polynuclear aromatic substances it acts as a coupling agent.

The fluorine atom in fluorobenzanthrone is in the 2- or 3- position of the *benz* ring. This is unusual since most reagents substitute in the 1-position in this ring.

MONTREAL, CANADA
AKRON, OHIO

RECEIVED JUNE 19, 1937

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

Vapor–Liquid Equilibria of Methylcyclohexane–Toluene Mixtures

BY DOROTHY QUIGGLE AND MERRELL R. FENSKE

During the course of work on the fractionation and composition of straight-run gasolines, efficient large scale fractionating columns have been developed. It has been found that binary mixtures of hydrocarbons are most suitable for determining the efficiencies of such columns. The equilibria of a number of binary hydrocarbon mixtures have already been presented.[1,2] However, in selecting a pair of hydrocarbons for such efficiency tests, particularly on large scale columns taking a charge of many gallons of material, consideration must be given to the ease of analyzing the equilibrium mixtures obtained, the purity possible of the starting materials, the ease with which they may be further purified if necessary, and their cost and availability. Because methylcyclohexane and toluene seemed to be a pair of hydrocarbons which fulfilled these prerequisites, their vapor–liquid equilibria have been obtained at normal pressures.

Properties of Materials

The methylcyclohexane was a technical grade obtained from the Eastman Kodak Company. It was purified by shaking with concentrated sulfuric acid, neutralizing with sodium carbonate, washing with water, and fractionating. Two different lots of methylcyclohexane were used and they had the following properties:

	No. 1	No. 2
Boiling point at 760 mm., °C.	100.85	100.85
Density, d^{20}_4	0.7695	0.7692
Refractive index, n^{20}_{D}	1.4234	1.4235

Later work in this Laboratory has shown that methylcyclohexane of sufficient purity without any treatment, for testing fractionating columns, may be obtained from the Rohm and Haas Company of Philadelphia.

The toluene for equilibrium determinations was obtained by carefully fractionating a nitration grade obtained from the Barrett Company of New York. Two different lots were used and had the following properties.

	No. 1	No. 2
Boiling point at 760 mm., °C.	110.6	110.6
Density, d^{20}_4	0.8658	0.8663
Refractive index, n^{20}_{D}	1.4965	1.4965

For test purposes the nitration grade of toluene as purchased is not of sufficient purity. Experience has shown that its fractionation in batch columns having up to 75 perfect plates yields only 50 or 60% of suitable material, the first 20–30% and the last 15–20% being unsuitable. A high reflux ratio should be maintained during the separation of the initial undesirable material, though it may be reduced appreciably when the middle portion is being fractionated.

Procedure

The equilibrium mixtures were obtained at ordinary barometric pressure by means of the Othmer equilibrium still[3] used in previous work.[2] Analyses of these mixtures were made by density, refractive index, and boiling point determinations as before.[2] Density and refractive index measurements are probably accurate to within ±0.0002 while boiling point measurements are probably accurate to no better than ±0.05 to ±0.1°. Because of the possible inaccuracy of the latter it cannot be too strongly stressed that definite conclusions as to the validity of equilibrium data should not be drawn from this property alone as has been done by Beatty and Calingaert.[1]

Results

The equilibrium data obtained on mixtures of methylcyclohexane and toluene are the result of two entirely separate investigations by different experimenters. The 69 points of equilibria obtained from density, refractive index, and boiling point measurements were plotted on a large curve 100 cm. square similar to the smaller curve shown in Fig. 1 and the best representative curve was drawn. Because the refractive index and density determinations were more accurate than the boiling points, greater weight was given to them in drawing the equilibrium curve. The data presented in Table I are points taken from this large smoothed curve. The refractive index,

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[1] Beatty and Calingaert, *Ind. Eng. Chem.*, **26**, 504, 904 (1934).

[2] Bromiley and Quiggle, *ibid.*, **25**. 1136 (1933).

[3] Othmer. *Ind. Eng. Chem.*, **20**, 743 (1928); *ibid.*, *Anal. Ed.*, **4**. 233 (1932).

TABLE I

DATA ON KNOWN MIXTURES

Mole fraction methylcyclohexane	Density, d^{20}_4	Refractive index, n^{20}_D	B. p. °C./760 mm.
0.00	0.8661	1.4965	110.6
.05	.8596	1.4916	109.55
.10	.8535	1.4871	108.55
.15	.8479	1.4825	107.65
.20	.8422	1.4782	106.9
.25	.8367	1.4740	106.2
.30	.8313	1.4699	105.6
.35	.8260	1.4660	105.0
.40	.8208	1.4620	104.5
.45	.8156	1.4582	104.0
.50	.8107	1.4544	103.55
.55	.8060	1.4509	103.15
.60	.8014	1.4474	102.75
.65	.7970	1.4440	102.45
.70	.7928	1.4408	102.15
.75	.7888	1.4376	101.90
.80	.7848	1.4345	101.65
.85	.7807	1.4315	101.4
.90	.7767	1.4286	101.20
.95	.7730	1.4260	101.00
1.00	.7694	1.4235	100.85

TABLE II

EQUILIBRIUM DATA AT NORMAL PRESSURE

Mole Fraction of Methylcyclohexane		
	Vapor	
Liquid	Found	Calcd.[a]
0.00	0.000	.....
.05	.075	(0.076)
.10	.143	(.146)
.15	.210	(.213)
.20	.270	(.273)
.25	.326	(.330)
.30	.378	(.379)
.35	.424	(.426)
.40	.470	(.473)
.45	.515	(.519)
.50	.560	(.564)
.55	.604	(.608)
.60	.650	(.654)
.65	.694	(.697)
.70	.737	(.738)
.75	.778	(.778)
.80	.818	(.820)
.85	.860	(.863)
.90	.906	(.909)
.95	.954	(.955)
1.00	1.000	.....

[a] Calculated by method based on the Duhem–Margules equation.[1]

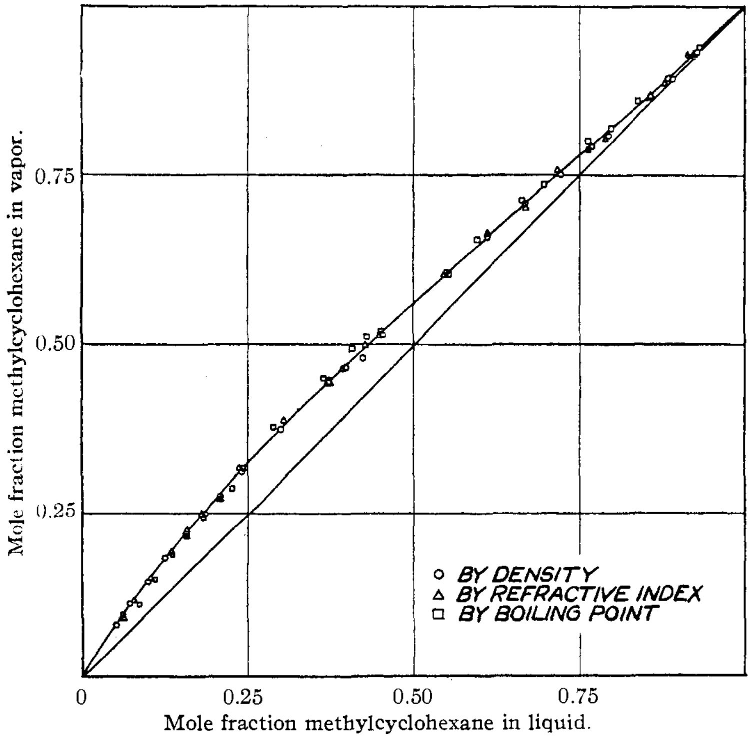

Fig. 1.—Equilibrium diagram.

density, and boiling point data obtained on the known mixtures for the purpose of serving in the analysis of the vapor and liquid equilibrium samples were treated similarly to the equilibrium data and are given in Table II. Each curve was established by a total of 22 points.

Inspection of Fig. 1 shows that the methylcyclohexane–toluene mixtures are suitable for testing, under total reflux, batch fractionating columns having not more than 20–30 theoretical plates. For columns operating continuously where the stripping and enriching lines are used in theoretical plate calculations,[4] the mixture may serve for testing columns having more than 20–30 theoretical plates, depending on the slope of these lines. In all cases, for the greatest accuracy, it is advisable to work with the sections of the equilibrium curve which are the farthest distant from the 45° line. That is, the range 10–75 mole per cent. methylcyclohexane (in liquid) would be more desirable to work in than the 25–90 mole per cent. range. Since most industrial fractionating columns do not have more than 20–30 theoretical plates, this

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(4) Walker, Lewis and McAdams, "Principles of Chemical Engineering," 2d edition, McGraw-Hill Book Co., Inc., New York, 1927, p. 600.

mixture should prove easy and adequate for testing because of the availability of the components in large quantities, their cheapness, and the ease of analysis of the mixtures obtained. This binary system has been used successfully in testing semi-works scale fractionating columns.

Discussion of Method of Checking the Reliability of Equilibrium Data

Beatty and Calingaert[1] have published a means of determining the reliability of vapor–liquid equilibrium data by a method based on the Duhem–Margules equation. Agreement between activity coefficients determined from experimental results and by graphical integration of the Duhem–Margules equation is supposed to indicate the accuracy of the equilibrium data. Adjustments are made until the data as a whole are satisfied. In the determination of the activity coefficients by each method, however, use is made of the boiling points of the equilibrium mixtures and the vapor pressures of the pure components over the boiling range worked with. Inasmuch as boiling point data are seldom more accurate than ±0.05 to ±0.1°, and moreover since adequate vapor pressure data from different sources which agree are seldom available in the literature, undue emphasis should not be put on this method of checking equilibrium data, especially when data obtained by other methods of analysis are given. Small differences in vapor pressure or in boiling point make considerable differences in the results.

Using the above method to check the experimental data listed in Table II and shown in Fig. 1, the equilibrium data presented in the column headed "Calculated" were obtained. The vapor pressures of methylcyclohexane and toluene used in the calculations were a combination of the best data available in the literature and of results obtained in this Laboratory. The vapor pressure of methylcyclohexane may be expressed by the equation $\log P = 7.3476 - 1670.7/T$ and that of toluene by the equation $\log P = 7.5635 - 1796.9/T$ where P is the vapor pressure in millimeters of mercury at any temperature T°K. Figure 2 shows the activity curves for both methylcyclohexane and toluene as determined by both methods. Because the experimental values are the result of 69 determinations using three different analytical methods they are probably more to be relied upon than the calculated values.

Departure of System from Ideality

Figure 2 shows that the mixtures of methylcyclohexane and toluene are not ideal as would be the case if both activity coefficient curves had a value of 1.0 throughout. However, each component does follow Raoult's law when it is present to the extent of 85–90 mole per cent. or more, and when it is present at low concentrations as a solute it follows Henry's law.

The shapes of the activity coefficient curves explain the unsymmetrical shape of the equilibrium curve. With low percentages of methylcyclohexane, while the toluene is acting ideally, *i. e.*, according to Raoult's law, the methylcyclohexane is acting abnormally, its vapor pressure in solution being higher than if it were acting ideally; hence the mole fraction of methylcyclohexane in the vapor is larger and the equilibrium curve in Fig. 1 is well bowed out from the 45° line. Likewise, for high mole fractions of methylcyclohexane where the latter is behaving ideally the toluene is behaving abnormally, and has a higher vapor pressure in solution than it would have under ideal conditions. The result is that the mole fraction of methylcyclohexane in the vapor is less than it would be under ideal conditions and hence the equilibrium curve swings in much closer to the 45° line at the upper end than at the lower end.

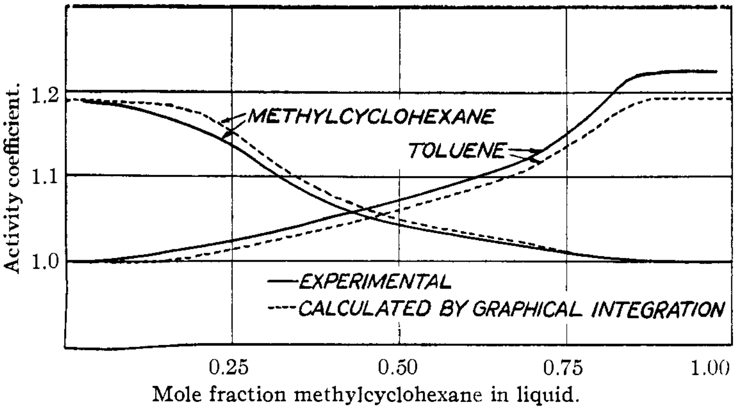

Fig. 2.—Departure of system from ideality.

Acknowledgment.—Acknowledgment is due Messrs. P. Birnsteil, H. S. Smith and P. W. Volk, who obtained most of the experimental data in the

course of their undergraduate thesis work (1934–1935) at this College.

Conclusions

Vapor–liquid equilibrium data have been obtained for methylcyclohexane–toluene mixtures at normal barometric pressures, as well as data for the analysis of liquid mixtures of these two hydrocarbons by density, refractive index and boiling point. This binary hydrocarbon mixture has proved to be entirely practical for testing fractional distillation equipment.

STATE COLLEGE, PA. RECEIVED JUNE 18, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF RHODE ISLAND STATE COLLEGE]

The Vapor Pressure and Dissociation of Tungsten Hexachloride in the Gas Phase[1]

BY ARTHUR A. VERNON

In the course of an investigation dealing with incandescent lamps, the vapor pressure of tungsten hexachloride was determined. A study of its dissociation in the gaseous state yielded preliminary values for the equilibrium constant of the reaction

$$WCl_6(g) \rightleftarrows W(s) + 3Cl_2(g) \qquad (1)$$

The tungsten hexachloride was prepared by passing purified chlorine gas over C. P. tungsten heated to redness in an oxygen-free atmosphere.

Vapor Pressure Measurements

A current of hydrogen was passed over tungsten hexachloride in a glass container inside a small heating furnace. A coil immersed in liquid air was connected to the outlet of the furnace to condense the tungsten hexachloride carried over by the hydrogen. A known amount of gas was passed through the apparatus and the vapor pressure of tungsten hexachloride calculated from the increase in weight of the coil. The results are given in Table I.

TABLE I

VAPOR PRESSURE OF TUNGSTEN HEXACHLORIDE

Temp., °C.	Vapor pressure, mm.
25	5×10^{-3}
50	2.6×10^{-2}
100	1.01×10^{-1}
150	25.1

The results conform to a log p *vs.* $1/T$ plot with a maximum deviation of measured point from the straight line of 5%. The heat of vaporization calculated from the slope of the line is 23,800 cal. per mole and the equation for the line is log $p = 3.1 - 1198/T$.

Dissociation Measurements

In preliminary experiments dissociation data were obtained by the use of tungsten filaments of known diameter mounted in glass bulbs which were evacuated and baked. The filaments were sintered while the bulbs were on the vacuum system and solid tungsten hexachloride introduced before being sealed off. Four filaments of the same diameter were burned at different current ratings and the changes in cold resistance noted at intervals. The tungsten hexachloride vapor was decomposed by the hot filaments and tungsten deposited on the wire. When equilibrium was reached, the resistance of the wires became constant. From the change in resistance of the filaments, the amount of tungsten deposited was calculated and from this the chlorine present at equilibrium could be found. The final temperatures of the filaments were determined by the method of Forsythe and Worthing.[2]

More accurate data presented here were obtained by a modification of this method in which the filaments were burned at a constant temperature determined by comparison with an optical pyrometer. To determine the vapor pressure of tungsten hexachloride more accurately and to have a check on the chlorine pressures as calculated from resistance changes, a quartz fiber manometer was attached to the stem of the bulb. The time for the amplitude of vibration of the fiber to drop from a value I to i was determined and the damping coefficient calculated by means of the expression $d = (1/t) \log (I/i)$. Haber and Kerschbaum[3] found that for a mixture of gases $\alpha = a + b\,[P_A\sqrt{M_A} + P_B\sqrt{M_B}]$ where a is the value of α in a vacuum and P and M are pres-

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[1] The data upon which this paper is based were obtained while the author was employed by the General Electric Company.

(2) Forsythe and Worthing, *Astrophys. J.*, **61**, 146–85 (1925).

(3) Haber and Kerschbaum, *Z. Elektrochem.*, **20**, 296 (1914).