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THE VAPOR-PARTICLE PARTITIONING OF n-ALKANES*

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ABSTRACT

A mixed-phase partitioning model has been proposed to predict the distribution of n-alkanes between the vapor and particle phases in the atmosphere. n-Alkanes having terrestrial plant wax and petroleum origins are assumed to be associated with atmospheric particles as microcrystalline solids and subcooled liquids, respectively. The fraction of n-alkanes on atmospheric particles having plant wax and petroleum origins is estimated with carbon preference indices. Hypothetical terrestrial plant wax and petroleum mixtures are used to estimate the mole fractions of the n-alkanes in each phase and the molecular weights of the phases. Solid and subcooled liquid phase n-alkane vapor pressures are used in the model to predict the fraction of n-alkanes associated with particles in the atmosphere. Trends in the prediction of vapor-particle partitioning using these assumptions agree well with field observations. However, the fraction of particle phase n-alkanes predicted by the model was significantly different from the field observations.

INTRODUCTION

n-Alkanes are distributed in the atmosphere between the vapor and particle phases (Eichmann et al., 1979 and 1980; Broddin et al., 1980; Zafiriou et al., 1985; Doskey and Andren, 1986). The "true" partitioning cannot be measured directly because adsorption and desorption of n-alkanes to and from particles collected on filter media can occur during sampling (Van Vaeck et al., 1984). Zafiriou et al. (1985) examined the vapor-particle partitioning of n-alkanes by comparing rain scavenging ratios of C₂₁-C₃₆ n-alkanes and scavenging ratios of clay particles at a remote marine site. These investigators assumed that the hydrophobicity of the long-chain n-alkanes precluded precipitation scavenging of vapor phase n-alkanes and that the scavenging ratios of clay particles and n-alkanes in the particle phase were similar. Theoretical concentrations of n-alkane vapor in equilibrium with n-alkanes in crystalline solid and subcooled liquid phases were determined. The crystalline solid and subcooled liquid phases were used to represent the physical states of the n-alkanes in terrestrial plant waxes and petroleum mixtures, respectively. The authors found that rain scavenging ratios that were predicted by assuming that the vapor phase n-alkanes were in equilibrium with crystalline solid n-alkanes agreed with observed scavenging ratios of clay particles.

Doskey and Andren (1986) found that the vapor-particle partitioning of odd- and even-carbon-numbered n-alkanes over the range of C₂₂-C₃₂ at a semiremote, continental site followed independent trends. Poor agreement was found between observations and predictions that were based on the assumption that the vapor phase n-alkanes were in equilibrium with crystalline solid n-alkanes.

In the present work, the data set of Doskey and Andren (1986) is used to develop a mixed-phase partitioning model to support the hypothesis that particle phase n-alkanes having terrestrial plant wax origins exist in the atmosphere as microcrystalline solids, while n-alkanes derived from petroleum exist as subcooled liquids on particles. Solid and subcooled liquid vapor pressures, melting points, and entropies of fusion for n-alkanes are presented and used in the model to predict the vapor concentrations of n-alkanes in equilibrium with a model mixture of petroleum and terrestrial plant wax. The results of the model are compared with field data obtained via a high-volume sampling methodology.

PHYSICOCHEMICAL DATA AND MIXED-PHASE PARTITIONING MODEL

Physicochemical data for C₂₂-C₃₂ n-alkanes are presented in Table 1. The KLH equation (Mackay et al., 1982) and an additive estimation method (Stein, 1981) were used to calculate subcooled liquid phase vapor pressures, while the modified Watson correlation (Grain, 1982) was used to estimate vapor pressures for solid phase n-alkanes. Vapor pressures for solid n-alkanes were also calculated by applying a melting point correction to subcooled liquid vapor pressures as follows (Mackay et al., 1980):

$$\ln(p^{\circ}_s) = \ln(p^{\circ}_l) + (\Delta S_f/R) [1 - (T_m/T)] \quad (1)$$

Here p°_s = vapor pressure for a substance in the solid state (atm),

p°_l = vapor pressure for a substance in the subcooled, liquid state
(atm),

ΔS_f = entropy of fusion (cal mole⁻¹ deg⁻¹),

R = ideal gas law constant ($\text{cal mole}^{-1} \text{deg}^{-1}$),

T_m = melting point ($^{\circ}\text{K}$), and

T = ambient temperature ($^{\circ}\text{K}$).

The entropies of fusion in Table 1 were calculated from the following equation (Yalkowsky, 1979):

$$\Delta S_f = 13.5 + 2.5 (N_c - 5) \quad (2)$$

Here N_c = number of carbon atoms.

The melting points presented in Table 1 were derived from a plot of available data on melting points from Warth (1956) and Weast (1973) versus the number of carbon atoms in the n-alkanes.

A mixed-phase partitioning model can be developed to calculate the equilibrium partial pressure of an n-alkane above atmospheric particles by using the concept of fugacity (see, e.g., Prausnitz, 1973; Thibodeaux, 1979; Mackay and Paterson, 1981). In our proposed system, we have n-alkanes in three phases -- air (phase 1), a solid microcrystalline plant wax (phase 2), and a subcooled liquid petroleum mixture (phase 3). The four equations that describe this system are as follows:

$$p_{a1} = y_{a1} P_T \quad (3)$$

$$f_{a1} = y_{a1} \gamma_{a1} f^{\circ}_{a1} \quad (4)$$

$$f_{a2} = x_{a2} \gamma_{a2} f^{\circ}_{a2} \quad (5)$$

$$f_{a3} = x_{a3} \gamma_{a3} f^{\circ}_{a3} \quad (6)$$

Here p_{a1} = partial pressure
 x_a, y_a = mole fraction,
 γ_a = activity coefficient (on a Raoult's law convention),
 f_a = fugacity (atm),
 f°_a = reference fugacity (atm), and
 P_T = total pressure of the system (atm).

At equilibrium, the fugacities are equal, and therefore the partial pressure of an n-alkane above the plant wax (phase 2) and the petroleum mixture (phase 3) would be given by the following equations:

$$p_{a1} = x_{a2} P_T (f^{\circ}_{a2} \gamma_{a2} / f^{\circ}_{a1} \gamma_{a1}) \quad (7)$$

$$p_{a1} = x_{a3} P_T (f^{\circ}_{a3} \gamma_{a3} / f^{\circ}_{a1} \gamma_{a1}) \quad (8)$$

At a system pressure (P_T) of one atmosphere, the reference fugacities for an n-alkane in the plant wax (f°_{a2}) and petroleum mixture (f°_{a3}) are equal to the vapor pressures of the n-alkane in the crystalline solid and subcooled liquid states, respectively, and the reference fugacity for an n-alkane in air (f°_{a1}) is one atmosphere. The plant wax and petroleum mixture are treated as an ideal solid and a subcooled liquid solution, respectively, and because the n-alkanes are not expected to associate in the gas phase, their activity coefficients in the three phases are assumed to be equal to one. The equilibrium concentration (c_{a1T}) of an n-alkane in air above a mixture of a plant wax and a petroleum mixture

containing the n-alkane at the system pressure is the sum of the partial pressures of the n-alkanes above the two phases and is given as

$$c_{a1T} = (x_{a2} f_{a2} + x_{a3} f_{a3}) / RT, \quad (9)$$

where c_{a1T} = moles m^{-3} .

To determine c_{a1T} , the mole fraction of the n-alkanes in the plant wax and subcooled liquid phases must be known; therefore, the average molecular weights of the phases must also be known. Because the exact compositions of plant waxes and the subcooled liquid phase on atmospheric particles are unknown, it will be assumed that they are composed entirely of n-alkanes. For the plant wax this assumption probably produces a molecular weight that is reasonable because the wax also contains homologous series of alcohols, aldehydes, acids, acetals, and ketones distributed similarly to those of the n-alkanes, although the ratios of odd to even numbered homologs are different for the different classes of hydrocarbons (see, e.g., Caldicott and Eglinton, 1973; Kolattukudy et al., 1981). Furthermore, the plant waxes exist in the atmosphere as particles of micron and submicron dimensions, distinct from other atmospheric particles. The surface wax of a plant is composed of microcrystals or hollow tubes of wax of micron and submicron dimensions (Baker and Holloway, 1971). These protrusions are sloughed from surfaces by wind and erosion by dust particles (Hall and Donaldson, 1963). A petroleum residue probably composes only a fraction of the subcooled liquid phase of atmospheric particles. The subcooled liquid phase most likely consists of a complex mixture of saturated, unsaturated, aromatic, oxygenated, nitrogenous, and halogenated hydrocarbons that became associated with atmospheric particles during gas-to-particle conversion and condensation

reactions. Therefore, it would be more correct to use the average molecular weight of the particle-phase total organic carbon (TOC) to represent the molecular weight of the subcooled liquid phase and the mass of the TOC to determine mole fractions of the n-alkanes in the subcooled liquid phase. Unfortunately, the average molecular weight of the TOC is unknown. Our assumption therefore precludes an accurate prediction of the distribution of n-alkanes between the vapor and particle phases. However, the overall trend in the vapor particle-partitioning of n-alkanes can still be determined.

n-Alkane distributions can be mathematically described by using the carbon preference index (CPI) of the n-alkanes, which is simply defined as the ratio of the mole fractions of the odd- to even-numbered homologs (Bray and Evans, 1961). Plant waxes normally have CPIs greater than 10 (Caldicott and Eglinton, 1973). n-Alkanes having a petroleum origin exhibit a uniform distribution of n-alkanes and a CPI of one (Blumer and Sass, 1972). An unresolved complex mixture (UCM) of branched and cyclic aliphatic hydrocarbons is also associated with petroleum residues on atmospheric particles (Simoneit, 1984).

n-Alkanes over the range of C₂₂-C₃₂ represent the greatest fraction of the particle phase n-alkanes in the data set of Doskey and Andren (1986). The greatest CPI value for the particle phase n-alkanes in this data set is 13. This value occurred in a sample collected during summer. The sample also contained a slight UCM. Assuming that the n-alkane distribution was composed of CPI 13 and CPI 1 distributions to represent the plant wax and petroleum fractions, respectively, Doskey and Andren (1986) calculated that n-alkanes with a CPI of 13 represented 95% of the total n-alkanes. Because n-alkanes of petroleum origin

made only a minor contribution to the n-alkane composition of this sample, the particle phase n-alkanes will be used to represent the n-alkane composition of a terrestrial plant wax. The mole fractions of the C₂₂-C₃₂ n-alkanes in the wax are presented in Table 2. A plant wax of this composition would have an average molecular weight of 379 g mole⁻¹. For a petroleum mixture containing n-alkanes over the range of C₂₂-C₃₂, the mole fraction of each n-alkane would be equal (Table 2), and the petroleum mixture would have an average molecular weight of 381 g mole⁻¹.

Field observations of the vapor-particle partitioning of n-alkanes will be compared to gas-particle distributions that are predicted from the concentration of aerosol surface area in the atmosphere and the vapor pressures of the n-alkanes. Junge (1977) simplified the multilayer adsorption model of Brunauer et al. (1938) into a linear Langmuir isotherm (Pankow, 1987) and derived the equation

$$\phi = c\theta/(c\theta + p^{\circ}), \quad (10)$$

where ϕ = fraction of adsorbed concentration to total concentration in air

c = a constant that depends on molecular weight and heat of condensation (0.13 for many organic compounds)

p° = vapor pressure (mm Hg)

θ = total surface area of the particles (cm² cm⁻³)

RESULTS AND DISCUSSION

Figure 1 is a plot of the fraction of adsorbed n-alkanes (ϕ) predicted by the Junge (1977) model of vapor-particle partitioning versus the number of carbon atoms in the n-alkanes over the range of C₂₂-C₃₂. The fractions of adsorbed n-alkanes calculated with vapor pressures estimated by the different predictive methods are markedly different. The best agreement appears to be between the modified Watson correlation and the additive estimation method. Table 3 compares experimental data for subcooled liquid phase n-alkanes (Macknick and Prausnitz, 1979; Sasse et al., 1988; Chirico et al., 1989) with predictions made with the additive estimation method (Stein, 1981) and the modified Watson correlation (Grain, 1982). The additive estimation method predictions appear to agree most closely with the experimental data. Trends that are evident in Junge model predictions for n-alkanes are (1) that the plot of fraction of adsorbed n-alkanes versus carbon chain length for the solid and subcooled liquid states exhibits smooth curves and (2) that the fraction sorbed for an n-alkane in the solid state is greater than the fraction sorbed for an n-alkane in the subcooled liquid state.

Figure 2 contains plots of ϕ versus carbon chain length for measurements of particle and vapor phase n-alkanes made by high-volume sampling methods (Van Vaeck et al., 1984; Doskey and Andren, 1986). The data sets exhibit an alternating pattern in the fraction of adsorbed n-alkanes. The vapor-particle partitioning of the n-alkanes in the data set of Doskey and Andren (1986) exhibited this behavior during summer, when most of the n-alkanes originated from plant waxes, with a smaller contribution from petroleum. The data could be explained by assuming that n-alkanes over the range of C₂₂-C₃₂ in these samples exist in two physical states -- with the odd homologs predominating as microcrystalline

solid n-alkanes in plant waxes and with a uniform distribution over the entire range of n-alkanes in a subcooled liquid phase containing petroleum residues.

To provide evidence for this hypothesis, a sample from the data set of Doskey and Andren (1986) will be used. The average temperature over the collection period was 19°C. The sample contained 102 µg of n-alkanes within the range of C₂₂-C₃₂, with 75% of the homologs exhibiting a CPI 13 distribution (plant wax) and 25% a CPI 1 distribution (petroleum). Using the average molecular weights of the model plant wax (379 g mole⁻¹) and the petroleum mixture (381 g mole⁻¹) indicates that the particles contained 0.20 µmole of microcrystalline plant wax and 0.067 µmole of subcooled liquid petroleum. The mole fractions of the n-alkanes in the plant wax (x_{a2}) and the petroleum mixture (x_{a3}) in the sample were calculated from the µmoles of each phase in the sample and the mole fraction of the n-alkane in the model phases (Table 2). The predicted concentration of vapor phase n-alkanes in the sample was calculated from equation 9 by using vapor pressures derived by the additive estimation method and the concentrations of particle phase n-alkanes in the sample. The fractions of each n-alkane adsorbed onto atmospheric particles versus the number of carbon atoms in the n-alkane for the field observations and the mixed-phase partitioning model are presented in Figure 2. Model predictions indicate that a lower fraction is adsorbed than was observed for C₂₂-C₂₈ n-alkanes and that a greater fraction is adsorbed for C₃₀-C₃₂ homologs. This finding is not unusual because some uncertainty exists in the vapor pressure estimation techniques and the calculation of the mole fractions of the n-alkanes in each phase. The trends, however, are very similar.

The similarity of the observed and predicted trends of n-alkane vapor particle partitioning provide evidence that n-alkanes having origins in plant wax and petroleum residue exist as crystalline solids and a subcooled liquid phase on atmospheric particles, respectively. The vapor-particle partitioning of petroleum residues on atmospheric particles may reasonably be determined by subcooled liquid vapor pressures. Petroleum residues in the atmosphere probably originate during the volatilization of petroleum products or as residues on particles produced during the combustion of petroleum products. Various hydrocarbons, including n-alkanes, have been detected on particles in automobile exhaust (Simoneit, 1984). The vapor-particle partitioning of polyaromatic hydrocarbons (PAHs), which originate during the combustion of organic matter and are also components of automobile exhaust, is determined by their subcooled liquid vapor pressures (Yamasaki et al., 1982; Bidleman et al., 1986; Foreman and Bidleman, 1987; Bidleman, 1988). The n-alkanes in petroleum residues apparently behave similarly. The vapor-particle partitioning of organochlorine pesticides and polychlorinated biphenyls (PCBs) in field and laboratory studies also appears to be determined by their subcooled liquid vapor pressures (Bidleman et al., 1986; Foreman and Bidleman, 1987; Bidleman, 1988). Organochlorine pesticides and PCBs evaporate from agricultural and urban areas and condense onto aerosols and probably do not form a crystal lattice. Some of the n-alkanes may evaporate and condense onto aerosols in a similar fashion. Unlike petroleum residues, plant waxes are microcrystalline materials composed of normal and branched alkanes, alcohols, acids, aldehydes, acetals, and ketones (see, e.g., Caldicott and Eglinton, 1973; Kolattukudy et al., 1981). These waxes can be eroded by wind from leaf surfaces and enter the atmosphere. The vapor-particle partitioning of n-alkanes in plant waxes appears to be determined by their solid phase vapor pressures.

CONCLUSIONS

A mixed-phase partitioning model has been proposed to predict the distribution of n-alkanes between the vapor and particle phases. The partitioning between n-alkanes in the gas phase and n-alkanes in terrestrial plant waxes and petroleum residues associated with atmospheric particles was assumed to be determined by the vapor pressures of solid and subcooled liquid n-alkanes, respectively. Trends in the predictions of vapor-particle partitioning based on these assumptions agreed nicely with field observations made by Doskey and Andren (1986) and further confirm the hypothesis proposed by Zafiriou et al. (1985).

While trends in the model predictions and the field observations were similar, the agreement between the fractions of adsorbed n-alkanes was rather poor. These differences could be caused by temperature variations over the sampling period. Better agreement between model predictions and observations might be obtained for shorter sampling intervals. The accuracy of the predictions would also be improved with experimental measurements of n-alkane vapor pressures and a better knowledge of the composition of the subcooled liquid phase of atmospheric particles.

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REFERENCES

- Baker E. A. and Holloway P. J. (1971) Scanning electron microscopy of waxes in plant surfaces. *Micron*. **2**, 364-380.
- Bidleman T. F. (1988) Atmospheric processes. *Environ. Sci. Technol.* **22**, 361-367.
- Bidleman T. F., Billings W. N. and Foreman W. T. (1986) Vapor-particle partitioning of semivolatile organic compounds: Estimates from field collections. *Environ. Sci. Technol.* **20**, 1038-1043.
- Blumer M. and Sass J. (1972) Indigenous and petroleum-derived hydrocarbons in a polluted sediment. *Mar. Pollut. Bull.* **3**, 92-94.
- Bray E. E. and Evans E. D. (1961) Distribution of n-paraffins as a clue to recognition of source beds. *Geochim. Cosmochim. Acta* **22**, 2-15.
- Broddin G., Cautreels W. and Van Cauwenberghe K. (1980) On the aliphatic and polyaromatic hydrocarbon levels in urban and background aerosols from Belgium and the Netherlands. *Atmospheric Environment* **14**, 895-910.
- Brunauer S., Emmett P. H. and Teller E. (1938) Adsorption of gases in the multimolecular layers. *J. Am. Chem. Soc.* **60**, 309-319.
- Caldicott A. B. and Eglinton G. (1973) Surface waxes. In *Phytochemistry III: Inorganic Elements and Special Groups of Chemicals* (edited by Miller L. P.), pp. 162-194. Van Nostrand/Reinhold, New York.
- Chirico R. D., Nguyen A., Steele W. V. and Strube M. M. (1989) Vapor pressure of n-alkanes revisited. New high-precision vapor pressure data on n-decane, n-eicosane, and n-octacosane. *J. Chem. Eng. Data* **34**, 149-156.
- Doskey P. V. and Andren A. W. (1986) Particulate- and vapor-phase n-alkanes in the northern Wisconsin atmosphere. *Atmospheric Environment* **20**, 1735-1744.
- Eichmann R., Ketseridis G., Schebeske G., Jaenicke R., Hahn J., Warneck P. and Junge C. (1980) n-Alkane studies in the troposphere-II: Gas and particulate concentrations in Indian Ocean air. *Atmospheric Environment* **14**, 695-703.
- Eichmann R., Neuling P., Ketseridis G., Hahn J., Jaenicke R. and Junge C. (1979) n-Alkane studies in the troposphere: I. Gas and particulate concentrations in North Atlantic air. *Atmospheric Environment* **13**, 587-599.
- Foreman W. T. and Bidleman T. F. (1987) An experimental system for investigating vapor-particle partitioning of trace organic pollutants. *Environ. Sci. Technol.* **21**, 869-875.

- Grain C. F. (1982) Vapor pressure. In *Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds* (edited by Lyman W. J., Reehl W. F. and Rosenblatt D. H.), pp. (14-1)-(14-20). McGraw-Hill Books, New York.
- Hall D. M. and Donaldson L. A. (1963) The ultrastructure of wax deposits on plant leaf surfaces: 1. Growth of wax on leaves of *Trifolium repens*. *Ultrastr. Res.* **9**, 259-267.
- Junge C. E. (1977) Basic consideration about trace constituents in the atmosphere as related to the fate of global pollutants. In *Fate of Pollutants in the Air and Water Environments. Part I. Mechanisms of Interaction Between Environments and Mathematical Modeling and the Physical Fate of Pollutants* (edited by Suffet I. H.), pp. 7-25. John Wiley and Sons, Inc., New York.
- Kolattukudy P. E., Espelie K. E. and Soliday C. L. (1981) Hydrophobic layers attached to cell walls. Cutin, suberin, and associated waxes. In *Plant Carbohydrates II. Extracellular Carbohydrates* (edited by Tanner W. and Loewus F. A.), pp. 225-248. Springer-Verlag, New York.
- Mackay D., Bobra A., Chan D. W. and Shiu W. Y. (1982) Vapor pressure correlations for low-volatility environmental chemicals. *Environ. Sci. Technol.* **16**, 645-649.
- Mackay, D., Bobra A. and Shiu W. Y. (1980) Relationships between aqueous solubility and octanol-water partition coefficients. *Chemosphere* **9**, 701-711.
- Mackay D. and Paterson S. (1981) Calculating fugacity. *Environ. Sci. Technol.* **15**, 1006-1014.
- MacKnick A. B. and Prausnitz J. M. (1979) Vapor pressures of high-molecular weight hydrocarbons. *J. Chem. Eng. Data* **24**, 175-178.
- Pankow J. F. (1987) Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. *Atmospheric Environment* **21**, 2275-2283.
- Prausnitz J. M. (1973) *The Molecular Thermodynamics of Fluid Phase Equilibrium*. Prentice Hall, Englewood Cliffs.
- Sasse et al. (1988) *Fluid Phase Equilibria* **42**, 287.
- Simoneit B. R. T. (1984) Organic matter of the troposphere-III. Characterization and sources of petroleum and pyrogenic residues in aerosols over the Western United States. *Atmospheric Environment* **18**, 51-67.
- Stein S. E. (1981) Application of additive estimation methods to vaporization properties of liquids. *J. Chem. Soc. Faraday Trans.* **77**, 1457-1467.

Thibodeaux L. J. (1979) *Chemodynamics. Environmental Movement of Chemicals in Air, Water, and Soil*. John Wiley & Sons, Inc., New York.

Van Vaeck L., Van Cauwenberghe K. and Janssens J. (1984) The gas-particle distribution of organic aerosol constituents: Measurement of the volatilisation artefact in hi-vol cascade impactor sampling. *Atmospheric Environment* **18**, 417-430.

Warth A. H. (1956) *The Chemistry and Technology of Waxes*, p. 12. Reinhold Publishing Corporation, New York.

Weast R. C. (1973) *Handbook of Chemistry and Physics*. pp. (C-75) - (C-542). The Chemical Rubber Company, Cleveland.

Yalkowsky S. H. (1979) Estimation of entropies of fusion of organic compounds. *Ind. Eng. Chem. Fundam.* **18**, 108-111.

Yamasaki H., Kuwata K. and Miyamoto H. (1982) Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* **16**, 189-194.

Zafiriou O. C., Gagosian R. B., Peltzer E. T., Alford J. B. and Loder T. (1985) Air-to-sea fluxes of lipids at Enewetak Atoll. *J. Geophys. Res.* **90**, 2409-2423.

Table 1. Physicochemical data for C₂₂-C₃₂ n-alkanes

N _c	T _m (°C)	ΔS_f (cal mole ⁻¹ deg ⁻¹)	p_l^o (atm)		p_s^o (atm)
			KLH ^a	Additive ^b	MWC ^c
22	44.5	56.0	1.3×10^{-7}	2.2×10^{-9}	1.4×10^{-10}
23	47.7	58.5	6.7×10^{-8}	7.4×10^{-10}	5.0×10^{-11}
24	51.3	61.0	3.6×10^{-8}	2.4×10^{-10}	1.8×10^{-11}
25	54.3	63.5	2.0×10^{-8}	7.9×10^{-11}	7.0×10^{-12}
26	56.5	66.0	1.1×10^{-8}	2.6×10^{-11}	2.6×10^{-12}
27	59.6	68.5	6.6×10^{-9}	8.6×10^{-12}	1.0×10^{-12}
28	62.1	71.0	3.8×10^{-9}	2.9×10^{-12}	4.2×10^{-13}
29	63.8	73.5	2.3×10^{-9}	9.3×10^{-13}	1.7×10^{-13}
30	65.9	76.0	1.4×10^{-9}	3.2×10^{-13}	7.5×10^{-14}
31	68.0	78.5	8.6×10^{-10}	1.0×10^{-13}	3.3×10^{-14}
32	69.8	81.0	5.2×10^{-10}	3.4×10^{-14}	1.3×10^{-14}

a, b, c Vapor pressures at 25°C were calculated by using the KLH equation (Mackay *et al.*, 1982), an additive estimation method (Stein, 1981), and the modified Watson correlation (Grain, 1982), respectively.

Table 2. The mole fractions of n-alkanes in a model mixture of terrestrial plant wax and petroleum residue

N _c	Molecular Weight (g mole ⁻¹)	Mole Fraction			
		Plant Wax		Petroleum Residue	
		Model	Sample	Model	Sample
22	310.61	0.0046	0.0034	0.091	0.023
23	324.64	0.054	0.042	0.091	0.023
24	338.67	0.011	0.0083	0.091	0.023
25	352.69	0.22	0.16	0.091	0.023
26	366.72	0.028	0.021	0.091	0.023
27	380.75	0.40	0.30	0.091	0.023
28	394.78	0.016	0.012	0.091	0.023
29	408.80	0.17	0.13	0.091	0.023
30	423.55	0.011	0.0082	0.091	0.023
31	436.95	0.077	0.056	0.091	0.023
32	450.98	0.0051	0.0037	0.091	0.023

Table 3. Comparison of experimental data on subcooled liquid phase n-alkane vapor pressures (atm) with estimated values

N_c	A^a	B^b	C^c	Additive ^d	MWC ^c
18	2.51×10^{-7}	-	-	2.0×10^{-7}	9.6×10^{-8}
20	2.59×10^{-8}	2.07×10^{-8}	1.63×10^{-8}	2.1×10^{-8}	3.6×10^{-9}
22	-	-	1.57×10^{-9}	2.2×10^{-9}	9.2×10^{-10}
24	-	-	2.71×10^{-11}	2.4×10^{-10}	2.8×10^{-10}
28	-	5.68×10^{-12}	-	2.9×10^{-12}	3.6×10^{-11}

^aMacKnick and Prausnitz (1979).

^bChirico et al. (1989).

^cSasse et al. (1988)

^{d,e}Vapor pressures at 25°C were calculated by using an additive estimation method (Stein, 1981) and the modified Watson correlation (Grain, 1982).

Figure Captions

- Fig. 1. Junge plots of the fractions of adsorbed solid and subcooled liquid phase n-alkanes versus the number of carbon atoms in the n-alkanes over the range of C₂₂-C₃₂ [$T = 25^{\circ}\text{C}$, $c = 0.13$, $\theta = 1 \times 10^{-6}$ (typical of a total suspended particle concentration of $30 \mu\text{g m}^{-3}$)] (MWC, modified Watson correlation, ADD, additive estimation method, KLH, KLH equation, ℓ , liquid, s, solid).
- Fig. 2. A Junge plot of n-alkane data from Van Vaeck et al. (1984) and Doskey and Andren (1986), (VV, VanVaeck, DA, Doskey and Andren).

Figure 1.

Figure 2.

DATE

FILMED

5/12/94

END