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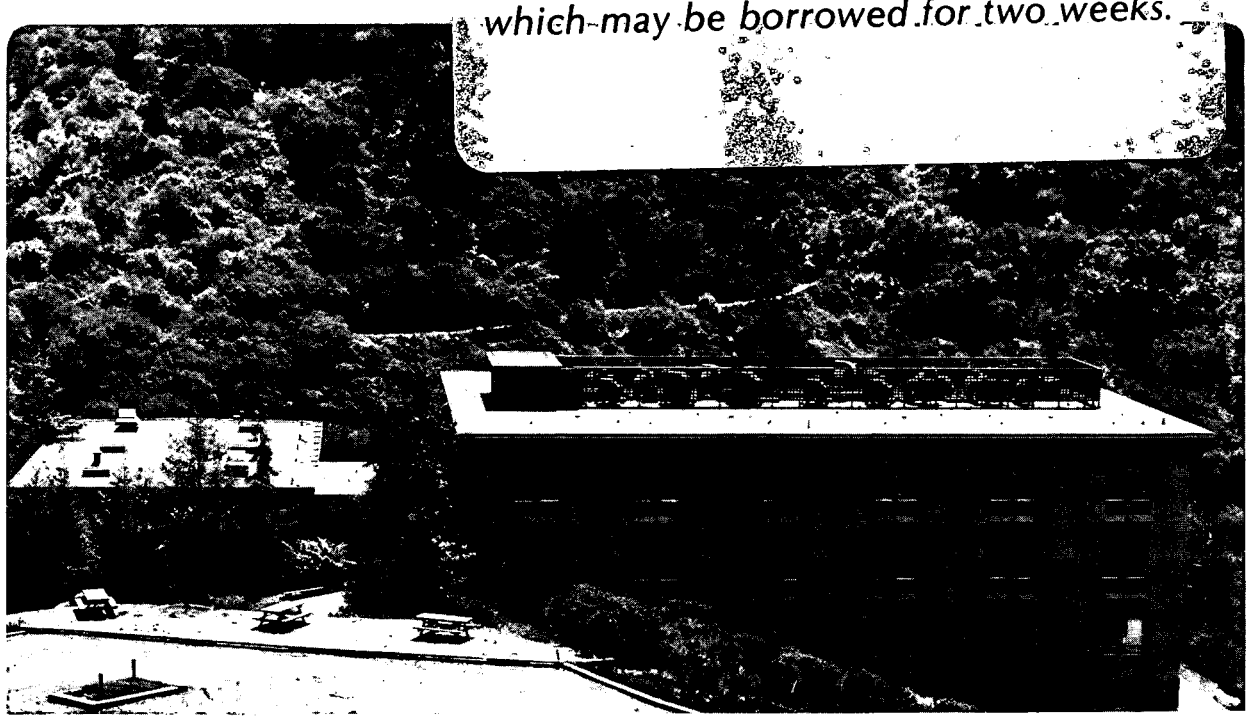

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PHASE EQUILIBRIA FOR HIGH-BOILING FOSSIL-FUEL DISTILLATES

1. CHARACTERIZATION

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ABSTRACT

An experimental procedure is described for characterizing high-boiling, distillable fossil-fuel mixtures to facilitate estimation of thermodynamic properties for process design calculations. A mixture is first separated into narrow-boiling fractions using a spinning-band column operating at low pressure and high reflux. Each fraction is considered to be a pseudocomponent of the mixture. Each pseudocomponent is characterized by structural properties per average molecule: carbon, alpha hydrogen, beta hydrogen, gamma hydrogen, hydroxyl, ether oxygen, primary amine, secondary amine, pyridinic nitrogen, and thiophenic sulfur. These structural properties are obtained from elemental analysis, proton-nuclear-magnetic-resonance spectra, infra-red spectra, and cryoscopic measurements. The proposed characterization procedure is illustrated with an Exxon-Donor-Solvent product, a Lurgi creosote, five crude-oil fractions from Belridge, California, and five crude-oil fractions from Hendrick Station, Texas. The molecular-structure properties obtained from characterization data are used to calculate equation-of-state constants as discussed in the following article.

To design processes for high-boiling fossil-fuel feed stocks, it is necessary to estimate thermodynamic properties of such feeds. Particularly important are the equilibrium ratios (K factors) as obtained from an equation of state. Typically, three or more equation-of-state constants are required for each component, as well as binary-interaction constants for each pair of components. As the number of components in a high-boiling feed is prohibitively large, it is efficient to consider the feed to be a mixture of a relatively small number of pseudocomponents. By correlating equation-of-state constants with physically significant characterization data for model compounds, it is then possible to use characterization data for pseudocomponents to obtain their equation-of-state constants. This work presents a method for obtaining such characterization data for distillable ($T_{b,atm}$ < 450°C), high-boiling, fossil-fuel liquids.

Traditional methods of characterization are now about fifty years old. These methods rely on liquid-density and boiling-point data (eg. API gravity and Watson characterization factor) which are easily measured and sufficiently informative for characterizing low-boiling paraffinic feeds; however, they are often inadequate for characterizing more complex fluids. Efforts to upgrade highly aromatic or heteroatom-rich fuels extracted from coal, shale, tar sands and petroleum residues have stimulated interest in developing better characterization procedures. For example, Brulé, et. al. (1983) reported that characterization of complex fluids is a primary problem in design of supercritical-fluid extraction of fossil-fuel feedstocks. Recently, it has been shown that novel approaches to characterizing fossil-fuels in terms of functional-group concentrations are useful for calculating properties such as heat capacities on a mass basis without proposing representative molecules (Allen, et. al., 1984; Petrakis, et. al., 1983); however, molecular size must be considered for phase-equilibrium calculations. Ruzicka, et. al. (1983) have extended the UNIFAC group-

contribution method to low-boiling fossil-fuel fractions characterized by true-boiling-point, paraffin-naphthene-aromatic analyses, and liquid densities. This method assumes that distilled fractions of the fuel are each composed of three representative model compounds: a paraffin, a naphthene, and an aromatic compound. Currently, however, published data for high-boiling compounds are insufficient to extend UNIFAC to high-boiling fuels.

Although sophisticated analytical techniques are available for obtaining detailed molecular-structure data, many of these techniques are expensive and time-consuming and require special expertise. Our purpose here is to propose an experimental characterization method that is easy to use and that requires only standard "off-the-shelf" analytical instruments.

While traditional characterization procedures have used macroscopic (bulk) properties, modern analytical methods make it possible to use microscopic (molecular-structure) properties. To reflect molecular structure, we have chosen new characterization properties for the pseudocomponents. These are (per number-average molecule): the number of carbon, aromatic hydrogen, alpha hydrogen, beta hydrogen, and gamma hydrogen atoms (as explained below in the section on proton-NMR). For heteroatom-containing feeds, we include also (per number-average molecule) the number of hydroxyl-oxygen, ether-oxygen, primary-amine, secondary-amine, pyridinic-nitrogen, and thiophenic-sulfur atoms.

To obtain these characterization properties, the feed is first fractionated by distillation to produce several narrow-boiling fractions or pseudocomponents. Each fraction is analyzed by standard combustion / gravimetric techniques to obtain its atomic composition (wt%). In addition, proton-NMR spectroscopy is used to obtain the hydrogen distribution of each fraction. If the oxygen or nitrogen content of a fraction is significant, IR spectroscopy is used

to measure hydroxyl and amine concentrations per mass of fraction. The above data are then used to estimate the aromaticity of each pseudocomponent. Aromaticity and a representative boiling point (obtained during fractionation) are used to provide a preliminary estimate of the molecular weight of the fraction. This estimate is used to prepare dilute solutions of each fraction in nitrobenzene for molecular-weight measurement by cryoscopy. After obtaining the number-average molecular weight, the experimental data are used to calculate the characterization properties of each pseudocomponent.

When the single-pseudocomponent assumption is inadequate for accurate design calculations for systems involving the characterized fraction, a further step may be useful. Rather than characterizing a larger number of narrower-boiling fractions, "true-boiling-point" distributions, obtained from distillation or gas chromatography, are used to estimate the molecular-size distribution within each fraction. These data are then used to describe a set of "micro-pseudocomponents" which have the same relative structure as the pseudocomponent, but differ in size. The number of micro-components is chosen as necessary to achieve the optimum balance between accuracy and computing cost.

The following sections give details of these techniques including illustrative results for several fossil-fuel fractions.

FRACTIONATION AND VAPOR-PRESSURE MEASUREMENT

The fossil-fuel liquid is fractionated in a Perkin-Elmer Model 251 Annular Still shown in Figure 1. The still has been slightly modified: the head thermowell was replaced with a septum through which a 1.59 mm (1/16-inch) diameter, monel-sheathed copper-constantan thermocouple (not shown) was inserted into the head for accurate temperature measurement. Although only one receiver is shown in Figure 1, the apparatus has four 25-ml receiver tubes so that four fractions can be taken before vacuum is broken. Both a digital temperature comparator and a liquid-level controller are used to terminate collection of each fraction automatically upon exceeding a set head temperature or a set liquid level in the receiver. Heated condenser water and an infrared lamp maintain the head of the column at an elevated temperature to reduce distillate viscosity and to facilitate collection of the fractions.

A preliminary distillation is used to prepare a plot of distillate volume as a function of head temperature. This plot is used to estimate the required charge and the boiling-point cutoff temperatures for fractionation. Subsequent characterization experiments require only about 225 mg of each fraction.

After charging the pot for fractionation, the column is purged with nitrogen and evacuated to 67 millibar (50 torr), allowing operation of the still at temperatures sufficiently low to inhibit thermal decomposition, yet sufficiently high to prevent solidification of anthracene in the condenser. To protect the silicone seals in the still head, the maximum head temperature is limited to 250°C. The pot temperature is limited to 300°C by the Kalrez® (Du Pont registered trademark) O-ring used to seal the pot to the column. Typically, eight samples (boiling-range about 20°C) are collected with a boil-up rate of approximately 30 μl of liquid per second and a reflux ratio of 10:1. After collection, each fraction is stored under nitrogen in a sealed container and refri-

gerated.

A representative boiling point is useful for estimating molecular weight and for developing accurate vapor-pressure correlations for the pseudocomponents; therefore, the head temperature and pressure are recorded at the beginning and at the end of fraction collection. Rather than separately measuring a bubble point for the fraction, the arithmetic average of the initial and final head temperatures at the arithmetic average of the corresponding head pressures is used as the representative boiling point for the fraction. Table 1 shows measurements of the initial, final, and average temperatures and pressures for fractions from an Exxon-Donor-Solvent sample, from a Lurgi-Creosote sample, from five crude-oil fractions from Belridge, California, and from five pipeline-mix crude-oil fractions from Hendrick Station, Texas. The crude-oil fractions were prepared by Chevron Research Co. using a packed column operated at 1.01 bar for the first fraction in both sets, 67 millibar (50 torr) for the second and third cuts, and 1.3 millibar (1 torr) (unpacked) for the fourth and fifth cuts. Actual distillation data were not available; however, the estimated initial and final normal boiling points, obtained by the Maxwell-Bonnell method (Maxwell and Bonnell, 1957), were provided. Fraction 8 of the Exxon-Donor-Solvent sample and fraction 5 of the Lurgi-Creosote sample are non-distillable residues.

ELEMENTAL ANALYSIS

Analyses for weight percents of hydrogen, carbon and nitrogen are obtained using a Perkin-Elmer 240 Analyzer. Weight percent sulfur is determined by the Grote combustion method and, assuming that the only other heteroatom is oxygen, weight percent oxygen is found by mass balance. Only 3 mg of sample are required for elemental analysis.

Table 2 shows elemental analyses for the previously indicated fractions.

PROTON-NMR SPECTROSCOPY

A proton-NMR spectrum was obtained for each fossil-fuel fraction using a Varian EM 390-NMR spectrometer operating at 90 MHz. Samples were prepared by syringing 25 μl of hexamethyldisiloxane (HMDS), 50 μl of fraction, and 400 μl of D_5-pyridine into a preweighed 2-mm NMR tube. The weight of each fluid added was determined by difference. The tube was sealed with a polyethylene cap to limit evaporation, water contamination, and oxidation. The tube was repeatedly inverted until the solution was homogeneous. To achieve homogeneity for very viscous fractions, it was necessary to sonicate the tube briefly by immersing it in a warm-water bath agitated by ultrasonic waves. A blank sample containing no fossil fuel was also prepared to quantify background absorption due to small amounts of non-deuterated pyridine in the solvent.

Proton-NMR spectrometry gives the hydrogen-atom distribution for a fossil-fuel fraction. Figure 2 shows a typical NMR spectrum. The electronic environment of each hydrogen atom determines its resonance frequency, commonly expressed as a relative shift from the resonance frequency of tetramethylsilane (TMS); for example, the hydrogen atoms in hexamethyldisiloxane (HMDS), used as an internal reference, resonate at 0.02 δ_{TMS}.

In complex hydrocarbon mixtures, proton-NMR measurements can be used to distinguish four types of hydrogen atoms (Clutter, et. al., 1972). These are listed below with their corresponding resonance-frequency ranges:

(1) H_{aro} = hydrogen attached to an aromatic carbon ($6.0 - 9.0\ \delta_{TMS}$)

(2) H_{α} = hydrogen attached to an aliphatic carbon which is alpha to an aromatic carbon ($1.7 - 4.0\ \delta_{TMS}$)

(3) H_{β} = hydrogen attached to non-alpha, non-terminal, aliphatic carbon ($0.9 - 1.7\ \delta_{TMS}$)

(4) H_{γ} = hydrogen attached to non-alpha, terminal, aliphatic carbon ($0.5 - 0.9\ \delta_{TMS}$)

The number of hydrogen atoms of a given type in the sample is proportional to the integral of the absorption over the corresponding resonance-frequency range. As the proportionality constant is independent of frequency, the corresponding integrals ($I_{H\alpha}$, $I_{H\beta}$, $I_{H\gamma}$, and I_{Haro}) can be used to calculate the hydrogen distribution for each fraction.

The hydrogen atoms of pyridine resonate in the region attributed to H_{aro}; therefore, deuterated pyridine is used as the solvent. However, since D_5-pyridine reacts slowly with atmospheric water to form trace quantities of non-deuterated pyridine, a background correction is required. The spectrum of the blank sample gives the peak area for pyridine in the solvent ($I_{pyridine}$) relative to that of HMDS (I_{HMDS}). The corrected peak area (I^{*}_{Haro}) is calculated from:

$$I^{*}_{Haro} = I_{Haro} - \left[\frac{I_{HMDS}}{m_{HMDS}}\right]_{sample} \left[\frac{(I/m)_{pyridine}}{(I/m)_{HMDS}}\right]_{blank} \quad (1)$$

where I is the NMR-spectrum peak area corresponding to a specific type of hydrogen atom and m is the mass of the fluid in the NMR tube.

For each of the four types of hydrogen atoms, the fraction of carbon-bonded hydrogen of type j is given by

$$F_j = \frac{I_j}{I_{Ht}} \quad (2)$$

where I_{Ht} is the sum of the integrals due to carbon-bonded hydrogen

$$I_{Ht} = I^{*}_{Haro} + I_{H\alpha} + I_{H\beta} + I_{H\gamma} \quad (3)$$

Parameters $I_{H\alpha}$, $I_{H\beta}$, and $I_{H\gamma}$ are given by the areas under the corresponding proton-NMR peaks.

INFRARED SPECTROSCOPY FOR HYDROXYLS AND AMINES

Infrared spectroscopy is used to measure the concentration of hydroxyl (OH), primary-amine (NH_2), and secondary-amine (NH) groups per gram of pseudocomponent. For each fraction, IR transmission spectra were obtained with a Perkin-Elmer Model 1430 IR spectrophotometer. Two matched quartz cells with optical path lengths of 2 mm were used. A solution of pseudocomponent in methylene chloride was placed in the sample cell, and pure methylene chloride was placed in the reference cell. IR transmittance was measured at the peaks near 3585 (OH), 3465 (NH and NH_2), and 3390 (NH_2) cm^{-1}. Each measurement was corrected for baseline absorption arising from small differences in IR transmittance through the cells. The solutions were sufficiently dilute to neglect the effect on transmittance due to the reduced concentration of the solvent in the sample cell.

For each functional group (OH, NH, NH_2), the Lambert-Beer law is used to determine concentrations from IR absorbance due to a given species:

$$A = a\,b\,c \tag{4}$$

where A is absorbance ($A = -\log_{10}$ transmittance), a is molar absorptivity (liter–mole^{-1}–mm^{-1}), b is path length (mm), and c is functional-group concentration (mole/liter). Absorbances due to OH and NH_2 groups are obtained directly from the corrected transmittances at 3585 and 3390 cm^{-1}, respectively. The absorbance at 3465 cm^{-1} due to the NH group is calculated by correcting for the overlap of the NH_2 peak at 3465 cm^{-1}.

The calibration functions for each functional group were obtained by measuring the absorbances of pure compounds containing these groups. Figure 3 shows absorbance as a function of concentration for each pure compound. In each case the Lambert-Beer law is obeyed over the concentration range studied.

Five compounds were used to relate the concentration of OH to its absorbance:

$$[OH] = 0.0372\ A_{3585}\ (\pm 4\%\ \text{at}\ 95\%\ \text{c.l.}) \tag{5}$$

where [OH] is concentration in moles/liter and A_{3585} is the peak-height absorbance near 3585 cm^{-1}.

Eight pure compounds containing the NH_2 group were used to obtain

$$[NH_2] = 0.1011\ A_{3390}\ (\pm 21\%\ \text{at}\ 95\%\ \text{c.l.}) \tag{6}$$

The large error in this function follows from the variation of extinction coefficients of the pure compounds. This is reflected in Figure 3 by the different slopes of the NH_2-containing compounds.

NH_2 also has an asymetrical deformation near 3465 cm^{-1}. This directly overlaps with the NH absorbance band. To correct for the overlap, the mean ratio of NH_2 absorbance at 3465 to that at 3390 cm^{-1} was calculated as 0.54 for the eight primary amines studied. Since the absorbances are additive, the absorbance at 3465 cm^{-1} due to NH can be determined by difference.

The calibration function for NH concentration is

$$[NH] = 0.0233\ A_{3465}\ (\pm 7\%\ \text{at}\ 95\%\ \text{c.l.}) \tag{7}$$

where A_{3465} is the peak-height absorbance due to NH corrected for the NH_2 overlap. Three compounds were used to obtain Equation 7.

Although the Lambert-Beer law holds for each group over the concentration range used, higher concentrations than those shown in Figure 3 may cause deviations from ideality. If an IR analysis indicates that the concentration of OH, NH, or NH_2 is above the calibrated range, a more dilute solution must be prepared and the analysis repeated. To reduce the need for repeated analyses,

elemental-analysis data are used to prepare samples with appropriate concentrations for IR measurements. (To calculate the appropriate concentrations, we assume that all oxygen atoms are hydroxyl and that all nitrogen atoms are in secondary amines.)

For each heteroatomic group i, the number of moles of i per gram of pseudocomponent is given by

$$(ha)_i = \frac{A_i}{a_i \, b \, c_F'} \tag{8}$$

where c_F' is the concentration (in grams per unit volume) of the fraction in methylene chloride.

CALCULATION OF ETHER-, PYRIDINE-, AND THIOPHENE-GROUP CONCENTRATIONS

The concentrations of ether oxygens, thiophenic sulfurs, and pyridinic nitrogens were determined by mass balance, assuming:

(1) All sulfur is in thiophenic form.

(2) All nitrogen is in primary-amine, secondary-amine or pyridinic form.

(3) All oxygen is in ether or hydroxyl form.

From these assumptions, the number of moles of oxygen, nitrogen, and sulfur atoms per gram of fraction is found from

$$(ha)_i = \frac{w_i}{(AW)_i} \tag{9}$$

where w_i is the weight fraction of heteroatom i in the fraction and $(AW)_i$ is the

atomic mass of heteroatom i. Next, $(ha)_i$ for ether oxygens and for pyridinic nitrogens is found by atom balance:

$$(ha)_{Np} = (ha)_N - (ha)_{NH} - (ha)_{NH2} \tag{10}$$

$$(ha)_{Oe} = (ha)_O - (ha)_{OH} \tag{11}$$

If Assumption (2) is not suitable, a non-aqueous potentiometric titration (Koros, et. al., 1967) may be used to obtain more detailed quantitative analysis of pyridinic compounds.

ESTIMATION OF AROMATICITY

Aromaticity is the fraction of carbon atoms which are in aromatic rings; it is used to obtain a first estimate of the molecular weight of the fraction for use in molecular-weight measurements. Aromaticity is estimated using data obtained from elemental analysis, proton-NMR, and IR:

$$FA = \frac{n_{Caro}}{n_{Ct}} \tag{12}$$

$$= 1 - \frac{n_{Cali}}{n_{Ct}} \tag{13}$$

$$= 1 - \left[\frac{n_{Hc}}{n_{Ct}}\right]\left[\frac{n_{C\alpha} + n_{C\beta} + n_{C\gamma}}{n_{Hc}}\right] \tag{14}$$

$$= 1 - \left\{\frac{n_{Hc}}{n_{Ct}}\right\}\left\{\left[\frac{n_{C\alpha}}{n_{H\alpha}}\right]\left[F_{H\alpha}\right] + \left[\frac{n_{C\beta}}{n_{H\beta}}\right]\left[F_{H\beta}\right] + \left[\frac{n_{C\gamma}}{n_{H\gamma}}\right]\left[F_{H\gamma}\right]\right\} \tag{15}$$

where FA is the aromaticity, F_j is the fraction of carbon-bonded hydrogen atoms which are of type j, n_{Hc} is the total number of atoms of carbon-bonded hydrogen per molecule and n_{Ct} is the total number of atoms of carbon per molecule. The factor n_{Hc}/n_{Ct} is obtained using

$$n_{Hc}/n_{Ct} = (n_{Ht}/n_{Ct})\,(n_{Hc}/n_{Ht}) \tag{16}$$

where

$$(n_{Ht}/n_{Ct}) = (w_H/w_C)\,[(AW)_C/(AW)_H] \tag{17}$$

and where

$$n_{Hc}/n_{Ht} = 1 - \frac{(ha)_{OH} + (ha)_{NH} + 2\,(ha)_{NH2}}{w_H/(AW)_H} \tag{18}$$

Several structural assumptions are required to estimate the ratios $(n_{C\alpha}/n_{H\alpha})$, $(n_{C\beta}/n_{H\beta})$, and $(n_{C\gamma}/n_{H\gamma})$. For petroleum fractions, the following assumptions are reasonable:

(1) Few heteroatoms are present.

(2) Few alpha carbons are terminal.

(3) Few branches are at aliphatic carbons.

(4) Few olefins are present.

With these assumptions,

$$(n_{C\alpha}/n_{H\alpha}) = 1/2 \tag{19}$$
$$(n_{C\beta}/n_{H\beta}) = 1/2 \tag{20}$$
$$(n_{C\gamma}/n_{H\gamma}) = 1/3 \tag{21}$$

Therefore,

$$FA = 1 - \left[\frac{n_{Hc}}{n_{Ct}}\right]\left[\frac{F_{H\alpha} + F_{H\beta}}{2} + \frac{F_{H\gamma}}{3}\right] \tag{22}$$

with the restriction:

$$FA \geq 0 \tag{23}$$

Integrals $I_{H\alpha}$, $I_{H\beta}$, $I_{H\gamma}$, and I_{Haro} are given by the areas under the corresponding proton-NMR peaks.

While the previous assumptions are reasonable for petroleum, they may not accurately describe liquids from coal-gasification processes. For such severely cracked, highly aromatic fractions, many alpha carbons are terminal due to beta-scission. For such fractions, Equation 19 should be replaced by:

$$(n_{C\alpha} / n_{H\alpha}) = 1/3 \tag{24}$$

When other assumptions are more appropriate, corresponding values for $(n_{C\alpha} / n_{H\alpha})$, $(n_{C\beta} / n_{H\beta})$, and $(n_{C\gamma} / n_{H\gamma})$ should be used.

Table 3 gives hydrogen-atom distributions and estimated aromaticities using Equation 24 for the coal-liquid fractions and using Equation 19 for the petroleum fractions.

MOLECULAR-WEIGHT MEASUREMENT

For each fraction, the number-average molecular weight is determined by freezing-point-depression (FPD) measurements using a Precision-Systems, Automatic, High-Sensitivity Cryette with nitrobenzene as solvent.

The accuracy of the FPD measurement is a function of solute concentration in nitrobenzene solution. At extremely low concentrations, the resolution of the instrument limits accuracy. However, high concentrations violate the assumption of solution ideality. Thus, an optimum concentration range exists for molecular-weight determinations.

The optimum concentration range was determined by measuring the molecular weights of pure compounds and those of known mixtures of pure compounds at a variety of concentrations, as indicated in Figure 4. The

optimum concentration range lies between 0.04 and 0.07 molal.

For any fraction, approximate values for aromaticity and normal boiling point provide an estimate of the optimum solution concentration, as shown in Figure 5 (Macknick, 1979). The normal boiling temperature of a fraction is estimated by adding 100°C to the average saturation temperature at 67 millibar (50 torr). This rough estimate is sufficient for preparing the solution.

Sample solutions of optimum concentration are prepared by dissolving a known weight of sample (estimated from Figure 5) in 25 ml of nitrobenzene. As consistent sample volume is essential, a precision pipet is used to place 2.500 ml of the sample solution in the FPD sample tube. The sample is then subcooled one degree Celsius below the freezing point of nitrobenzene (5.76°C). After seeding the solution by vibration, the freezing-point depression of the sample solution is measured with a platinum-resistance thermometer, previously calibrated with standard solutions of pyrene in nitrobenzene.

For dilute solutions, number-average molecular weight is calculated by:

$$(MW)_F = \frac{m_F K_f}{m_{NB} (T_{NB} - T_{soln})} \tag{25}$$

where $(MW)_F$ = Number-average molecular weight of fossil-fuel fraction (g/mole)

m_{NB} = Mass of nitrobenzene (kg)

m_F = Mass of fossil-fuel fraction (g)

K_f = Freezing-point depression constant for nitrobenzene (6.852°C-kg/mole)

T_{NB} = Freezing point of nitrobenzene (5.76°C)

T_{soln} = Freezing point of solution (°C)

An initial calibration of the cryette thermister is made using pure nitrobenzene and a dilute solution of known concentration of pyrene in nitrobenzene. After this initial zero and gain adjustment, the effective T_{NB} is determined by averaging the apparent FPD of pure nitrobenzene samples. An effective K_f is given by the arithmetic mean of the K_f's calculated from Equation 25 using the measured FPD's of six standard pyrene solutions spanning the optimum concentration range. The effective T_{NB} and K_f are used to calculate the molecular weights of unknown solutions. In a typical experiment, the standard deviation of the effective K_f was 0.272°C–kg/mole. This standard deviation provides an estimate of the accuracy of our molecular-weight measurements (about ±10% at 95% confidence limits).

Molecular-weight measurements may be distorted by association of the solute molecules under some conditions (Moschopedis, et. al., 1976; Schwagar, et. al., 1977; Sharma, et. al., 1983); however, this is not important in sufficiently dilute solutions (Speight and Moschopedis, 1977). Within the optimum concentration range used here, association is not significant even for large, polar molecules dissolved in nitrobenzene. Table 4 gives examples of molecular-weight determinations for synthetic solutions. The measurements are all within the expected accuracy.

Table 5 gives number-average molecular-weight measurements for the previously indicated fractions.

CALCULATION OF NUMBER-AVERAGE MOLECULAR STRUCTURAL PROPERTIES

The measured molecular weight is used to normalize the other data to a per-average-molecule basis, yielding the number of carbon atoms per molecule, the number of each type of hydrogen atom per molecule, and the number of each type of heteroatomic group per molecule $(HA)_i$.

Tables 5 and 6 give molecular-structure properties for the previously indicated fractions.

Each pseudocomponent is a mixture of real components. When the fossil-fuel fraction is partially vaporized, the compositions of the vapor phase and the liquid phase are not identical, nor is either equal to that of the whole fraction. In contrast to pure compounds, the average molecular structure in each phase is different from that of the unseparated fraction. Therefore, it is not correct to apply the overall characterization of the unseparated fraction to the partially vaporized or partially condensed portion of that fraction. The error is small for narrow-boiling fractions, but it may be appreciable when the boiling range exceeds (about) 10°C. Clearly, the error may be reduced by characterizing a larger number of narrower-boiling fractions.

Alternatively, however, relatively wide-boiling, characterized fractions may be analyzed further to obtain "true-boiling-point" (TBP) data. TBP data may be obtained by distillation (ASTM-86) or by gas chromatography, as discussed by O'Donnell (1973), Gouw, et. al. (1967), Green, et. al. (1964), and Petrocelli, et. al. (1964). The Appendix gives some details on the use of gas chromatography to obtain TBP data in the form of carbon-number distributions for fossil-fuel distillates. Carbon-number distributions are used to characterize a set of hypothetical, narrow-boiling "microfractions" which constitute each fraction. This characterization is made by assuming that for each microfraction, the characterization properties (i.e., number of carbon atoms, each type of

hydrogen atom, and each type of heteroatom per molecule) are proportional to those of its parent-fraction. The proportionality constant is assumed to be the ratio of the average number of carbon atoms per molecule in the microfraction to the average number of carbon atoms per molecule in the macrofraction. When a more detailed description of the fuel is desired, characterizing microfractions is likely to be simpler than preparing and characterizing a large number of narrower-boiling macrofractions. Carbon-distributions are desirable for those macrofractions that are too wide-boiling to be treated accurately as single pseudocomponents.

CONCLUSIONS

While classical methods for characterizing fossil-fuel feed stocks are simple and fast, they may not be adequate for those feeds which are highly aromatic or, perhaps, rich in heteroatoms. On the other hand, sophisticated analytical techniques are expensive, slow, and require experienced personnel. The characterization procedure presented here is a compromise suitable for engineering work. Using standard, "off-the-shelf" analytical instruments, a high-boiling but distillable fossil fuel is first fractionated into about eight narrow-boiling fractions, considered to be pseudocomponents of the fuel. Then, for each fraction, measurements are made of one vapor-pressure datum (from distillation), elemental composition (from combustion / gravimetric analyses), hydrogen distribution (from proton-NMR), hydroxyl and amine concentrations (from IR), and number-average molecular weight (from cryoscopy). To illustrate, characterization data are given for an Exxon-Donor-Solvent sample, a Lurgi-Creosote sample, a Belridge-Crude-Oil sample, and a Hendrick-Station-Pipeline-Mix sample.

Since only standard analytical instruments are used, and since all experimental work is relatively simple, the characterization procedure described here

is suitable for routine engineering applications. Characterization properties of the pseudomolecules representing the fractions can be calculated from the data obtained using this procedure. The following paper shows that, using correlations obtained from experimental data for model compounds, it is possible to use the characterization properties proposed here to calculate equation-of-state constants. These constants may then be used to calculate phase equilibria for systems containing high-boiling fossil-fuels that include aromatic or heteroatom-rich components in addition to more common paraffins.

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NOMENCLATURE

A = absorbance

a = absorptivity

AW = atomic weight

b = optical path length

C = average number of carbon atoms per molecule

c = molar concentration

c′ = mass concentration

c.l. = confidence limit

F_j = fraction of carbon-bonded hydrogen atoms which are of type j

FA = moles of aromatic carbon atoms per mole of carbon atoms (aromaticity)

$(HA)_i$ = moles of heteroatomic group i per number-average mole of fossil-fuel fraction (heteroatomicity)

$(ha)_i$ = moles of heteroatomic group i per gram of fossil-fuel fraction (heteroatomicity)

I_j = area of proton-NMR peak due to hydrogen atoms of type j

k = number of carbon atoms per molecule of n-alkane

K_f = freezing-point depression constant

m = mass

n = number of moles

MW = number-average molecular weight

P = pressure

T = temperature

V = volume

w = mass fraction

Subscripts

aro = aromatic hydrogen atoms

b = boiling-point

blank = blank proton-NMR sample

C = carbon atoms

c = carbon-bonded

Cali = aliphatic carbon atoms

Caro = aromatic carbon atoms

Ct = total carbon atoms

$C\alpha$ = aliphatic carbon atoms directly bonded to aromatic ring

$C\beta$ = non-alpha, non-terminal aliphatic carbon atoms

$C\gamma$ = non-alpha, terminal aliphatic carbon atoms

est = estimated

F = fossil-fuel fraction

H = hydrogen atoms

Hali = aliphatic hydrogen atoms

Haro = aromatic hydrogen atoms

Hc = carbon-bonded hydrogen atoms

Ht = total hydrogen atoms

$H\alpha$ = hydrogen atoms attached to $C\alpha$

$H\beta$ = hydrogen atoms attached to $C\beta$

$H\gamma$ = hydrogen atoms attached to $C\gamma$

HMDS = hexamethyldisiloxane

i = heteroatom-containing functional group i

j = hydrogen-atom type j

max = maximum

N = nitrogen atoms

Np = pyridinic nitrogen atoms

NB = nitrobenzene

NH = secondary amine functional groups

NH2 = primary amine functional groups

O = oxygen atoms

Oe = ether functional groups

OH = hydroxyl functional groups

S = sulfur atoms

sample = proton-NMR sample containing fraction

soln = solution

t = total

TMS = tetramethylsilane

Superscripts

* = corrected for background absorption due to trace pyridine in proton-NMR solvent

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APPENDIX: CARBON-NUMBER-DISTRIBUTION DETERMINATION

For some of the fractions studied here, a carbon-number distribution was determined from a simulated "true-boiling-point" separation via gas chromatography. This distribution can be used to characterize relatively wide-boiling fractions in terms of a greater number of narrow-boiling pseudocomponents or, alternately, it may be used to fit a statistical model of the fraction as described by Cotterman, et. al. (1984). A Varian Model 3700 gas chromatograph with an OV-101-coated, glass-capillary column and a flame-ionization detector was used to obtain the distribution. One minute after injecting a 1 μl sample of the oil, the column was heated from 80°C to 250°C at 7°C/min. Carbon-atom concentrations were measured at 0.02-sec intervals and integrated by an online, Commodore Model 8032 microcomputer. The resulting data give an estimate of the mass percent of fraction as a function of retention time. Normal-alkane reference compounds were used to relate retention time to n-alkane carbon number. Next, the data were used to calculate mole percent of fraction eluting between n-alkanes of carbon number k-1 and k (excluding the former but including the latter). The carbon number associated with each range was estimated as that of the n-alkane having a retention time equal to the mean retention time of compounds integrated within the interval. The mean carbon number per average molecule (determined by molecular-weight and elemental analyses) was then used to normalize the carbon numbers associated with the intervals. The number of each type of hydrogen atom and heteroatom associated with each interval was estimated as the number of each type of hydrogen atom and heteroatom in the bulk fraction (as determined from

characterization data) multiplied by the ratio of the normalized carbon number associated with the interval to the mean carbon number per average molecule. The number of carbons, hydrogens, and heteroatoms associated with each interval characterize a "micro-component". These micro-components can be lumped as necessary to achieve the desired resolution of characterization.

Tables 7 and 8 give distribution data, obtained in this manner, for four Belridge (California) crude-oil fractions and four Hendrick-Station (Texas) pipeline-mix oil fractions.

TABLE 1

DISTILLATION DATA FOR FOSSIL-FUEL FRACTIONS

Sample	Fraction	Initial Boiling P (torr)	Initial Boiling T (°C)	Final Boiling P (torr)	Final Boiling T (°C)	P^s (torr)	T^s (°C)
Exxon	1	51.4	106.2	50.9	126.1	51.1	116.2
Donor	2	50.9	126.1	52.3	142.0	51.6	134.0
Solvent	3	52.3	142.0	52.0	159.8	52.2	150.9
Process	4	52.0	159.8	51.3	182.4	51.6	171.1
Product	5	51.3	182.4	51.1	201.0	51.2	191.7
	6	51.1	201.0	52.9	223.6	52.0	212.3
	7	52.9	223.6	52.3	243.6	52.6	233.6
	8	52.3	243.6	----	----	----	----
Lurgi	1	52.4	180.0	51.5	198.0	51.9	189.0
Creosote	2	52.0	194.6	51.5	211.1	51.8	202.9
	3	50.6	208.2	50.9	233.6	50.8	220.9
	4	48.9	224.8	49.0	243.6	48.9	234.2
	5	49.1	239.0	----	----	----	----
Belridge	1	760	149	760	205	760	177
Crude Oil	2	760	205	760	260	760	232
	3	760	260	760	344	760	302
	4	760	344	760	432	760	388
	5	760	432	760	538	760	485
Hendrick	1	760	149	760	205	760	177
Station	2	760	205	760	260	760	232
Pipeline	3	760	260	760	344	760	302
Mix	4	760	344	760	441	760	392
	5	760	441	760	538	760	489

P^s = Saturation Pressure (linear average)

T^s = Saturation Temperature (linear average)

TABLE 2

ELEMENTAL COMPOSITION OF FOSSIL-FUEL FRACTIONS

Sample	Fraction	Wt% C	Wt% H	Wt% N	Wt% S	Wt% O*	Molar H/C
Exxon	1	88.60	10.26	0.09	0.08	0.97	1.380
Donor	2	88.37	10.57	0.16	0.03	0.87	1.425
Solvent	3	88.74	10.48	0.20	0.05	0.53	1.407
Process	4	89.03	10.46	0.21	0.05	0.25	1.400
Product	5	88.60	10.14	0.30	0.03	0.93	1.364
	6	89.46	9.19	0.21	0.00	1.13	1.229
	7	89.14	9.41	0.36	0.02	1.07	1.258
	8	89.37	8.59	0.71	0.04	1.29	1.145
Lurgi	1	86.57	8.24	1.11	0.29	3.79	1.134
Creosote	2	86.73	8.47	1.01	0.48	3.31	1.075
	3	88.38	8.18	1.01	0.37	2.06	0.992
	4	86.17	8.46	1.40	0.31	3.66	0.992
	5	86.45	8.13	1.42	0.27	3.73	0.992
Belridge	1	86.30	13.50	0.00	0.13	0.07	1.864
Crude Oil	2	86.59	12.68	0.01	0.72	0.00	1.744
	3	86.58	12.13	0.08	0.79	0.42	1.669
	4	86.41	11.62	0.38	0.78	0.81	1.603
	5	86.37	11.64	0.60	0.89	0.50	1.606
hendrick	1	85.81	13.26	0.02	0.53	0.38	1.841
Station	2	86.23	13.30	0.00	0.47	0.00	1.838
Pipeline	3	85.81	12.58	0.00	1.61	0.00	1.747
Mix	4	85.67	12.26	0.04	1.66	0.37	1.705
	5	85.79	11.55	0.10	1.62	0.94	1.604

* Obtained by difference

TABLE 3

HYDROGEN-ATOM DISTRIBUTIONS AND AROMATICITY
FOR FOSSIL-FUEL FRACTIONS

Sample	Fraction	F_α	F_β	F_γ	F_{aro}	Aromaticity
Lurgi	1	0.306	0.265	0.087	0.342	0.649
Creosote	2	0.301	0.278	0.089	0.332	0.633
	3	0.256	0.276	0.087	0.381	0.676
	4	0.258	0.335	0.091	0.316	0.619
	5	0.266	0.342	0.088	0.304	0.632
Donor	2	0.248	0.385	0.185	0.182	0.460
Solvent	3	0.242	0.405	0.167	0.186	0.465
Process	4	0.261	0.411	0.150	0.178	0.458
Product	5	0.235	0.400	0.159	0.206	0.493
	6	0.266	0.314	0.164	0.256	0.574
	7	0.289	0.348	0.146	0.217	0.538
	8	0.265	0.324	0.121	0.290	0.618
Belridge	1	0.091	0.473	0.396	0.040	0.226
Crude	2	0.095	0.474	0.382	0.049	0.277
Oil	3	0.145	0.489	0.310	0.056	0.300
	4	0.152	0.500	0.296	0.052	0.322
	5	0.166	0.538	0.247	0.049	0.304
Hendrick	1	0.102	0.479	0.368	0.051	0.236
Station	2	0.085	0.534	0.334	0.047	0.230
Pipeline	3	0.082	0.540	0.328	0.050	0.266
Mix	4	0.177	0.574	0.199	0.050	0.246
	5	0.152	0.560	0.229	0.059	0.306

F_α = Number of alpha hydrogen atoms per total number of carbon-bonded hydrogen atoms (PCBH)

F_β = Number of beta hydrogen atoms (PCBH)

F_γ = Number of gamma hydrogen atoms (PCBH)

F_{aro} = Number of aromatic hydrogen atoms (PCBH)

Aromaticity = Number of aromatic carbon atoms per total carbon atoms

TABLE 4

FREEZING-POINT-DEPRESSION MEASUREMENTS
FOR SOLUTIONS OF MODEL COMPOUNDS IN NITROBENZENE

Solute	Wt %	Molecular Weight	
		Calculated	Measured
Pyrene	0.836	202.26	197
	1.258		200
Hexadexane	1.160	226.45	229
	1.337		228
Anthracene	0.522	206.9	199
Hexadecane	0.280		
Hexadecane	0.386	177.8	179
Quinaldine	0.137		
2-Naphthol	0.207		
Hexadecane	0.490	184.6	188
Quinaldine	0.143		
2-Naphthol	0.175		
Hexadecane	0.598	180.3	183
Quinaldine	0.242		
2-Naphthol	0.237		

TABLE 5

STRUCTURAL DATA FOR FOSSIL-FUEL FRACTIONS:
CARBON AND HYDROGEN ATOMS PER AVERAGE MOLECULE
AND MOLECULAR WEIGHT

Sample	Fraction	C	H_α	H_β	H_γ	H_{aro}	MW
Lurgi	1	13.5	4.6	4.0	1.3	5.2	187
Creosote	2	15.0	5.2	4.8	1.5	5.8	208
	3	15.3	4.3	4.6	1.5	6.4	208
	4	16.3	4.9	6.4	1.7	6.0	227
	5	22.0	6.5	8.3	2.1	7.4	305
Exxon	1	9.8	3.3	4.6	2.3	3.3	133
Donor	2	10.7	3.8	5.9	2.8	2.8	146
Solvent	3	11.4	3.9	6.5	2.7	3.0	154
Process	4	12.2	4.5	7.0	2.6	3.0	165
Product	5	12.8	4.1	7.0	2.8	3.6	174
	6	13.7	4.5	5.3	2.8	4.3	184
	7	14.0	5.1	6.1	2.6	3.8	189
	8	17.3	5.2	6.4	2.4	5.7	232
Belridge	1	10.6	1.8	9.4	7.8	0.8	148
Crude	2	13.6	2.3	11.3	9.1	1.2	189
Oil	3	17.7	4.3	14.4	9.1	1.7	245
	4	24.5	5.9	19.6	11.6	2.0	340
	5	33.4	8.9	28.8	13.2	2.6	464
Hendrick	1	11.0	2.1	9.7	7.5	1.0	154
Station	2	13.6	2.1	13.3	8.3	1.2	189
Crude	3	17.6	2.5	16.6	10.1	1.5	247
Oil	4	24.5	7.4	24.0	8.3	2.1	344
	5	36.4	8.9	32.7	13.4	3.4	510

C = Number of carbon atom per average molecule (PAM)

H_α = Number of hydrogen atoms (PAM)
bonded to aliphatic carbon atoms
which are in turn bonded to aromatic carbon atoms

H_β = Number of hydrogen atoms (PAM)
bonded to non-terminal, non-alpha, aliphatic carbon atoms

H_γ = Number of hydrogen atoms (PAM)
bonded to terminal, non-alpha, aliphatic carbon atoms

H_{aro} = Number of hydrogen atoms (PAM)
bonded to aromatic carbon atoms

MW = Number-average molecular weight in g/mole

TABLE 6

STRUCTURAL DATA FOR FOSSIL-FUEL FRACTIONS:
HETEROATOMIC GROUPS PER 1000 MOLECULES

Sample	Fraction	NH	NH_2	N_p	OH	O_e	S
Lurgi	1	15	3	130	170	273	17
Creosote	2	1	4	145	140	290	31
	3	9	3	138	85	183	24
	4	2	19	206	92	427	22
	5	2	35	272	110	601	26
Exxon	1	0	0	8	20	61	3
Donor	2	2	0	15	21	58	1
Solvent	3	2	1	19	20	31	2
Process	4	3	4	18	17	9	3
Product	5	4	1	32	35	66	2
	6	4	1	23	26	104	0
	7	4	0	45	32	94	1
	8	22	15	81	69	118	3
Belridge	1	0	0	0	0	6	6
Crude	2	0	0	1	0	0	42
Oil	3	1	0	13	1	63	60
	4	35	18	39	6	166	83
	5	66	27	106	8	137	129
Hendrick	1	0	0	2	1	36	25
Station	2	0	0	0	0	0	28
Pipeline	3	0	0	0	0	0	124
Mix	4	5	0	5	11	80	178
	5	14	0	22	11	289	258

NH_2 = Primary Amine

NH = Secondary Amine

N_p = Pyridinic Nitrogen

OH = Hydroxyl

O_e = Ether Oxygen

S = Thiophenic Sulfur

TABLE 7

CARBON-NUMBER DISTRIBUTION DATA
FOR FOUR BELRIDGE CRUDE OIL FRACTIONS

Fraction 1		Fraction 2		Fraction 3		Fraction 4	
C	Mole%	C	Mole%	C	Mole%	C	Mole%
8.3	1.11	10.5	0.17	13.6	0.43	16.9	0.09
9.3	21.93	11.5	8.36	14.6	11.02	17.8	0.98
10.4	39.26	12.6	28.13	15.7	24.18	18.8	3.87
11.4	28.42	13.6	30.31	16.7	14.65	19.7	7.18
12.4	8.80	14.6	21.80	17.8	11.74	20.6	9.47
13.5	0.48	15.7	9.99	18.8	10.47	21.6	10.18
		16.7	1.24	19.8	10.69	22.5	6.74
				20.9	9.41	23.5	10.28
				21.9	5.32	24.4	6.95
				23.0	1.63	25.3	7.20
				24.0	0.41	26.3	7.51
				25.1	0.05	27.2	10.78
						28.2	6.06
						29.1	2.28
						30.0	3.61
						31.0	2.48
						31.9	1.73
						32.8	1.09
						33.8	0.68
						34.7	0.42
						35.7	0.25
						36.6	0.12
						37.5	0.05

C = average number of carbon atoms per molecule within micro-fraction

TABLE 8

CARBON-NUMBER DISTRIBUTION DATA
FOR FOUR HENDRICK STATION CRUDE OIL FRACTIONS

Fraction 1		Fraction 2		Fraction 3		Fraction 4	
C	Mole%	C	Mole%	C	Mole%	C	Mole%
7.5	0.34	10.5	1.93	13.4	0.20	16.7	0.003
8.6	2.58	11.6	11.09	14.4	6.40	17.6	0.45
9.7	22.79	12.6	25.05	15.4	22.15	18.6	3.14
10.8	36.10	13.68	28.03	16.5	15.19	19.5	7.92
11.8	27.63	14.7	23.10	17.5	15.56	20.4	8.29
12.9	9.42	15.8	9.98	18.5	12.37	21.3	8.14
14.0	1.14	16.8	0.82	19.6	12.90	22.3	6.09
				20.6	11.11	23.2	10.09
				21.6	3.81	24.1	7.95
				22.7	0.31	25.0	8.37
						26.0	7.90
						26.9	11.37
						27.8	6.37
						28.8	2.45
						29.7	3.89
						30.6	3.19
						31.6	1.74
						32.5	1.11
						33.4	0.67
						34.3	0.41
						35.3	0.23
						36.2	0.12
						37.1	0.04

C = average number of carbon atoms per molecule within micro-fraction

CAPTIONS FOR FIGURES

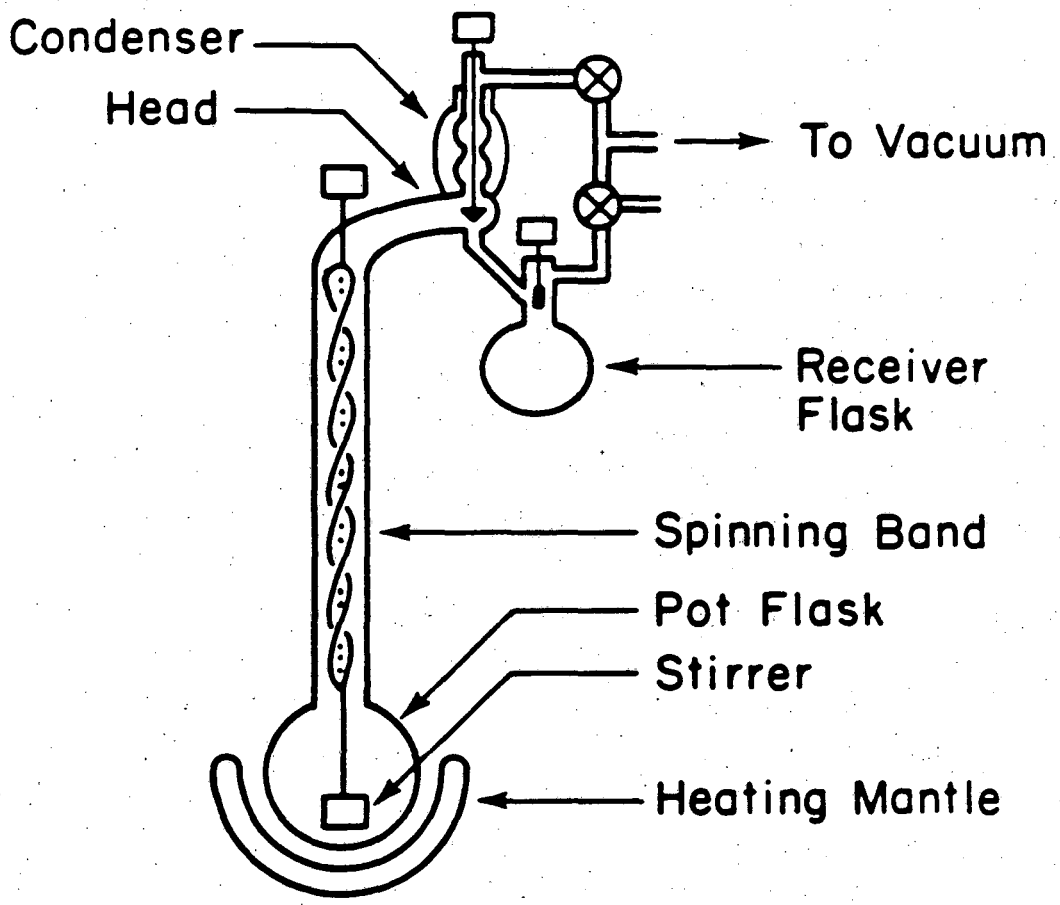
Figure 1: Perkin-Elmer Annular Still

Figure 2: Typical Proton-NMR Spectrum

Figure 3: Infra-Red Absorbance of Pure Phenolics and Amines Dissolved in Methylene Chloride at 20°C

Figure 4: Freezing-Point-Depression Measurements Showing Optimum Solute-Concentration Range (0.04 - 0.07 molal)

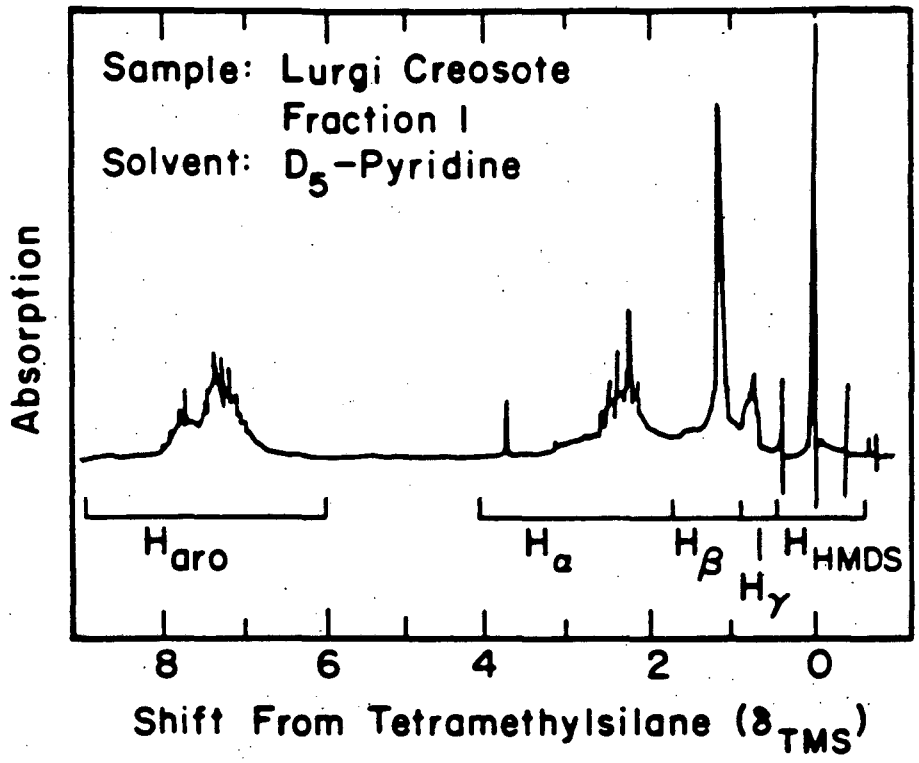
Figure 5: Estimation of Optimum Concentration for Molecular-Weight Determination by Freezing-Point Depression of Nitrobenzene (Adapted from Macknick, 1979)



Still: Perkin-Elmer Model 251 Annular Still
Spinning Band: 0.91 × 0.01 m Monel Mesh
Reflux Ratio: 10:1
Maximum Head Temperature: 250°C
Maximum Pot Temperature: 300°C
Boiling-Point Range of Fraction: ~20°C

Figure 1

Perkin-Elmer Annular Still



H = Hydrogen Atom

aro = Attached to Aromatic Carbon Atom (6.0 → 9.0 δ_{TMS})

α = Attached to Carbon Atom Alpha to Aromatic Carbon (1.7 → 4.0 δ_{TMS})

β = Attached to Non-alpha, Non-terminal Aliphatic Carbon Atom (0.9 → 1.7 δ_{TMS})

γ = Attached to Non-alpha, Terminal Aliphatic Carbon Atom (0.5 → 0.9 δ_{TMS})

HMDS = Hexamethyldisiloxane (0.02 δ_{TMS})

Figure 2

Typical Proton-NMR Spectrum

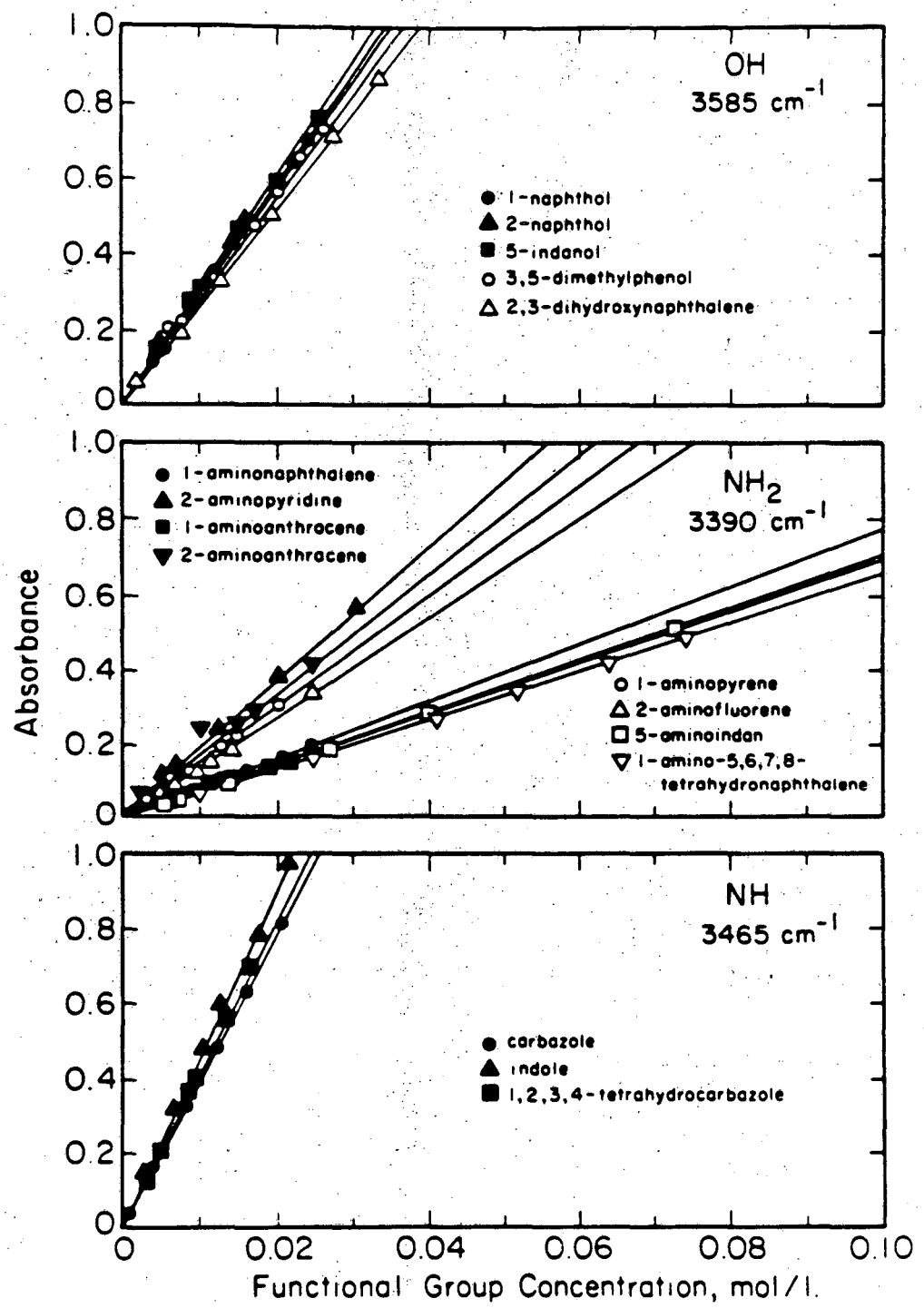


Figure 3

Infra-Red Absorbance of Pure Phenolics and Amines Dissolved in Methylene Chloride at 20°C

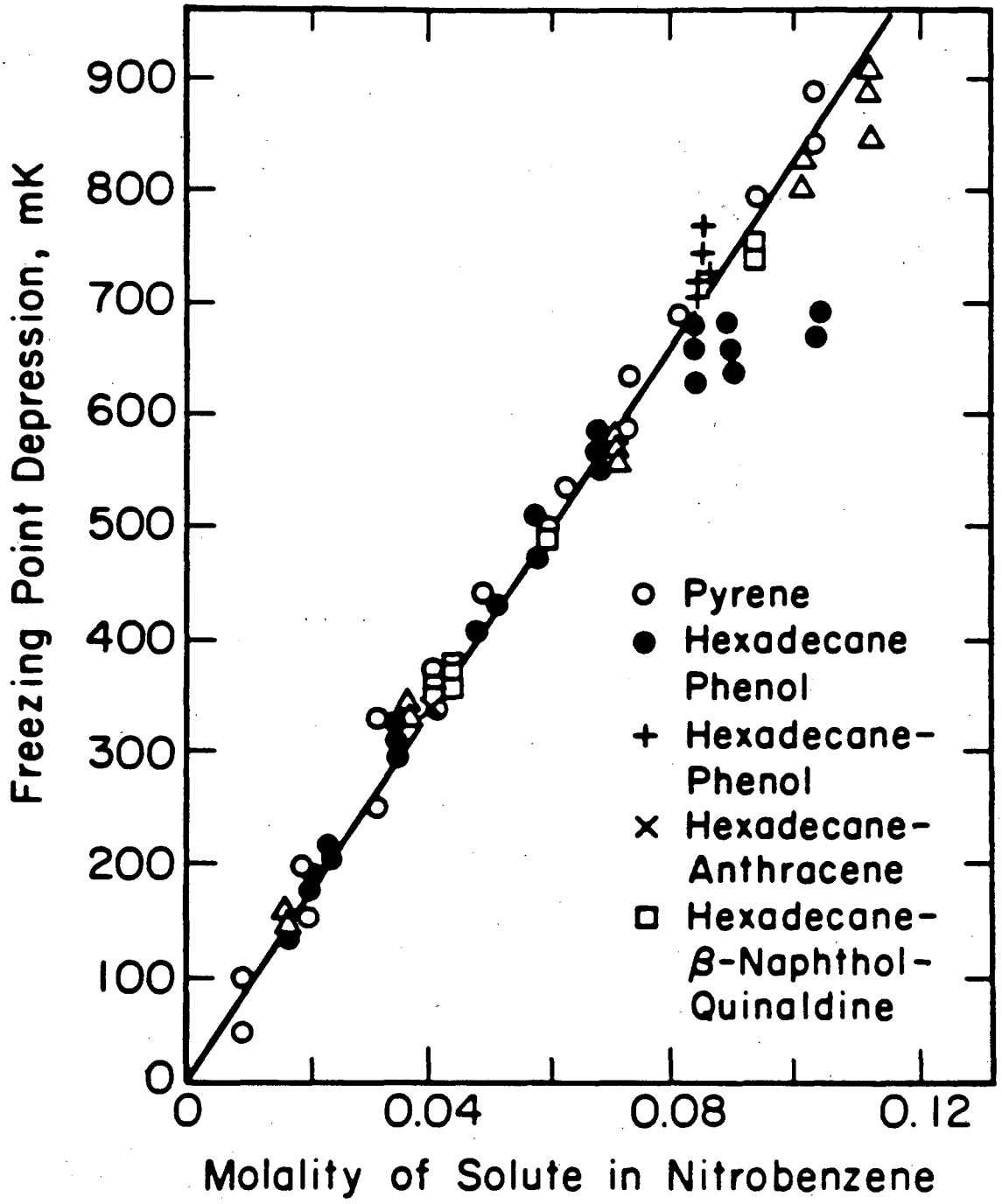


Figure 4

Freezing-Point-Depression Measurements
Showing Optimum Solute-Concentration Range
(0.04 - 0.07 molal)

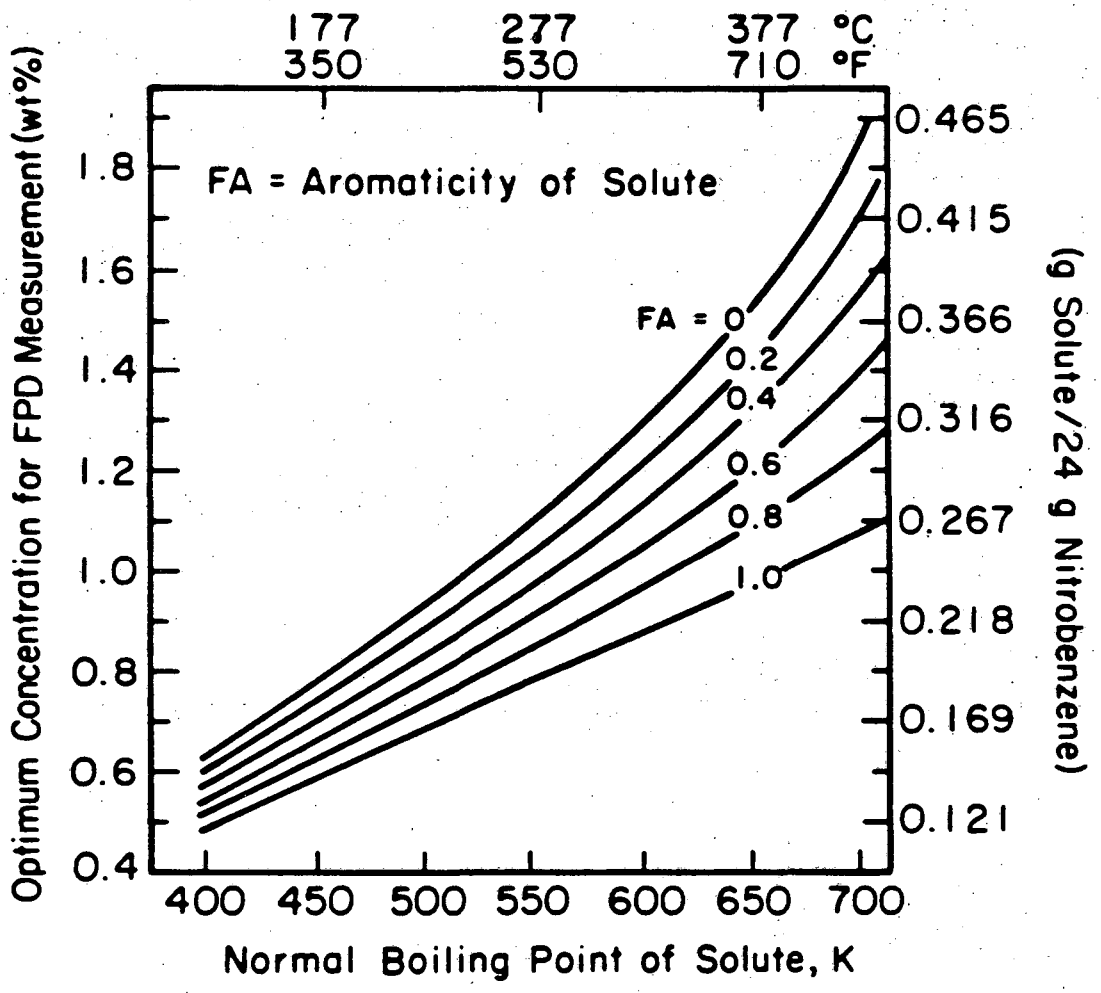


Figure 5

Estimation of Optimum Concentration
for Molecular-Weight Determination
by Freezing-Point Depression of Nitrobenzene
(Adapted from Macknick, 1979)

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