Vapor-Liquid Equilibria for Mixtures of 2,4- and 2,6-Toluene Diisocyanate

HALBERT N. COLE
Elastomer Chemicals Department, E. I. du Pont de Nemours & Co., Inc., Penns Grove, N. J.

Although organic isocyanates were discovered over 100 years ago, they have only recently attained commercial importance with the development of polyurethanes which are finding wide application in manufacture of polyurethane foams, solid elastomers, and resins. Toluene diisocyanate is widely used in the manufacture of polyurethanes. It exists in several isomeric forms, the 2,4- and 2,6-isomers of which are the most important. This article presents vapor-liquid equilibrium data for the system 2,4-, 2,6-toluene diisocyanate obtained at the Chambers Works Plant Technical Section Laboratory of the Du Pont Elastomer Chemicals Department. Measurements were made at three pressures: 5, 30, and 60 mm. of mercury absolute. The method used to correlate the data can be used with any system having symmetrical activity coefficients and relative volatilities close to 1.

EXPERIMENTAL PROCEDURE

A series of 9 to 15 equilibrium determinations was made at each pressure using an equilibrium still (Figure 1). The procedure outlined by Othmer (*3, 4*) was followed. The still was connected in series with a manometer, a 12-liter flask, and a manostat to a laboratory vacuum pump. The 12-liter flask was used to increase the volume of the system, thus reducing pressure fluctuations. At 5 mm., the pressure was measured using a McLeod gage instead of a manometer. The pressure was held constant to within ±1 mm. The equilibrium temperature in the still was measured by means of an iron-constantan thermocouple to an estimated accuracy of ±1 °C.

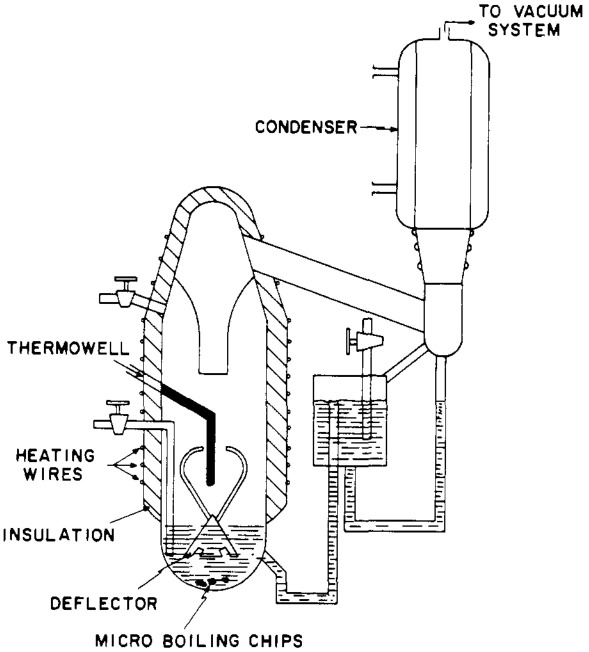

Figure 1. Equilibrium still

High purity 2,4-toluene diisocyanate of the following analysis prepared from pure 2,4-dinitrotoluene was used in the determinations:

Analysis	Results	Method
Purity	99.99%	Determined as toluene diisocyanate by reaction of toluene diisocyanate in tetrahydrofuran with a measured excess of di-*n*-butyl amine. Di-*n*-butyl amine was back-titrated with standard hydrochloric acid
Hydrolyzable chlorine	0.006%	Sample reacted with isopropyl alcohol and some water. Chloride was then titrated potentiometrically with standard silver nitrate
Toluene insolubles	Nil	Sample dissolved in dry toluene, filtered, and insoluble matter was dried and weighed
True freezing point	22.0 °C.	
2,6-Isomer content	1%	Infrared (*2*)

A similar high purity 2,6-toluene diisocyanate was prepared from pure 2,6-dinitrotoluene. All material was redistilled before use.

The desired quantities of each isomer were charged to the still to give a total of 100 ml., which filled the still and the condensate chamber to the desired level. When constant pressure was achieved, the toluene diisocyanate was brought gradually to the boiling point and, after boiling commenced, was cycled in the still for approximately 1 hour to achieve equilibrium. At the end of this time, the still was cooled and 10-ml. samples of the still residue and condensate were withdrawn.

The samples were analyzed for isomer ratio by infrared spectrophotometry (*2*). Duplicate analyses were run on about half of the samples to determine standard deviation.

The vapor pressure curves for 2,4- and 2,6-toluene diisocyanate were determined by means of an isoteniscope (*5*). The pressure was measured with a calibrated closed-leg mercury manometer with an inside diameter of 20 mm. The manometer was read to an accuracy of ±0.1 mm. by means of a cathetometer.

CORRELATION OF DATA

The relative volatility, α, was calculated for each determination by means of Equation 1.

$$\alpha = \frac{x_2 y_1}{x_1 y_2} \tag{1}$$

Any determination which was obviously in error—e.g., if the vapor was enriched in 2,4-isomer instead of 2,6- or if the result was outside the range of probable error—was repeated.

Equations 2, 3, and 4 were used to correlate the data.

$$\ln \gamma_1 = A x_2^2 \tag{2}$$

$$\ln \gamma_2 = A x_1^2 \tag{3}$$

$$\ln \frac{(\gamma_1)}{(\gamma_2)} = A(1 - 2x_1) \tag{4}$$

These equations result from both the Van Laar and Margules equations when the constants are equal (symmetrical activity coefficient curves) (*1*). This simplifying assumption was made because the equilibrium data were not sufficiently precise to show any finite difference between the two small constants. These constants are small

Table I. Equilibrium Data at 5 Mm.

(Temperature, 109°-10°C.)

x_1	x_2	y_1	y_2	Rel. Vol.
0.114	0.886	0.125	0.875	1.110
0.132	0.868	0.145	0.855	1.115
0.139	0.861	0.147	0.853	1.067
0.291	0.709	0.302	0.698	1.054
0.305	0.695	0.319	0.681	1.067
0.422	0.578	0.442	0.558	1.085
0.438	0.562	0.455	0.545	1.072
0.693	0.307	0.703	0.297	1.048
0.867	0.133	0.871	0.129	1.036

Table II. Equilibrium Data at 30 Mm.

(Temperature, 145°-46°C.)

x_1	x_2	y_1	y_2	Rel. Vol.
0.114	0.886	0.124	0.876	1.100
0.199	0.801	0.219	0.781	1.128
0.342	0.658	0.354	0.646	1.054
0.439	0.561	0.459	0.541	1.084
0.467	0.533	0.483	0.517	1.066
0.590	0.410	0.611	0.389	1.091
0.696	0.304	0.708	0.292	1.058
0.797	0.203	0.806	0.194	1.058
0.904	0.096	0.910	0.090	1.073

because the activity coefficients are close to 1. Equation 5 follows from the definition of activity coefficients,

$$\alpha = \frac{P_1\gamma_1}{P_2\gamma_2} \tag{5}$$

$$\ln\alpha = \ln\frac{(P_1)}{(P_2)} + \ln\frac{(\gamma_1)}{(\gamma_2)} \tag{6}$$

and Equation 6 is obtained by taking the natural logarithm of Equation 5. An expression for $\ln\alpha$ in terms of x (Equation 7) can now be obtained by substituting, for $\ln\frac{(\gamma_1)}{(\gamma_2)}$ in Equation 6, $f(x)$ from Equation 4.

$$\ln\alpha = \ln\frac{P_1}{P_2} + A(1-2x_1) \tag{7}$$

Because all values of α obtained were very close to 1, $\alpha - 1$ was substituted for $\ln\alpha$, resulting in a linear relationship between α and x (Equation 8).

Table III. Equilibrium Data at 60 Mm.

(Temperature, 165°-66°C.)

x_1	x_2	y_1	y_2	Rel. Vol.
0.132	0.868	0.141	0.859	1.079
0.230	0.770	0.247	0.753	1.098
0.278	0.722	0.298	0.702	1.102
0.342	0.658	0.360	0.640	1.082
0.411	0.589	0.430	0.570	1.081
0.586	0.414	0.605	0.395	1.081
0.670	0.330	0.686	0.314	1.076
0.752	0.248	0.764	0.236	1.067

$$\alpha = 1 + \ln\frac{P_1}{P_2} + A(1-2x_1) \tag{8}$$

Based on the above, a straight line was fitted to the α vs. x_1 data at each pressure by the method of least squares. Smooth equilibrium data were then calculated, based on values of α taken from the straight line at 5-mole % intervals.

It can be seen from Equation 4 that $\frac{\gamma_1}{\gamma_2} = 1$ when $x_1 = 0.5$. Thus,

$$\alpha = \frac{P_1\gamma_1}{P_2\gamma_2} = \frac{P_1}{P_2}$$

at $x_1 = 0.5$. Hence, a comparison of the ratio of pure component vapor pressures determined from the equilibrium still data with the ratio obtained from the vapor pressure curves affords a qualitative test of the data.

RESULTS

The measured vapor-liquid equilibrium data for 5, 30, and 60 mm. and corresponding relative volatilities are shown in Tables I, II, and III. Figure 2 shows plots of relative volatility vs. mole per cent of 2,6-toluene diisocyanate in the liquid at the three pressures. The standard deviation in 34 duplicate infrared determinations was ±0.3%. This deviation would cause an error of ±0.026 in the calculated value of α at a concentration range of 50-50. At 90-10 concentrations, the error becomes ±0.071.

The average relative volatilities (or ratios of pure component vapor pressures) from the equilibrium still data at 5, 30, and 60 mm. are 1.065, 1.080, and 1.081, respectively. The system apparently becomes more nearly ideal as the

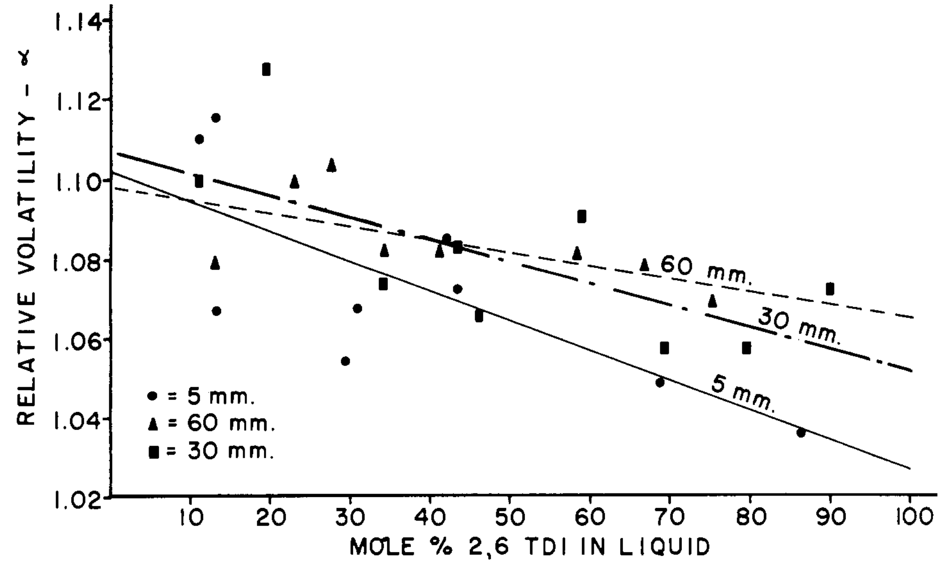

Figure 2. Relative volatility plots

pressure is increased—i.e., the plot of α vs. x_1 becomes more nearly horizontal. Relative volatility decreases with increasing 2,6-toluene diisocyanate in the liquid. Table IV gives the calculated smooth equilibrium curve data at 5% intervals for the three pressures. It is seen from these data that the three curves are almost coincidental. The equilibrium or x-y diagram for 30 mm. is shown in Figure 3. The other diagrams can be produced in full or in part from the data in Table IV.

The vapor pressure curves for the pure isomers are expressed by the following equations:

$$\log P_1 = \frac{-4522.85}{T} - 8.1211 \log T + 33.5939$$

$$\log P_2 = \frac{-4116.04}{T} - 5.7901 \log T + 26.4743$$

The vapor pressures obtained from these equations are believed to be accurate to ±0.1 mm. over a temperature range of 100° to 180°C. Table V shows a comparison between the ratio of pure component vapor pressures obtained from the equilibrium still data and those calculated from the vapor pressure curves.

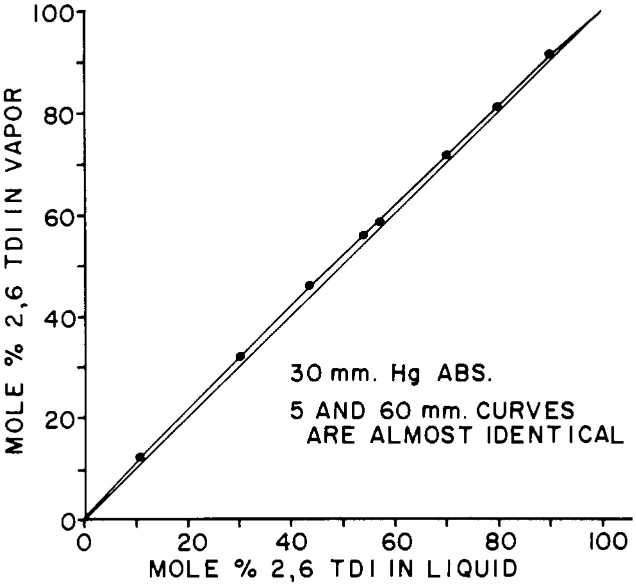

Figure 3. Vapor-liquid equilibrium diagram

Table IV. Smooth Equilibrium Data

x_1	y_1 – 60 Mm.	y_1 – 30 Mm.	y_1 – 5 Mm.
0.05	0.055	0.055	0.055
0.10	0.108	0.109	0.108
0.15	0.162	0.162	0.162
0.20	0.214	0.215	0.214
0.25	0.266	0.267	0.265
0.30	0.318	0.319	0.316
0.35	0.369	0.369	0.367
0.40	0.420	0.420	0.417
0.45	0.470	0.470	0.466
0.50	0.520	0.519	0.516
0.55	0.569	0.568	0.565
0.60	0.618	0.617	0.613
0.65	0.667	0.666	0.662
0.70	0.715	0.714	0.710
0.75	0.763	0.762	0.758
0.80	0.811	0.810	0.807
0.85	0.858	0.857	0.855
0.90	0.906	0.905	0.903
0.95	0.953	0.953	0.951

Table V. Vapor Pressure Ratio Comparison

Pressure, Mm. Hg	P_1/P_2 (Equil. Still)	P_1/P_2 (V.P. Curves)
5	1.065	1.070
30	1.080	1.086
60	1.081	1.081

The activity coefficients for this system can be calculated from Equations 2 and 3. They are very close to 1 as would be expected.

ACKNOWLEDGMENT

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NOMENCLATURE

x_1 = mole fraction 2,6-toluene diisocyanate in liquid
x_2 = mole fraction 2,4-toluene diisocyanate in liquid
y_1 = mole fraction 2,6-toluene diisocyanate in vapor
y_2 = mole fraction 2,4-toluene diisocyanate in vapor
γ_1 = activity coefficient for 2,6-toluene diisocyanate
γ_2 = activity coefficient for 2,4-toluene diisocyanate
A = constant of Margules equation
α = relative volatility
P_1 = vapor pressure of pure 2,6-toluene diisocyanate, mm. of mercury
P_2 = vapor pressure of pure 2,4-toluene diisocyanate, mm. of mercury
T = absolute temperature, °K.

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