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## Viscosity prediction of Athabasca bitumen using the extended principle of corresponding states

Susan E. Johnson, William Y. Svrcek, and Anil K. Mehrotra

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$I_1$  = integral defined by eq 6  
 $K$  = coefficient in the expansion of the modified Van Driest equation,  $9.1033 \times 10^{-4}$   
 $k_c^0$  = mass-transfer coefficient for no reaction  
 $k_R$  = first-order homogeneous reaction rate constant  
 $M = k_R D / (k_c^0)^2$   
 $Q = (ScK)^{1/3} R^+$   
 $R$  = duct radius  
 $R^+$  = dimensionless duct radius, equal to  $Ru^*/\nu$   
 $r$  = radial coordinate  
 $Re$  = Reynolds number, equal to  $uD/\nu$   
 $Sc$  = Schmidt number, equal to  $\nu/D_A$   
 $Sh$  = Sherwood number  
 $u$  = mean axial velocity  
 $u^*$  = friction velocity, equal to  $u(f/2)^{1/2}$   
 $x$  = axial distance  
 $y$  = distance from the wall  
 $y^+$  = dimensionless distance from the wall, equal to  $yu^*/\nu$

#### Greek Symbols

$\alpha = \gamma K^{-2/3} (R^+)^{-2} Sc^{1/3}$   
 $\epsilon_D$  = eddy diffusivity of mass  
 $\epsilon_D^+ = \epsilon_D / \nu$   
 $\gamma = k_R R^2 / \nu$

$\nu$  = kinematic viscosity  
 $\phi$  = enhancement factor

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## Viscosity Prediction of Athabasca Bitumen Using the Extended Principle of Corresponding States

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The viscosity of gas-free and gas-saturated Athabasca bitumen was predicted by using the extended principle of corresponding states. Bitumen was characterized as a mixture of several pseudocomponents, and the Kesler-Lee correlations were used to estimate the critical temperature and pressure and the acentric factor of each pseudocomponent. The critical volume was calculated by using the method of Riedel. With methane as the reference fluid and paraffinic shape factors, the viscosity predictions were completely inadequate. To improve viscosity predictions, four compounds of aromatic-naphthenic nature were screened as possible reference fluids. Of these, 1,2,3,4,5,6,7,8-octahydrophenanthrene (PSU 625) gave the bitumen viscosity predictions that were within an average absolute deviation of 6% from the experimental data over a temperature range of 20–130 °C. Subsequently, the viscosity predictions were extended to gas-saturated bitumen. For the CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>-saturated bitumen viscosity data, average absolute deviations of 19%, 29%, and 7%, respectively, were obtained.

The thermodynamic and transport properties of bitumen/gas systems have been presented in numerous studies. Ward and Clark (1950) reported the viscosity and specific gravity of a number of different samples of Athabasca bitumen. Jacobs et al. (1980) measured the viscosity of gas-free Athabasca bitumen and Athabasca bitumen saturated with CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>. Viscosity, density, and gas-solubility data for Athabasca bitumen saturated with CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, CO, and C<sub>2</sub>H<sub>6</sub> and a synthetic combustion gas were provided by Svrcek and Mehrotra (1982) and Mehrotra and Svrcek (1982, 1985a). Data for bitumens from other oil sand deposits in Canada were also provided by Mehrotra and Svrcek (1984, 1985b,c).

Numerous correlations and prediction methods have been developed to predict the variation of viscosity with

temperature. A number of correlations, which were developed for oils, were examined by Jacobs (1978). Mehrotra and Svrcek (1982, 1984) presented correlations for the viscosity and solubility of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>-saturated Athabasca bitumen. Modified forms of the Eyring and Hildebrand equations to predict the viscosity of gas-free Athabasca bitumen were proposed by Khan et al. (1984). Khan et al. also presented two empirical correlations for gas-free bitumen. A graphical method for the viscosity of gas-free bitumen was developed by Sarkar (1984).

All of the existing correlations for gas-free and gas-saturated bitumen viscosity are empirical in nature. In each case, viscosity data are required to fit the correlation constants. In this paper, we present a predictive method based on the extended corresponding states principle to calculate the viscosity of gas-free and gas-saturated bitumen. For gas-saturated bitumen, the viscosity predictions from a three-parameter generalized corresponding states

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**Table I. Characterization of Abasand Bitumen Based on the Analysis of Boyd and Montgomery (1963)**

fraction	wt %	$M$ , g/mol	SG	NBP, K	$T_c$ , K	$P_c$ , MPa	$V_c$ , cm <sup>3</sup> /mol	$\omega$
A	0.52	363	0.8762	682.6	836.4	1.082	1393	1.021 125
B	10.24	360	0.8876	682.9	840.9	1.132	1345	1.004 072
C	1.27	317	0.9025	650.6	824.0	1.393	1104	0.882 456
D	0.55	643	0.9279	891.8	995.0	0.495	3109	1.527 243
E	3.17	582	0.9263	852.4	969.1	0.597	2599	1.424 655
F	2.52	431	0.9437	753.2	911.1	1.026	1557	1.117 435
G	1.85	369	0.9592	708.9	886.8	1.321	1226	0.967 472
H	0.56	341	0.9694	688.1	876.1	1.495	1092	0.885 493
J	12.42	340	0.9923	693.8	889.0	1.574	1058	0.862 746
CCl <sub>4</sub> (I)	8.55	519	1.0599	868.0	1037.4	0.979	1806	1.218 998
CCl <sub>4</sub> (II)	4.50	592	1.0619	925.6	1076.6	0.777	2265	1.361 532
CCl <sub>4</sub> (III)	1.37	577	1.0539	909.5	1062.4	0.806	2171	1.336 359
C <sub>6</sub> H <sub>6</sub>	4.78	821	1.1180	1146.2	1244.8	0.378	4764	1.762 204
CHCl <sub>3</sub>	16.73	976	1.0869	1222.7	1276.8	0.222	7576	1.987 363
CH <sub>3</sub> OH	7.97	834	1.0869	1122.9	1214.8	0.362	4802	1.774 874
asphaltenes	23.00	2492	1.1601	1323.3	1376.9	0.200	9366	2.034 313
av		1048	1.045					

method are also presented. The method is predictive in that no mixture (i.e., bitumen) physical or transport properties are required as input data. The only data required are the critical properties, acentric factor, and mole fraction of each of the bitumen pseudocomponents.

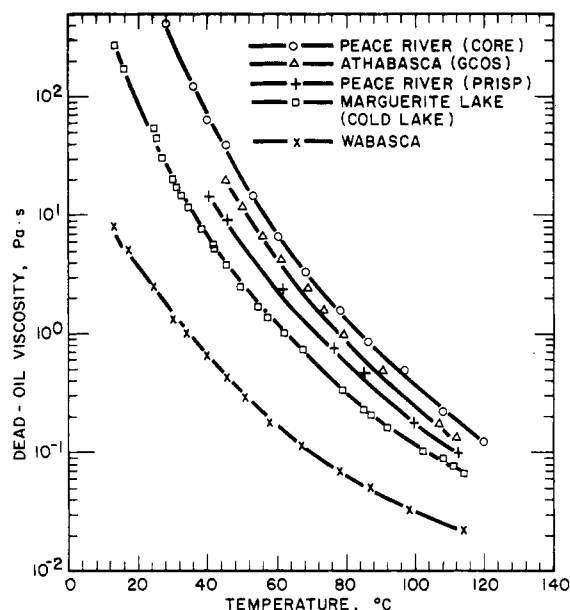
### Bitumen Characterization

It is well-known that bitumens from different locations can have significantly different viscosities. In Figure 1, the viscosity versus temperature curves for a number of gas-free Alberta bitumens are shown. All of the bitumen viscosity data in Figure 1 were obtained by using a Contraves DC44 concentric cylinder viscometer (Mehrotra and Svrcek, 1985c). Due to its complex nature, bitumen is commonly fractionated into two major components for analysis: the maltene and the asphaltene fractions. Further division of the maltenes into distillable and undistillable fractions is done in the SIMDIST analysis using an arbitrary cutoff normal boiling point of 600 °C.

The pseudocomponent approach, a characterization method extremely useful for undefined mixtures, was applied to bitumen by Bishnoi et al. (1977). Mehrotra et al. (1985a) used this five-pseudocomponent scheme to obtain satisfactory vapor-liquid equilibrium predictions for gas-saturated bitumens. The pseudocomponent approach for bitumens has been shown to give satisfactory vapor-liquid equilibrium (Sarkar, 1984), surface tension (Mehrotra et al., 1985b), and mass diffusivity (Mehrotra et al., 1987) predictions.

To characterize bitumen, it is necessary to obtain at least the specific gravity and the normal boiling point and/or the molecular weight of each pseudocomponent (Newman, 1981). If these properties are known for each fraction, the critical properties and acentric factor can be estimated by using available correlations. Mehrotra et al. (1985a) examined a number of these correlations for Alberta bitumens and found that the Kesler-Lee (1976) correlations were the most appropriate for bitumen/gas systems. Hence, we used the Kesler-Lee correlations to estimate the critical temperature, critical pressure, and acentric factor. The critical volume was calculated by using the method of Riedel (Reid et al., 1977).

**Abasand Bitumen.** Relatively abundant data are available for the maltene-distillable and the asphaltene fractions (Strausz, 1977; Svrcek and Mehrotra, 1982; Yen and Dickie, 1968; Bunger et al., 1975; Winniford, 1963). However, the only data available in the literature with analyses for each fraction of bitumen were published by Boyd and Montgomery (1961a,b, 1962, 1963). Boyd and Montgomery employed a solvent separation technique



**Figure 1.** Viscosity of Alberta bitumens (Mehrotra and Svrcek, 1985c).

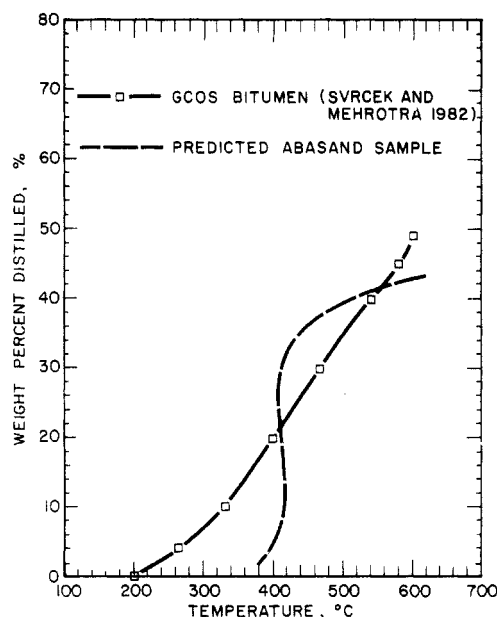
coupled with chromatographic elution to divide an Athabasca bitumen from the Abasand quarry into 16 fractions. For each fraction the molecular weight, specific gravity, and several other properties were given. Table I presents the experimental and calculated properties of the 16 pseudocomponents. A pseudodistillation curve for the Abasand bitumen using the predicted normal boiling point for each fraction is shown in Figure 2.

The viscosity predictions using the Boyd-Montgomery characterization for the Abasand bitumen could not be verified due to a lack of the viscosity data for their bitumen. In order to verify the bitumen viscosity predictions, it was necessary to work with a bitumen for which both viscosity and bitumen property data were available. For the Athabasca (GCOS) bitumen samples investigated by Svrcek and Mehrotra (1982), the viscosity data and the simulated distillation (SIMDIST) curves were available.

**GCOS Bitumen.** By use of the Abasand characterization as a base, several characterization schemes for the GCOS bitumen were developed (Johnson, 1985). Two of the characterization schemes, schemes 1a and 1b, were developed with the assumption that a change in the molecular weight of each Abasand bitumen fraction would be sufficient to account for the differences in the two bitumens. In these characterization schemes, the mole frac-

**Table II. Characterization of Pseudocomponents of GCOS Bitumen Scheme 2: Comparative Analysis [Based on the Data of Svrcek and Mehrotra (1982)]**

fraction	wt %	<i>M</i> , g/mol	SG	NBP, K	<i>T<sub>c</sub></i> , K	<i>P<sub>c</sub></i> , MPa	<i>V<sub>c</sub></i> , cm <sup>3</sup> /mol	ω
1	8.08	200	0.9769	550.7	774.2	2.715	594	0.505 556
2	31.52	374	1.0508	743.2	947.4	1.555	1130	0.901 369
3	41.20	610	1.0819	952.6	1103.3	0.752	2382	1.389 634
4	19.20	1089	1.1601	1421.1	1437.1	0.120	17800	2.215 240
av		595	1.077					

**Figure 2.** SIMDIST curves for the maltenes fraction in Athabasca bitumen.

tions, mass fractions, and specific gravities of the pseudocomponents were kept constant. In scheme 1a, the molecular weight of each Abasand bitumen fraction was multiplied by the ratio of the molecular weights of the GCOS and the Abasand bitumens. In scheme 1b, the molecular weight of each Abasand bitumen fraction was multiplied by the ratio of the GCOS bitumen molecular weight and the mole-average Abasand bitumen molecular weight.

In the third characterization scheme, scheme 2, a different approach was used. In this scheme, termed the comparative analysis scheme, the pseudodistillation curve was compared with the SIMDIST curve for the GCOS bitumen, Figure 2. The relative compositions of the two bitumens, in terms of the fraction of the bitumens comprising the maltene-distillable, maltene-undistillable, and asphaltene fractions, were also compared. By examining the differences and similarities in the distillation curves, the compositions, and the bitumen molecular weights and specific gravities, a four-pseudocomponent characterization, Table II, was developed for the GCOS bitumen.

The fourth characterization, scheme 4, was that of Bishnoi et al. (1977). The last characterization scheme, scheme 5, consisted of only one pseudocomponent which had the molecular weight and specific gravity of the GCOS bitumen (Johnson, 1985).

### General Corresponding States Theory and Model Development

The corresponding states method has proven to be one of the most useful methods for predicting the properties of fluids. The principle states that the dimensionless groups of properties of two pure fluids at corresponding reduced conditions have the same numerical value (Leach, 1967). Thus, the properties of a fluid are predicted from

the knowledge of the physical parameters and the known properties of another (reference) fluid.

**The Method of Ely and Hanley.** If two fluids correspond, the transport coefficients of one fluid,  $\alpha$ , at a particular temperature and density can be expressed in terms of the other fluid, the reference fluid,  $o$ . According to Hanley (1976), for fluid  $\alpha$ ,

$$\eta_{\alpha}(\rho, T) = \eta_o[\rho(\rho_{co}/\rho_{ca}), T(T_{co}/T_{ca})] \times (M_{\alpha}/M_o)^{1/2}(\rho_{ca}/\rho_{co})^{2/3}(T_{co}/T_{ca})^{1/2} \quad (1)$$

The principle of corresponding states was extended to mixtures by Mo and Gubbins (1974) who used the van der Waals one-fluid approximation to equate the mixture to an equivalent pure fluid and developed the following equation for a binary mixture,  $x$ :

$$\eta_x(\rho, T) = \eta_o[\rho(\rho_{co}/\rho_{cx}), T(T_{co}/T_{cx})] \times (M_x/M_o)^{1/2}(\rho_{cx}/\rho_{co})^{2/3}(T_{co}/T_{cx})^{1/2} \quad (2)$$

To extend the framework to polyatomic fluids and nonconformal mixtures, the shape factor approach developed by Leach et al. (1966) was employed by Ely and Hanley (1981a,b). The following relations were used:

$$f_{\alpha,o} = (T_{co}/T_{co})\Theta_{\alpha,o} \quad (3)$$

$$h_{\alpha,o} = (\rho_{co}/\rho_{ca})\Phi_{\alpha,o} \quad (4)$$

where the shape factors are given by

$$\Theta_{\alpha,o}(T_{ra}, V_{ra}, \omega_{\alpha}) = 1 + A_t(\omega_{\alpha} - \omega_o)(a_1 + b_1 \ln T_{\alpha}^+ + (c_1 + d_1/T_{\alpha}^+)(V_{\alpha}^+ - 0.5)) \quad (5)$$

$$\Phi_{\alpha,o}(T_{ra}, V_{ra}, \omega_{\alpha}) = [1 + (\omega_{\alpha} - \omega_o)(a_2 A_p(V_{\alpha}^+ + b_2 A_p)) + c_2 A_p(V_{\alpha}^+ + d_2 A_p) \ln T_{\alpha}^+] Z_{co}/Z_{ca} \quad (6)$$

and

$$T_{\alpha}^+ = \min [2, \max \{T_{ra}, 0.5\}] \quad (7)$$

$$V_{\alpha}^+ = \min [2, \max \{V_{ra}, 0.5\}] \quad (8)$$

In the Ely-Hanley method, the original restriction imposed by Leach et al. (1966) on  $T_r$  (eq 7) is eliminated. In eq 5 and 6,  $A_t$  and  $A_p$  are two multiplying factors which were introduced in this work to correctly predict bitumen density.

The shape factors,  $\Theta_{\alpha,o}$  and  $\Phi_{\alpha,o}$ , vary weakly with temperature and density. Including these in the expression for the viscosity coefficient of a mixture gives

$$\eta_x(\rho, T) = \eta_o(\rho h_{x,o}, T/f_{x,o})(M_x/M_o)^{1/2} h_{x,o}^{-2/3} f_{x,o}^{1/2} \quad (9)$$

$$h_{x,o} = \sum_{\alpha} \sum_{\beta} X_{\alpha} X_{\beta} h_{\alpha\beta,o} \quad (10)$$

$$f_{x,o} h_{x,o} = \sum_{\alpha} \sum_{\beta} X_{\alpha} X_{\beta} f_{\alpha\beta,o} h_{\alpha\beta,o} \quad (11)$$

$$f_{\alpha\beta,o} = (1 - k_{\alpha\beta})(f_{\alpha,o} f_{\beta,o})^{1/2} \quad (12)$$

$$h_{\alpha\beta,o} = (1 - l_{\alpha\beta})(\frac{1}{2} h_{\alpha,o}^{1/3} + \frac{1}{2} h_{\beta,o}^{1/3})^3 \quad (13)$$

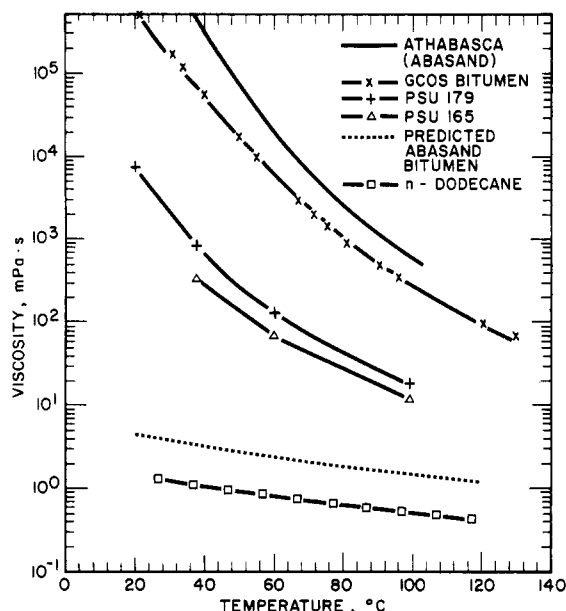


Figure 3. Measured and predicted viscosities of bitumen and pure compounds.

In eq 12 and 13, the interaction parameters  $k_{\alpha\beta}$  and  $l_{\alpha\beta}$  were assumed to be zero due to a lack of data for bitumen. The Ely-Hanley method incorporates all of the mixing rules derived by Mo and Gubbins (1974) except for the mass mixing rule

$$h_{x,0}^{4/3} f_{x,0}^{1/2} M_x^{1/2} = \sum_{\alpha} \sum_{\beta} X_{\alpha} X_{\beta} h_{\alpha\beta,0}^{4/3} f_{\alpha\beta,0}^{1/2} M_{\alpha\beta}^{1/2} \quad (14)$$

### Viscosity Predictions for Gas-Free Bitumen

**Methane as the Reference Fluid.** Ely-Hanley Shape Factors for *n*-Paraffins. As a first attempt, the TRAPP (Transport Properties Prediction) program developed by Ely and Hanley (1981b) was used to calculate the viscosity of the Abasand bitumen using the 16-component characterization, Table I. As the density of each component was known at 20 °C, the program was used to predict the density and viscosity of each component at this temperature. Convergence problems were encountered for the components with molecular weight greater than approximately 400 g/mol. The predicted densities for the components for which convergence was achieved were extremely high (Johnson, 1985). The large deviations in the predicted densities suggested that the paraffin shape factors would have to be modified.

**Modification of the Paraffin Shape Factors.** At low-to-moderate densities, hydrocarbon shape factors are known to be only temperature dependent. However, at high densities the shape factors also become density dependent (Leach et al., 1966). The shape factor ( $\Phi_{\alpha,0}$ ) is more density dependent than  $\Theta_{\alpha,0}$ . Hence, it was decided to reduce the influence of  $\Theta_{\alpha,0}$  and thus make the prediction more density dependent. It is emphasized that the shape factors were modified to improve the density predictions for the "heavier" hydrocarbons.

The shape factors were modified by introducing two multiplying factors,  $A_t$  and  $A_p$ , in eq 5 and 6, respectively. The multiplication factors were evaluated by a trial and error procedure using the experimental density as a basis for comparison (Johnson, 1985). The multiplication factor  $A_p$  was found to be a function of the acentric factor when the multiplication factor  $A_t$  was set to 0.1. The optimized  $A_p$  correlations with  $\omega$  that yielded the best density pre-

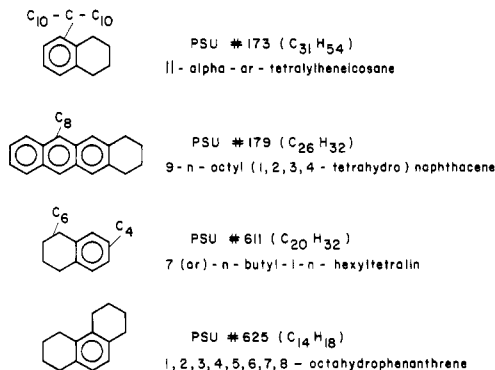


Figure 4. Molecular structure of aromatic-naphthenic compounds used as reference fluids.

dictions (AAD = 0.57%) for all 16 components in Table I are given as eq 15. The bitumen density predictions improved dramatically with these simple shape factor modifications (Johnson, 1985).

$$A_p = \begin{cases} 0.1337367\omega + 0.7690133 & \text{NBP} \leq 685 \text{ K} \\ 0.0819147\omega + 0.7933043 & 685 \text{ K} < \text{NBP} \leq 1000 \text{ K} \\ -0.0081948\omega + 0.9327518 & 1000 \text{ K} < \text{NBP} \leq 1275 \text{ K} \\ 0.8416 & \text{NBP} > 1275 \text{ K} \end{cases} \quad (15)$$

Figure 3 gives a comparison of the predicted viscosity of the Abasand bitumen and the viscosities of some other compounds. The predicted viscosities are very low, and these actually follow the pattern of a *n*-paraffin as evidenced by the viscosity-temperature curve for *n*-dodecane. Also shown in Figure 3 are the viscosity data (API, 1966) for a fused-ring aromatic compound (PSU 179) and a fused-ring naphthenic compound (PSU 165). The viscosity-temperature curves of these compounds, however, do follow the same trend as the curves for the bitumens.

It is apparent from Figure 3 that the modification of the shape factors with simple multiplying factors is not sufficient to predict the viscosity of bitumen. It is possible that this failure is due to the inability of the shape factors to account for the extreme differences in the potential energy functions of the fluid of interest, bitumen, and the reference fluid, methane. It was postulated that if the reference fluid and the fluid of interest were members of the same class of compounds (e.g., paraffins, naphthenes, aromatics, etc.), the functional form of the shape factor correlations may not have to be altered. Consequently, a reference fluid was sought which possessed molecular characteristics similar to bitumen.

**Aromatic-Naphthenic Reference Fluids.** Four high molecular weight hydrocarbons, which had the same type of molecular configuration as bitumen, were chosen as the trial reference fluids from API Research Project 42 (1966). The molecular structures of these branched aromatic/naphthenic compounds are shown in Figure 4. For each reference fluid, an equation of state and a reference fluid density-temperature correlation were developed. The multiplication factors,  $A_t$  and  $A_p$ , were again determined. For PSU 179,  $A_p$  was found to be a function of acentric factor. For the remaining three reference fluids,  $A_p$  was found to be a function of critical pressure. The data, calculated properties, and developed correlations for PSU 625 are given in Table III.

The viscosity predictions for the Abasand bitumen are shown in Figure 5. Noting that the Abasand bitumen is heavier than GCOS bitumen, PSU 625 was selected as the reference fluid for the prediction of the GCOS bitumen viscosity. Figure 6 presents the GCOS bitumen viscosity

**Table III. Data and Correlations for the Reference Fluid PSU 625**

	20 °C	37.8 °C	60 °C	98.9 °C
$\rho$ , g/cm <sup>3</sup>	1.0241	1.0123	0.9973	0.9709
$\eta$ , mPa·s	17.34	8.227	4.260	1.945
$M$ , g/mol	186.3 (C <sub>14</sub> H <sub>18</sub> )	$P_c$ , MPa	3.081	
NBP, K	546.8	$V_c$ , cm <sup>3</sup> /mol	536	
$T_c$ , K	786.6	$\omega$	0.438 434	

density-temp correlation (to fit the above data)

$$\rho = 1.221 - 0.000673T$$

viscosity-temp correlation (to fit the above data)

$$\ln \ln (10^4 \eta) = 48.5307 - 15.0799 \ln T + 1.2279 (\ln T)^2$$

size-shape factor multiplier correlation with  $P_c$ 

$$A_p = 1.676142 - 1.085622P_c + 0.393115P_c^2 \text{ for NBP} \leq 685 \text{ K}$$

$$A_p = 0.935480 + 0.216607P_c - 0.394615P_c^2 + 0.225268P_c^3 - 0.048578P_c^4 \text{ for } 685 \text{ K} < \text{NBP} \leq 1275 \text{ K}$$

$$A_p = 0.865853 \text{ for NBP} > 1275 \text{ K}$$

constants for the Alani-Kennedy equation of state

$$V^3 - [RT/P + mT + c]V^2 + (ke^{n/T}/P)[V - mT + c] = 0$$

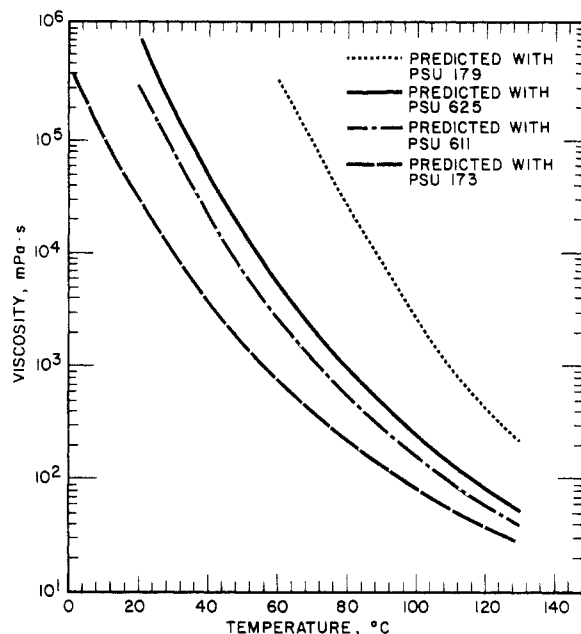
where

$$c = 2.382 432$$

$$k = 2.160 864 \times 10^5$$

$$m = 4.373 353 \times 10^{-4}$$

$$n = -1.592 656 \times 10^2$$

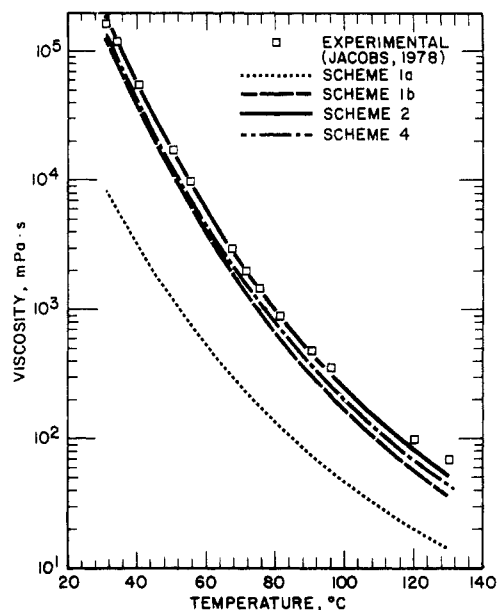
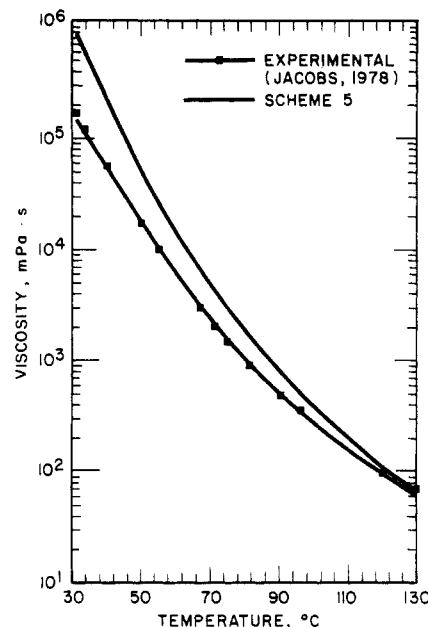
**Figure 5.** Viscosity predictions for Athabasca (Abasand) bitumen with aromatic-naphthenic reference fluids.

predictions for the four multicomponent schemes. It is evident that the comparative analysis scheme, Table II, provided the best characterization of the GCOS bitumen. The predicted viscosities using this characterization are within an average absolute deviation of 6% from the data of Jacobs (1978).

Figure 7 presents the predicted viscosity for the GCOS bitumen using scheme 5, the one-pseudocomponent characterization. Clearly, for this case the predicted viscosities are much higher than the data with an average deviation of 155% (Johnson, 1985). Hence, a one-pseudocomponent scheme is inadequate for bitumen viscosity prediction.

### Viscosity Predictions for Gas-Saturated Bitumen

**The Teja-Rice Corresponding States Method.** The generalized corresponding states method of Teja and Rice (1981) relates the reduced viscosity ( $\eta\xi$ ) of any substance

**Figure 6.** Viscosity predictions for Athabasca (GCOS) bitumen with multicomponent characterization schemes.**Figure 7.** Viscosity predictions for Athabasca (GCOS) bitumen with one-pseudocomponent scheme.

to the viscosities of two nonspherical reference fluids,  $r_1$  and  $r_2$ , at the same reduced temperature and pressure

$$\ln (\eta \xi) = \ln (\eta \xi)^{r_1} + \frac{\omega - \omega^{r_1}}{\omega^{r_2} - \omega^{r_1}} [\ln (\eta \xi)^{r_2} - \ln (\eta \xi)^{r_1}] \quad (16)$$

where

$$\xi = V_c^{2/3} T_c^{-1/2} M^{-1/2} \quad (17)$$

The two reference fluids are selected such that they are similar to the fluid of interest or, in the case of mixtures, to the key components. For mixtures,  $T_{cm}$ ,  $V_{cm}$ ,  $\omega_m$ , and  $M_m$  are calculated from eq A1-A6 in the Appendix. In eq A5, the binary interaction parameter  $\Psi_{ij}$  can be evaluated from experimental data. In this study, the binary interaction parameter was assumed to be unity due to a lack of experimental data for bitumen.

Wong et al. (1983) developed two sets of mixing rules to predict vapor-liquid and vapor-liquid-liquid equilibria in mixtures containing paraffinic and aromatic hydrocarbons, alcohols, and water. Their first set of mixing rules, referred to as mixing rule set 2, is given by eq A7-A12. The second set of mixing rules of Wong et al., referred to as mixing rule set 3, consists of eq A8-A11 along with eq A3. In this study, the adjustable parameters  $\alpha_{ij}$  (eq A10) and  $\beta_{ij}$  (eq A11) were set to unity due to a lack of experimental data. For the mixing rules of Wong et al.,  $\xi$  is calculated by replacing  $V_c$  in eq 17 with  $T_c/P_c$ , and the results are in eq A13.

**Extension of the Reference Fluid Equation of State.** The reference fluid correlations for the viscosity and density were extended from the liquid to the dense and dilute gas-phase regions. To determine the best prediction methods for these properties in each phase, a comprehensive study of the viscosity and the density prediction methods available in the literature was undertaken (Johnson, 1985). For the gas phase, the Soave-Redlich-Kwong (SRK) equation of state (Soave, 1972) was chosen to predict the reference fluid molar volume. The method of Reichenberg (Reid et al., 1977) was used to predict the viscosity of the dilute gas. For the dense gas phase, the best method proved to be a combination of the method of Reichenberg, for the contribution of dilute gas to the dense gas viscosity, and the method of Stiel and Thodos for polar gases (Reid et al., 1977), for the contribution of the dense gas to the dense gas viscosity. These methods gave predictions that compared well with published data for a number of paraffinic and aromatic compounds (Johnson, 1985).

For the liquid phase, the equation of state of Alani and Kennedy (1960) predicted the liquid molar volume with good accuracy. The constants  $c$ ,  $k$ ,  $m$ , and  $n$  for PSU 625 are given in Table III. A correlation developed by Briggs et al. (1984) for CO<sub>2</sub>-saturated Cold Lake bitumen, eq 18, was used to obtain the viscosity of gas-free bitumen at higher pressures. In this study, the CO<sub>2</sub> composition correction in eq 18 was not used; i.e.,  $X = 0$ .

$$\ln \eta_{P,T,X} = \ln \eta_{T(P=0,X=0)} + B_T P - C_T X \quad (18)$$

**Variations in the Three Bitumen Samples.** In order to predict the viscosities of the bitumen samples used in the gas-saturated experiments of Svrcek and Mehrotra (1982), it was necessary to obtain good characterizations for each of the samples. The comparative analysis scheme, Table II, was developed for the bitumen sample used in the CO<sub>2</sub>-bitumen experiments by Svrcek and Mehrotra (1982), and this sample was very similar to that of Jacobs (1978). However, the samples used for the CH<sub>4</sub>- and N<sub>2</sub>-saturated experiments had somewhat lower viscosities. It was, therefore, necessary to modify the bitumen characterization to account for the lower viscosity values. For each of the bitumen samples, Svrcek and Mehrotra (1978) had provided a SIMDIST curve. These SIMDIST curves differed slightly, although the bitumen samples were obtained from the same batch of Athabasca oil sand. The differences in the SIMDIST curves were attributed to a different amount of toluene in each sample which may have been left in the toluene-extraction step. The amount of toluene in the bitumen was estimated by using the extended corresponding states approach. For toluene,  $A_t$  was set to 0.1 and  $A_p$  was calculated as 0.295. By use of a trial and error procedure, the predicted results were matched with the data of Svrcek and Mehrotra, and in this way an estimate of the toluene content of the samples was obtained. The samples used in the N<sub>2</sub> and CH<sub>4</sub> experiments were estimated to have toluene contents of 1.575%

Table IV. Comparison of Predictive Methods for Gas-Saturated Bitumen Viscosity

	av abs dev, %		
	CO <sub>2</sub> satd.	CH <sub>4</sub> satd.	N <sub>2</sub> satd.
Extended Corresponding States Method			
shape factor set 1: $A_t = A_p = 1.0$	29.0		
shape factor set 2: $A_t = 0.1, A_p = 1.0$	24.0	35.1	7.2
shape factor set 3: $A_t = A_p = 0.1$	21.9	30.0	7.4
shape factor set 4: $A_t = A_p = 0.0$	19.3	29.0	7.4
Teja-Rice Corresponding States Method			
mixing rule set 1			
case 1: gas evaluated at $P$ and $T$ of mixture	53.6	36.5	9.3
case 2: gas evaluated at $P$ and $T$ of PSU 625	23.5	32.7	9.5
mixing rule set 2			
case 1: gas evaluated at $P$ and $T$ of mixture	99.8	99.4	99.6
case 2: gas evaluated at $P$ and $T$ of PSU 625	99.0	99.2	99.7
mixing rule set 3			
case 1: gas evaluated at $P$ and $T$ of mixture	62.1	41.7	13.8
case 2: gas evaluated at $P$ and $T$ of PSU 625	28.0	38.5	14.3

and 2%, respectively (Johnson, 1985).

**Predictions Using the Extended Method of Corresponding States.** According to the corresponding states theory, a fluid is in corresponding states with a reference fluid if the two substances are at the same reduced temperature and pressure. When considering a gas in solution it must be realized that the reduced temperature and pressure which would correspond to the state of the gas/bitumen mixture are not the same reduced temperature and pressure that would correspond to the state of the pure gas. Thus, to predict gas-saturated bitumen viscosities, it is necessary to accurately predict the density of the gas in all phases. In order to predict the density of the gas adequately, the correct shape factors must be known. That is, it was necessary to obtain a correlation for the shape factors along the vapor-liquid saturation lines. The gas shape factor corrections were found to change with both temperature and pressure; hence, this approach was not successful. Instead, simple correction factors were determined for each state of the gas. The following multiplying factor sets were found to adequately predict the density of the gases in the following states: [ $A_t = 1.0, A_p = 1.0$ ] for the gaseous state; [ $A_t = 0.1, A_p = 1.0$ ] for the liquid state; and [ $A_t = 0.0-0.1, A_p = 0.0-0.1$ ] for the dense liquid state.

Since a correlation for the corrected shape factors was not found, the gas/bitumen mixture viscosities were predicted with all of the above shape factor combinations. The results are summarized in Table IV. The best viscosity predictions from the extended corresponding states method are shown in Figures 8, 9, and 10 for the CO<sub>2</sub>-, CH<sub>4</sub>-, and N<sub>2</sub>-saturated bitumen, respectively. The overall average deviations of 19%, 29%, and 7% from the data of Svrcek and Mehrotra (1982) for the CO<sub>2</sub>-, CH<sub>4</sub>-, and N<sub>2</sub>-saturated bitumen cases are satisfactory.

**Predictions Using the Teja-Rice Corresponding States Method.** The gas-saturated bitumen viscosities were also calculated by using the Teja-Rice method with the three sets of pseudocritical rules given in the Appendix. The two nonspherical reference fluids were taken as the gas and the gas-free bitumen. The gas-free bitumen viscosity was calculated by using the extended method of corresponding states as described previously, while the pure gas viscosity was calculated by using the TRAPP program (Ely and Hanley, 1981b) with methane as the reference fluid. The pure gas viscosity was calculated at two sets of conditions. These conditions were the mixture temperature and pressure (case 1) and the PSU 625 reference fluid temperature and pressure corresponding to the temperature and pressure of the bitumen assuming no



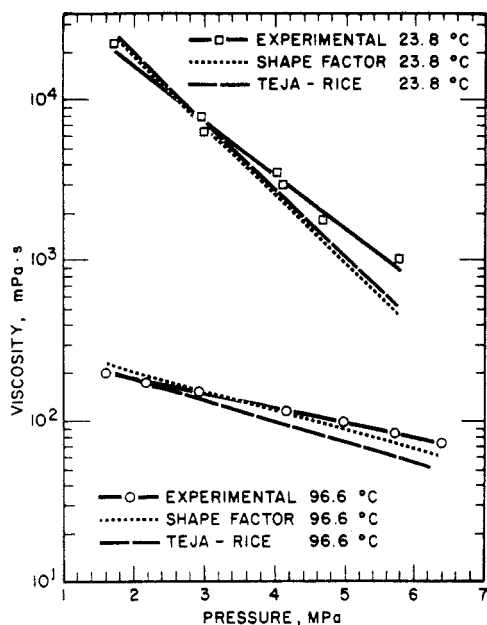


Figure 8. Prediction of  $\text{CO}_2$ -saturated bitumen viscosity with shape factor set 4 and Teja-Rice mixing rule 1 (case 2).

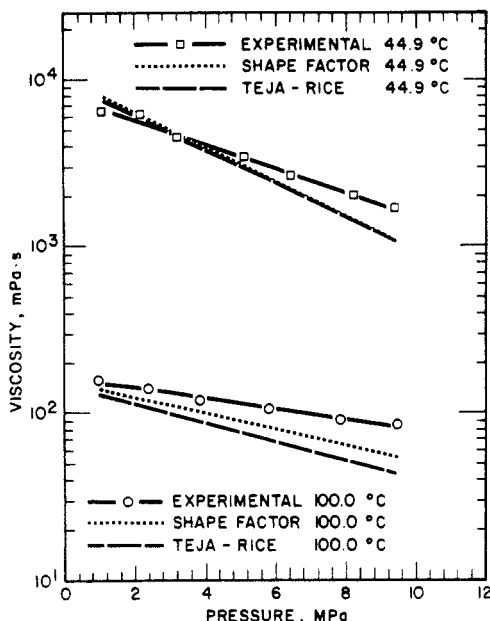


Figure 9. Prediction of  $\text{CH}_4$ -saturated bitumen viscosity with shape factor set 4 and Teja-Rice mixing rule 1 (case 2).

gas saturation (case 2). For case 2, all pure gases existed in the liquid or the dense gas phase rather than the dilute gas phase.

The results, Table IV, show clearly that mixing rule set 2 for the Teja-Rice method is inadequate for viscosity prediction. Mixing rule set 1 of Teja and Rice (1981) gave the best viscosity predictions. It is interesting to note that shape factor sets 3 and 4, and case 2 for the Teja-Rice method, both of which evaluate the gases at conditions where these are dense liquids, gave the best results. This indicates that the gases should be modeled as "pseudoliquids" in solution.

In Figures 8, 9, and 10, the experimental data of Svrcek and Mehrotra (1982) are compared with the predictions obtained by using the extended method of corresponding states and the Teja-Rice method with mixing rule set 1. It should be noted that the comparison in these figures is shown only for a high and a low temperature. In Figure

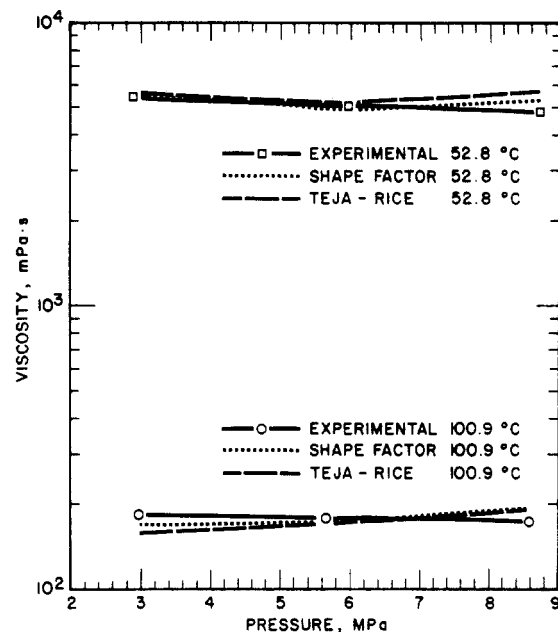


Figure 10. Prediction of  $\text{N}_2$ -saturated bitumen viscosity with shape factor set 4 and Teja-Rice mixing rule 1 (case 2).

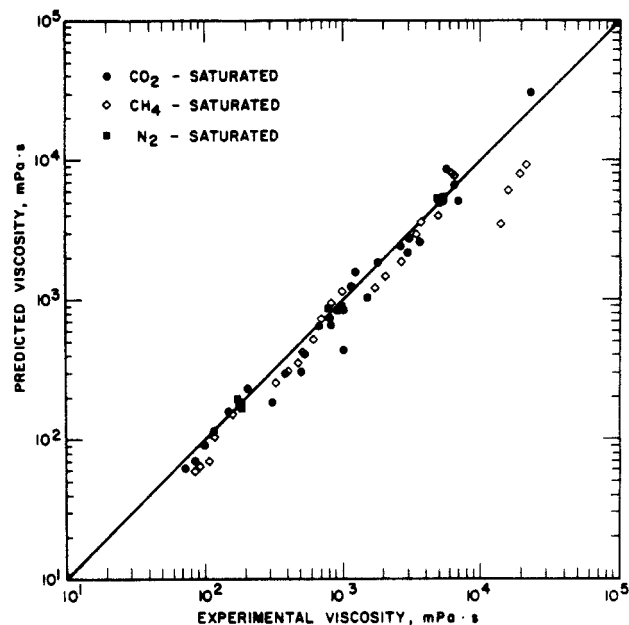


Figure 11. Comparison of experimental and predicted gas-saturated bitumen viscosities.

11, all of the experimental data for the three gases are compared with the predictions from the extended corresponding states method.

## Conclusions

The extended principle of corresponding states was successfully used to predict the viscosity of gas-free Athabasca bitumen by modification of existing shape factor correlations. The viscosity predictions achieved with 1,2,3,4,5,6,7,8-octahydrophenanthrene as the reference fluid were in good agreement, less than 6% deviation, with the published viscosity data.

The accuracy of the bitumen viscosity predictions was found to be dependent on the bitumen characterization used. A one-pseudocomponent characterization scheme was shown to be inadequate for bitumen viscosity predictions, whereas a characterization scheme employing four

pseudocomponents was shown to provide extremely good viscosity predictions.

For gas-saturated bitumen viscosity, the extended corresponding states method and the Teja-Rice corresponding states method (with the original mixing rules) gave the best predictions. It is also concluded that the gases dissolved in bitumen should be modeled as "pseudoliquids".

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### Nomenclature

$A_p$  = multiplying factor in eq 6  
 $A_t$  = multiplying factor in eq 5  
 $f$  = equivalent substance temperature reducing ratio  
 GCOS = Great Canadian oil sands  
 $h$  = equivalent substance volume reducing ratio  
 $k$  = binary interaction parameter  
 $l$  = binary interaction parameter  
 $M$  = molecular weight  
 NBP = normal boiling point  
 $P$  = absolute pressure  
 $P_c$  = critical pressure  
 $P_r$  = reduced pressure  
 SG = specific gravity  
 SIMDIST = simulated distillation analysis  
 $T$  = absolute temperature  
 $T_c$  = critical temperature  
 $T_r$  = reduced temperature  
 $V$  = molar volume  
 $V_c$  = critical volume  
 $V_r$  = reduced volume  
 $X$  = mole fraction  
 $Z_c$  = critical compressibility factor

### Greek Symbols

$\alpha$  = interaction parameter  
 $\beta$  = interaction parameter  
 $\eta$  = dynamic viscosity  
 $\rho$  = density  
 $\rho_c$  = critical density  
 $\omega$  = Pitzer's acentric factor  
 $\Psi$  = binary interaction parameter  
 $\Theta$  = energy shape factor  
 $\Phi$  = size shape factor

### Subscripts

$i, j$  = components  
 $m$  = mixture  
 $o$  = reference fluid  
 $x$  = fluid, pure or mixture  
 $\alpha, \beta$  = components  
 $\alpha\beta$  = binary pair

### Superscripts

$+$  = modifier in eq 7 and 8  
 $r1, r2$  = reference fluids

### Appendix

#### Mixing Rule Set 1 (Teja and Rice, 1981).

$$T_{cm} V_{cm} = \sum_i \sum_j X_i X_j T_{cij} V_{cij} \quad (A1)$$

$$V_{cm} = \sum_i \sum_j X_i X_j V_{cij} \quad (A2)$$

$$\omega_m = \sum_i X_i \omega_i \quad (A3)$$

$$M_m = \sum_i X_i M_i \quad (A4)$$

The cross parameters ( $i \neq j$ ) are given by

$$T_{cij} V_{cij} = \Psi_{ij} (T_{ci} V_{ci} T_{cj} V_{cj})^{1/2} \quad (A5)$$

$$V_{cij} = 1/8 (V_{ci}^{1/3} + V_{cj}^{1/3})^3 \quad (A6)$$

#### Mixing Rule Set 2 (Wong et al., 1983).

$$\omega_m (T_{cm}/P_{cm})^{2/3} = \sum_i \sum_j X_i X_j \omega_{ij} (T_{cij}/P_{cij})^{2/3} \quad (A7)$$

$$T_{cm}/P_{cm} = \sum_i \sum_j X_i X_j T_{cij}/P_{cij} \quad (A8)$$

$$T_{cm}^2/P_{cm} = \sum_i \sum_j X_i X_j T_{cij}^2/P_{cij} \quad (A9)$$

$$T_{cij} = \alpha_{ij} (T_{ci} T_{cj})^{1/2} \quad (A10)$$

$$P_{cij} = 8 T_{cij} / \{ \beta_{ij} [(T_{ci}/P_{ci})^{1/3} + (T_{cj}/P_{cj})^{1/3}]^3 \} \quad (A11)$$

$$\omega_{ij} = (\omega_i + \omega_j)/2 \quad (A12)$$

**Mixing Rule Set 3 (Wong et al., 1983).** The set is eq A3, A8–A11, and A13.

$$\xi = T_c^{1/6} P_c^{-2/3} M^{-1/2} \quad (A13)$$

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# Rapid Expansion of Supercritical Fluid Solutions: Solute Formation of Powders, Thin Films, and Fibers

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Supercritical fluids (or dense gases) have been established as suitable solvents for many nonvolatile or thermally labile compounds. The rapid ( $<10^{-5}$  s) solute condensation occurring during the expansion of a supercritical fluid solution through a nozzle results from solute nucleation and particle growth processes which may be impacted by a variety of experimental parameters. The qualitative effects of solute concentration and of the presence of electrolytes on the physical characteristics of material formed during this process have been explored. The technique is shown to be applicable to both inorganic ( $\text{SiO}_2$ ) and organic materials (polymers) using a range of supercritical solvents and thus has potential for a variety of applications involving the formation of powders, thin films, and fibers. It is shown that an intimately mixed powder of two inorganic materials ( $\text{SiO}_2$  and KI) or an inorganic and organic combination (KI and poly(vinyl chloride)) can be obtained, suggesting the feasibility for the formation of unique amorphous mixtures.

## I. Introduction

Supercritical fluids, dense gases above their critical temperatures and pressures, have been shown to have a number of unique solvent characteristics (McHugh and Krukonis, 1986) and can often be used to dissolve solutes having negligible vapor pressures (Smith and Udseth, 1983; Randall, 1983; Paulaitis et al., 1983). Furthermore, the rapid expansions of highly dilute supercritical fluid solutions through a nozzle have been shown to allow transfer of individual molecular species of low volatility to the gas phase, where mass spectrometric techniques may be used for their study (Smith and Udseth, 1983; Randall, 1983). Rapid expansions of more concentrated supercritical fluid solutions containing low vapor pressure solutes can be used to produce powders and films, resulting from homogeneous nucleation of the solute species present in the solutions prior to expansion (Smith, 1986).

The production of particles upon decompression of supercritical fluid solutions was first noted over a century ago (Hannay and Hogarth, 1880), and the formation of particles during the expansion of supercritical solutions through a valve has more recently been observed for a number of different systems (Paulaitis et al., 1983; McHugh and Krukonis, 1986; Larson and King, 1986). We are currently investigating the rapid expansion of the supercritical fluid solutions (RESS) process, which involves an expansion of the solution through a well-defined orifice under conditions which allow some degree of control over the solute nucleation and growth phenomena during the expansion. This technology offers the potential to produce thin films, fine powders with narrow size distributions, and intimate mixtures of amorphous materials under the nonequilibrium conditions inherent in the RESS expansion (Petersen et al., 1986; Matson et al., 1986a,b). Theoretical models for free jet expansions (e.g., Anderson (1971), Shapiro (1953), and Murphy and Miller (1984)) provide a basis for understanding the details of the RESS expan-

Table I. Critical Properties of Solvents Used in This Study

solvent	critical pressure, bar	critical temp, °C	critical density, g/mL
propane	42.5	96.8	0.217
ammonia	114.0	132.4	0.234
n-pentane	33.7	196.6	0.237
ethanol	63.8	243.1	0.276
water	221.2	374.1	0.325

sion process which affect solute nucleation and growth and, therefore, the physical properties of RESS products. This understanding will allow some degree of control over the RESS process and permit the tailoring of RESS product morphologies to meet specific requirements for any number of possible applications. The RESS technique has potential for use with a wide range of both inorganic and organic materials. This report discusses the results of some of our initial investigations involving a number of ceramic and preceramic materials, as well as a variety of organic polymers.

## II. Experimental Section

**A. The RESS Apparatus.** The RESS process utilizes the dramatic change in dissolving power experienced by a solvent as it is rapidly expanded from conditions where it exists as a supercritical fluid to a much lower pressure (and temperature) environment where it exists as a gas. This transition of the solvent from a supercritical fluid having significant dissolving capacity to a gas having negligible dissolving power encourages the rapid nucleation and growth of low vapor pressure solute particles, provided sufficient solute density exists in the expansion jet. The RESS process is therefore considered a general technique, useful for any solvent-solute systems that can be maintained as a solution at supercritical fluid conditions. Consequently, the process has been applied to a number of different solute materials using solvents having a range