A Process for Extracting High Molecular Weight Hydrocarbons from a Solid Phase in Equilibrium with a Liquid Hydrocarbon Phase: Solubility-Selectivity Behavior of Certain Organic Groups

DARYLL CORDEIRO, KRAEMER D. LUKS, and JAMES P. KOHN

Department of Chemical Engineering
University of Notre Dame, Notre Dame, Indiana 46556

In a recent paper (Cordeiro et al., 1972), the authors demonstrated that methane pressurization of solutions of *n*-decane and *n*-dotriacontane in equilibrium with a solid phase of *n*-dotriacontane will enhance the solubility of the high-molecular-weight paraffin *n*-dotriacontane. The experimental method and data correlation using the Flory-Huggins model were presented in detail. The significance of this work lies in its potential application to petroleum recovery, specifically recovery of those high-molecular-weight materials left behind after primary and secondary recovery techniques have been employed. Salient features of this methane pressurization process are enhanced solubilities of high-molecular-weight materials due to methane swelling of the liquid phase, increased fluidity of the liquid phase caused by the presence of the methane, and subsequent ease of methane by outgassing.

This note reports the effect of methane pressurization on a second prototype ternary three-phase system in which the role of paraffin *n*-dotriacontane is played by the aromatic phenanthrene. Included is an assessment of the process in terms of its selectivity in solubilizing aromatics versus paraffins in a liquid phase containing *n*-decane.

Thermodynamically speaking, in addition to liquid phase composition, the process derivatives

$$\xi_1 \equiv \left[\frac{\partial (x_H/x_{10})}{\partial P} \right]_T$$

and

$$\xi_2 \equiv (\partial N_H/\partial P)_T/(\partial N_1/\partial P)_T$$

are helpful in clarifying the nature of the process. If $\xi_1 > 0$, then solid material is dissolved upon pressurization. If $\xi_1 < 0$, then precipitation occurs. ξ_2 is a measure of the yield of the process, for example, moles of phenanthrene dissolved per mole of methane, although it must be noted that the chemical nature of the liquid phase can strongly affect the solubility of methane gas at a given pressure.

The experimental plan of attack pursued before (Cordeiro et al.) was again followed. For the prototype system with phenanthrene (denoted by subscript 14), the temperature range studied was broader, since the freezing point depression of the phenanthrene was greater due to the addition of *n*-decane. Furthermore, to expedite the Flory-Huggins correlation for the phenanthrene system, a less suitable candidate for that model, it was found necessary to include composition dependence, by no means insignificant in this case, into $\overline{V}_i$. We found

$$\overline{V}_1 = 0.3331T + 11.9628(x_{10}/x_{14}) - 87.56 \quad \text{cc/g-mole}$$

$$\overline{V}_{10} = 0.18T + 6.9662(x_{10}/x_{14}) + 134.47 \quad \text{cc/g-mole}$$

$$\overline{V}_{14} = 0.1031T - 0.3182(x_{10}/x_{14}) + 129.12 \quad \text{cc/g-mole}$$

$$\Delta U_{1,10} = 1266.46 \text{ cal/g-mole}$$

$$\Delta U_{1,14} = 2764.41 \text{ cal/g-mole}$$

$$\Delta U_{10,14} = 838.1 \text{ cal/g-mole}$$

which are suitable in the temperature range 350 to 370°K. As well at $T = T_m = 371.77$°K, we found

$$\Delta H_{14}{}^m = 4556 \text{ cal/g-mole}$$

and, in the range 350 to 370°K,

$$\Delta V_{14}{}^m = (\Delta H_{14}{}^m/12076.5)(T_m/T)^{2.49} \quad \text{cc/g-mole}$$

Figure 1 is a diagram of the ternary three-phase surface studied. The isotherms shown have the same values of T/T_m as our earlier work with *n*-dotriacontane. Table 1 maps out methane pressurization of the new system at 369.15°K ($T/T_m = 0.9930$) while Table 2, via a sample calculation, demonstrates in moles the same isothermal pressurization process.

Similarities between the two processes studied (that is, aromatic and paraffinic solid phases) are that $\xi_1 > 0$ always and ξ_2 is a strong function of T/T_m, demonstrating that solids near their melting points are preferentially dissolved. At $T/T_m = 0.9930$, both phenanthrene and *n*-dotriacontane exhibit a limiting pressure, at which point one can simply dissolve solid with methane indefinitely. This behavior is indicated in Figure 1 by the isotherm 369.15°K intersecting the $x_{10} = 0$ plane between 55 and 60 atm pressure. At $T/T_m = 0.9930$, ξ_2 for phenanthrene greatly exceeds ξ_2 for *n*-dotriacontane, but mainly because methane is less soluble in phenanthrene mixtures.

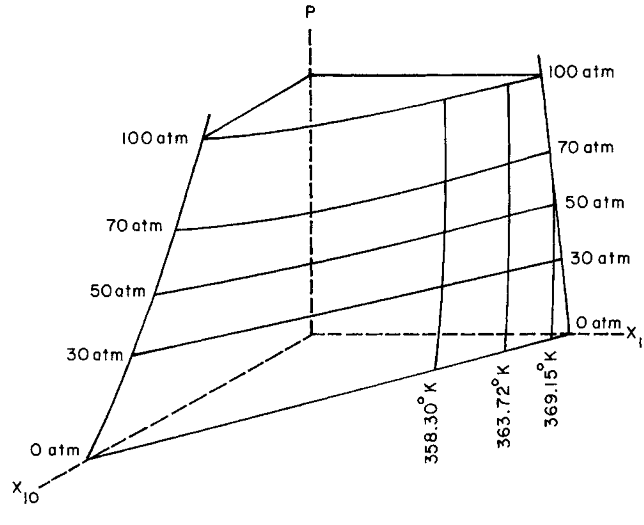

Fig. 1. Diagram of the ternary 3-phase state surface for the prototype system methane-normal decane-phenanthrene.

Correspondence concerning this note should be addressed to K. D. Luks.

Table 1. Liquid Phase Compositions and the Coefficients ξ_1 and ξ_2 as Functions of Pressure along a 3-Phase Isotherm for the Ternary System Methane-n-Decane-Phenanthrene; Temperature = 369.15·K

Pressure, atm.	Mole fraction methane	Mole fraction phenanthrene	ξ_1 (atm.)$^{-1}$	ξ_2
0.00	0.0	0.9630	0.5996	16.5543
5.00	0.0066	0.9606	0.7148	15.8772
10.00	0.0130	0.9582	0.8582	15.4395
15.00	0.0192	0.9557	1.0941	15.2827
20.00	0.0253	0.9532	1.4148	15.0735
25.00	0.0312	0.9507	1.8939	14.9205
30.00	0.0369	0.9482	2.7075	14.8477
35.00	0.0425	0.9458	4.1227	14.6974
40.00	0.0479	0.9433	7.0702	14.6083
45.00	0.0532	0.9409	14.3048	14.5050
50.00	0.0583	0.9384	47.8271	14.5083
55.00	0.0634	0.9360	1176.0910	14.4797

Table 2. Variation with Pressure in the Number of Moles of Methane and Phenanthrene in the Liquid Phase—Based on 1,000 Moles of Liquid at Zero Pressure—along an Isotherm on the Ternary 3-Phase Surface. Number of Moles of n-Decane in Solution = 37.0; Temperature = 369.15·K

Pressure, atm.	Moles of methane in solution	Moles of phenanthrene in solution
0.00	0.0	963.0
5.00	7.5	1,085.0
10.00	16.7	1,228.9
15.00	28.3	1,407.8
20.00	43.4	1,636.9
25.00	63.1	1,925.7
30.00	91.8	2,357.1
35.00	133.5	2,972.3
40.00	201.3	3,965.1
45.00	329.5	5,829.7
50.00	663.8	10,681.0
55.00	3,661.8	54,104.6

An interesting question to pose is which species, aromatic or paraffinic, will be selectively chosen in the methane pressurization process with n-decane present in the liquid phase. The two HMW materials differ too much in T_m to make any quartenary study meaningful. However, consideration of the two prototype systems studied at $T/T_m = 0.9930$ and their comparison at low values of P suggests that the methane pressurization process would be selective. The following admittedly over-simplified arguments are put forth:

1. If the solid HMW solubilities were ideal, then

$$\left(\frac{\partial \ln x_H}{\partial P}\right)_T = \frac{-\Delta V_H{}^m}{RT}$$

2. Methane would go into solution according to Henry's law, that is,

$$x_1 = P/K_1$$

where K_1 is the Henry's law constant.

3. Now consider the case where the HMW neither dissolves nor precipitates, that is,

$$\xi_1 = 0 = \left[\frac{\partial(x_H/x_{10})}{\partial P}\right]_T$$

From these relationships, a value of K_1 can be found such that $\xi_1 = 0$. This value of K_1 is larger than that at which $\xi_1 > 0$, as methane dissolution is necessary to enhance HMW dissolution. At $T/T_m = 0.9930$

$$K_1\ (\xi_1 = 0,\ n\text{-dotriacontane}) = 678.43 \text{ atm}$$

$$K_1\ (\xi_1 = 0,\ \text{phenanthrene}) = 1911.39 \text{ atm}$$

while, as $P \rightarrow 0$ at $T/T_m = 0.9930$, the actual laboratory values of the Henry's law constants are

$$K_1\ (n\text{-dotriacontane}) = 151.75 \text{ atm}$$

$$K_1\ (\text{phenanthrene}) = 746.27 \text{ atm}$$

Looking at the ratio of $K_1\ (\xi_1 = 0)/K_1(\text{actual})$ for each HMW, one sees that

$$K_1 - \text{Ratio}\ (n\text{-dotriacontane}) = 4.47$$

$$K_1 - \text{Ratio}\ (\text{phenanthrene}) = 2.56$$

which would seem to suggest that the paraffin is much more prone to dissolve than the aromatic under similar conditions.

A detailed accounting of the study of these two prototype systems is contained in Cordeiro (1972).

The phenanthrene used was manufactured by the Aldrich Chemical Company and was certified to be better than 98 mole % pure.

ACKNOWLEDGMENT

The authors are grateful for support of this work provided by the American Petroleum Institute (Research Project No. 135).

NOTATION

K_1 = Henry's law constant
N_i = number of moles of component i
P = pressure
R = universal gas constant
T = temperature
T_m = temperature of melting
ΔU_{ij} = interchange energy between components i and j (Flory-Huggins model)
$\overline{V}_i$ = partial molar volume of component i
x_i = mole fraction of component i

Greek Letters

ξ_1 = process function describing whether the HMW is precipitated or dissolved
ξ_2 = process function describing the "efficiency" of the process

Subscripts

1	refers to methane
10	refers to n-decane
14	refers to phenanthrene
H	refers to HMW, that is, high-molecular-weight material

LITERATURE CITED

Cordeiro, D. J., "The Effect of Methane under Pressure on the Liquid Solubilities of High Molecular Weight Hydrocarbon Components in a Liquid Hydrocarbon Phase," Ph.D. dissertation, University of Notre Dame, Indiana (1972).

———., K. D. Luks, and J. P. Kohn, "A Process for Extracting High Molecular Weight Hydrocarbons from a Solid Phase in Equilibrium with a Liquid Hydrocarbon Phase," *Ind. Eng. Chem. Process Design Develop.* (in press).

Manuscript received October 5, 1972; note accepted October 6, 1972.