# Some Thermodynamic Aspects of Petroleum Recovery by Methane Pressurization

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In two previous papers (Cordeiro et al., 1973a, b) a methane pressurization process was described by which the solubility of high molecular weight hydrocarbons in a solid phase could be enhanced within a liquid hydrocarbon phase by pressurizing the solid-liquid system with methane gas. This solubility enhancement was demonstrated to occur for two diverse hydrocarbon solids in the following prototype systems:

System I: methane (gas)—normal decane (liquid)—normal dotriacontane (solid)
System II: methane (gas)—normal decane (liquid)—phenanthrene (solid)

and some speculation was offered concerning the selectivity of aromatic vs. paraffinic solids of similar melting point under methane pressurization with $n$-decane being the liquid solvent in each case.

In this paper, several thermodynamic aspects of the process are considered with respect to the Systems I and II and also

System III: methane (gas)—trans decalin (liquid)—normal dotriacontane (solid)

the study of which has been recently completed. These experimental results are presented below.

## EXPERIMENT-SYSTEM III

An experimental study of the phase equilibria behavior of the ternary system methane-trans decalin-normal dotriacontane was performed. The data was correlated with the Flory-Huggins model (Flory, 1942; Huggins, 1942) solely for the purpose of aiding the later thermodynamic analysis of the system with respect to process behavior. Our previous work (Cordeiro et al. 1973a) presents the equations of this model in detail. The model works as well as with System I, and better than with System II, using the following partial molar volume and interaction parameter data:

$$\begin{aligned}
\overline{V}_1 &= 0.12T + 6.65 && \text{cc/g-mole}\\
\overline{V}_{td} &= 0.149T + 114.76 && \text{cc/g-mole}\\
\overline{V}_{32} &= 2.8T - 385.0 && \text{cc/g-mole}\\
\Delta U_{1,td} &= 1478.61 && \text{cal/g-mole}\\
\Delta U_{1,32} &= 3058.4 && \text{cal/g-mole}\\
\Delta U_{td,32} &= 234.52 && \text{cal/g-mole}
\end{aligned}$$

where $T$ is °K. The data are applicable in the range of 323-340°K up to pressures of 70 atm. These data were obtained from the following laboratory experiments, each of which was reproduced at least once. The purpose of these experiments is discussed in detail in Cordeiro et al. (1973a):

1. Trans decalin-normal dotriacontane solid-liquid equilibria: Freezing points were taken at 8 compositions at 1 atm.
2. Methane-trans decalin vapor-liquid equilibria: Liquid compositions and volumes were obtained at 70° and 100°C up to pressures of 70 atm.
3. Methane-trans decalin-normal dotriacontane vapor-liquid equilibria: Liquid compositions and volumes were obtained at 70°C up to pressures of 70 atm for the following initial molar compositions (that is, no methane present):

21.58% trans decalin

50.65% trans decalin

63.76% trans decalin

4. Methane-trans decalin-normal dotriacontane solid-liquid-vapor equilibria: To test the predictions of the Flory-Huggins model, two loci of constant $(x_{td}/x_{32})$, where

$$x_{td}/x_{32} = 0.2753$$
$$x_{td}/x_{32} = 1.1008$$

were established.

The data on pure normal dotriacontane and methane-normal dotriacontane mixtures obtained by Cordeiro et al. (1973a) were also used. Noteworthy is the fact that there was no significant change in $\overline{V}_1$ and $\overline{V}_{32}$, comparing System I to System III, the same temperature dependence being maintained in both Systems.

Table 1 presents the isotherm $T/T_m = 0.993$ for System III.

## THERMODYNAMICS AND MODELING

The two thermodynamic functions chosen to describe the economics of the methane pressurization process are (Cordeiro et al., 1973a, b):

$$\xi_1 \equiv \left[\frac{\partial(x_H/x_M)}{\partial P}\right]_T = \frac{1}{N_M}\left(\frac{\partial N_H}{\partial P}\right)_T$$

$$\xi_2 \equiv \frac{(\partial N_H/\partial P)_T}{(\partial N_1/\partial P)_T} = \frac{(1-x_1)\left(\frac{\partial x_H}{\partial P}\right)_T + x_H\left(\frac{\partial x_1}{\partial P}\right)_T}{(1-x_H)\left(\frac{\partial x_1}{\partial P}\right)_T + x_1\left(\frac{\partial x_H}{\partial P}\right)_T}$$

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$\xi_1$ determines whether the high molecular weight (HMW) hydrocarbon dissolves or precipitates upon pressurization,

$$\xi_1 > 0, \quad \text{dissolution of HMW}$$

$$\xi_1 < 0, \quad \text{precipitation of HMW}$$

while $\xi_2$ compares the rate at which HMW and the compressing gas methane go into solution (or HMW precipitates if $\xi_1$, and thus $\xi_2$, are negative).

Table 2 gives $\xi_1$ and $\xi_2$ as a function of pressure at $T/T_m = 0.993$ for the three systems studied. Systems I and III are quite similar in behavior. If any comparison can be made, it seems to favor the presence of the naphthenic liquid being present from the standpoint of process yield of dissolved HMW paraffins. Cordeiro et al. (1973b) have presented arguments earlier that show that, despite the high values of $\xi_2$ in System II, HMW paraffins will probably be preferentially dissolved over HMW aromatics.

This classification of Systems I and III as being more favorable for process yield than System II is further justified by examining the excess Gibbs energy $\Delta G_E$ for the liquid phase using the Flory-Huggins model. It was found that

$$\Delta G_E < 0 \quad \text{for Systems I and III}$$

$$\Delta G_E > 0 \quad \text{for System II}$$

The nonideal effects apparently enhance dissolution in Systems I and III and oppose it in System II, although it does not prohibit it in the latter case.

The computation of composition as a function of pressure at any given $T/T_m$ is fairly lengthy when one uses the Flory-Huggins model. See Cordeiro et al. (1973a). Furthermore, they are restricted to particular prototype systems about which, hopefully, generalizations can be made. Our goal here is to offer some suggestions concerning modeling the pressurization process in general in a manner simpler and less detailed than a Flory-Huggins description. For example, one might propose an ideal pressurization described by

$$x_1 = P/P_0{}^1$$

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

$$x_1 + x_M + x_H = 1$$

which, when combined with freezing point depression data, will generate $\{x_i\}$ as a function of $P$ at some $T < T_m$, where $i = 1, M, H$. To get the hypothetical vapor pressure of a supercritical gas like methane, one might use the equation proposed by Hougen et al. (1959):

$$\log_{10} P_r = \frac{-A(1 - T_r)}{T_r} - 10^{-8.68(T_r - b)^2}$$

where

$$A = 16.25 - 73.85\, z_c + 90\, z_c{}^2$$

$$b = 1.8 - 6.2\, z_c$$

Such a description ignores the nature of the liquid phase mixture. Use of this description for the three systems showed that it did a fair job at describing System II, slightly overestimating the solubility of methane, but was poor for Systems I and III, being as much as three-fold short on predicting $x_1 = x_1(P)$ at $T/T_m = 0.993$. The effect on $(\xi_1, \xi_2)$ at $P = 0$ is accordingly mispredicted. It is noteworthy, however, that the expression for $(\partial \ln x_H/\partial P)_T$ was found to be a reasonably good representation of the experimental process behavior.

Table 1. Composition and the Parameters $(\xi_1, \xi_2)$ as a Function of Pressure for the System Methane-trans Decalin-Normal Dotriacontane at 340°K ($T/T_m = 0.993$). Nonphysical Means That This Pressure Can Never be Reached (That is, $x_{td} < 0$)

| $P$ atm | $x_1$ mole fraction | $x_{32}$ mole fraction | $\xi_1$ atm$^{-1}$ | $\xi_2$ |
|---|---|---|---|---|
| 0 | 0.0 | 0.8853 | 0.3544 | 6.189 |
| 5 | 0.0324 | 0.8798 | 0.5828 | 6.182 |
| 10 | 0.0636 | 0.8740 | 1.098 | 6.118 |
| 15 | 0.0937 | 0.8682 | 2.807 | 6.087 |
| 20 | 0.1227 | 0.8624 | 17.44 | 6.071 |
| 25 | | | nonphysical | |

Table 2. Values of $\xi_1$ and $\xi_2$ as a Function of Pressure at $T/T_m = 0.993$, Where $T_m$ is the Melting Temperature of the HMW Material, for the Three Systems Studied. The Tabulations are Terminated at Those Pressures Where $x_{10}$ or $x_{td}$ Computes $< 0$

| $P$ | System I | | System II | | System III | |
|---|---|---|---|---|---|---|
| atm | $\xi_1$(atm$^{-1}$) | $\xi_2$ | $\xi_1$(atm$^{-1}$) | $\xi_2$ | $\xi_1$(atm$^{-1}$) | $\xi_2$ |
| 0 | 0.1887 | 4.3091 | 0.5996 | 16.5543 | 0.3544 | 6.189 |
| 5 | 0.2465 | 4.2640 | 0.7148 | 15.8772 | 0.5828 | 6.182 |
| 10 | 0.3594 | 4.2267 | 0.8582 | 15.4395 | 1.098 | 6.118 |
| 15 | 0.5724 | 4.1980 | 1.0941 | 15.2827 | 2.807 | 6.087 |
| 20 | 1.0463 | 4.1810 | 1.4148 | 15.0735 | 17.44 | 6.071 |
| 25 | 2.5005 | 4.1634 | 1.8939 | 14.9205 | | |
| 30 | 12.1909 | 4.1579 | 2.7075 | 14.8477 | | |
| 35 | | | 4.1227 | 14.6974 | | |
| 40 | | | 7.0702 | 14.6083 | | |
| 45 | | | 14.3048 | 14.5050 | | |
| 50 | | | 47.8271 | 14.5083 | | |
| 55 | | | 1,176.0977 | 14.4797 | | |
| 60 | | | — | — | | |

Use of an equation for liquid phase fugacity developed by Lee and Edmister (1971) in union with the Lewis and Randall rule to predict the liquid solubilities of methane achieves good agreement with experiment for Systems I and III, but is worse than the ideal prediction for II. Table 3 compares the predicted $(\xi_1, \xi_2)$ for Systems I-III with experiment.

## USE OF ETHANE FOR PRESSURIZATION

One of the main reasons that the methane pressurization process successfully enhances solubilization of HMW materials is that the dissolving methane swells the liquid phase available. It would seem that if another gas were chosen that were more soluble in the liquid phase than methane but of similar chemical nature, the process might be carried out at lower pressures. A likely candidate gas is ethane.

A computer simulation of the system ethane (gas)—normal decane (liquid)—normal dotriacontane (solid) was carried out for purposes of comparison with System I. The Flory-Huggins interchange energies $\Delta U_{2,10}$ and $\Delta U_{2,32}$ and the partial molar volume $\overline{V}_2$ were needed. Kohn and co-workers (1967, 1968, 1969, 1970) have investigated the systems of ethane with normal octane, normal dodecane, normal eicosane, and normal octacosane. Their results were analyzed and, based on these results, values for $\Delta U_{2,10}$, $\Delta U_{2,32}$ and $\overline{V}_2$ were estimated as best possible, if somewhat crudely. The results obtained for the temperature range

TABLE 3. A COMPARISON OF THE VALUES OF $\xi_1$ AND $\xi_2$ FOR SYSTEMS I TO III AT $P = 0$ AND $T/T_m = 0.993$ BETWEEN EXPERIMENT AND THOSE PREDICTED USING LEE-EDMISTER FUGACITIES IN CONJUNCTION WITH THE LEWIS-RANDALL RULE

| | | $\xi_1$ (atm$^{-1}$) | $\xi_2$ |
|---|---|---|---|
| System I | experimental | 0.1887 | 4.31 |
| | predicted | 0.2118 | 4.30 |
| System II | experimental | 0.5996 | 16.55 |
| | predicted | 5.3046 | 25.98 |
| System III | experimental | 0.3544 | 6.189 |
| | predicted | 0.4265 | 6.256 |

TABLE 4. COMPOSITION AND THE PARAMETERS ($\xi_1$, $\xi_2$) AS A FUNCTION OF PRESSURE PREDICTED FOR THE SYSTEM ETHANE-NORMAL DECANE-NORMAL DOTRIACONTANE AT 340°K ($T/T_m = 0.993$). THE TABLE HAS BEEN TERMINATED AT THOSE PRESSURES AT WHICH $x_{10}$ COMPUTES $< 0$. NOTE THAT $\xi_1 \to \infty$ AS $x_{10} \to 0$

| $P$ atm | $x_2$ mole fraction | $x_{32}$ mole fraction | $\xi_1$ (atm$^{-1}$) | $\xi_2$ | $\Delta G_E$ cal/g-mole |
|---|---|---|---|---|---|
| 0 | 0.0 | 0.8412 | 0.8636 | 5.087 | −14.50 |
| 1 | 0.0270 | 0.8403 | 1.215 | 5.086 | −15.01 |
| 2 | 0.0530 | 0.8394 | 1.800 | 5.083 | −15.46 |
| 3 | 0.0786 | 0.8385 | 2.955 | 5.071 | −15.88 |
| 4 | 0.1035 | 0.8375 | 5.691 | 5.063 | −16.28 |
| 5 | 0.1279 | 0.8366 | 15.28 | 5.063 | −16.66 |
| 6 | 0.1517 | 0.8356 | 116.4 | 5.061 | −17.02 |

330-340°K were

$$\Delta U_{2,10} = 712.21 \quad \text{cal/g-mole}$$

$$\Delta U_{2,32} = 2048 \quad \text{cal/g-mole}$$

$$\overline{V}_2 = 0.12T + 26.7 \quad \text{cc/g-mole}$$

Table 4 presents an ethane pressurization process at $T/T_m = 0.993$, which would be analogous to System I at the same temperature. See Cordeiro et al. (1973a or b). Noteworthy is the occurrence of the singularity in $\xi_1$ at a much lower pressure. This is the pressure at which gas and HMW material are dissolved continuously in fixed proportion without any further increase in pressure. Furthermore, $\xi_2$ is greater than in System I and, in conjunction, the solubility of ethane is greater.

## REMARKS

There are two aspects of this study worthy of reemphasis. First of all, not only is the process successful for all systems so far investigated but there is hope that some simple correlations can provide meaningful, approximate predictions of the process behavior without involving oneself with the complexity of the liquid phase composition. Secondly, the prospect of using gases other than methane is a promising area of consideration, ethane being an example of one such substitution.


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## NOTATION

$(A, b)$ = constants in equation of Hougen et al. (1959) for vapor pressure
$\Delta G_E$ = excess molar Gibbs free energy of mixing
$N_i$ = number of moles of component $i$
$P$ = pressure
$P_c$ = critical pressure
$P_r$ = reduced pressure = $P/P_c$
$P_0^1$ = vapor pressure of component methane
$T$ = temperature
$T_m$ = melting point temperature of HMW material
$T_c$ = critical temperature
$T_r$ = reduced temperature = $T/T_c$
$\Delta U_{i,j}$ = Flory-Huggins interchange energy between components $i$ and $j$
$v$ = molar volume
$\overline{V}_i$ = partial molar volume of component $i$
$\Delta v_m$ = change of molar volume upon melting
$x_i$ = mole fraction of component $i$
$z_c$ = critical compressibility factor
$(\xi_1, \xi_2)$ = process derivative functions defined in Section II

### Subscripts

$H$, HMW = refer to high molecular weight material
$M$ = refers to liquid component, for example, $n$-decane or trans decalin
$i, j$ = refers to species $i$ or $j$
$td$ = trans decalin
1 = methane
2 = ethane
10 = normal decane
32 = normal dotriacontane
$m$ = melting point

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