analytics, Medical Academy, 80-416 Gdańsk, Poland

Liquid-vapor phase equilibria have been studied under isobaric conditions, and total vapor pressures were measured at 20 °C. In the three binary systems studied, large positive deviations from the ideal behavior have been observed. An azeotrope in the hexamethyldisiloxane (HMDS)-1-butanol system was formed at 0.725 mole fraction HMDS at 765 mmHg. In the hexamethyldisiloxane-2-methyl-1-propanol system the minimum boiling point occurred at 0.615 mole fraction HMDS at 766 mmHg. In the third binary system, an azeotrope contained 0.540 mole fraction HMDS at 754 mmHg.

A variety of physicochemical techniques, including ebulliometry, have been employed for studying intermolecular interactions. As there are only a few reports in the literature (*1-3*) on molecular interaction between hexamethyldisiloxane and alcohols, this work has been confined to the measurements of vapor pressures and boiling points in the systems including hexamethyldisiloxane and isomeric butanols. Results of these measurements can provide a basis for evaluation of the nature of deviation of the systems from ideal state.

Experimental Section

Materials. Prior to measurements all reagents were purified by repeated distillation. Their boiling points (bp), densities (d^{20}_4) and refraction indices (n^{20}_D) were as follows: hexamethyldisiloxane (HMDS) bp 100-100.5 °C, d^{20}_4 0.7636 g cm^{-3}, n^{20}_D 1.3774; 1-butanol bp 118 °C, d^{20}_4 0.8104 g cm^{-3}, n^{20}_D 1.3987; 2-butanol bp 99-100 °C, d^{20}_4 0.8080 g cm^{-3}, n^{20}_D 1.3972; 2-methyl-1-propanol bp 108-109 °C, d^{20}_4 0.8020 g cm^{-3}, n^{20}_D 1.3958.

Procedure. For each of the systems studied, a series of solutions was prepared by covering the whole concentration range of both components.

Table I. Liquid-Vapor Equilibria under Isobaric Conditions, Total Vapor Pressure, *P*, Density d^{20}_4, and Refractive Index n^{20}_D in the Systems Hexamethyldisiloxane-Butyl Alcohols

	HMDS mole fraction				
temp, °C	vapor	liquid	d^{20}_4	n^{20}_D	*P*, mmHg (20 °C)
P = 765 mmHg		Hexamethyldisiloxane-1-Butanol			
98.4	0.840	0.904	0.7661	1.3788	37.0
97.2	0.772	0.795	0.7698	1.3801	37.5
97.0	0.725	0.725	0.7736	1.3817	37.8
97.5	0.719	0.610	0.7786	1.3836	35.5
98.1	0.690	0.500	0.7826	1.3856	35.0
99.3	0.675	0.404	0.7856	1.3878	34.0
100.6	0.648	0.299	0.7916	1.3904	30.5
103.9	0.622	0.200	0.7976	1.3932	26.0
109.2	0.530	0.102	0.8024	1.3962	21.4
118.0		0.000	0.8104	1.3992	6.0
P = 766 mmHg		Hexamethyldisiloxane-2-Methyl-1-propanol			
97.9	0.815	0.902	0.7677	1.3784	35.0
96.6	0.743	0.800	0.7724	1.3791	35.2
95.0	0.645	0.692	0.7756	1.3804	35.4
94.6	0.615	0.615	0.7789	1.3819	35.5
95.1	0.580	0.507	0.7832	1.3837	35.0
95.3	0.535	0.493	0.7880	1.3852	32.5
96.5	0.480	0.300	0.7919	1.3874	30.0
99.0	0.400	0.205	0.7956	1.3899	27.4
102.6	0.310	0.100	0.7987	1.3928	22.1
108.0		0.000	0.8020	1.3958	8.0
P = 754 mmHg		Hexamethyldisiloxane-2-Butanol			
97.0	0.730	0.895	0.7664	1.3782	36.8
93.2	0.645	0.792	0.7712	1.3792	36.9
91.9	0.590	0.700	0.7715	1.3804	37.0
91.4	0.560	0.604	0.7775	1.3818	37.3
91.2	0.540	0.540	0.7777	1.3827	37.5
91.3	0.520	0.503	0.7784	1.3832	35.5
91.7	0.500	0.409	0.7833	1.3853	35.0
92.3	0.472	0.297	0.7878	1.3877	32.5
93.7	0.404	0.201	0.7933	1.3902	30.5
96.3	0.325	0.105	0.8010	1.3946	25.0
100.0		0.000	0.8080	1.3972	12.0

Total vapor pressure of the systems was measured in a device reported by Szarawara (*4*, *5*). Before each measure-

0021-9568/80/1725-0230$01.00/0