change, and purity increase, often being seen in supercritical fluid extraction testing.)

Although the amount of solubility data on the dihydroxybenzenes is by no means as extensive as for the hydroxybenzoic acids, the solubility behavior given in Table III does lend credence to the statement that the solubility in supercritical carbon dioxide of isomers in a family is related to the melting point, the solubility decreasing with increasing melting point.

The hydroxybenzoic acids are frequently desired in relatively pure ortho and para forms for subsequent conversion to other compounds, and they most commonly must be separated from each other in a mixture not usually containing the meta isomer. The two isomers can be separated by other methods, by crystallization, for example, promoted by lowering the pH of a solution (of high pH) containing both compounds (in ionic form), advantage being taken of the fact that the p*K* for the para acid is higher than that of the ortho acid, resulting in a preferential precipitation of the para acid form. A relatively pure para isomer fraction can usually be prepared by such a process, but the remaining ortho isomer is usually contaminated with some previously unprecipitated para isomer as the pH is lowered further (*17*). Other studies which are to be carried out will test the ability of supercritical carbon dioxide to separate mixtures of *o*- and *p*-hydroxybenzoic acids.

Conclusions

With two families of disubstituted aromatic isomers, it has been demonstrated that solubility in supercritical carbon dioxide is related to the melting point; at a constant pressure and temperature of the carbon dioxide the solubility decreases with increasing melting point. The large difference in solubility between the ortho and para isomers suggests that supercritical fluid extraction might prove to be an effective way to separate a mixture of these isomers.

Registry No. CO_2, 124-38-9; *o*-hydroxybenzoic acid, 69-72-7; *m*-hydroxybenzoic acid, 99-06-9; *p*-hydroxybenzoic acid, 99-96-7; *o*-dihydroxybenzene, 120-80-9; *m*-dihydroxybenzene, 108-46-3; *p*-dihydroxybenzene, 123-31-9.

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Vapor–Liquid Equilibria for the Binary Systems Formed by Hexamethyldisiloxane, 1-Pentanol, and 2-Methyl-4-butanol

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The total vapor pressure was determined at 293.15 K, and liquid–vapor equilibria have been studied under isobaric conditions for binary systems hexamethyldisiloxane (HMDS)–1-pentanol and HMDS–2-methyl-4-butanol. In both systems a large positive deviation from the ideal behavior was observed, as evidenced by the vapor pressure maximum on the isotherm and the boiling point minimum under isobaric conditions.

In continuation of our studies (*1-4*), liquid-vapor phase equilibria have been studied in systems containing hexamethyldisiloxane (HMDS) and two alcohols. The nature of deviations from the ideal behavior could be estimated by measuring total vapor pressures under isothermic conditions and boiling points under isobaric conditions.

Introduction

HMDS can widely be used as a nonpolar solvent, owing to its physicochemical properties. It is a nontoxic and poorly reactive solvent (*5, 6*). Therefore, HMDS can replace a variety of common solvents such as benzene or toluene. This is the reason that prompted us to study the liquid–liquid and liquid–vapor equilibria of systems formed by HMDS. The information about the equilibria is useful in the application and separation of HMDS in technological processes.

Experimental Section

Reagents. Hexamethyldisiloxane (HMDS) was commercial product. After purification it had bp 100.8–101 °C, $d^{20}{}_4$ 0.7634 g cm^{-3}, and $n^{20}{}_D$ 1.3777. 1-Pentanol had bp 137 °C, $d^{20}{}_4$ 0.8133 g cm^{-3}, and $n^{20}{}_D$ 1.4103. 2-Methyl-4-butanol boiled at 130.5–131 °C, and had $d^{20}{}_4$ 0.8120 g cm^{-3} and $n^{20}{}_D$ 1.4076.

Measurements. Total vapor pressure over the whole concentration range of the system was measured in the previously described apparatus (*1*). Before carrying out the measurements, we checked the apparatus by using two-component benzene–toluene mixtures. Measurements of the total vapor pressure were carried out at 20 ± 0.05 °C.

Isobaric experiments were carried out by using the modified Swietoslawski ebulliometer (*7, 8*). The values of the total vapor pressure and outside pressure were measured with a precision of ±0.006 kPa and the temperature was measured with a precision of ±0.05 °C. Tables I and II contain the mean values of the measurements run in triplicate. The composition of the liquid and of the condensate was determined refracto-

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Table I. Liquid–Vapor Equilibria under Isobaric Conditions, Density, $d^{20}{}_4$, and Refractive Index, $n^{20}{}_D$, in the Systems HMDS–Alcohol

temp, K	[HMDS], mole fraction vapor	[HMDS], mole fraction liquid	$d^{20}{}_4$	$n^{20}{}_D$
p = 101.733 kPa, HMDS–1-Pentanol				
373.86	0.950	0.949	0.7659	1.3787
374.65	0.915	0.902	0.7687	1.3796
375.77	0.875	0.800	0.7757	1.3817
376.48	0.855	0.698	0.7808	1.3842
377.06	0.834	0.604	0.7849	1.3869
379.15	0.815	0.501	0.7901	1.3898
380.23	0.794	0.393	0.7951	1.3932
383.65	0.782	0.305	0.7996	1.3968
388.78	0.760	0.199	0.8047	1.4008
397.31	0.673	0.103	0.8096	1.4051
403.35	0.591	0.064	0.9042	1.4112
p = 102.420 kPa, HMDS–2-Methyl-4-butanol				
396.66	0.343	0.051	0.8081	1.4058
393.15	0.463	0.103	0.8039	1.4035
386.62	0.666	0.200	0.7969	1.3995
381.66	0.690	0.298	0.7903	1.3956
378.23	0.750	0.402	0.7840	1.3992
375.90	0.771	0.500	0.7790	1.3889
374.58	0.805	0.597	0.7748	1.3862
374.41	0.826	0.704	0.7709	1.3838
374.24	0.840	0.809	0.7673	1.3918
372.46	0.852	0.854	0.7655	1.3807
372.97	0.881	0.908	0.7644	1.3797
373.18	0.920	0.953	0.7631	1.3787

Table II. Values of Total Vapor Pressures at 293.15 K for the HMDS–Alcohol Systems

HMDS–1-pentanol [HMDS], mole fraction	HMDS–1-pentanol vapor press., kPa	HMDS–2-methyl-4-butanol [HMDS], mole fraction	HMDS–2-methyl-4-butanol vapor press., kPa
0.949	4.603	0.953	4.486
0.902	4.598	0.908	4.628
0.800	4.414	0.854	4.656
0.698	4.402	0.809	4.506
0.604	4.299	0.704	4.438
0.501	4.056	0.597	4.372
0.393	3.879	0.500	4.164
0.305	3.599	0.402	3.908
0.199	3.095	0.298	3.629
0.103	2.271	0.200	3.232
		0.103	2.337
		0.051	1.603

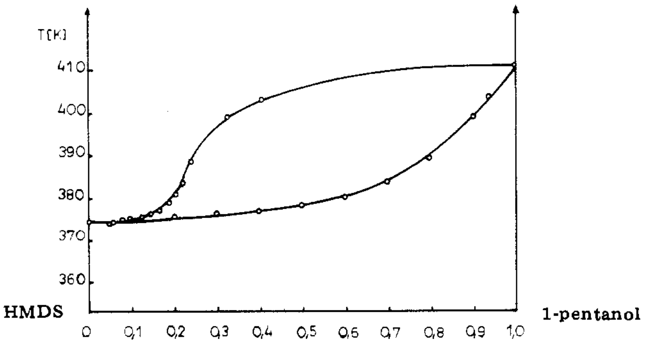

Figure 1. Boiling point vs. composition in the system HMDS–1-pentanol at 1017.33 hPa.

metrically by using an experimentally plotted $n^{20}{}_D$ vs. composition graph.

Results and Conclusions

The liquid–vapor phase equilibria of two binary systems, HMDS–1-pentanol and HMDS–2-methyl-4-butanol, were investigated under isothermic and isobaric conditions. The results, shown in Table I and Figures 1–4, indicate that there are large positive deviations from the ideal behavior. Azeotropic mixtures occur in both systems. The minimum of the boiling point under isobaric conditions (Figures 1 and 3) correspond to the maximum vapor pressure on the isotherms (Figures 2 and 4).

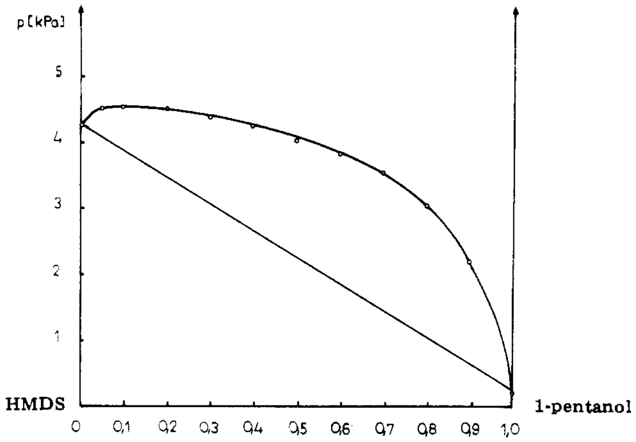

Figure 2. Total Vapor pressure in the system HMDS–1-pentanol at 293.15 K.

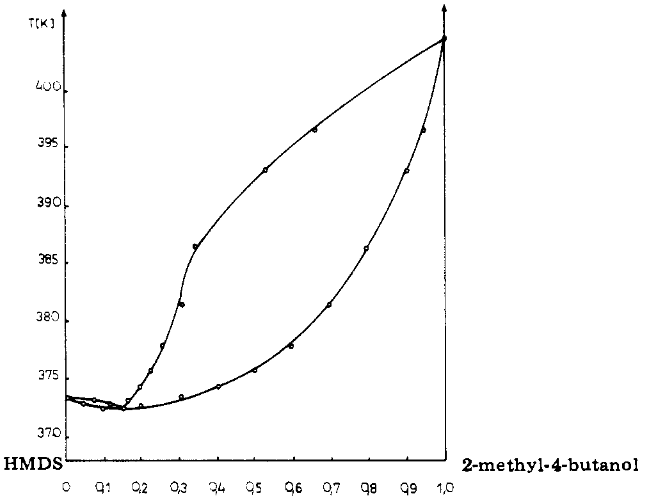

Figure 3. Boiling point vs. composition in the system HMDS–2-methyl-4-butanol at 1024 hPa.

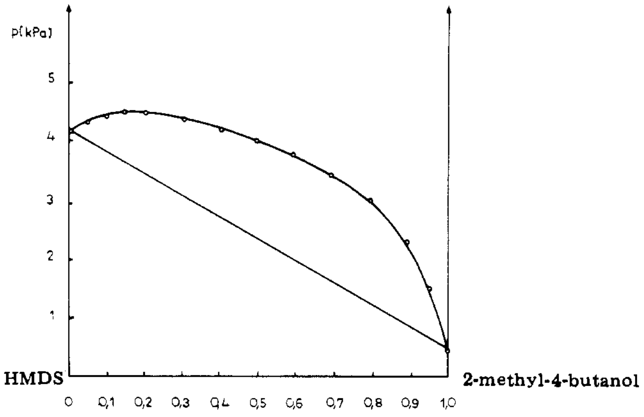

Figure 4. Total vapor pressure in the system HMDS-2-methyl-4-butanol at 293.15 K.

In the system HMDS–1-pentanol, the minimum of the boiling point amounts to 373.86 K under a pressure of 1017.33 hPa at a HMDS mole fraction of 0.949. In the system HMDS–2-methyl-4-butanol, the boiling point of the azeotrope is 372.46

K under a pressure of 1024.2 hPa and falls at a mole fraction of HMDS of 0.854.

Registry No. HMDS, 107-46-0; 1-pentanol, 71-41-0; 2-methyl-4-butanol, 123-51-3.

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Liquid–Liquid Equilibria for Three Methyl Alcohol–Trimethyl Borate–*n*-Alkane Systems

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Liquid–liquid equilibria for the solvent–solute pair methyl alcohol–trimethyl borate with *n*-hexane, *n*-heptane, and *n*-nonane have been measured at 298.15 ± 0.1 K. Data have been correlated by various means.

The binodal solubility curves and representative tie-line data were measured for three ternary systems. These systems contained the solvent–solute pair methyl alcohol–trimethyl borate and extractant liquids *n*-hexane, *n*-heptane, and *n*-nonane. Measurements were made at atmospheric pressure and 298.15 ± 0.1 K. The titration method of analysis (*1*) for the binodal curve was used. Titrations were made into a glass container which was immersed in a constant temperature bath controlled to ±0.1 K. The container had three openings to accommodate a stirrer, which was used intermittently, a calcium chloride drying tube, and a buret.

For tie-line data a mixture of the three components was added to a clean container. Amounts of methyl alcohol or hydrocarbon were then added in order to form two liquid layers of comparable volumes. Mixtures were alternately stirred for periods of about 5 min and then allowed to settle. These cycles were repeated for up to 8 h and then allowed an extended settling time. The container had septa through which long needles were placed in the two layers, and samples withdrawn by hypodermic syringe.

Analysis of the two layers was made by a combination of chemical analysis and physical property measurements. This method has been described previously (*2*) and involves titration for the borate, and measurement of mixture densities and refractive indices. Physical property measurements were made at 300.15 ± 0.1 K to ensure the liquid sample did not separate into two layers.

Materials Used

All chemicals received had purities in excess of 99.5% with the exception of the trimethyl borate which was about 98% purity. Methyl alcohol and the hydrocarbons were analyzed for water by the Karl Fisher method and showed traces less than 0.01%. All chemicals were subsequently subjected to simple distillations retaining the central portions for the experimental work. Only about 40% of the trimethyl borate was retained, and it assayed at 99.8% purity. The refractive indices and densities of the five chemicals compared with literature data are shown in Table I.

Results

The experimental data are given in Tables II–IV and plotted in Figure 1. Binodal points have been omitted for clarity. Correlation of the tie-line data and estimation of the plait points were made by the method of Hand (*3*). These are shown in Figure 2. Distribution coefficients

$$m = X_{CA}/X_{CB} \tag{1}$$

were calculated as a function of concentration X_{CA} and found to be linear. Data were extrapolated to $X_{CA} = 0$ in order to obtain values of the distribution coefficient, m_0, at infinite dilution. The distribution coefficient data correlated as

$$m = m_0 + ZX_{CA} \tag{2}$$

with values of m_0 and Z given in Table V. As suggested by Alders (*4*), the distribution coefficient at infinite dilution for a given solvent–solute pair can be directly related to the carbon number of an alkane extractant liquid. The data for the three systems reported here follow the form suggested by Alders and represent the experimental values of m_0 ± 0.001.

$$\log m_0 = -0.015C_N + 0.052 \tag{3}$$

Alders also noted that for a given solvent–solute pair, e.g., methyl alcohol–trimethyl borate, the ratio of distribution coefficients at equal solute concentrations is relatively independent of concentration for a homologous series of extractants. This implies that the value of Z in eq 2 should approximate a single value for the homologous series. As seen in Table V, this is true for the data reported here.

Van Laar coefficients for the methyl alcohol–hydrocarbon pairs were calculated from the mutual solubility data by using the procedure suggested by Colburn and Schoenborn (*5*) and are reported in Table VI. Methods for estimating the activity coefficient at infinite dilution (equivalent to the Van Laar coefficient) from structural relationships have been summarized by Smith (*6*). For methyl alcohol–*n*-alkanes these simplify to relations involving only the number of carbon atoms in the *n*-alkanes. Constants for these simplifications were evaluated from the experimental data, and the resulting equations are

$$A_{AB} = 0.8655 + 0.0149(1 - C_N)^2 \tag{4}$$

$$A_{BA} = -1.190 + 0.4025C_N - 0.0215(C_N - 1)^2 \tag{5}$$

Equation 4 predicts the value of the Van Laar coefficient to

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