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Supplementary Material Available: Experimental PVT data and Table IV (60 pages). Ordering information is given on any current masthead page.

The Densities of Methylcyclohexane–*n*-Heptane Mixtures

Phoebus M. Christopher, Walden L. S. Laukhuf,* and Charles A. Plank
Department of Chemical Engineering, University of Louisville, Louisville, Kentucky 40208

Despite the popularity of the methylcyclohexane–*n*-heptane mixture for testing laboratory fractionating columns, extensive physical property data for the combination are somewhat lacking. The results of this investigation offer some help in this regard by giving correlations of experimentally observed densities as a function of temperature and composition. The empirical equations to which the data were fitted may be employed, along with appropriate cross-plots, for the estimation of density over the entire composition range, and for temperatures up to and including the normal boiling points of the various mixtures.

For many years, the *n*-heptane–methylcyclohexane system has been used for distillation studies. As far back as 1939, Ward (*10*) cited this as an excellent system for testing laboratory fractionating columns. Despite the continued use of this system, extensive measurements of the various physical properties necessary for comparison and correlation have not yet been made. Densities of the pure components have been cited in Egloff (*5, 6*), Driesbach (*3, 4*), Mussche and Verhoeye (*8*), and API Research Project 44 (*1*). Bromiley and Quiggle (*2*) observed mixture densities at 20 °C, and also measured the normal boiling points of various solution compositions.

The present work gives the results of measurements of the densities for the pure components as well as mixtures, and correlates these as a function of temperature and composition of the mixtures. Extrapolation of these data to the boiling point provides requisite data for distillation correlations.

Experimental Section

The methylcyclohexane, practical grade, and the *n*-heptane, reagent grade, used for this work were supplied by Matheson, Coleman and Bell. The former boiled over the range of 100.5–101.5 °C which included the normal boiling point (100.934 °C in ref 1) while the latter boiled between 98 and 99 °C which also included its normal boiling point (98.427 °C in ref 1).

A Robertson pycnometer, with graduated capillary arms (*9*), was used for the density measurements. Pure, deionized water (specific resistance between 400 000 and 450 000 ohms), at 25.0 °C, was used for calibrating the volumes of the pycnometer corresponding to the various graduated markings. All observations were carried out in a water bath, which was maintained to within ±0.1 °C; readings of the capillary heights were facilitated by the use of a cathetometer. Complete calibration details are in ref 7.

The compositions of the pure components and all of the binary mixtures were ascertained refractometrically. For this purpose, a Bausch and Lomb precision refractometer was used, and observations were recorded to within ±0.000 03 units at 25.0 °C, for the sodium D-line. This corresponds to ±0.196% in composition.

Results and Discussion

Densities of pure *n*-heptane and methylcyclohexane were measured from 25 to 80 °C at 5 °C intervals. These observations were compared with the data of Egloff (*5, 6*), Driesbach (*3, 4*), Mussche (*8*), and the API Research Project 44 results (*1*) and are presented in Table I. The largest difference between data of this study and that reported in the literature is 0.26%.

Since the purpose of this work was to supply data for large scale distillation studies, practical and reagent grade materials were used. To verify whether these grades would yield data comparable to that of pure materials, densities of chromatographic quality methylcyclohexane and *n*-heptane at 25 °C were also measured. These density values are compared with other data from this study in Table II. It should be noted that there is less than a 0.012% difference which indicates reliable applicability of the data taken using practical and reagent grade chemicals.

Densities of known composition for five mixtures of the two components were determined under similar conditions. Compositions of the mixtures were checked before and after determinations to be assured that the compositions were unaltered during the heating and cooling processes. These data, along with extrapolations to the boiling point are shown in Table III.

Table I

Temp, °C	Density (g ml⁻¹) n-Heptane This study	n-Heptane Lit. (ref)	Methylcyclohexane This study	Methylcyclohexane Lit. (ref)
25.0	0.679 18	0.679 63 (5)	0.764 61	0.765 06 (3)
		0.679 55 (5)		0.765 10 (8)
		0.679 50 (8)		0.765 06 (1)
		0.679 51 (4)		
		0.679 46 (1)		
30.0	0.674 97	0.675 22 (5)	0.760 31	0.760 60 (6)
		0.675 50 (5)		0.760 30 (6)
		0.675 25 (4)		0.760 7 (1)
		0.675 16 (1)		
35.0	0.670 79		0.756 03	
40.0	0.666 36	0.666 23 (5)	0.751 69	0.752 0 (1)
		0.666 70 (5)		
		0.666 5 (1)		
42.1				0.751 20 (6)
45.0	0.662 17		0.747 39	
50.0	0.657 79	0.657 70 (5)	0.742 99	0.7432 (1)
		0.657 50 (5)		
		0.657 70 (1)		
55.0	0.653 37		0.738 62	
60.0	0.649 02	0.648 30 (5)	0.734 29	0.734 4 (1)
		0.648 80 (1)		
62.1				0.734 40 (6)
65.0	0.644 47		0.730 09	
70.0	0.640 60	0.639 50 (5)	0.725 64	0.725 7 (1)
		0.639 20 (5)		
		0.639 80 (1)		
75.0	0.636 12		0.721 23	
78.8				0.717 40 (1)
80.0	0.631 64	0.630 00 (5)	0.716 78	0.716 9 (1)
		0.630 70 (1)		
90.0		0.621 40 (1)		0.708 0 (1)
98.4	0.615 55[a]			
100.0				0.699 2 (1)
100.8			0.698 47[a]	

[a] Extrapolated to biling point data of Bromiley and Quiggle (2).

Table II. Pure Component Densities at 25 °C

	This study Table I	Chromo-quality	% difference
Methylcyclohexane	0.76461	0.76452	0.0118
n-Heptane	0.67918	0.67917	0.0015

Table III

Temp °C	Density of n-heptane–methylcyclohexane mixtures (g/ml) Mole fraction of n-heptane 0.2216	0.3965	0.5916	0.8107
25.0	0.742 59	0.727 03	0.710 78	0.694 22
30.0	0.738 32	0.722 82	0.706 41	0.690 01
35.0	0.733 84	0.718 62	0.702 40	0.685 76
40.0	0.729 68	0.714 29	0.697 99	0.681 47
45.0	0.725 45	0.710 04	0.693 67	0.677 14
50.0	0.721 02	0.705 59	0.689 31	0.672 74
55.0	0.716 66	0.701 29	0.684 99	0.668 55
60.0	0.712 80	0.696 89	0.680 69	0.663 97
65.0	0.708 69	0.692 58	0.676 26	0.659 63
70.0	0.704 26	0.688 24	0.671 82	0.655 19
75.0	0.699 18	0.683 68	0.667 24	
80.0	0.694 67	0.679 15	0.662 91	0.646 21
98.66(bp)[a]				0.629 13
99.03(bp)[a]			0.645 58	
99.52(bp)[a]		0.661 51		
100.04(bp)[a]	0.676 83			

[a] Extrapolated values using boiling point data of Bromiley and Quiggle (2).

Table IV. Results of n-Heptane–Methylcyclohexane Mixture Densities as a Function of Temperature[a]

Composition mole fraction of n-heptane	$A \times 10$	$(-B) \times 10^4$	$(-C) \times 10^7$	Std. error of estimate $\times 10^4$
0.0000	7.859 53	8.490 49	1.871 66	0.551 36
0.2216	7.628 61	8.045 37	5.541 82	2.983 00
0.3965	7.478 08	8.181 18	4.927 93	0.602 44
0.5916	7.315 03	8.174 07	5.073 54	0.758 95
0.8107	7.149 76	8.159 45	5.490 60	0.533 26
1.0000	7.005 83	8.489 52	1.548 26	1.351 15

[a] Coefficients in eq 1.

The density data for the pure components and mixtures as functions of temperature have been fitted to the following empirical equation

$$\rho = A + BT + CT^2 \quad (1)$$

where T is in degrees Celsius. Values of A, B, and C were obtained through a standard least-squares analysis of the data and are summarized in Table IV. The excellent fit of the data is indicated by the maximum standard error of estimate being 2.9820×10^{-4}.

Isothermal density data have also been fitted to the following empirical equation

$$\rho = a + bX + cX^2 + dX^3 \quad (2)$$

Table V. Results of *n*-Heptane–Methylcyclohexane Mixture Densities as a Function of Composition[a]

Temp, °C	$a \times 10$	$(-b) \times 10$	$c \times 10^2$	$(-d) \times 10^2$	Std. error of estimate $\times 10^4$
25.0	7.646 46	1.075 87	3.807 77	1.588 23	2.604
30.0	7.603 48	1.072 21	3.704 07	1.510 70	3.376
35.0	7.560 29	1.079 31	4.008 48	1.735 60	2.172
40.0	7.517 16	1.073 66	3.854 01	1.645 76	2.820
45.0	7.474 15	1.065 39	3.602 35	1.465 82	2.808
50.0	7.430 14	1.068 61	3.689 35	1.519 29	2.455
55.0	7.386 52	1.073 12	3.895 28	1.684 03	3.160
60.0	7.343 59	1.046 02	3.085 56	1.150 10	3.102
65.0	7.301 86	1.045 80	3.007 34	1.108 12	4.346
70.0	7.257 12	1.030 86	2.514 64	0.707 18	3.362
75.0	7.212 09	1.047 69	2.797 91	0.830 48	1.745
80.0	7.167 90	1.070 07	3.529 34	1.340 17	1.473

[a] Coefficients in eq 2.

where X = mole fraction of *n*-heptane in the mixture. The values of *a, b, c,* and *d* were also determined by a least-squares analysis. The maximum standard error of estimate for these data was 4.35×10^{-4} at 65 °C. The constants so determined are presented in Table V.

Isothermal density data when plotted exhibited only slight curvature, indicating nearly ideal liquid solutions. Extrapolated values of the densities at the boiling points were correlated as a function of composition by eq 2,

$$\rho(\text{bp}) = 0.615\,48 + 0.533\,77X - 1.394\,08X^2 + 0.941\,96X^3 \quad (3)$$

with a standard error of estimate for the density of 7.222×10^{-3}.

The data and equations here, along with suitable crossplots, will allow the estimation of densities of mixtures of *n*-heptane and methylcyclohexane up to and including the mixture boiling points at atmospheric pressure. Densities determined with either eq 1 or eq 2 differ from the literature data of Table I by a maximum of 0.265%. This occurs for both equations at 80 °C and with the data of Egloff (*5*).

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Glossary

a,b,c,d	constants in eq 2
A,B,C	constants in eq 1
T	degrees Celsius
X	mole fraction of *n*-heptane
bp	normal boiling point, °C
ρ	density, g ml^{-1}

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