Some Physical Properties of the Ternary System Benzene–Cyclohexane–*n*-Hexane

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In the ternary system benzene–cyclohexane–*n*-hexane and its three associated binary systems the following physical properties have been measured over the complete composition range: refractive index, density, surface tension, viscosity, heat of mixing, solid-liquid equilibrium, and isobaric vapor-liquid equilibrium at 760 mm. of Hg. A six-stage equilibrium still unit was used to obtain distillation lines on the ternary diagram.

THE BENZENE-cyclohexane–*n*-hexane system has been studied in some detail because it is the simplest representative petroleum system, containing an aromatic, a cycloparaffin, and a straight-chain aliphatic hydrocarbon; furthermore, the three components are close-boiling, so that the isobaric and isothermal vapor-liquid equilibria are not very different. One object of the investigation was to provide a comprehensive set of experimental physical property measurements on a system, and these are presented here. A further object was to compare the measured data with predictions made on the basis of regular solution theory, using an interchange energy term obtained by direct calculation. This comparison has been made and will be published elsewhere. The calculation was based upon the known molecular shape and lattice; distances between pairs of atoms or active centers in adjacent molecules were calculated, and the interaction energy between them was computed using a Lennard-Jones potential.

MATERIALS

Benzene ("for molecular weight determination") and cyclohexane ("special for spectroscopy") were obtained from the British Drug Houses, Ltd., and *n*-hexane from the Phillips Petroleum Co. The authors considered that these materials were sufficiently pure for the measurement of all properties except density and refractive index. Small quantities of each were purified as follows: Benzene was dried over sodium wire and fractionally distilled, rejecting the first and last 10%. Cyclohexane and *n*-hexane were stirred with chlorosulfonic acid to remove branched-chain hydrocarbons, then washed with sulfuric acid, sodium carbonate solution, and water as recommended by Shepard and Henne (*11*). The properties of the materials as purchased and after purification are compared with literature values in Table I.

DATA FOR BINARY SYSTEMS

The experimental method for all the measurements has been described (*1*).

Refractive Index. Mixtures were made up by weighing into glass-stoppered weighing bottles. Refractive indices at 25° C. were determined with a Bellingham and Stanley Abbe-type refractometer to an accuracy of 0.0001 (Table II).

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Table I. Physical Properties of Components

	As Purchased	Purified	Literature Value (*6*)
Benzene			
Refractive index, 25° C.	1.4979	1.4979	1.49790
Density, 25° C. g./ml.	0.87390	0.87358	0.87368
Boiling point, ° C.	80.10	80.10	80.103
Cyclohexane			
Refractive index, 25° C.	1.4229	1.4235	1.42354
Density, 25° C. g./ml.	0.77210	0.77385	0.77389
Boiling point, ° C.	80.70	80.72	80.738
***n*-Hexane**			
Refractive index, 25° C.	1.3725	1.3723	1.37226
Density, 25° C. g./ml.	0.65490	0.65480	0.65480
Boiling point, ° C.	68.70	68.70	68.740

Density. Densities were measured by weighing made-up mixtures in Sprengel-Ostwald pycnometers. Weighing was carried out on a Stanton SM2 semimicrobalance, and densities were reproducible to 0.00006 gram per ml. on the average (Table III).

Surface Tension. A Cambridge torsion balance was used to determine the force necessary to detach a platinum ring, diameter 0.5 inch, from the liquid. Determinations were made in a controlled temperature room at 20° ± 1° C. The results are given in Table IV and are accurate to about ±0.2 dyne per cm.

Viscosity. This was measured with an Ostwald viscometer. With the usual precautions, replicate efflux times usually agreed to 0.1 second, corresponding to a reproducibility in the viscosity of 0.001 centipoise (Table IV).

Heat of Mixing. Twenty-milliliter quantities of one pure component were added to 350 ml. of mixtures of various compositions in a Dewar vessel at 25° C. The temperature change was measured. Because the added amount of pure component was small, differential heats of mixing could be obtained in calories per gram of added pure component.

Table II. Refractive Index in the Binary Systems

Mole Fraction Benzene	Refractive Index, 25° C.
Benzene-Cyclohexane	
0.0000	1.4235
0.1146	1.4291
0.2242	1.4350
0.4574	1.4501
0.6190	1.4623
0.7463	1.4728
0.8473	1.4824
1.0000	1.4979
Benzene–*n*-Hexane	
0.0000	1.3723
0.2018	1.3893
0.3583	1.4045
0.4969	1.4204
0.6885	1.4454
0.8121	1.4645
0.9173	1.4824
1.0000	1.4979
Mole Fraction Cyclohexane	
Cyclohexane–*n*-Hexane	
0.0000	1.3723
0.1611	1.3793
0.3660	1.3885
0.4747	1.3935
0.6247	1.4013
0.7624	1.4089
0.8903	1.4169
1.0000	1.4235

Table III. Densities of the Binary Systems

Mole Fraction Benzene	Density, 25° C., G./Ml.
Benzene-Cyclohexane	
0.0000	0.77385
0.1260	0.78249
0.2463	0.79144
0.4552	0.80946
0.6153	0.82554
0.7090	0.83602
0.8609	0.85460
1.0000	0.87358
Benzene–*n*-Hexane	
0.0000	0.65480
0.1358	0.67524
0.2431	0.69264
0.3733	0.71584
0.5307	0.74785
0.6914	0.78561
0.7950	0.81358
0.9145	0.84762
1.0000	0.87358
Mole Fraction Cyclohexane	
Cyclohexane–*n*-Hexane	
0.0000	0.65480
0.1930	0.67453
0.3330	0.68957
0.4805	0.70607
0.6502	0.72640
0.7809	0.74325
0.8455	0.75196
1.0000	0.77385

Table IV. Surface Tension and Viscosity in the Binary Systems

Mole Fraction Benzene	Surface Tension 20° C., Dynes/Cm.	Viscosity 25° C., Centipoise
Benzene-Cyclohexane		
0.0000	24.84	0.8690
0.1282	25.00	0.7622
0.2174	25.14	0.7122
0.3364	25.43	0.6599
0.4874	25.84	0.6124
0.6470	26.54	0.5879
0.7814	27.20	0.5830
0.9033	27.88	0.5926
1.0000	28.87	0.6059
Benzene–*n*-Hexane		
0.0000	18.95	0.3008
0.1281	19.53	0.3134
0.2665	20.22	0.3270
0.4050	21.05	0.3471
0.5704	22.16	0.3822
0.7216	23.43	0.4254
0.8811	25.97	0.5139
1.0000	28.87	0.6059
Mole Fraction Cyclohexane		
Cyclohexane–*n*-Hexane		
0.0000	18.95	0.3008
0.1714	19.39	0.3405
0.2742	19.90	0.3670
0.4498	20.40	0.4234
0.5873	21.30	0.4846
0.7520	22.54	0.5887
0.9034	23.81	0.7347
1.0000	24.84	0.8690

By plotting the differential heat of mixing against composition for each component, the integral heat of mixing was obtained at regular intervals of composition. These values have a precision of about 1%. The differential (or partial) and the total heats of mixing at rounded values of mole fractions are given in Table V.

Solid-Liquid Equilibrium. Cooling curves were obtained by connecting a copper-constantan thermocouple, immersed in the liquid sample, to a Kent recorder. The liquid sample, held in a boiling tube, was suspended within a larger diameter boiling tube, and the outer tube immersed in liquid nitrogen. With this arrangement, the sample cooled at the convenient rate of about 3° C. per minute. From the arrest-points on the cooling curves the phase diagrams could be plotted, and the three binary diagrams are shown in Figure 1.

Vapor-Liquid Equilibrium. Measurements were made at 760-mm. pressure, using six Ellis-type equilibrium stills (*3*) connected in series to improve accuracy and to reduce the time needed to obtain the data points required to characterize a system. At equilibrium in a series type of experiment, the vapor of one stage is identical in composition to the liquid in the next stage; this can be observed as a cross-correlation in Table VI.

DATA FOR THE TERNARY SYSTEM

The triangular diagram was covered by making up a number of stock mixtures of two of the components. The compositions of these mixtures were evenly spaced along one of the sides of the triangle. Addition of known amounts of the third component then gave mixtures lying on lines crossing the triangle and converging on the third component apex (Tables VII, VIII, and IX).

The ternary heats of mixing were determined by adding small amounts (20 ml.) of the pure components to large

Table V. Partial and Total Heats of Mixing at 25° C. in the Binary Systems

Mole Fraction Benzene	Partial Heat B in CH,[a] Cal./G.	Partial Heat CH in B, Cal./G.	Total Heat, Cal./G. Mole
	Benzene-Cyclohexane		
0.1	8.28	0.11	72.92
0.2	6.40	0.32	121.30
0.3	4.86	0.73	156.75
0.4	3.64	1.38	183.10
0.5	2.60	2.20	193.65
0.6	1.74	3.20	188.95
0.7	1.07	4.37	168.45
0.8	0.49	5.89	129.38
0.9	0.14	7.64	74.03
	Benzene-*n*-Hexane		
0.1	7.86	0.06	65.96
0.2	6.52	0.20	115.59
0.3	5.28	0.53	155.70
0.4	4.27	1.10	189.85
0.5	3.15	1.92	205.60
0.6	2.18	3.04	206.80
0.7	1.31	4.59	190.20
0.8	0.63	6.78	156.30
0.9	0.20	9.54	96.28
Mole Fraction Cyclohexane			
	Cyclohexane-*n*-Hexane		
0.1	1.68	0.00	14.13
0.2	1.43	0.02	25.43
0.3	1.18	0.05	32.98
0.4	0.95	0.12	38.21
0.5	0.71	0.27	41.49
0.6	0.49	0.55	43.70
0.7	0.30	0.94	41.98
0.8	0.10	1.53	33.02
0.9	−0.07	2.28	14.34

[a] Heat absorbed in calories per gram of added benzene.

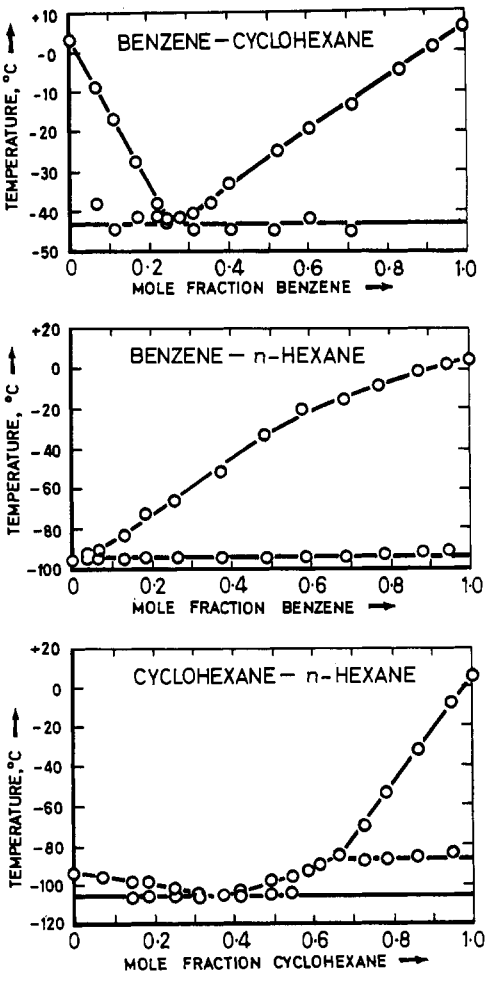

Figure 1. Solid-liquid equilibrium in the three binary systems

amounts (350 ml.) of ternary mixtures of various compositions. Sufficient determinations were carried out to enable a contour plot of the differential heat of addition of each pure compound to be made. From these plots the total or integral heat of mixing could be found. The results of the determinations of the differential heats of mixing are given in Table X.

The integral heats of mixing for the ternary system are shown in the triangular plot in Figure 2.

Solid-Liquid Equilibrium. The ternary diagram was covered by adding benzene to stock solutions of cyclohexane–*n*-hexane and obtaining a cooling curve for each mixture. The results are presented as a triangular plot in Figure 3.

Vapor-Liquid Equilibrium. The six-stage unit was employed and has the advantage that the results give the course of a distillation line on the ternary diagram—that is, the alternate liquid and vapor compositions are those which would be obtained in an ideal plate-type distillation column operating at total reflux. A few such lines give a better idea of the general pattern of the vapor-liquid equilibrium for the system than would a much larger number of liquid-vapor tie lines of the type obtained by making measurements with a single equilibrium still. The results for 18 distillation lines are given in Table XI. Because the vapor of one stage and the liquid of the next have the same composition, the same correlation in adjacent columns of the table is found as occurs in Table VI for the binary systems.

AGREEMENT WITH OTHER WORKERS

For the majority of the measurements reported here, there are no data in the literature with which comparison can be made. This is particularly true of the ternary system, where the only property which has previously been examined is the heat of mixing, and here the results obtained by Mathieson and Thynne (*9*) agree in all cases to within 5% of values interpolated from Figure 2.

A more detailed comparison of the authors' results with literature values for the binary systems is given in the doctoral thesis (*1*) from which this paper is derived. No cases of divergence arose.

Thermodynamic Consistency Tests. Herington (*4*) and Redlich and Kister (*10*) have described a test for binary vapor-liquid equilibrium data in which the logarithm of the ratio of the activity coefficients, $\ln(\gamma_1/\gamma_2)$, is plotted against composition. The data are consistent if

$$\int_0^1 \ln(\gamma_1/\gamma_2) \cdot dx_1 = 0$$

in the sense that they satisfy the Gibbs-Duhem equation. A small correction is recommended for isobaric data, the test equation being

$$\int_0^1 \frac{-\Delta H^M}{RT^2} \frac{dT}{dx} dx_1 + \int_0^1 \ln(\gamma_1/\gamma_2)\, dx_1 = 0$$

where ΔH^M is the heat of mixing. In close-boiling systems such as those investigated by the present authors, the first

Table VI. Vapor-Liquid Equilibrium at 760 Mm. in the Binary Systems

Mole Fraction Benzene		Boiling Pt., ° C.
Liquid	Vapor	
Benzene-Cyclohexane		
0.077	0.096	79.80
0.096	0.118	79.50
0.118	0.145	79.25
0.145	0.176	79.05
0.176	0.208	78.85
0.208	0.243	78.70
0.245	0.280	78.50
0.280	0.314	78.25
0.314	0.346	78.10
0.346	0.375	77.95
0.375	0.402	77.85
0.402	0.426	77.75
0.507	0.512	77.60
0.512	0.516	77.60
0.516	0.519	77.60
0.519	0.522	77.55
0.522	0.524	77.55
0.524	0.526	77.55
0.628	0.612	77.65
0.645	0.628	77.70
0.663	0.645	77.75
0.685	0.663	77.80
0.712	0.685	77.90
0.742	0.712	78.00
0.775	0.744	78.05
0.806	0.775	78.30
0.836	0.806	78.55
0.865	0.836	78.80
0.892	0.865	79.05
0.916	0.892	79.25
Benzene–*n*-Hexane		
0.080	0.078	68.70
0.082	0.080	68.75
0.085	0.082	68.75
0.088	0.085	68.80
0.091	0.088	68.80
0.095	0.091	68.80
0.144	0.137	68.85
0.152	0.144	68.90
0.160	0.152	68.95
0.170	0.160	68.95
0.183	0.170	69.00
0.199	0.183	69.00
0.252	0.226	69.00
0.281	0.252	69.15
0.318	0.281	69.35
0.366	0.318	69.65
0.430	0.366	70.05
0.512	0.430	70.65
0.583	0.489	71.35
0.690	0.583	72.70
0.797	0.690	74.55
0.881	0.797	76.65
0.940	0.881	78.10
0.972	0.940	79.10
Mole Fraction Cyclohexane		
Liquid	Vapor	
Cyclohexane–*n*-Hexane		
0.123	0.096	70.05
0.160	0.123	70.40
0.203	0.160	70.85
0.260	0.203	71.40
0.329	0.260	72.05
0.409	0.329	72.90
0.477	0.398	73.70
0.562	0.477	74.70
0.616	0.532	75.40
0.647	0.562	75.70
0.700	0.616	76.40
0.730	0.647	76.75
0.774	0.700	77.35
0.833	0.774	78.20
0.879	0.833	79.00
0.918	0.879	79.50

Table VII. Refractive Index in the Ternary System Benzene–Cyclohexane–*n*-Hexane at 25° C.

Mole Fraction Benzene	Mole Fraction Cyclohexane	Mole Fraction *n*-Hexane	Refractive Index n_D^{25}
0.1146	0.8854	0.1070	1.4249
		0.2325	1.4132
		0.4216	1.4008
		0.5264	1.3959
		0.6470	1.3891
		0.7015	1.3866
		0.7806	1.3824
		0.9444	1.3750
0.2242	0.7758	0.0989	1.4269
		0.2379	1.4168
		0.3410	1.4096
		0.4965	1.3996
		0.6446	1.3907
		0.7093	1.3872
		0.7888	1.3830
		0.8375	1.3805
		0.9098	1.3766
0.4574	0.5426	0.1875	1.4315
		0.3976	1.4134
		0.5938	1.3985
		0.6943	1.3914
		0.8166	1.3831
		0.8719	1.3797
		0.9182	1.3768
0.6190	0.3810	0.1789	1.4414
		0.3018	1.4281
		0.4085	1.4180
		0.5107	1.4085
		0.5857	1.4018
		0.6852	1.3941
		0.7241	1.3905
		0.8181	1.3826
0.7463	0.2537	0.1165	1.4562
		0.1945	1.4464
		0.4182	1.4213
		0.5890	1.4045
		0.7306	1.3922
		0.7572	1.3900
		0.8208	1.3849
		0.9176	1.3777
0.8473	0.1527	0.1545	1.4580
		0.3663	1.4311
		0.4637	1.4198
		0.5155	1.4141
		0.6108	1.4042
		0.7131	1.3950
		0.8253	1.3849

Table VIII. Density in the Ternary System Benzene–Cyclohexane–*n*-Hexane at 25° C.

Mole Fraction Cyclohexane	Mole Fraction *n*-Hexane	Mole Fraction Benzene	Density at 25° C., G./Ml.
0.1930	0.8070	0.2643	0.71309
		0.4720	0.74931
		0.6139	0.77918
		0.7127	0.80086
0.3358	0.6642	0.2744	0.72720
		0.5201	0.76787
		0.6598	0.79500
		0.7752	0.81930
0.4805	0.5195	0.3072	0.74511
		0.5455	0.78232
		0.6485	0.80095
		0.7789	0.82567
0.6502	0.3498	0.2215	0.75087
		0.4976	0.78661
		0.7424	0.82483
		0.8650	0.84698
0.7809	0.2191	0.1834	0.76132
		0.4913	0.79611
		0.7018	0.82499
		0.8315	0.84496
0.8455	0.1545	0.2179	0.77141
		0.4175	0.79210
		0.6399	0.81918
		0.7856	0.83965

Table IX. Surface Tension and Viscosity in the Ternary System Benzene–Cyclohexane–*n*-Hexane at 20° C.

Mole Fraction Cyclohexane	Mole Fraction *n*-Hexane	Mole Fraction Benzene	Surface Tension at 20° C., Dynes/Cm.	Viscosity at 25° C., Centipoise
0.1714	0.8286	0.1998	20.30	0.3523
		0.3764	21.48	0.3720
		0.5285	22.50	0.3991
		0.6781	23.38	0.4397
		0.8394	25.62	0.5073
		0.9584	27.76	0.5774
0.2742	0.7258	0.1444	20.72	0.3746
		0.3488	21.51	0.3897
		0.6080	23.74	0.4390
		0.7850	25.19	0.4957
		0.8978	27.00	0.5489
0.4498	0.5502	0.1385	21.06	0.4250
		0.3447	22.15	0.4359
		0.5081	22.98	0.4498
		0.6515	23.89	0.4794
		0.7510	25.37	0.5100
		0.9163	27.24	0.5680
0.5873	0.4127	0.1436	22.11	0.4743
		0.3017	22.97	0.4714
		0.4836	23.50	0.4786
		0.6676	24.44	0.5025
		0.8251	26.15	0.5394
		0.9229	27.80	0.5754
0.7520	0.2480	0.1461	23.19	0.5570
		0.2681	23.50	0.5380
		0.4231	24.02	0.5283
		0.5664	24.67	0.5303
		0.7122	25.55	0.5396
		0.8756	27.09	0.5694
0.9034	0.0966	0.1231	24.10	0.6731
		0.2662	24.40	0.6223
		0.4094	25.00	0.5913
		0.5700	25.61	0.5720
		0.7122	26.08	0.5685
		0.8941	27.70	0.5860

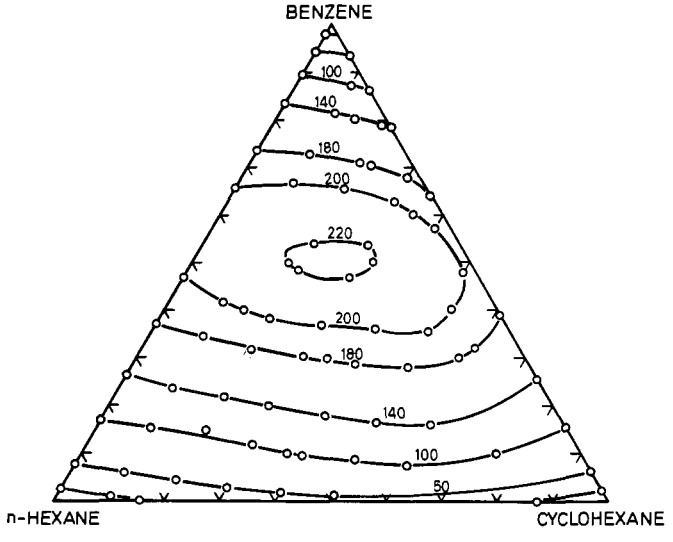

Figure 2. Integral heats of mixing for the ternary system benzene–cyclohexane–*n*-hexane at 25° C.
Contour figures are cal. per mole of mixture

term is negligible. The maximum value for $(\Delta H^M/RT^2) \cdot (dT/dx)$ was 0.008 or 0.5% of the end value of ln (γ_1/γ_2). Expressing the area differences as a percentage of the total area, the discrepancies for the binary systems were benzene-cyclohexane 3.1%, benzene–*n*-hexane 5.5%, and cyclohexane–*n*-hexane 1.3%.

Colburn and Schoenborn (2) and Herington (5) have proposed graphical integration methods for testing ternary data, but they involve much graphical interpolation and extrapolation. A more easily applied test is that of Li

Table X. Differential Heats of Mixing in the Ternary System Benzene–Cyclohexane–*n*-Hexane

Mean Mole Fractions			Temperature Change, ° C.	Heat of Mixing, Cal./G.
Benzene	Cyclohexane	*n*-Hexane		
		Addition of Benzene		
0.036	0.779	0.185	−0.991	8.78
0.039	0.450	0.511	−0.992	8.65
0.142	0.171	0.687	−0.756	6.65
0.200	0.499	0.301	−0.683	5.88
0.209	0.372	0.419	−0.669	5.75
0.234	0.294	0.472	−0.656	5.62
0.317	0.583	0.100	−0.504	4.35
0.373	0.135	0.492	−0.480	4.08
0.415	0.383	0.202	−0.396	3.46
0.471	0.138	0.391	−0.368	3.18
0.516	0.232	0.252	−0.305	2.68
0.559	0.326	0.115	−0.242	2.09
0.692	0.103	0.205	−0.123	1.08
0.758	0.164	0.078	−0.077	0.67
		Addition of Cyclohexane		
0.658	0.113	0.229	−0.399	3.96
0.357	0.123	0.520	−0.164	1.62
0.460	0.127	0.413	−0.238	2.37
0.712	0.175	0.113	−0.452	4.51
0.149	0.176	0.675	−0.119	1.26
0.491	0.236	0.273	−0.235	2.37
0.238	0.284	0.478	−0.118	1.17
0.324	0.312	0.364	−0.135	1.34
0.564	0.314	0.122	−0.286	2.85
0.405	0.381	0.214	−0.180	1.75
0.121	0.400	0.479	−0.087	0.85
0.177	0.499	0.324	−0.074	0.74
0.305	0.586	0.109	−0.103	0.91
0.070	0.756	0.174	−0.017	0.17
		Addition of *n*-Hexane		
0.327	0.578	0.095	−0.214	2.50
0.751	0.153	0.096	−0.569	6.58
0.593	0.300	0.107	−0.378	4.46
0.067	0.742	0.191	−0.138	1.61
0.427	0.360	0.231	−0.200	2.28
0.687	0.097	0.216	−0.414	4.80
0.520	0.218	0.262	−0.239	2.78
0.187	0.495	0.318	−0.077	0.91
0.340	0.302	0.358	−0.115	1.34
0.478	0.131	0.391	−0.175	2.01
0.235	0.275	0.472	−0.054	0.63
0.127	0.394	0.479	−0.038	0.44
0.388	0.126	0.486	−0.094	1.09
0.158	0.161	0.681	−0.018	0.21

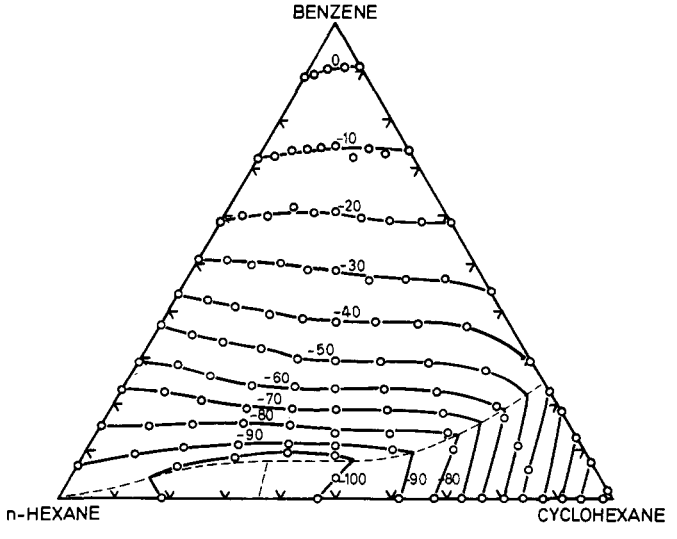

Figure 3. Solid-liquid equilibrium in the ternary system benzene–cyclohexane–*n*-hexane

Table XI. Vapor-Liquid Equilibrium in the Ternary System Benzene–Cyclohexane–*n*-Hexane

Run No.	Liquid Mole Fraction			Vapor Mole Fraction			Boiling Pt., °C.
	Benzene	Cyclohexane	*n*-Hexane	Benzene	Cyclohexane	*n*-Hexane	
1	0.861	0.066	0.073	0.806	0.067	0.127	77.45
	0.806	0.067	0.127	0.732	0.068	0.200	76.05
	0.732	0.068	0.200	0.637	0.070	0.293	74.55
	0.637	0.070	0.293	0.544	0.071	0.383	73.15
	0.544	0.071	0.383	0.461	0.067	0.472	71.95
	0.461	0.067	0.472	0.409	0.052	0.539	71.05
2	0.512	0.110	0.378	0.443	0.096	0.461	72.15
	0.443	0.096	0.461	0.395	0.079	0.526	71.25
	0.395	0.079	0.526	0.342	0.064	0.594	70.70
	0.342	0.064	0.594	0.304	0.053	0.643	70.25
	0.304	0.053	0.643	0.279	0.037	0.684	69.85
	0.279	0.037	0.684	0.250	0.025	0.725	69.55
3	0.157	0.503	0.340	0.176	0.414	0.410	74.35
	0.176	0.414	0.410	0.180	0.347	0.473	73.30
	0.180	0.347	0.473	0.183	0.267	0.550	72.55
	0.183	0.267	0.550	0.183	0.214	0.603	71.80
	0.183	0.214	0.603	0.176	0.179	0.645	71.10
	0.176	0.179	0.645	0.171	0.138	0.691	70.60
4	0.078	0.289	0.633	0.081	0.231	0.688	71.75
	0.081	0.231	0.688	0.079	0.173	0.748	71.05
	0.079	0.173	0.748	0.077	0.122	0.801	70.50
	0.077	0.122	0.801	0.075	0.097	0.828	70.15
	0.075	0.097	0.828	0.073	0.074	0.853	69.80
	0.073	0.074	0.853	0.070	0.059	0.871	69.50
5	0.024	0.708	0.268	0.030	0.635	0.335	76.55
	0.030	0.635	0.335	0.036	0.540	0.424	75.50
	0.036	0.540	0.424	0.041	0.458	0.501	74.40
	0.041	0.458	0.501	0.048	0.363	0.589	73.25
	0.048	0.363	0.589	0.055	0.290	0.655	72.35
	0.055	0.290	0.655	0.057	0.227	0.716	71.60
6	0.081	0.843	0.076	0.109	0.786	0.105	78.70
	0.109	0.786	0.105	0.128	0.730	0.142	78.00
	0.128	0.730	0.142	0.152	0.655	0.193	77.25
	0.152	0.655	0.193	0.169	0.579	0.252	76.35
	0.169	0.579	0.252	0.182	0.506	0.312	75.30
	0.182	0.506	0.312	0.195	0.420	0.385	74.30
7	0.315	0.648	0.037	0.345	0.605	0.050	77.80
	0.345	0.605	0.050	0.375	0.554	0.071	77.35
	0.375	0.554	0.071	0.397	0.511	0.092	77.00
	0.397	0.511	0.092	0.411	0.457	0.132	76.45
	0.411	0.475	0.132	0.413	0.415	0.172	75.80
	0.413	0.415	0.172	0.404	0.365	0.231	75.15
8	0.425	0.451	0.125	0.423	0.408	0.169	76.00
	0.423	0.408	0.169	0.413	0.364	0.223	75.35
	0.413	0.364	0.223	0.398	0.313	0.289	74.65
	0.398	0.313	0.289	0.381	0.270	0.349	73.80
	0.381	0.270	0.349	0.356	0.216	0.428	72.95
	0.356	0.216	0.428	0.330	0.180	0.490	72.15
9	0.254	0.276	0.470	0.248	0.220	0.532	72.25
	0.248	0.220	0.532	0.238	0.163	0.599	71.55
	0.238	0.163	0.599	0.227	0.130	0.643	71.05
	0.277	0.130	0.643	0.216	0.100	0.684	70.55
	0.216	0.100	0.684	0.200	0.078	0.722	70.10
	0.200	0.078	0.722	0.190	0.060	0.750	69.75
10	0.120	0.123	0.757	0.118	0.091	0.791	70.15
	0.118	0.091	0.791	0.116	0.064	0.820	69.85
	0.116	0.064	0.820	0.114	0.045	0.841	69.60
	0.114	0.045	0.841	0.111	0.036	0.853	69.45
	0.111	0.036	0.853	0.103	0.026	0.871	69.30
	0.103	0.026	0.871	0.097	0.023	0.880	69.15
11	0.310	0.577	0.113	0.336	0.505	0.159	76.50
	0.336	0.505	0.159	0.345	0.440	0.215	75.85
	0.345	0.440	0.215	0.344	0.386	0.270	75.10
	0.344	0.386	0.270	0.333	0.334	0.333	74.30
	0.333	0.334	0.333	0.318	0.278	0.404	73.50
	0.318	0.278	0.404	0.298	0.224	0.478	72.65
12	0.685	0.237	0.078	0.642	0.230	0.128	76.50
	0.642	0.230	0.128	0.591	0.219	0.190	75.65
	0.591	0.219	0.190	0.539	0.200	0.261	74.75
	0.539	0.200	0.261	0.480	0.180	0.340	73.70
	0.480	0.180	0.340	0.431	0.158	0.411	72.75
	0.431	0.158	0.411	0.383	0.130	0.487	71.95
13	0.898	0.080	0.022	0.849	0.112	0.039	78.75
	0.849	0.112	0.039	0.810	0.128	0.062	78.20
	0.810	0.128	0.062	0.749	0.138	0.113	77.40
	0.749	0.138	0.113	0.681	0.135	0.184	76.20
	0.681	0.135	0.184	0.610	0.129	0.261	74.95
	0.610	0.129	0.261	0.539	0.115	0.356	73.70
14	0.652	0.332	0.016	0.629	0.333	0.038	77.50
	0.629	0.333	0.038	0.600	0.329	0.071	77.15

(*Continued*)

Table XI. Vapor-Liquid Equilibrium in the Ternary System Benzene–Cyclohexane–n-Hexane (Continued)

Run No.	Liquid Mole Fraction			Vapor Mole Fraction			Boiling Pt., °C.
	Benzene	Cyclohexane	n-Hexane	Benzene	Cyclohexane	n-Hexane	
	0.600	0.329	0.071	0.573	0.320	0.107	76.75
	0.573	0.320	0.107	0.543	0.310	0.147	76.15
	0.543	0.310	0.147	0.511	0.289	0.200	75.40
	0.511	0.289	0.200	0.472	0.258	0.270	74.60
15	0.516	0.474	0.010	0.518	0.464	0.018	77.55
	0.518	0.464	0.018	0.519	0.452	0.029	77.45
	0.519	0.452	0.029	0.516	0.439	0.045	77.30
	0.516	0.439	0.045	0.512	0.419	0.069	77.00
	0.512	0.419	0.069	0.505	0.395	0.100	76.55
	0.505	0.395	0.100	0.492	0.366	0.142	76.05
16	0.250	0.674	0.076	0.277	0.613	0.110	77.35
	0.277	0.613	0.110	0.299	0.551	0.150	76.70
	0.299	0.551	0.150	0.315	0.482	0.203	76.05
	0.315	0.482	0.203	0.320	0.420	0.260	75.15
	0.320	0.420	0.260	0.316	0.358	0.326	74.30
	0.316	0.358	0.326	0.308	0.301	0.391	73.50
17	0.225	0.657	0.118	0.253	0.586	0.161	76.90
	0.253	0.586	0.161	0.272	0.514	0.214	76.15
	0.272	0.514	0.214	0.284	0.446	0.270	73.35
	0.284	0.446	0.270	0.289	0.380	0.331	74.45
	0.289	0.380	0.331	0.284	0.313	0.403	73.55
	0.284	0.313	0.403	0.273	0.246	0.481	72.65
18	0.093	0.712	0.195	0.112	0.630	0.258	76.85
	0.112	0.630	0.258	0.129	0.545	0.326	74.85
	0.129	0.545	0.326	0.139	0.469	0.392	74.85
	0.139	0.469	0.392	0.150	0.380	0.470	73.85
	0.150	0.380	0.470	0.153	0.307	0.540	72.90
	0.153	0.307	0.540	0.156	0.232	0.612	72.00

and Lu (7) which involves numerical integration round a loop of experimental points. The loops may be closed or open-ended, but there is a restriction that the points should not be widely separated, otherwise large errors are introduced by the numerical integration process. The condition for consistency is

$$\sum_{n=1}^{N} \sum_{i} x_{i(n)} [\ln \gamma_{i(n-1)} - \ln \gamma_{i(n+1)}] = 0$$

where n refers to the nth point in a loop of N points. For an open loop, $(n - 1)$ is put equal to 1 for the first point, and $(n + 1)$ is put equal to N when the last point is reached. The test was applied to the open loops of seven points obtained from each experimental run of the six-stage still. The average deviation on 20 runs was 19.9%. Li and Lu give no indication of what value is allowable, but two runs had deviations of 66.8 and 51.9% and were discarded. The mean deviation of the remaining 18 runs reported in Table XI is 15.5%. The Li-Lu test was refined by McDermott and Ellis (8), who suggested that the equation

$$D = \sum [x_{i(n)} + x_{i(n+1)}] [\ln \gamma_{i(n+1)} - \ln \gamma_{i(n)}] = 0$$

should be the consistency condition. The points are taken in pairs, and D could be allowed to be 0.01 for a sample composition measurement accurate to ±0.001 mole fraction. For 17 out of 100 pairs of points, D was greater than 0.01. Judgment is required as to which points to reject. Of the two loops rejected by the Li-Lu test, only one would be inconsistent on the McDermott-Ellis test. The other had no D value above 0.01, but four of its values were above 0.005. A rather more complicated test for consistency over a composition path has been suggested by Tao (12). Over the 20 composition paths, the average deviation was −1.9%. Excluding the two inconsistent runs reduced the average deviation to +1.5%. No criterion is suggested by Tao of how small the deviation must be for acceptability. One disadvantage of this test is that it cannot be used if the liquid compositions for one component are the same at both ends of a composition path, as in run 3 of Table XI.

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