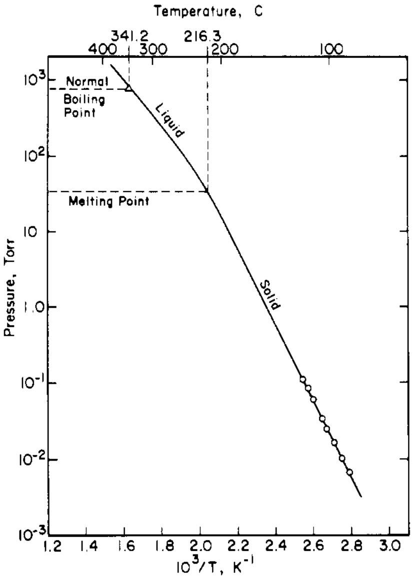

Figure 4. Extrapolation of vapor-pressure data for anthracene at near-ambient temperatures to the normal boiling point, by using the SWAP method (t_{mp} = 216.3 °C; $P(\text{sat})_{mp}$ = 33.4 torr; F_A = 1.0; F_B = F_N = 0.0).

average error in estimating T_{760} is 5.2 °C, or 11.1% in pressure.

For extrapolation of solid data to the normal boiling point, the melting point temperature must be known. However, the SWAP method is not highly sensitive to small errors in melting point temperatures. For anthracene, if the melting point temperature used is in error by ±10 °C, the subsequent error in predicting T_{760} is only ±4.7 °C.

Conclusions

The experimental technique used here yields reliable vapor-pressure data near ambient temperatures. Since the experiment is performed at convenient temperatures and pressures, it is simple to operate and provides good-quality data easily and rapidly. Using the SWAP method, we estimate vapor pressures for high-molecular-weight hydrocarbons in the range 10^{-3}–10^3 torr from experimental data at near-ambient temperature for both solids and liquids.

Glossary

A, B	Clapeyron equation constants
f	fugacity, torr
F_A, F_B, F_N	SWAP parameters: fraction of carbon atoms per molecule which are aromatic, branched paraffin, and naphthenic, respectively
n	number of carbon atoms per molecule of hydrocarbon
ppm-(CO_2)	concentration of CO_2, ppm by volume
P(atmo)	atmospheric pressure, torr
P(sample)	total pressure in equilibrium cell, torr
P(sat)	vapor pressure, torr
t	temperature, °C
T	temperature, K
x	mole fraction in condensed phase
y	mole fraction in vapor phase

Greek Letters

ϕ	fugacity coefficient
γ	activity coefficient

Subscripts

i	component i
mp	melting point
0.01, 10, 760	at pressures of 10^{-2}, 10, and 760 torr, respectively

Superscripts

c	condensed phase
o	standard state
v	vapor phase

Literature Cited

(1) Macknick, A. B., Winnick, J., Prausnitz, J. M., *AIChE J.*, **24**, 731 (1978).
(2) Osborn, A. G., Douslin, D. R., *J. Chem. Eng. Data*, **20**, 229 (1975).
(3) Sinke, G. C., *J. Chem. Thermodyn.*, **6**, 311 (1974).
(4) Smith, G., Winnick, J., Abrams, D. S., Prausnitz, J. M., *Can. J. Chem. Eng.*, **54**, 337 (1976).

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Use of Rational Functions for Representing Data

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The relative merits of polynomials and rational functions for the representation of data are illustrated by means of various fits to typical sets of physical data by using these two types of parameterization. In many situations rational functions provide superior fits with the same number of adjustable parameters (or fits with fewer parameters for the same degree of precision), greater stability of extrapolation to points outside the fitted range, and greater versatility in approximating diverse functional forms, including those showing singularities. A useful algorithm for the computation of rational fits is briefly discussed.

One popular method for representing data is to use a simple polynomial. For example Prausnitz (*6*) represents Henry's constants as a function of the variable β = 1000/T, where T is the temperature in K, in the form

$$\ln H = a_0 + a_1\beta + \ldots + a_M\beta^M \qquad (1)$$

where M, in some instances, is as high as 5. Many other examples of this approach can be found in the chemical engineering literature.

Polynomial parameterizations have certain serious theoretical limitations (*1*). For example, a power-series expansion for a given function has a radius of convergence which is equal to the distance from the point of expansion to the nearest singularity in the function, so even the exact power series, if it were known, would be completely useless beyond that point. These theo-

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Table I. Values of χ^2 Obtained from Linear Polynomial and Rational Fits to Data on Henry's Constants (*6*) for a Number of Binary Systems[a]

	polynomial fit		rational fit	
system	order	χ^2	order	χ^2
H_2–CH_4	[5, 0]	2.7×10^{-4}	[2, 1]	3.5×10^{-4}
H_2–C_2H_4	[5, 0]	4.2×10^{-4}	[2, 1]	1.9×10^{-4}
H_2–C_2H_6	[5, 0]	2.3×10^{-3}	[2, 1]	4.9×10^{-4}
H_2–C_3H_8[b]	[5, 0]	6.0×10^{-4}	[2, 1]	1.1×10^{-4}
H_2–C_3H_8[c]	[7, 0]	1.8×10^{-2}	[2, 1]	5.9×10^{-4}
H_2–*n*-C_6H_{14}	[5, 0]	7.8×10^{-4}	[2, 1]	1.2×10^{-4}
N_2–C_2H_6	[4, 0]	6.0×10^{-4}	[2, 1]	1.2×10^{-3}

[a] The data are quoted to three significant figures and the χ^2 values obtained with the [2, 1] rational fit are in each case consistent with this tabulation accuracy. [b] 160–500 K only. [c] 160–620 K.

retical weaknesses can be reflected in practice when real data are to be fitted since these data may well follow physical laws which are consistent with the appearance of singularities not far outside the range of interest.

It is the purpose of this paper to point out that in many situations rational functions (i.e., a ratio of two polynomials) can provide a better fit to data than is given by a simple polynomial with the same number of adjustable coefficients. For a fit of specified accuracy, it is rare for a rational function to require more adjustable coefficients than the corresponding simple polynomial; usually it is superior in this regard. This economy in coefficients can be useful from the point of view of data storage. Another advantage in the use of rational functions is that extrapolations tend to be more reliable; this probably arises from the greater versatility of rational functions in approximating the behavior of diverse functional forms without resort to the use of high powers in the independent variable. The properties of certain special forms of rational function, called Padé approximants, are well established and have recently been widely utilized in theoretical and experimental physics (*1*). Padé approximants are rational functions which either (I) give an exact fit to the value of a mathematical function and to its derivatives up to a specified order at a single point or (II) give an exact fit to the values of such a function at a specified set of points. Convenient algorithms have been developed which can be used to obtain the coefficients in the Padé functions from the values of the function and/or its derivatives in these two cases.

It has been found that Padé approximants have remarkable convergence properties and are, to a great extent, free from the limitations characteristic of polynomial approximations. These properties have been utilized in many situations, just one example being in the evaluation of the critical temperature and exponent from the Ising model for ferromagnets (*8*).

The situation considered in the present paper differs from that in standard Padé approximant theory in that real data, rather than the values of a mathematical function, are to be fitted. The data points are subject to experimental uncertainties so, instead of seeking an exact fit to specified points, a least-squares technique (*3*) has been used to obtain a best overall fit. In contrast to the Padé approximant case, the number of fitted parameters is normally much less than the number of data points.

Adopting the standard terminology used in the theory of Padé approximants, we say that the rational function

$$F(x) = \frac{a_0 + a_1x + \ldots + a_Mx^M}{1 + b_1x + \ldots + b_Nx^N} \tag{2}$$

is of order $[M, N]$. The special case $[M, 0]$ corresponds to a polynomial of degree M. By convention, the constant term in the denominator is taken to be equal to unity without loss of generality. There is no strict rule for selecting the optimum values of M and N for a fit with a specified number of coefficients, but in practice the best results are usually achieved with $M \simeq N$.

In order to illustrate the relative merits of linear polynomials ($N = 0$) and rational functions ($M \simeq N$) for fitting data, we have fitted various typical sets of physical data by using these two types of parameterization. In both cases the number of free parameters was increased until the fit was generally within the level of accuracy of the experimental data. The problem of finding the coefficients in a linear polynomial which give a best fit to a given set of data is straightforward, and the solution is necessarily unique. However, greater care is required in determining the least-squares coefficients for rational functions, since functional forms which are nonlinear in the parameters can lead to more than one minimum in parameter space. This difficulty can readily be overcome by inserting a reasonably accurate first approximation for the coefficients into the minimization program. The first approximation values may then be improved upon to give a best fit to the data by using one of several standard techniques which are available. The procedure described in ref 3 was used in the present work. It was found convenient to obtain the first approximation values for the coefficients by using the ν algorithm (*4*), which is described in the Appendix. This algorithm, which is sufficiently simple for computations on a hand-held calculator, generates the rational function which exactly fits a specified number of data points. If L such points are chosen, the algorithm generates a rational function of order $[(L/2), (L/2) - 1]$ for even L and $[(L - 1)/2, (L - 1)/2]$ for odd L. If these selected points are reasonably accurate and span the entire range of the independent variable under consideration, the set of coefficients obtained in this way is very useful as first approximation values for insertion in the minimization program. (Where checks were made, it was found that different sets of starting points always led to the same least-squares solution.)

The results of fitting some typical sets of physical data by using both linear polynomials and rational functions are summarized in Tables I–IV, Table I being for Henry's constant as a function of temperature for a number of systems (*6*). In each case ln H is parameterized as a function of the temperature-dependent variable β, as in eq 1, and the minimum is found for

$$\chi^2 = \sum_i (\ln H_i^{(\text{fit})} - \ln H_i^{(\text{exptl})})^2$$

where $H_i^{(\text{fit})}$ and $H_i^{(\text{exptl})}$ are the fitted and experimental values

Table II. Values of χ^2 and Also Extrapolated Values of the Critical Density Obtained from Linear Polynomial and Rational Fits to Density Data (*7*) for a Number of *n*-Alkanes[a]

				[3, 0]		[4, 0]		[2,1]	
substance	temp range, °C	critical density,[b] g/mL³	critical temp,[b] °C	density[c]	χ^2	density[c]	χ^2	density[c]	χ^2
n-hexane	−80 to +130	0.23	234.2	0.40	7.5×10^{-7}	0.36	6.4×10^{-7}	0.26	6.7×10^{-8}
n-heptane	−80 to +150	0.23	267.0	0.41	8.0×10^{-7}	0.39	1.6×10^{-7}	0.24	9.1×10^{-8}
n-octane	−50 to +150	0.23	295.6	0.42	9.0×10^{-8}	0.41	4.1×10^{-8}	0.28	9.4×10^{-9}
n-decane	−20 to +220	0.24	344.4	0.40	5.8×10^{-7}	0.37	3.6×10^{-7}	0.29	2.8×10^{-8}
n-dodecane	−10 to +250	0.24	384.55	0.40	7.4×10^{-7}	0.37	4.1×10^{-8}	0.29	3.1×10^{-8}

[a] The data are given with a tabulation precision corresponding to $\chi^2 \sim 5 \times 10^{-8}$. [b] Reference 7. [c] Extrapolated critical density, g/mL³.

Table III. Values of χ^2 Obtained from Linear Polynomial and Rational Fits for Compressibility Factor Data as a Function of Density for Ethane at a Series of Temperatures[a]

	values of $\chi^2 \times 10^8$			values of $\chi^2 \times 10^8$	
t, °C	[4, 0] fit	[2, 2] fit	t, °C	[4, 0] fit	[2, 2] fit
50	1.2×10^5	0.5×10^5	250	47	14
75	3.1×10^4	0.9×10^4	275	30	13
100	9.7×10^3	1.2×10^3	300	26	17
125	4.5×10^3	0.4×10^3	325	25	21
150	1.20×10^3	0.09×10^3	350	28	25
175	572	41			
200	147	17			
225	79	16			

[a] Reference 2. At temperatures of 175 °C and upward the χ^2 values obtained from the [2, 2] rational fit are consistent with the accuracy claimed for the data. The rational function gives a closer fit over the entire range than does the linear polynomial with the same number of coefficients, its superiority being particularly marked between 100 and 225 °C.

Table IV. Parameters in the Equation $\rho^s = (a_0 + a_1X + a_2X^2)/(1 + b_1X)$ $(X = ((T_c - T)/1000)^\beta)$ for the Saturated Gas and Liquid Densities of Ethane[a]

parameters	liquid	gas
a_0	6.801	6.801
a_1	13.733	−30.154
a_2	−2.174	34.028
b_1	−0.5763	−1.2004
β	0.33574	0.3700
T_c	305.35	
ρ_c	6.801	

[a] T is expressed in K and ρ^s in mol dm^{-3}. Data from ref 2 were fitted in the range 248–305.25 K. In constructing this table T_c and β were adjusted until a best fit was obtained to both the liquid and vapor density curves with a common value for ρ_c. The critical constants obtained are very close to, though not exactly equal to, those recorded in ref 2.

Table V. Array for Use with the ν Algorithm (See Appendix)

$$\begin{array}{llll}
\nu_1^{(1)} & & & \\
\nu_2^{(1)} & \nu_2^{(2)} & & \\
\nu_3^{(1)} & \nu_3^{(2)} & \nu_3^{(3)} & \ddots \\
\vdots & \vdots & \vdots & \\
\nu_n^{(1)} & \nu_n^{(2)} & \nu_n^{(3)} \cdots\cdots & \nu_n^{(n)}
\end{array}$$

of H at the ith data point. It can be seen from the table that the value of χ^2 for the [2, 1] rational fit (with four adjustable parameters) is comparable with, and often smaller than, the value of χ^2 for a polynomial fit with a larger number of parameters, leading to a more economical, and often more accurate, representation of the data. The superiority of the rational fit is particularly striking in the case of the H_2/C_3H_8 system.

Other examples of cases in which an economy in the number of coefficients can be achieved by the use of a rational function are provided in Table II, where saturated liquid density is fitted as a function of temperature, and in Table III, where the compressibility factor of ethane is fitted as a function of fluid density at a series of temperatures. The liquid densities in Table II were fitted over the bottom two-thirds of the full temperature range for which data were available (*7*). Usually this gave a fitted range of about 200 °C. It may be seen that the [2, 1] fit represents the data over this range to within the four-figure accuracy to which it was given. The [4, 0] fit (which involves the use of an extra coefficient) is required to achieve comparable precision by using a linear polynomial. The result of calculating a density at the critical temperature by using both the rational and linear parameterizations with coefficients obtained by fitting the data at the lower temperatures is also shown. The extrapolated density obtained from the [2, 1] fit is in every case substantially more accurate than that obtained from either of the linear polynomial fits tested. It should be pointed out that neither the rational function nor the linear polynomial in the forms given can provide an exact representation of density behavior at the critical point, since neither can exactly reproduce the critical condition ($(\mathrm{d}T/\mathrm{d}\rho^s)_{T=T_c} = 0$ for finite ρ^s (cf. Table IV)). Nevertheless the degree of approximation attainable by using a rational function is much closer. This is in accord with experience with Padé approximants; it is well-known that these can approximate the effects of various types of singularity by means of poles (*1*). In the cases analyzed in Table II a pole always occurred just above the critical temperature, with a zero close by. A fit with the correct analytical structure at the critical point can be obtained by representing ρ^s either as a rational function or as a linear polynomial in the variable $(T^c - T)^\beta$ (Table IV). However, this procedure is advantageous only when accurate data exist close to the critical point.

Table III shows the results of fitting the compressibility factor Z for ethane as a function of density (*2*) at each of a set of temperatures. It is apparent that the [2, 2] rational function

$$Z = \frac{1 + a_1\rho + a_2\rho^2}{1 + b_1\rho + b_2\rho^2}$$

gives a better fit for these data than does the linear [4, 0] polynomial with the same number of coefficients. In this context it is of interest to note that equations of state of the "Redlich-Kwong" type are of the [2, 2] form, though with restrictions on the coefficients. The familiar virial series in the density is a linear polynomial.

In conclusion, it can be claimed that some of the advantages which can result from the use of rational functions rather than linear polynomials for fitting data are apparent in the above examples. Principally these advantages are (1) the possibility of fitting data to a given degree of precision by using a smaller number of coefficients (2) greater stability of extrapolation, and (3) greater versatility in approximating diverse functional forms, including those showing singularities. Although there are some drawbacks in the use of rational functions, for example, integration and differentiation are not so straightforward, the advantages listed above suggest that the possibility of using a rational function as a possible alternative to the linear polynomial should always be considered when fitting data.

Appendix

Suppose that a function $F(\chi)$ takes the values $F_k = F(\chi_k)$ at some set of n points χ_k ($k = 1, ..., n$). The ν algorithm for constructing a rational function $R(\chi)$ which takes each of the values $R(\chi_k) = F_k$ is as follows.

We first define the quantities $\nu_k^{(1)} = F_k$ and list them as column 1 of an array (see Table V). In general, column m of the array consists of the entries $\nu_m^{(m)}$ to $\nu_n^{(m)}$, which are determined in terms of the entries of the preceding column by the recursion formula

$$\nu_k^{(m)} = \frac{\chi_k - \chi_{m-1}}{\nu_k^{(m-1)} - \nu_{m-1}^{(m-1)}}$$

Having constructed this array, and in particular having obtained the diagonal entries $\nu_1^{(1)}$ to $\nu_n^{(n)}$, we give the required rational function $R(\chi)$ by the continued fraction

$$R(\chi) = \nu_1^{(1)} + \cfrac{\chi - \chi_1}{\nu_2^{(2)} + \cfrac{\chi - \chi_2}{\nu_3^{(3)} + \ddots + \cfrac{\chi - \chi_{n-1}}{\nu_n^{(n)}}}}$$

Literature Cited

(1) Basdevant, J. L., *Fortschr. Phys.*, **20**, 283 (1972).
(2) Douslin, D. R., Harrison, R. H., *J. Chem. Thermodyn.*, **5**, 491 (1973).
(3) Fletcher, R., Powell, M. J. D., *Comput. J.*, **6**, 163 (1963).
(4) Genz, A., in "Padé Approximants", Graves-Morris, P. R., Ed., Institute of Physics, London, 1973, p 112.
(5) Ma, S. K., "Modern Theory of Critical Phenomena", W. A. Benjamin, Reading, Mass., 1976 pp 24, 25.
(6) Prausnitz, J. M., Chueh, P. L., "Computer Calculations for High-Pressure Vapor-Liquid Equilibria", Prentice-Hall, Englewood Cliffs, N.J., 1968, Appendix B and p 223.
(7) "Selected Values of Properties of Hydrocarbons and Related Compounds", API Research Project 44, Thermodynamics Research Center, Department of Chemistry, Texas A&M University, 1971.
(8) Stanley, H. E., "Introduction to Phase Transitions and Critical Phenomena", Oxford University Press, London, 1971, pp 158-163.

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Surface Tensions of Binary Liquid Mixtures of Some Polar and Nonpolar Liquids with Dimethyl Sulfoxide (Me_2SO)

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The surface tensions of binary liquid mixtures of dimethyl sulfoxide with chloroform, carbon tetrachloride, benzene, toluene, chlorobenzene, bromobenzene, and nitrobenzene have been measured at 30, 40, and 50 °C with an improved capillary-rise method. The excess surface tensions at different concentrations of these mixtures were calculated at equimolar concentrations, from surface tension data. Except for the dimethyl sulfoxide + nitrobenzene system, all other mixtures have negative excess surface tensions which indicate a strong attractive interaction in these systems. For the dimethyl sulfoxide + nitrobenzene system, excess surface tensions are positive.

Introduction

Molecular interactions in binary liquid mixtures have been studied by many workers using surface tension data (*4*, *6*, *8*). Me_2SO is a solvent of recent interest because it is highly polar (μ = 4.3 D) (*2*) which should promote strong dipole–dipole interaction. It is a solvent of medium dielectric constant ($\epsilon_{20\,^\circ\mathrm{C}}$ 48.9) (*2*) and has no significant hydrogen bonding (*5*). It is therefore a little surprising that only a few studies on surface tensions of binary liquid mixtures involving the Me_2SO as one of the two components have been reported (*1*, *9*). Clever and Sneed (*1*) studied the surface tensions of the mixtures of acetone and Me_2SO. These studies appear to be sketchy and a detailed investigation appears very desirable. It seems, therefore, fruitful to measure surface tensions of mixtures of some polar and nonpolar liquids such as chloroform, carbon tetrachloride, benzene, toluene, chlorobenzene, bromobenzene, and nitrobenzene with Me_2SO at 30, 40, and 50 °C.

Experimental Section

Me_2SO (Fluka purum) was dried over freshly ignited quicklime and was repeatedly distilled at reduced pressure until the electrical conductivity of the purified samples was reduced to $10^{-7}\ \Omega^{-1}$. The purified sample was kept in a drybox until used.

Chloroform, carbon tetrachloride, benzene, toluene, chlorobenzene, bromobenzene and nitrobenzene were purified as per standard procedures (*11*). The purity of the purified samples was checked by measuring densities, which were found to agree closely with the corresponding values given in the literature (*10*).

The solutions were made on a weight-to-weight ratio. Surface tensions of binary mixtures were measured with the help of an improved differential capillary-rise instrument shown in Figure 1. Two uniform-bore Pyrex glass capillaries of considerable different radii were fixed in a standard joint, Pyrex glass cell (specially designed for this purpose), which held the binary mixture. Uniformity of the bore of the capillary was checked by measuring the length and weight of the mercury thread in different parts of the capillary. The glass cell was filled with the binary mixture and calibrated capillaries were fixed at its mouth and the whole setup was placed in a thermostat running at the desired temperature. The variation in the temperature of the thermostat was ±0.01 in the lower and ±0.02 in the higher temperature range. The rise in the height of the liquid column in the capillaries was measured with a cathetometer (least count = 0.001 cm). The angle of contact of binary mixture and glass was taken as zero. Densities of the mixtures were measured using a calibrated dilatometer. A precaution taken to keep the solutions and solvent free from moisture as much as possible was to pass purified dry nitrogen through the empty part of the cell from time to time. The difference in the height of the liquids in two capillaries was noted and the surface tensions were calculated using the formula

$$\gamma'/\gamma = (\Delta h'/\Delta h)(\rho'/\rho)$$

where γ' is the surface tension of the binary mixtures of density ρ' and giving difference in height $\Delta h'$; γ, ρ, and Δh are the corresponding values for the Me_2SO (used as a reference liquid).

Table I. Density and Surface Tensions of Me_2SO at Various Temperatures

temp, °C	density, g/mL		surface tension, dyn/cm	
	exptl	lit. (*1*)	exptl	lit. (*1*)
30	1.0914	1.0913	42.41	42.41
40	1.0816	1.0816	41.17	41.17
50	1.0723	1.0721	40.05	40.05

Results

Accuracy of the measurements was checked by determining densities and surface tensions of Me_2SO at different temperatures. These values are compared with the literature values in Table I and are found to be in good agreement.

The surface tensions of binary liquid mixtures at 30, 40, and 50 °C are given in Table II.

Discussion

(I) Variation of Surface Tensions with Mole Fraction. From the data given in Table II, γ' vs. x_A curves were drawn. Those plots only for the dimethyl sulfoxide + carbon tetrachloride and

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