J. Chem. Eng. Data **1985**, *30*, 251-253

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 The container had septa through which long needles were placed in the two layers, and samples withdrawn by hypodermic syringe.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

$$m = X_{CA}/X_{CB} \qquad (1)$$

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

$$m = m_0 + ZX_{CA} \qquad (2)$$

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 $m_0 \pm 0.001$.

$$\log m_0 = -0.015C_N + 0.052 \qquad (3)$$

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

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

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

Equation 4 predicts the value of the Van Laar coefficient to

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Table I. Physical Properties of the Pure Components

	densities, kg/m^3			refractive index		
component	at 300.15 K	at 298.15 K	lit.[a] at 298.15 K	at 300.15 K	at 298.15 K	lit.[a] at 298.15 K
methyl alcohol	784.5	786.5	786.52	1.32478	1.32653	1.32657
trimethyl borate	921.7	927.2	927.3 (*7*)	1.35422	1.35503	1.3550 (*8*)
n-hexane	653.3	654.2	654.71	1.37138	1.37218	1.37226
n-heptane	678.4	679.7	679.51	1.38417	1.38506	1.38511
n-nonane	713.8	714.2	713.81	1.40220	1.40321	1.40311

[a] All literature citations are from ref 9 unless otherwise specified.

Table II. Solubility Data for Methyl Alcohol (A)-*n*-Hexane (B)-Trimethyl Borate (C) at 298.15 K

X_A	X_B	X_C	X_A	X_B	X_C
0.105	0.895	0	0.551	0.436	0.013
0.175	0.781	0.044	0.480	0.487	0.033
0.581	0.419	0	0.388	0.566	0.046
0.511	0.465	0.024	0.314	0.634	0.052
0.435	0.524	0.041	0.137	0.839	0.024
0.343	0.609	0.048	0.217	0.733	0.050
0.278	0.670	0.052	0.360[a]	0.592[a]	0.048[a]

Tie-Line Data

A-rich layer			B-rich layer		
X_A	X_B	X_C	X_A	X_B	X_C
0.544	0.442	0.014	0.129	0.856	0.015
0.469	0.495	0.036	0.165	0.797	0.038

[a] Plait point (estimated).

Table III. Solubility Data for Methanol (A)-*n*-Heptane (B)-Trimethyl Borate (C) at 298.15 K

X_A	X_B	X_C	X_A	X_B	X_C
0.759	0.241	0	0.169	0.683	0.148
0.583	0.335	0.082	0.285	0.562	0.153
0.724	0.262	0.014	0.059	0.916	0.025
0.629	0.312	0.059	0.075	0.855	0.070
0.689	0.284	0.027	0.111	0.783	0.106
0.536	0.364	0.100	0.143	0.720	0.137
0.488	0.397	0.115	0.230	0.618	0.152
0.057	0.943	0	0.448	0.426	0.126
0.068	0.884	0.048	0.407	0.459	0.134
0.096	0.815	0.089	0.342	0.514	0.144
0.118	0.758	0.124	0.341[a]	0.505[a]	0.154[a]

Tie-Line Data

A-rich layer			B-rich layer		
X_A	X_B	X_C	X_A	X_B	X_C
0.645	0.304	0.051	0.069	0.875	0.056
0.551	0.352	0.097	0.106	0.789	0.105
0.691	0.282	0.027	0.061	0.908	0.031
0.372	0.485	0.143	0.250	0.598	0.152

[a] Plait point (estimated).

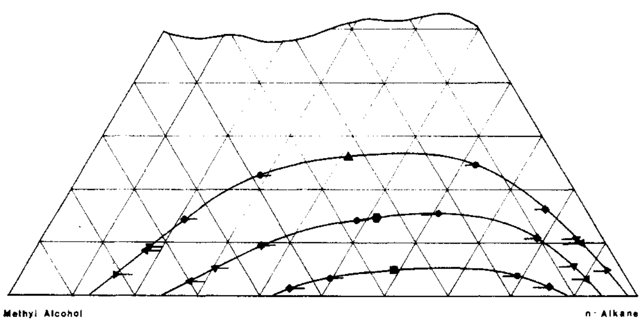

Figure 1. Ternary equilibrium data for methyl alcohol–*n*-alkane–trimethyl borate systems.

Table IV. Solubility Data for Methanol (A)-*n*-Nonane (B)-Trimethyl Borate (C) at 298.15 K

X_A	X_B	X_C	X_A	X_B	X_C
0.017	0.983	0	0.512	0.272	0.216
0.073	0.737	0.190	0.483	0.290	0.227
0.214	0.518	0.268	0.456	0.308	0.236
0.364	0.380	0.256	0.431	0.326	0.243
0.410	0.342	0.248	0.408	0.342	0.250
0.493	0.286	0.221	0.385	0.361	0.254
0.024	0.928	0.048	0.364	0.379	0.257
0.037	0.873	0.090	0.344	0.398	0.258
0.092	0.693	0.215	0.327	0.411	0.262
0.121	0.646	0.233	0.311	0.426	0.263
0.135	0.612	0.253	0.295	0.442	0.263
0.174	0.564	0.262	0.281	0.455	0.264
0.214	0.518	0.268	0.269	0.466	0.265
0.281	0.458	0.261	0.258	0.475	0.267
0.314	0.423	0.263	0.246	0.487	0.267
0.872	0.123	0	0.237	0.496	0.267
0.716	0.184	0.100	0.188	0.547	0.265
0.673	0.200	0.127	0.080	0.731	0.189
0.638	0.212	0.150	0.757	0.172	0.071
0.603	0.227	0.170	0.227	0.507	0.266
0.572	0.240	0.188	0.327[a]	0.408[a]	0.265[a]
0.541	0.256	0.203			

Tie-Line Data

A-rich Layer			B-rich layer		
X_A	X_B	X_C	X_A	X_B	X_C
0.738	0.179	0.083	0.035	0.867	0.098
0.647	0.121	0.142	0.064	0.774	0.162
0.487	0.288	0.225	0.128	0.623	0.249
0.807	0.153	0.040	0.021	0.932	0.047
0.733	0.175	0.092	0.040	0.853	0.107

[a] Plait point (estimated).

Table V. Constants for Eq 2

system no.[a]	m_0[b]	Z	X_{CA} range
1	0.916	0.385	0–0.048
2	0.884	0.389	0–0.154
3	0.826	0.360	0–0.265

[a] 1 = methyl alcohol (A)–*n*-hexane (B)–trimethyl borate (C); 2 = methyl alcohol (A)–*n*-heptane (B)–trimethyl borate (C); 3 = methyl alcohol (A)–*n*-nonane (B)–trimethyl borate (C). [b] Distribution coefficient at infinite dilution.

Table VI. Binary Van Laar Coefficients at 298.15 K for Liquid Systems Using Base 10 Logarithms

system	A_{AB}	A_{BA}
methanol (A)–hexane (B)	1.238	0.687
methanol (A)–heptane (B)	1.404	0.853
methanol (A)–nonane (B)	1.818	1.056

±0.002 and eq 5 must represent the data herein since only three points were available to determine the three constants.

Glossary

A	Van Laar coefficient associated with base 10 logarithms
C_N	number of carbon atoms in extractant alkane
m	distribution coefficient
m_0	value at infinite dilution

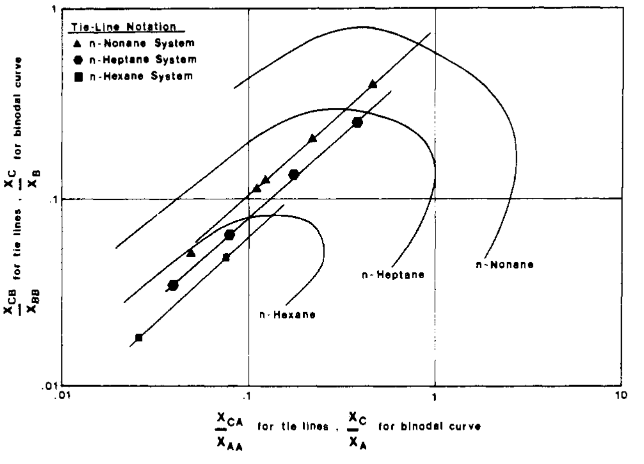

Figure 2. Hand (*3*) correlation for estimation of plait points.

X	weight fraction
Z	constant in eq 2

Subscripts

A	solvent liquid, methyl alcohol
B	extractant liquid, alkane
C	solute, trimethyl borate
AA	solvent in solvent rich layer
BB	extractant in extract layer
CA	solute in solvent rich layer
CB	solute in extract layer

Registry No. Methanol, 67-56-1; trimethyl borate, 121-43-7; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-nonane, 111-84-2.

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Density of Cyclodecane from 25 to 192 °C

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The density of a purified sample of cyclodecane has been measured from 25 to 192 °C by densimetry. The results are well described by $d/(\mathrm{g\ cm^{-3}}) = 0.87340 - (0.78424 \times 10^{-3})(t/°\mathrm{C}) + (0.5005 \times 10^{-6})(t/°\mathrm{C})^2 - (0.2018 \times 10^{-8})(t/°\mathrm{C})^3$ with a standard deviation of 5×10^{-5} g cm^{-3}.

During an investigation of the physical properties of binary mixtures containing cyclodecane (*1*) we have measured the orthobaric density of cyclodecane at 17 temperatures from 25.69 to 191.80 °C. The starting material was obtained from the Chemical Samples Company; it was dried over anhydrous calcium chloride and then fractionated in a 1-m column packed with glass helices. The impurity level estimated by gas-liquid chromatography using a column packed with FFAP on Diatomite CLQ, and flame-ionization detection, and nitrogen carrier gas was 99.5 mol%. The refractive index was found to be 1.4714 in exact agreement with the value reported by Plattner and Hulstkamp (*2*).

The density measurements were carried out by using the actual hydrostatic density balance described by Hales and Gundry (*3*). The cell was calibrated with twice-distilled water by using the densities reported by Kell (*4*). The temperature was measured to ±3 mK using a platinum resistance thermometer and an Automatic Systems Laboratory Ltd ac resistance bridge that had been calibrated at the National Physical Laboratory, London. The results of the measurements are listed in column 2 of Table I; we estimate their precision to be about $\pm 7 \times 10^{-4}$ g cm^{-3}. They are well described by the expression

$$d/(\mathrm{g\ cm^{-3}}) = 0.87340 - (0.78424 \times 10^{-3})(t/°\mathrm{C}) + (0.5005 \times 10^{-6})(t/°\mathrm{C})^2 - (0.2018 \times 10^{-8})(t/°\mathrm{C})^3 \quad (1)$$

Table I. Densities (*d*) of Cyclodecane at Different Temperatures (*t*)

t/°C	*d*/(g cm^{-3}) exptl	*d*/(g cm^{-3}) eq 1	*d*/(g cm^{-3}) lit.[a]
25.691	0.85362	0.85355	0.85421
29.691	0.85049	0.85051	0.85118
38.098	0.84405	0.84414	0.84489
45.952	0.83822	0.83823	0.83913
54.075	0.83214	0.83214	0.83329
62.584	0.82580	0.82580	0.82732
71.239	0.81935	0.81934	0.82140
80.222	0.81266	0.81267	0.81544
89.239	0.80600	0.80597	0.80965
99.034	0.79871	0.79868	0.80359
108.800	0.79143	0.79140	0.79780
120.056	0.78292	0.78297	0.79146
131.000	0.77470	0.77472	0.78564
142.289	0.76613	0.76613	
153.967	0.75715	0.75715	
166.250	0.74760	0.74758	
191.798	0.72716	0.72716	

[a] Reference 5.

with a standard deviation of 5×10^{-5} g cm^{-3}. Values calculated from this expression are listed in column 3 of Table I. The only other results we have been able to find in the literature that extend over a reasonable range of temperature are those of Meyer and Hotz (*5*) and the fourth column contains values at our temperatures calculated from their fitting equation. The agreement is reasonably good at the lower end of the common temperature range but becomes increasingly poor at the upper end of the range. At 20 °C our extrapolated value of 0.8579 compares reasonably well with that quoted by Plattner and

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