A Distribution Function for Oil Mixtures and Polymers

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The representation of the composition of various oil mixtures by continuous functions was discussed by Lederer (*1*) long ago. He also pointed out that algebraic distribution functions were desirable. Nowadays the need for algebraic functions is more pressing, since they are by far the best means of feeding extensive data into an automatic computer. The obvious independent variable for oil mixtures is the vapor pressure, and so the value of the distribution function $X(p)$ gives the mole fraction of the material that has a vapor pressure higher than p. Continuous distribution functions have been introduced also by Bowman and Edmister (*2*), although they did not use algebraic functions.

In a search for a useful distribution function the first choice will be, of course, the normal function dependent on an appropriate argument. Since the vapor pressure is essentially a partition coefficient, its value is just as significant as the value of its reciprocal. Whenever a quantity and its reciprocal are *a priori* equally significant, the best choice of a variable is usually the logarithm since a transformation from p to $1/p$ changes only the sign of $\log p$. Indeed the logarithmic-normal distribution furnishes a fairly good representation of quite a few oil mixtures. Still there are, in general, systematic deviations exceeding the limits of experimental error.

A much better representation is achieved by generalizing the log-normal function in the same way that the normal distribution function was generalized by Charlier (3). The Gram-Charlier series generalizes the Gaussian function by adding its derivatives, multiplied by empirical coefficients. The term of order zero is the Gaussian. The two coefficients of the Gaussian (mean and standard deviation) are always so chosen that the coefficients of the first and second order terms of the Gram-Charlier series are zero. Following Charlier, we restrict the expansion of the series to the terms of third and fourth order, thus obtaining a function containing four experimental parameters. It will be called the *nearly log-normal* function. Most of the properties of the nearly normal function are discussed in textbooks (3) and need not be repeated here. The values and significance of various means of the vapor pressure are of interest.

THE NEARLY LOG-NORMAL FUNCTION

We start from the Gaussian

$$G = (2\pi)^{-0.5} \exp(-0.5t^2) \qquad (1)$$

expressed in the reduced variable

$$t = (1/r) \log (p_m/p) \qquad (2)$$

We prefer to take $\log (1/p)$ as the independent variable rather than $\log p$, so that we may count the cumulative mole fraction, as usually, beginning with the light material and ending with the heavy material. The function G/r is then the log-normal frequency function of $1/p$; that is the mole fraction of substances with vapor pressures between p and $p + \Delta p$ is given by

$$(G/r)\Delta\log(1/p) = (2\pi)^{-0.5} \exp(-0.5t^2)\Delta t. \qquad (3)$$

For the nearly log-normal distribution we introduce, in addition to p_m and r, two more individual parameters h_3 and h_4. The frequency function is now given by

$$f\Delta\log(1/p) = G[1 - h_3(t^3 - 3t) + h_4(t^4 - 6t^2 + 3)]\Delta t \qquad (4)$$

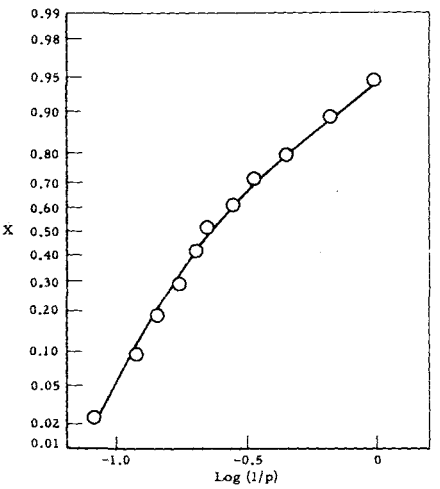

Fig. 1. Vapor-pressure distribution of a gas oil at 370°C. Curve: log $p_m = 0.585$; $r = 0.288$; $h_3 = -0.176$; $h_4 = -0.013$, pressure in atmospheres.

Integration furnishes the distribution function

$$X = \int_{-\infty}^{t} G(z)dz + G(t)[h_3(t^2 - 1) - h_4(t^3 - 3t)] \qquad (5)$$

which gives the cumulative mole fraction of the substances with vapor pressures above p.

For the determination of the coefficients we assume that average vapor pressures p_i have been found for a number of cuts containing mole fractions x_i of the oil mixture. The coefficients are then given by

$$\log p_m = \sum_i x_i \log p_i;$$

$$r^2 = \sum_i x_i [\log(p_m/p_i)]^2 \qquad (6)$$

$$h_3 = -\sum_i x_i [\log(p_m/p_i)]^3/6r^3 \qquad (7)$$

$$h_4 = \sum_i x_i [\log(p_m/p_i)]^4/24r^4 - 0.125 \qquad (8)$$

The vapor-pressure distribution of a gas oil at 370°C., as calculated from determinations of true boiling points, is shown in Figure 1. The ordinate is the cumulative mole fraction on a so-called "probability scale"; that is any distribution normal in the abscissa values (log normal in $1/p$ or p) appears as a straight line. The observations shown in Figure 1 can be crudely approximated by a straight line, but the deviations are systematic and by no means negligible; however, the curve, calculated according to (5), represents the measurements within the experimental errors. Other oil mixtures (kerosene, various refinery streams) have been found to show similar distributions.

POLYMERS

The nearly log-normal function is equally useful for polymers. Wesslau (4) and recently Chiang (5) discussed the use of the log-normal distribution function for polymers. Actually the situation is precisely the same as in the case of oil mixtures. As soon as reasonably accurate data are available, systematic deviations are found, which however are small enough to

allow a representation by Equations (4) and (5).

For polymers we replace $1/p$ by the molal weight, and so instead of (2) we have

$$t = (1/r)\log(M/M_m) \qquad (9)$$

Similar substitutions are made in (6), (7), and (8). In addition, we prefer to use weight fractions rather than mole fractions so that X in Equation (5) is replaced by the cumulative weight fraction W and x_i in (6) to (8) by the weight fraction w_i. It makes little difference which kind of variable we choose; indeed, it can be shown that a log-normal distribution for weight fractions implies a log-normal distribution for mole fractions with the same standard deviation (6).

Various average molal weights are of interest for polymers. In order to obtain a general result, we define the average molal weight of order g by

$$(M_g)^g = \int_{-\infty}^{\infty} M^g f d\log M \qquad (10)$$

We introduce the nearly normal frequency function (4) (after replacing $1/p$ by M) into (10) and obtain after a slightly involved calculation* for the average molal weight of order g:

$$\log M_g = \log M_m + 1.152\, gr^2 + g^{-1}\log[1 - h_3(2.3\, gr)^3 + h_4(2.3\, gr)^4] \qquad (11)$$

Thus we have quite convenient expressions for the number average molal weight $M_n(g = -1)$:

$$\log M_n = \log M_m - 1.152\, r^2 - \log[1 + h_3(2.3r)^3 + h_4(2.3r)^4], \qquad (12)$$

for the viscosity molal weight by writing the exponent a of the relation of Mark and Houwink for g in (11), and for the weight average molal weight $M_w(g = 1)$

$$\log M_w = \log M_m + 1.152\, r^2 + \log[1 - h_3(2.3r)^3 + h_4(2.3r)^4] \qquad (13)$$

The relations given by Chiang (5) for the log-normal distribution follow from (11) with $h_3 = h_4 = 0$.

In general one will interpret the terms containing h_3 and h_4 in all these relations as correction terms, representing small deviations from the log-normal distribution. In other words, h_3 and h_4 should be small compared with unity. Practically the permissible limits of h_3 and h_4 will depend on the magnitude of r and also on the specific application.

AVERAGE VAPOR PRESSURES

Returning to oil mixtures, we define the average ideal vapor pressure and the average reciprocal ideal vapor pressure by

$$p_a = \sum_i x_i p_i; \quad 1/p_r = \sum_i x_i/p_i \qquad (14)$$

The reciprocal vapor pressure determines the dew point of the mixture. Replacing M by $1/p$, we obtain from (13) and (12)

$$\log p_a = \log p_m + 1.151 r^2 + \log[1 + h_3(2.3r)^3 + h_4(2.3r)^4] \qquad (15)$$

$$\log p_r = \log p_m - 1.151 r^2 - \log[1 - h_3(2.3r)^3 + h_4(2.3r)^4] \qquad (16)$$

NOTATION

G = Gaussian [Equation (1)]
M = molal weight
M_g = average molal weight of order g
M_m = geometric average molal weight
M_n = number average molal weight
M_w = weight average molal weight
W = cumulative weight fraction
X = cumulative mole fraction
f = frequency function [Equation (4)]
h_3, h_4 = coefficients of the Hermitian terms
p = vapor pressure
p_i = vapor pressure of species i
p_m = geometric mean vapor pressure
p_a = average vapor pressure
p_r = average reciprocal vapor pressure
r = standard deviation
t = reduced distribution variable [Equations (2), (9)]
w_i = weight fraction of species i
x_i = mole fraction of species i

ACKNOWLEDGMENT

We are obliged to R. M. Smith and W. H. McFadden for help and discussions.

LITERATURE CITED

1. Lederer, E. L., *Petroleum*, **31**, No. 6, 1 (1935).
2. Bowman, J. R., *Ind. Eng. Chem.*, **41**, 2007 (1949); **43**, 2622 (1951). ———, and W. C. Edmister, *Chem. Eng. Progr. Symposium Ser. No. 2*, **48**, 112 (1952); **48**, No. 3, 76 (1952). Edmister, W. C., and D. H. Buchanan, *ibid.*, **49**, No. 6, 69 (1953). *Ind. Eng. Chem.*, **47**, 1685 (1955).
3. Charlier, C. V. L., "Vorlesungen über die Grundzüge der mathematischen Statistik," Lund, Sweden (1931). See also H. Cramér, "Mathematical Methods of Statistics," Princeton Univ. Press, Princeton, (1951).
4. Wesslau, H., *Makromol. Chem.*, **20**, 111 (1956).
5. Chiang, R., *J. Polymer Sci.*, **36**, 91 (1959).
6. Mussa, C., *J. Appl. Polymer Sci.*, **1**, 300 (1959).

* We substitute t for M with the aid of (9), transform to a new variable $y = t - 2.303\, gr$, and order the polynomial into Hermitian polynomials. Then the integration is easy because of the relation between Hermitian polynomials and the derivatives of G.

Liquid-side Mass Transfer Coefficients in Packed Towers

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In the June, 1959, issue of the *A.I.Ch.E. Journal*, Onda, Sada, and Murase (4) presented a correlation for liquid-phase mass transfer coefficients based on values of k_L for Raschig rings obtained by dividing the volumetric coefficient, by the wetted area of Fujita (2). Since the authors showed that their correlation does not provide insight into the mechanism of absorption, because the same correlation is obtained with either the two-film theory