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Curve Fitting in Science and Technology. II. Application to Relative Volatility, Bubble Point, and Dew Point of Ideal Binary Mixtures

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Curve Fitting in Science and Technology. II. Application to Relative Volatility, Bubble Point, and Dew Point of Ideal Binary Mixtures

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Abstract

The curve fitting technique in science and technology, introduced in a previous paper, is extended to fitting α vs t, the bubble point and dew point curves for binary ideal mixtures. It is found that α vs t and bubble point curves can be fitted quite accurately by the inverse linear curve while the dew point curve is fitted best by the logarithmic function. It is shown also that the errors resulting from utilizing different fitting functions are proportional to the asymmetry differences between the original and fitting functions. The dew point curve has an asymmetry of $m_0m_1 > 1$. Both the logarithmic and square-root functions also have asymmetries greater than 1, and fitting by these functions is accomplished through the exponential and quadratic fit, respectively.

In a previous paper [1] it was shown that several complex or implicit relations in science and technology can be represented quite accurately by simple explicit relations. The choice of the best fitting function for the relation $y = f(x)$ depends on comparing the asymmetry m_0m_1 of the function to be fitted with those of the different fitting functions at the same Z value. The best fitting function is the function which has the nearest asymmetry to that of the function under consideration. m_0 and m_1 are the normalized initial and final slopes, respectively, and Z is the normalized midordinate ratio.

$$Z = Y_{1/2} = \text{value of } Y \text{ at } X = \tfrac{1}{2}$$

If the normalized function is given by

$$Y = F(X)$$

then

$$Y = \frac{y - y_i}{y_f - y_i} \tag{1}$$

and

$$X = \frac{x - x_i}{x_f - x_i} \tag{2}$$

$$Z = Y_{1/2} = \frac{y_{1/2} - y_i}{y_f - y_i} \tag{3}$$

Subscripts i, f, and ½ refer to initial, final, and middle, respectively.

$$m_0 = m_i\theta \tag{4}$$

$$m_1 = m_f\theta \tag{5}$$

m_i and m_f are the initial and final slopes of the function $y = f(x)$:

$$\theta = \frac{x_f - x_i}{y_f - y_i} \tag{6}$$

and hence

$$m_0 m_1 = m_i m_f \theta^2 \tag{7}$$

The simple fitting functions in their normalized forms are expressed in terms of Z as follows:

Inverse linear

$$Y = \frac{ZX}{1 - Z + X(2Z - 1)} \tag{8}$$

Exponential

$$Y = \frac{\left(\frac{1 - Z}{Z}\right)^{2X} - 1}{\left(\frac{1 - Z}{Z}\right)^{2} - 1} \tag{9}$$

Quadratic

$$Y = (4Z - 1)X + 2(1 - 2Z)X^2 \tag{10}$$

Poisson

$$Y = X(2Z)^{2(1-X)} \tag{11}$$

The normalized asymmetries are given by the following equations:

Inverse linear

$$m_0 m_1 = 1 \tag{12}$$

Exponential

$$m_0 m_1 = \left[\frac{2Z(1 - Z)}{1 - 2Z} \ln \frac{1 - Z}{Z}\right]^2 \tag{13}$$

Poisson

$$m_0 m_1 = 4Z^2(1 - 2 \ln 2Z) \tag{14}$$

Quadratic

$$m_0 m_1 = (4Z - 1)(3 - 4Z) \tag{15}$$

There are no analytic expressions for the logarithmic function in terms of Z. However, analytic expressions can be derived in terms of $\bar{Z}$ where $\bar{Z} = X_{1/2}$ = value of X at $Y = ½$.

Fitting with a logarithmic function can be achieved through the exponential function. Another fitting function is the square-root function which is the inverse of the quadratic, and fitting with it can also be achieved via the quadratic function.

The logarithmic and square-root functions have asymmetries equal to the inverse of those for the exponential and quadratic functions, respectively, and fitting with them will be demonstrated later in the section dealing with fitting the dew point curve.

The relative volatility α, bubble point t_B, and dew point t_D depend on the vapor pressure of each component and its variation with temperature. The relation between vapor pressure and temperature for a large number of compounds and particularly hydrocarbons is given quite satisfactorily by the well-known Antoine equation:

$$\ln P = A - \frac{B}{t + C} \tag{16}$$

where P is the vapor pressure and t is the temperature, and A, B, and C are constants. Each compound has its own set of A, B, and C values. The Antoine constants for different compounds are tabulated in several handbooks and nomographs; see, for example, Ref. *2*.

The values of these constants for benzene, toluene, pentane, hexane, heptane, and octane based on P in mmHg and t in °C are given in Table 1. The normal boiling point t_b was calculated by substituting $P = 760$ mmHg in Eq. (16) and is also tabulated in Table 1.

The basic relationships needed for the development of this paper are the following:

$$\alpha = P_1/P_2 \tag{17}$$

where α is the relative volatility between Components 1 and 2 at a given temperature t, and P_1 and P_2 are the vapor pressures of pure Components 1 and 2 at temperature t.

For a binary ideal mixture, Raoult's law applies and we get

$$\pi = p_1 + p_2 = xP_1 + (1 - x)P_2 \tag{18}$$

or

$$x = \frac{\pi - P_2}{P_1 - P_2}$$

TABLE 1
Antoine Constants and Normal Boiling Points for Different Hydrocarbons

Compound	A	B	C	t_b
Benzene	15.9008	2788.51	220.79	80.10
Toluene	16.0137	3096.52	219.48	110.63
Pentane	15.8333	2477.07	233.21	36.04
Hexane	15.8366	2697.55	224.37	68.74
Heptane	15.8737	2911.32	216.64	98.43
Octane	15.9426	3120.29	209.52	125.66

where π is the total pressure, p_1 and p_2 are the partial pressures of Components 1 and 2, and x is the mole fraction of the more volatile Component 1 in the liquid phase.

Furthermore,

$$p_1 = y\pi = xP_1 \tag{19}$$

or

$$y = x\frac{P_1}{\pi}$$

where y is the mole fraction of Component 1 in the vapor phrase and p_1 is the partial pressure of Component 1.

To fit simple relations for the α vs t curve, t_B vs x (bubble point curve), and t_D vs y (dew point curve) for a binary ideal mixture under a given total pressure π, the temperature range of interest becomes fixed and lies between t_1 and t_2, which are the boiling points of pure Components 1 and 2 under the given total pressure. Since Component 1 is the more volatile, then $t_2 > t_1$.

Utilizing Eqs. (16)–(19), the values of P_1, P_2, α, x, and y were calculated for the following binary mixtures:

(1) Benzene–toluene
(2) Pentane–hexane
(3) Hexane–heptane

In each case the temperature range between the two boiling points t_2 and t_1 was divided into 10 equal intervals and calculations were performed at each temperature as shown in Table 2, where $\gamma = (t_2 - t)/(t_2 - t_1)$.

As pointed out before, in order to choose the best fitting function, one needs to calculate m_0/m_1, which depends on $d\alpha/dt$, dt/dx, and dt/dy at t_1 and t_2 for the above curves respectively.

By differentiation of Eq. (16),

$$\frac{dP}{dt} = \frac{PB}{(t + C)^2} \tag{20}$$

From Eqs. (17)–(20), one can easily deduce the following relations.

I. For the α vs t curve: From Eqs. (17) and (20).

TABLE 2
Calculated Values of α, x, and y for Different Binary Ideal Mixtures

γ	t (°C)	P_1 (mmHg)	P_2 (mmHg)	α	x	y
			I. Benzene–Toluene			
0	110.6	1784	760	2.348	0.000	0.000
0.1	107.6	1650	696	2.370	0.067	0.145
0.2	104.5	1524	637	2.393	0.139	0.278
0.3	101.5	1405	582	2.416	0.217	0.401
0.4	98.4	1293	530	2.440	0.301	0.513
0.5	95.4	1189	482	2.465	0.393	0.615
0.6	92.3	1091	438	2.490	0.493	0.708
0.7	89.3	999	397	2.517	0.603	0.792
0.8	86.2	914	357	2.544	0.723	0.869
0.9	83.2	834	324	2.572	0.855	0.938
1.0	80.1	760	292	2.601	1.000	1.000
			II. Pentane–Hexane			
0	68.7	2058	760	2.708	0.000	0.000
0.1	65.5	1882	685	2.747	0.063	0.155
0.2	62.2	1716	616	2.786	0.131	0.295
0.3	58.9	1563	553	2.828	0.205	0.422
0.4	55.7	1420	494	2.871	0.287	0.536
0.5	52.4	1287	441	2.917	0.377	0.638
0.6	49.1	1164	393	2.964	0.476	0.729
0.7	45.8	1050	349	3.013	0.586	0.810
0.8	42.6	945	308	3.065	0.709	0.882
0.9	39.3	849	272	3.119	0.846	0.945
1.0	36.0	760	239	3.176	1.000	1.000
			III. Hexane–Heptane			
0	98.4	1772	760	2.331	0.000	0.000
0.1	95.5	1640	696	2.356	0.068	0.146
0.2	92.5	1515	636	2.381	0.141	0.280
0.3	89.5	1398	581	2.406	0.219	0.403
0.4	86.6	1288	529	2.433	0.304	0.516
0.5	83.6	1184	481	2.461	0.396	0.618
0.6	80.6	1088	437	2.489	0.497	0.711
0.7	77.6	997	396	2.519	0.606	0.795
0.8	74.7	912	358	2.550	0.725	0.871
0.9	71.4	833	323	2.582	0.856	0.939
1.0	68.7	760	291	2.615	1.000	1.000

$$\left(\frac{d\alpha}{dt}\right)_{\substack{t=t_2\\x=0}} = \alpha_2\left[\frac{B_1}{(t_2+C_1)^2} - \frac{B_2}{(t_2+C_2)^2}\right] \tag{21}$$

$$\left(\frac{d\alpha}{dt}\right)_{\substack{t=t_1\\x=1}} = \alpha_1\left[\frac{B_1}{(t_1+C_1)^2} - \frac{B_2}{(t_1+C_2)^2}\right] \tag{22}$$

II. For the bubble point curve (t_B vs x): From Eqs. (18) and (20).

$$\left(\frac{dt}{dx}\right)_{\substack{x=0\\t=t_2}} = \frac{1}{\left(\frac{dx}{dt}\right)_{\substack{x=0\\t=t_2}}} = -\frac{(\alpha_2-1)(t_2+C_2)^2}{B_2} \tag{23}$$

$$\left(\frac{dt}{dx}\right)_{\substack{x=1\\t=t_1}} = \frac{1}{\left(\frac{dx}{dt}\right)_{\substack{x=1\\t=t_1}}} = -\frac{(\alpha_1-1)(t_1+C_1)^2}{\alpha_1 B_1} \tag{24}$$

III. For the dew point curve: From Eqs. (19), (20), and dt/dx.

$$\left(\frac{dt}{dy}\right)_{\substack{y=0\\t=t_2}} = \frac{1}{\left(\frac{dy}{dt}\right)_{\substack{y=0\\t=t_2}}} = -\frac{(\alpha_2-1)(t_2+C_2)^2}{\alpha_2 B_2} \tag{25}$$

$$\left(\frac{dt}{dy}\right)_{\substack{y=1\\t=t_1}} = \frac{1}{\left(\frac{dy}{dt}\right)_{\substack{y=1\\t=t_1}}} = -\frac{(\alpha_1-1)(t_1+C_1)^2}{B_1} \tag{26}$$

ILLUSTRATIVE EXAMPLES

The following three numerical examples are based on data given in Table 2.

Example 1. Fitting the α vs t Curve for the Ideal Binary Mixture. Benzene–Toluene under Atmospheric Pressure

In this case

$$Y = F(X)$$

where

$$Y = \frac{\alpha - \alpha_2}{\alpha_1 - \alpha_2} = \frac{\alpha - 2.3480}{2.6006 - 2.3480} \qquad \text{(A)}$$

$$X = \frac{t_2 - t}{t_2 - t_1} = \frac{110.63 - t}{110.63 - 80.10} \qquad \text{(B)}$$

$$Z = Y_{1/2} = \frac{2.4648 - 2.3480}{2.6006 - 2.3480} \qquad \text{(C)}$$

$$\text{at } t = t_2;\ X = 0,\ Y = 0$$

$$\text{at } t = t_1;\ X = 1,\ Y = 1$$

$$m_i = \left(\frac{d\alpha}{dt}\right)_{\substack{x=0\\ t=110.63}},\ m_f = \left(\frac{d\alpha}{dt}\right)_{\substack{x=1\\ t=80.10}}$$

$$\theta^2 = \left(\frac{t_f - t_i}{\alpha_f - \alpha_i}\right)^2 = \left(\frac{110.63 - 80.10}{2.6006 - 2.3480}\right)^2$$

m_i and m_f are calculated from Eqs. (21) and (22) after substituting for α_1, α_2, and the Antoine constants from Table 2.

The asymmetry of the α vs t curve is then obtained from Eq. (7), leading to $m_0/m_1 = 0.9988$ as given in Table 3. The corresponding asymmetries at the same value of Z for the different fitting functions were calculated from Eqs. (12)–(15) and are given also in Table 3. By comparing the asymmetry of the original function with those of the fitting functions, it is evident that the nearest asymmetry is that of the inverse linear.

As indicated in the previous paper, the error resulting from fitting with different functions is proportional to the difference between the asymmetry of the original and fitting functions. Applying this rule to the asymmetries given in Table 3, one finds

$$|E_{\text{I.L.}}| = 0.2|E_{\text{Exp}}| = 0.12|E_{\text{Poiss}}| = 0.06|E_{\text{Quad}}| \qquad \text{(D)}$$

Substituting for Y, X, and Z as given by Eqs. (A), (B), and (C) into Eq. (8) gives the required simple relation between α and t, and we get

$$\alpha = 2.3480 + \frac{7.116 \times 10^{-3}(110.63 - t)}{1 - 4.582 \times 10^{-3}(110.63 - t)} \qquad (27)$$

α was calculated for the same values of t given in Table 2, and the results are given in Column 5 of Table 4. As expected from the almost identical values of $m_0 m_1$ of the original and fitting functions, the calculated values are identical with the actual values to the 4th decimal place.

Example 2. Fitting the Bubble Point Curve (t_B vs x) for Benzene-Toluene under Atmospheric Pressure

In this case it is easier to find the best fit for the x vs t_B curve in which Case Z is determined directly as can be seen from Table 2. Once the function x vs t is known, one solves for t to get the explicit relation for the bubble point curve. This is easily accomplished for all fitting functions mentioned in this paper except for the Poisson fitting function where an explicit relation in t_B would not be possible.

In this case

$$Y = F(X)$$

where

$$Y = x \tag{A'}$$

and

$$X = \frac{110.63 - t}{110.63 - 80.10} \tag{B'}$$

$$\text{at } t = t_2;\ Y = 0, X = 0$$

$$\text{at } t = t_1;\ Y = 1, X = 1$$

$$Z = Y_{1/2} = x \text{ at } \gamma = \tfrac{1}{2}$$

where

$$\gamma = \frac{t_2 - t}{t_2 - t_1}$$

From Table 2,

$$Z = 0.39305 \tag{C'}$$

TABLE 3

Comparison between the Asymmetries of the α vs t, x vs t, and y vs t Functions for Binary Ideal Mixtures with Those of Different Fitting Functions

Benzene–Toluene, bp range 80.1–110.6°C

	P vs t						
	Benzene	Toluene	α vs t, $\theta = 120.8$	x vs t, $\theta = 30.5$	t vs x, bubble	y vs t, $\theta = 30.5$	t vs y, dew
m_0m_1	0.942	0.927	0.999	0.983	1.017	0.888	1.126
Z	0.419	0.406	0.462	0.393		0.615	
m_0m_1 (IL)	1	1	1	1		1	
m_0m_1 (Ex)	0.965	0.953	0.993	0.939		0.930	
m_0m_1 (P)	0.950	0.934	0.989	0.915		0.887	
m_0m_1 (Q)	0.894	0.860	0.977	0.817		0.789	

Pentane–Hexane, bp range 36.0–68.7°C

	P vs t						
	Pentane	Hexane	α vs t, $\theta = 69.9$	x vs t, $\theta = 32.7$	t vs x, bubble	y vs t, $\theta = 32.7$	t vs y, dew
m_0m_1	0.922	0.896	0.997	0.980	1.0203	0.836	1.196
Z	0.406	0.388	0.4462	0.377		0.6382	
m_0m_1 (IL)	1	1	1	1		1	
m_0m_1 (Ex)	0.953	0.933	0.985	0.920		0.899	
m_0m_1 (P)	0.934	0.907	0.978	0.889		0.834	
m_0m_1 (Q)	0.858	0.799	0.954	0.758		0.694	

Hexane-Heptane, bp range 68.7–98.4°C

	P vs t						
	Hexane	Heptane	α vs t, $\theta = 104.6$	x vs t, $\theta = 29.7$	t vs x, bubble	y vs t, $\theta = 29.7$	t vs y, dew
$m_0 m_1$	0.942	0.923	0.998	0.985	1.015	0.877	1.140
Z	0.419	0.406	0.456	0.397		0.618	
$m_0 m_1$ (IL)	1	1	1	1		1	
$m_0 m_1$ (Ex)	0.965	0.953	0.990	0.943		0.926	
$m_0 m_1$ (P)	0.951	0.934	0.985	0.921		0.880	
$m_0 m_1$ (Q)	0.896	0.859	0.970	0.829		0.776	

TABLE 4
Testing the Accuracy of Eqs. (27), (28), and (29) for Benzene–Toluene
(boiling point range is divided into 5 equal intervals)

Exact values				Eq. (27), α vs t,	Eq. (28) bubble point,	Eq. (29) dew point,
t	α	x	y	α_{calc}	t_{calc}	t_{calc}
110.63	2.3480	0	0	2.3480	110.63	110.63
104.52	2.3927	0.1388	0.2783	2.3927	104.55	104.58
98.42	2.4400	0.3012	0.5126	2.4400	89.43	98.45
92.31	2.4903	0.4932	0.7079	2.4903	92.30	92.27
86.21	2.5437	0.7227	0.8689	2.5437	86.17	86.13
80.10	2.6006	1.0000	1.0000	2.6006	80.10	80.10
$\Sigma\|E\|$	(for 10 intervals)			0	.20	.44

$$m_i = \left(\frac{dx}{dt}\right)_{\substack{t=t_2\\x=0}}, \quad m_f = \left(\frac{dx}{dt}\right)_{\substack{t=t_1\\x=1}}$$

$$\theta^2 = \left(\frac{t_f - t_i}{x_f - x_i}\right)^2 = \left(\frac{110.63 - 80.10}{1 - 0}\right)^2$$

m_i and m_f are calculated from Eqs. (23) and (24) on substituting the values of t_1, t_2, α_1, α_2, and the Antoine constants as given in Table 2. Again on substituting the values of m_i, m_f, and θ^2 in Eq. (7), one gets $m_0 m_1 = 0.9833$. The corresponding values of $m_0 m_1$ at $Z = 0.39305$ for the different fitting functions were calculated from Eqs. (12)–(15) and are given in Table 3 together with that of the original function. The same values may be obtained by interpolation in Table 2 or Fig. 3 of the original paper (*1*).

Again, the I.L. function has the nearest asymmetry and is, therefore, the best fitting function.

Substituting the values of Y, X, and Z as given by Eqs. (A′), (B′), and (C′) in Eq. (8) and solving for t gives the bubble point function for benzene–toluene under atmospheric pressure:

$$t_B = 110.63 - \frac{47.15x}{1 + 0.5442x} \tag{28}$$

The relative errors from using other fitting functions can also be calculated as in Example 1, leading to

$$|E_{\text{I.L.}}| \cong 0.38|E_{\text{Exp}}| \cong 0.25|E_{\text{Poiss}}| \cong 0.10|E_{\text{Quad}}| \tag{D′}$$

To test the accuracy of Eq. (28), t_B was calculated from it at the same values of x given in Table 2, and the values obtained are given in Column 6 of Table 4. Comparing the calculated values with the actual values shows that the fit is quite good.

Example 3. Fitting a Simple Explicit Relation for the Dew Point Curve (t_D vs y) for Benzene–Toluene under Atmospheric Pressure

An equation for the dew point curve should be explicit in t_D. As in the case of the bubble point curve, it is more convenient to fit the y vs t curve due to the availability of Z from Table 2. One can solve for t from the y vs t equation, which is readily done except in the case of the Poisson fitting function.

In this case, and similar to the bubble point,

$$Y = y \tag{A''}$$

$$X = \frac{t_2 - t}{t_2 - t_1} = \frac{110.63 - t}{110.63 - 80.10} \tag{B''}$$

$$Z = 0.61481 \text{ (from Table 2)} \tag{C''}$$

m_0/m_1 is calculated by substituting in the expression for m_i and m_f as given by Eqs. (25) and (26). θ^2 is the same as in the bubble point curve, leading to $m_0/m_1 = 0.8879$. At the same value of Z, the asymmetries of the fitting functions were calculated and are given in Table 3. The closest asymmetry is that of the Poisson where $m_0/m_1 = 0.8869$, indicating that the Poisson function gives a very close fit to the y vs t curve. However, with the Poisson fit it is not possible to solve for t, and an explicit relation in t cannot be obtained. The second best fit is the exponential which has an asymmetry equal to 0.9302, and an explicit relation for t vs x is possible.

Substituting from Eqs. (A″), (B″), and (C″) into Eq. (9) leads to the simple relation for the dew point curve and we get

$$t_D = 32.645 \ln\left(\frac{1 - 0.6075y}{0.03375}\right) \tag{29}$$

t_D was calculated for the same values of y given in Table 2, and the calculated values are given in Table 4 for comparison with the actual values. As can be seen from Table 4, the fit is quite satisfactory but not as good as the bubble point curve fit due to a bigger difference between the asymmetries of the original and fitting functions.

To show again that the error is proportional to the asymmetry difference, the same dew point curve was fitted by both the inverse linear and quadratic functions, also by fitting the y vs t curve and then solving for t_D, leading respectively to another inverse linear and a square-root function.

By substituting from Eqs. (A″), (B″), and (C″) into Eqs. (8) and (10) and solving for t_D, the following equations were deduced.

Inverse linear

$$t_D = 110.63 - \frac{19.128y}{1 - 0.3735y} \tag{30}$$

Quadratic

$$t_D = 62.12 + 48.51\sqrt{1 - 0.86265y} \tag{31}$$

t_D was calculated from Eqs. (30) and (31) for the same values of y given in Table 2. The calculated values are listed in Table 5 together with those calculated from Eq. (29), and $|E|$ was determined in each case.

If

$|D|$ = difference between $m_0 m_1$ for original and fitting function, then from table 3

TABLE 5

Comparison between the Log, Square Root, and Inverse Linear Fit for the Dew Point Curve of Benzene–Toluene. The Log Fit Gives the Least Error

t	y	Eq. (29), t_{calc} log	E	Eq. (31), t_{calc} square root	E	Eq. (30), t_{calc} inverse log	E
110.63	0	110.63	0	110.63	0	110.63	0
104.52	0.2783	104.58	+0.06	104.41	−0.11	104.69	+0.17
98.42	0.5126	98.45	+0.03	98.35	−0.07	98.50	+0.08
92.31	0.7079	92.27	−0.04	92.39	+0.08	92.22	−0.09
86.21	0.8689	86.13	−0.08	86.40	+0.19	86.02	−0.19
80.10	1.0000	80.10	0	80.10	0	80.10	0
$\Sigma\|E\|$ (for 10 intervals)			.44		.95		1.11

$$|D|_{\text{Exp}}:|D|_{\text{Quad}}:|D|_{\text{I.L.}} = 1:2.3:2.6$$

and from Table 5

$$|E|_{\text{Exp}}:|E|_{\text{Quad}}:|E|_{\text{I.L.}} = 1:2.2:2.5$$

which shows that the linear relationship between $|E|$ and $|D|$ holds fairly well in this case.

From the above equation,

$$|E|_{\text{Exp}} = 0.45|E|_{\text{Quad}} = 0.40|E|_{\text{I.L.}} \qquad \text{(D}''\text{)}$$

Relative Error $|E|r$ and Accuracy of the Fit

The absolute errors given in Tables 4 and 5 do not tell much about the accuracy of the fit. In order to make them meaningful, they should be compared with some reference error. The most logical error to be used as reference is probably the error resulting from the linear fit which is accomplished by fitting the original equation by two straight lines connecting the two end points to the middle point at $X = 0.5$.

The linear fit error was calculated for the above three examples, leading to:

For the α vs t curve, $|\Sigma E|_{\text{Lin}} = 0.01525$

For the bubble point curve, $|\Sigma E|_{\text{Lin}} = 5.29$

For the dew point curve, $|\Sigma E|_{\text{Lin}} = 5.73$

From these values, the absolute errors given in Tables 4 and 5 and from Eqs. (D), (D′), and (D″), the following relative errors were deduced.

For the α vs t curve:

$$|E|_{r,\text{I.L.}} = 0.6\%, \qquad |E|_{r,\text{Exp}} = 3.0\%$$

$$|E|_{r,\text{Poiss}} = 5.0\%, \qquad |E|_{r,\text{Quad}} = 10.0\%$$

For the bubble point curve:

$$|E|_{r,\text{I.L.}} = 3.8\%, \qquad |E|_{r,\text{Exp}} = 10.0\%$$

$$|E|_{r,\text{Poiss}} = 15.2\%, \qquad |E|_{r,\text{Quad}} = 38.0\%$$

For the dew point curve:

$$|E|_{r,\text{Log}} = 7.7\%, \qquad |E|_{r,\text{Sq.Rt.}} = 17.1\%$$

$$|E|_{r,\text{I.L.}} = 19.3\%$$

As can be seen from these relative error values, the inverse linear fit of the α vs t curve is practically a perfect fit, the inverse linear fit of the bubble point curve with only 3.8% relative error is also very good, and the logarithmic fit of the dew point curve is quite satisfactory. Any fit that leads to a relative error of less than 10% should be considered a good fit.

In getting the relative error values for the α vs t curve, it was necessary to calculate the absolute error for the Poisson fit which has a much larger error than that for the I.L. fit. From Eq. (D), the other errors were calculated.

CONCLUSION

The α vs t and the bubble point curve for benzene–toluene are fitted quite accurately by the simple inverse linear function while the dew point curve is represented best by the logarithmic function. This finding applies to other hydrocarbons and particularly to the paraffinic hydrocarbons, as can be seen from Table 3. The variation of α with concentration during distillation also follows the inverse linear curve.

In fact, the constant Z in the normalized Eq. (8) may be expressed in terms of the carbon number n by a simple relation which is characteristic of each of the above three relations, leading to general formulas which apply to all binary mixtures of the series.

The application of the present technique to the variation of α with composition x should be important in distillation calculations but is outside the scope of the present paper.

APPENDIX

Linear Fit Error, α vs t (Benzene–Toluene)

The two straight lines connecting the end points to the middle point at $X = 0.5$ are

$$\alpha_{\text{left}} = 2.34798 + 7.651 \times 10^{-3}(110.624 - t)$$
$$= 3.19436 - 7.651 \times 10^{-3}t$$

$$\alpha_{\text{right}} = 2.46475 + 8.9038 \times 10^{-3}(95.364 - t)$$
$$= 3.31385 - 8.9038 \times 10^{-3}t$$

The Poisson fitting function is obtained by substituting for Y, X, and Z from Eqs. (A), (B), and (C) into Eq. (11), leading to

$$\alpha = 2.34798 + 0.01251(110.626 - t)(0.924326)^{0.065522t}$$

The calculated values of α for both fits are given in Table 6 together with Error E in each case.

$$|E|_{r,\text{Poiss}} = \frac{0.00076}{0.01525} \times 100 = 5.0\%$$

From Eq. (D):

$$|E|_{r,\text{I.L.}} = 5 \times 0.12 = 0.60\%$$

$$|E|_{r,\text{Exp}} = 5 \times \frac{0.12}{0.2} = 3.0\%$$

TABLE 6

t	α_{exact}	α_{calc}, linear fit	E	α_{calc}, Poisson fit	E
110.626	2.34798	2.34798	0	2.34798	0
107.574	2.36999	2.37131	0.00132	2.36991	−0.00008
104.521	2.39265	2.39467	0.00202	2.39254	−0.00011
101.469	2.41598	2.41802	0.00204	2.41587	−0.00011
98.416	2.44000	2.44138	0.00138	2.43994	−0.00005
95.364	2.46475	2.46475	0	2.46475	0
92.312	2.49027	2.49192	0.00165	2.49032	+0.00005
89.259	2.51658	2.51911	0.00253	2.51669	+0.00011
86.207	2.54371	2.54628	0.00257	2.54384	+0.00013
83.154	2.57172	2.57346	0.00174	2.57183	+0.00011
80.102	2.60064	2.60064	0	2.60064	0
$\Sigma\lvert E\rvert$			0.01525		0.00076

$$|E|_{r,\text{Quad}} = 5 \times \frac{0.12}{0.06} = 10.0\%$$

Linear Fit Error, Bubble Point Curve (Benzene-Toluene)

The two straight lines connecting the end points to the middle point are

$$t_{\text{left}} = 110.626 - \frac{15.262}{0.39305}x$$

$$= 110.626 - 38.83x$$

$$t_{\text{right}} = 95.364 - \frac{15.262}{0.60695}(x - 0.39305)$$

$$= 95.364 - 25.145(x - 0.39305)$$

$$= 105.247 - 25.145x$$

The calculated values of t are given in Table 7 in Column 4 together with the error E.

TABLE 7

x	y	t_{exact}	$t_{\text{calc}}^{\text{Bubble}}$, linear fit	E	$t_{\text{calc}}^{\text{dew}}$, linear fit	E
0	0	110.626	110.63	0	110.626	0
0.066785	0.145011	107.574	108.04	+0.47	107.026	−0.548
0.138819	0.278335	104.521	105.24	+0.72	103.717	−0.804
0.216723	0.400649	101.469	102.21	+0.74	100.680	−0.789
0.301199	0.512599	98.416	98.93	+0.51	97.901	−0.515
0.393050	0.614811	95.364	95.36	0	95.364	0
0.493190	0.707888	92.312	92.85	+0.54	91.676	−0.636
0.602662	0.792403	89.259	90.09	+0.83	88.327	−0.932
0.722669	0.868911	86.207	87.08	+0.87	85.296	−0.911
0.854587	0.937942	83.154	83.76	+0.61	82.561	−0.593
1	1	80.102	80.10	0	80.102	0
$\Sigma\|E\|$				5.29		5.728

Linear Fit Error, Dew Point Curve (Benzene-Toluene)

In this case, the two straight lines connecting the end points with the middle point of $X = ½$ are given by

$$t_{\text{left}} = 110.626 - \frac{15.262}{0.614811} y$$
$$= 110.626 - 24.824y$$

$$t_{\text{right}} = 95.364 - \frac{15.262}{0.385189} (y - 0.614811)$$
$$= 119.724 - 39.622y$$

The calculated temperatures according to these formulas are given in Table 7 in Column 6 together with the error E in each case.

The relative errors in the case of the bubble point curve are calculated from $\Sigma|E|$ for the I.L. fit in Table 4 and $\Sigma|E|$ for the linear fit, leading to

$$|E|_{r,\text{I.L.}} = \frac{0.20}{5.29} \times 100 = 3.8\%$$

From Eq. (D′):

$$|E|_{r,\text{Exp}} = 3.8 \times \frac{1}{0.38} = 10.0\%$$

$$|E|_{r,\text{Poiss}} = 3.8 \times \frac{1}{0.25} = 15.2\%$$

$$|E|_{r,\text{Quad}} = 3.8 \times \frac{1}{0.1} = 38.0\%$$

Similarly for the dew point curve from $\Sigma|E|$ for log fit in Table 5 and $\Sigma|E|$ for linear fit, one finds:

$$|E|_{r,\log} = \frac{0.44}{5.728} \times 100 = 7.7\%$$

From Eq. (D″) one gets

$$|E|_{r,\mathrm{Sq.Rt.}} = 7.7 \times \frac{1}{0.45} = 17.1\%$$

$$|E|_{r,\mathrm{I.L.}} = 7.7 \times \frac{1}{0.4} = 19.3\%$$

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