# Viscosities and Activation Parameters of Viscous Flow of Sodium and Potassium Halides in Aqueous *N*,*N*-Dimethyloctylamine Oxide Solutions

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**Viscometric investigations have been carried out on sodium and potassium halides in aqueous solutions of *N*,*N*-dimethyloctylamine oxide. Two different concentrations of amine oxide solutions were employed as solvent to study the influence of micelles on viscometric properties of the alkali metal halides. Activation parameters of viscous flow were calculated and are discussed in terms of structure-making or -breaking properties of electrolytes in aqueous amine oxide solution.**

Viscosity measurements are very useful in providing information regarding ion-solvent interactions and the modifications induced by ions on solvent structure. Numerous studies have been made in studying the behavior of electrolytes in pure solvents by viscometric techniques (*1-5*), while little research has been carried out on ternary systems of electrolytes (*6-8*). This paper continues our investigation of the physicochemical properties of alkali metal halides in aqueous ternary systems (*9-11*). In the present communication we report the results of viscosity and density measurements of sodium and potassium halides in aqueous *N*,*N*-dimethyloctylamine oxide ($DC_8NO$) solution. The choice of $DC_8NO$ is based on its ability to act as a nonionic surfactant. Two different concentrations of aqueous $DC_8NO$ were used as solvent in preparing the electrolyte solution to examine the effect of monomers and micelles on the viscometric properties of alkali metal halides in solution. Viscosity data were analyzed in terms of different viscosity equations to obtain information about ionic interactions prevalent at high concentrations of electrolytes. Various thermodynamic parameters of viscous flow were also determined.

## Experimental Section

Analytical reagent grade samples of alkali metal halides obtained from B.D.H. or Merck were employed for the present work without further purification. The surfactant is prepared according to the procedures of Desnoyers et al. (*12*). Aqueous solutions of 0.0375 and 0.2137 M in $DC_8NO$ were used as stock solutions. Viscosity and density measurements of various electrolyte solutions in the concentration range of 0.05-2.5 M were obtained by the methods and with the appartus described previously (*9-11*).

## Results and Discussion

Viscosity *B* coefficients are shown to be valuable in discussing the structure-making (SM) or structure-breaking (SB) properties of solute molecules (*13*, *14*). Three different procedures were employed to obtain *B* coefficients. The values of *B* and *D* coefficients were obtained by using the modified Jones-Dole (*15*) equation:

$$\eta_{rel} = 1 + BC + DC^2 \qquad (1)$$

Viscosity data were fitted into the Goldsack-Franchetto equation (*16*)

$$\ln \eta_{rel} (1 + XV) = XE \qquad (2)$$

where *E* and *V* are parameters characteristic of electrolytes and *X* is the mole fraction of the electrolyte in solution. The values of *E* and *V* were obtained by means of nonlinear least-squares method and approximate values of *B* coefficients were obtained by using the relation

$$B = (E - V)/55.51 \qquad (3)$$

The average reduced volume $\bar{V}_e$ obtained from Breslau-Miller's equation (*17*) and the experimental viscosity is used to obtain *B* coefficients for 1:1 electrolytes

$$B = 2.90\bar{V}_e - 0.018 \qquad (4)$$

All these values are presented in Table I. The values of *B* coefficients obtained by the three different procedures are of the same order of magnitude. Slight, observed differences in the values of *B* coefficients could be attributed to different approximations involved in the derivation of these equations. It has been shown that the *B* coefficient is related to the size and shape of the solute molecule and to solvation effects, whereas the coefficient *D* includes solute-solute interactions and also those solute-solvent interactions that were not accounted for by the *BC* term in Jones-Dole's equation at higher concentrations (*18*). The values of *D* are in general higher in the ternary systems compared to the corresponding values in aqueous systems. It has been shown that an estimate of the influence of long-range Coulombic forces on *D* can be obtained from conductivity measurements (*3*). The contribution is of the order of 0.003 to the value of *D* and certainly not negligible with alkali metal halide solutions in our investigation. The *B* values of sodium and potassium halides in dilute $DC_8NO$ (0.0375 M) solutions are slightly lower than in pure water. In 0.2137 M $DC_8NO$ solution, the *B* values for sodium halides are slightly higher than the corresponding values in water. Since $DC_8NO$ can act as a nonionic surfactant and the critical micelle concentration (cmc) value is $\cong$0.200 M, the experimental concentrations of $DC_8NO$ used in the present investigation represent concentrations above and below cmc values. In dilute solutions where only $DC_8NO$ monomers are present and undergo hydrophobic hydration (*12*), $DC_8NO$ acts as a structure maker in aqueous solutions. Slightly higher values of *B* for alkali halides in $DC_8NO$ solution (above cmc) indicate a decrease in the structure-making ability of $DC_8NO$ at higher concentrations.

Ionic $B_\pm$ coefficients at various temperatures were calculated according to the procedures described by Kaminsky (*19*) and are presented in Table II.

The high values of the *B* coefficients found for $Na^+$ with $dB/dT < 0$, show that it is strongly solvated in aqueous $DC_8NO$ solution and behaves as a structure maker. In contrast, the low *B* coefficients values and $dB/dT > 0$ for $K^+$, $Cl^-$, $Br^-$, and $I^-$ ions show that they interact weakly with the solvent molecules. The structure-breaking ability is in the order $I^- > Br^- > Cl^- \cong K^+$. Ionic molar volumes $\bar{V}_\pm$ can be obtained from the $B_\pm$ values by employing the relation

$$B_\pm = 2.5\bar{V}_\pm \qquad (5)$$

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**Table I. *B* Values of Alkali Metal Halides in Aqueous Solutions of *N*,*N*-Dimethyloctylamine Oxide**

| | $T$ = 298 K | | | | $T$ = 303 K | | | | $T$ = 308 K | | | | $T$ = 313 K | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | eq[a] | | eq 2[a] | eq 3[a] | eq 1 | | eq 2 | eq 3 | eq 1 | | eq 2 | eq 3 | eq 1 | | eq 2 | eq 3 |
| salt | *B* | *D* | *B* | *B* | *B* | *D* | *B* | *B* | *B* | *D* | *B* | *B* | *B* | *D* | *B* | *B* |
| | | | | | | | | In 0.0375 M Solution | | | | | | | | |
| NaCl | 0.0723 | 0.0185 | 0.0704 | 0.0727 | 0.0824 | 0.0145 | 0.0819 | 0.0815 | 0.0954 | 0.0088 | 0.0954 | 0.0925 | 0.0802 | 0.0176 | 0.0766 | 0.0773 |
| NaBr | 0.0531 | 0.0130 | 0.0518 | 0.0489 | 0.0615 | 0.0117 | 0.0604 | 0.0577 | 0.0667 | 0.0119 | 0.0645 | 0.0623 | 0.0710 | 0.0130 | 0.0698 | 0.0673 |
| NaI | 0.0030 | 0.0150 | 0.0047 | −0.0008 | 0.0150 | 0.0134 | 0.0249 | 0.0272 | 0.0238 | 0.0111 | 0.0439 | 0.0544 | 0.0269 | 0.0112 | 0.0451 | 0.0544 |
| KCl | −0.0090 | 0.0059 | −0.0093 | −0.0234 | 0.0051 | 0.0042 | 0.0050 | −0.0085 | 0.0220 | 0.0005 | 0.0222 | 0.0082 | 0.0365 | 0.0018 | 0.0133 | −0.0234 |
| KBr | −0.0430 | 0.0090 | −0.0478 | −0.0688 | −0.0366 | 0.0110 | −0.0274 | −0.0303 | −0.0316 | 0.0116 | −0.0070 | 0.0067 | −0.0209 | 0.0096 | −0.0038 | 0.0007 |
| KI | −0.0917 | 0.0207 | −0.0964 | −0.1182 | −0.0766 | 0.0191 | −0.0695 | −0.0793 | −0.0661 | 0.0197 | −0.0506 | −0.0474 | −0.0603 | 0.0209 | −0.0536 | −0.0552 |
| | | | | | | | | In 0.2136 M Solution | | | | | | | | |
| NaCl | 0.0896 | 0.0112 | 0.0704 | 0.0668 | 0.0950 | 0.0104 | 0.0819 | 0.0893 | 0.0982 | 0.0121 | 0.0954 | 0.0988 | 0.0990 | 0.0100 | 0.0766 | 0.0998 |
| NaBr | 0.0610 | 0.0080 | 0.0518 | 0.0325 | 0.0682 | 0.0088 | 0.0604 | 0.0573 | 0.0743 | 0.0094 | 0.0645 | 0.0681 | 0.0836 | 0.0086 | 0.0698 | 0.0737 |
| NaI | 0.0129 | 0.0127 | 0.0047 | 0.0121 | 0.0320 | 0.0059 | 0.0250 | 0.0330 | 0.0357 | 0.0095 | 0.0439 | 0.0342 | 0.0502 | 0.0058 | 0.0451 | 0.0522 |
| KCl | −0.0146 | 0.0077 | −0.0093 | −0.0409 | 0.0008 | 0.0060 | 0.0049 | −0.0082 | 0.0147 | 0.0037 | 0.0222 | −0.0006 | 0.0209 | 0.0048 | 0.0133 | 0.0160 |
| KBr | −0.0399 | 0.0090 | −0.0478 | −0.0819 | −0.0289 | 0.0092 | −0.0273 | −0.0465 | −0.0119 | 0.0063 | −0.0070 | −0.0651 | −0.0057 | 0.0074 | −0.0038 | −0.0143 |
| KI | −0.0850 | 0.0170 | −0.0963 | −0.1081 | −0.0646 | 0.0131 | −0.0701 | −0.0790 | −0.0541 | 0.0124 | −0.0506 | −0.0538 | −0.0362 | 0.0083 | −0.0536 | −0.0361 |

[a] Equation 1, Jones–Dole equation; eq 2, Goldsack–Franchetto equation; eq 3 Breslau–Miller equation.

and the hydration number $N_B$ of ions can be calculated (*20*) from the equation

$$\bar{V}_{\pm} = \bar{V}^0_{\text{ion}} + N_B \bar{V}^0_S \tag{6}$$

The values of $N_B$ and $\bar{V}_{\pm}$ are presented in Table II. The values of $\bar{V}_{\pm}$ and $N_B$ increase with temperature for all ions except for $Na^+$ ions. Thus, our results are similar to those of Millero (*20*), thereby confirming the structure-making properties of $Na^+$ ions and the breaking properties for all other ions. The negative hydration numbers for the structure-breaking ions could be attributed to the ability of these ions in solution to disrupt the water structure by pushing the water molecules apart in both primary and secondary hydration spheres around them (*21–22*). From the magnitude of hydration numbers, one can conclude that the structure-breaking ability of ions in aqueous $DC_8NO$ solution at 298 K is in the order: $I^- > Br^- > Cl^- > K^+ > Na^+$.

The Gibb's energy of activation $\Delta G^{\ddagger}_{\text{vis}}$ for viscous flow of a solution for a given composition can be calculated by using Eyring's equation (*23*)

$$\Delta G^{\ddagger}_{\text{vis}} = RT \ln (v\eta / hN) \tag{7}$$

The $\Delta G_{\text{vis}}$ thus determined at different temperatures for a given composition were fitted into the equation

$$\Delta G^{\ddagger}_{\text{vis}} = a + bT + cT^2 \tag{8}$$

The entropy and enthalpy of activation ($\Delta S_{\text{vis}}$ and $\Delta H_{\text{vis}}$, respectively) were then obtained according to the following equations:

$$\Delta S^{\ddagger}_{\text{vis}} = -\frac{\partial}{\partial T}(\Delta G^{\ddagger}_{\text{vis}}) \tag{9}$$

$$\Delta H^{\ddagger}_{\text{vis}} = \Delta G^{\ddagger}_{\text{vis}} + T\Delta S^{\ddagger}_{\text{vis}} \tag{10}$$

The dependencies of these thermodynamic parameters on composition were fitted into the following empirical equation with reasonable accuracy as suggested by Tamamushi et al. (*24*)

$$\Delta Y^{\ddagger}_{\text{vis}} = \Delta Y^0_{\text{vis}} + \beta_y X + \gamma_y X^2 \quad (y = G, H, \text{and } S) \tag{11}$$

where $\Delta Y^0_{\text{vis}}$ is the activation parameter for the pure solvent and $X$ is the mole fraction of the solute. The relationship between $\beta_y$ and $\gamma_y$ ($y = G$, $H$, and $S$) is given by

$$\beta_G = \beta_H - T\beta_S; \quad \gamma_G = \gamma_H - T\gamma_S$$

These coefficients were determined by the least-squares method and are presented in Table III. Using these empirical coefficients the activation parameters of most of the solutions studied can be reproduced with standard deviations of <0.02 kJ mol$^{-1}$, <0.1 kJ mol$^{-1}$, and <0.5 J mol$^{-1}$ K$^{-1}$ for $\Delta G^{\ddagger}_{\text{vis}}$, $\Delta H^{\ddagger}_{\text{vis}}$, and $\Delta S_{\text{vis}}$, respectively. Initial effects of solutes on the activation parameters for viscous flow can be discussed in terms of $\beta_y$ coefficients. Positive values of these coefficients represent an initial increase in the activation parameters $\Delta Y_{\text{vis}}$ with an increase in concentration. It is observed (*24*) that for structure-making ions $\beta_G > 0$ and $\beta_S$ and $\beta_H < 0$ and for structure-breakers all the values are negative. It is also observed that for all salts (except NaCl) the $\Delta G^{\ddagger}_{\text{vis}}$ remained constant within the experimental error up to very high concentrations. This effect is probably due to complete compensation for change in $\Delta H^{\ddagger}_{\text{vis}}$ with concentration by that in $\Delta S^{\ddagger}_{\text{vis}}$. This type of phenomena was observed for all structure breakers in our previous studies (*9–11*).

The limiting values of the activation parameters at infinite dilution of the electrolytes were calculated according to the procedures of Feakins et al. (*7*) and are presented in Table IV. Normally for the net structure maker in solution, the free energy change $\Delta\mu^0_2{}^{\ddagger}$ is always greater than that of the pure solvent

**Table II. Values of Ionic Parameters of Alkali Metal Halides in Aqueous Solutions of *N*,*N*-Dimethyloctylamine Oxide**[a]

| | $T$ = 298 K | | | $T$ = 303 K | | | $T$ = 308 K | | | $T$ = 313 K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ion | $B_\pm$ | $V_\pm$ | $N_B$ | $B_\pm$ | $V_\pm$ | $N_B$ | $B_\pm$ | $V_\pm$ | $N_B$ | $B_\pm$ | $V_\pm$ | $N_B$ |
| | | | | | | In 0.0375 M Solution | | | | | | |
| $Na^+$ | 0.0768 | 30.72 | 4.31 | 0.0798 | 31.94 | 4.50 | 0.0844 | 33.76 | 4.77 | 0.0620 | 24.78 | 3.42 |
| $K^+$ | −0.0045 | −1.80 | −1.17 | 0.0026 | 1.02 | −0.74 | 0.0110 | 4.40 | −0.23 | 0.0182 | 7.30 | 0.21 |
| $Cl^-$ | −0.0045 | −1.80 | −2.53 | 0.0026 | 1.02 | −2.10 | 0.0110 | 4.40 | −1.59 | 0.0182 | 7.30 | −1.15 |
| $Br^-$ | −0.0385 | −15.40 | −5.15 | −0.0392 | −15.66 | −5.19 | −0.0426 | −17.04 | −5.40 | −0.0392 | −15.66 | −5.19 |
| $I^-$ | −0.0872 | −34.88 | −9.15 | −0.0792 | −31.66 | −8.66 | −0.0771 | −30.84 | −8.54 | −0.0786 | −31.42 | −8.63 |
| | | | | | | In 0.2136 M Solution | | | | | | |
| $Na^+$ | 0.0969 | 38.76 | 5.53 | 0.0946 | 37.84 | 5.39 | 0.0908 | 36.32 | 5.16 | 0.0886 | 35.55 | 5.04 |
| $K^+$ | −0.0073 | −2.92 | −1.34 | 0.0004 | 0.16 | −0.87 | 0.0074 | 2.94 | −0.45 | 0.0104 | 4.18 | −0.26 |
| $Cl^-$ | −0.0073 | −2.92 | −2.70 | 0.0004 | 0.16 | −2.23 | 0.0074 | 2.94 | −1.81 | 0.0104 | 4.18 | −1.63 |
| $Br^-$ | −0.0326 | −13.04 | −4.79 | −0.0293 | −11.72 | −4.59 | −0.0192 | −7.70 | −3.98 | −0.0162 | −6.46 | −3.80 |
| $I^-$ | −0.0777 | −31.08 | −8.57 | −0.0650 | −26.00 | −7.81 | −0.0614 | −24.58 | −7.59 | −0.0466 | −18.66 | −6.70 |

[a] Values of $B_\pm$ in L mol$^{-1}$; values of $V_\pm$ in cm$^3$ mol$^{-1}$.

**Table III. Values of $\beta$ and $\gamma$ Coefficients of Alkali Metal Halides in Aqueous *N*,*N*-Dimethyloctylamine Oxide Solutions at 298 K**[a]

| salt | $10^{-2}\beta_G$ | $10^{-2}\gamma_G$ | $10^{-2}\beta_H$ | $10^{-2}\gamma_H$ | $\beta_S$ | $\gamma_S$ |
|---|---|---|---|---|---|---|
| | | | In 0.0375 M Solution | | | |
| NaCl | 0.05 | 1.03 | −0.44 | 10.0 | −0.17 | 3.07 |
| NaBr | 0.01 | 1.00 | 0.18 | −14.5 | 0.06 | −5.17 |
| NaI | −0.04 | 0.86 | −0.95 | 12.6 | −0.31 | 3.94 |
| KCl | −0.07 | 0.66 | −1.15 | 9.61 | −0.36 | 3.00 |
| KBr | −0.11 | 0.60 | −0.63 | −1.80 | −0.17 | −0.83 |
| KI | −0.18 | 1.44 | −1.05 | 1.29 | −0.29 | 0.04 |
| | | | In 0.2136 M Solution | | | |
| NaCl | 0.07 | 0.40 | −0.65 | 3.89 | −0.27 | 2.10 |
| NaBr | 0.03 | 0.34 | −0.39 | −4.29 | −0.14 | −1.55 |
| NaI | −0.03 | 0.69 | −1.06 | 11.6 | −0.35 | 3.70 |
| KCl | −0.07 | 0.48 | −1.07 | 6.55 | −0.34 | 2.05 |
| KBr | −0.10 | 0.53 | −0.81 | −9.18 | −0.24 | −0.48 |
| KI | −0.16 | 1.03 | −1.60 | 16.3 | −0.48 | 5.11 |

[a] Values of $\Delta G$ and $\Delta H$ in kJ mol$^{-1}$ and $\Delta S$ in kJ mol$^{-1}$ K$^{-1}$.

**Table IV. Thermodynamic Parameters of Activation of Flow at Infinite Dilution of Alkali Metal Halides in Aqueous Solutions of *N*,*N*-Dimethyloctylamine Oxide**[a]

| salt | $\Delta\mu^0{}_2{}^\ddagger$ | $T\Delta S^0{}_2{}^\ddagger$ | $\Delta H^0{}_2{}^\ddagger$ | ions | $T\Delta S^0{}_2{}^\ddagger$ | $\Delta H^0{}_2{}^\ddagger$ |
|---|---|---|---|---|---|---|
| | | | In 0.0375 M Solution[b] | | | |
| NaCl | 18.13 | −47.7 | −29.5 | $Na^+$ | −17.6 | −4.0 |
| NaBr | 17.41 | −53.5 | −36.1 | $K^+$ | −30.0 | −25.5 |
| NaI | 13.73 | −56.3 | −42.6 | $Cl^-$ | −30.0 | −25.5 |
| KCl | 9.07 | −60.1 | −51.0 | $Br^-$ | −34.1 | −33.3 |
| Kbr | 5.35 | −64.1 | −58.8 | $I^-$ | −55.5 | −59.6 |
| KI | 0.42 | −85.6 | −85.2 | | | |
| | | | In 0.2136 M Solution[c] | | | |
| NaCl | 21.66 | −53.9 | −32.2 | $Na^+$ | −13.6 | −3.2 |
| NaBr | 18.87 | −57.9 | −39.0 | $K^+$ | −40.3 | −35.5 |
| NaI | 15.10 | −63.7 | −48.6 | $Cl^-$ | −40.3 | −35.5 |
| KCl | 9.59 | −80.5 | −70.9 | $Br^-$ | −50.8 | −49.1 |
| KBr | 6.47 | −91.0 | −84.5 | $I^-$ | −54.0 | −56.2 |
| KI | 2.59 | −94.2 | −91.6 | | | |

[a] Values in kJ mol$^{-1}$. [b] $\Delta\mu^0{}_1{}^\ddagger$(solvent) = 9.22 kJ mol$^{-1}$. [c] $\Delta\mu^0{}_1{}^\ddagger$ (solvent) = 9.73 kJ mol$^{-1}$.

$\Delta\mu^0{}_1{}^\ddagger$. The values of free energy changes indicate that halides of sodium and potassium act as structure makers at infinite dilution. This may be due to the dominance of the structure-making ability of cations over anions. The values $T\Delta S^0{}_2{}^\ddagger$ and $\Delta H^0{}_2{}^\ddagger$ are negative for all ions suggesting that the transition state is associated with bond making and an increase in order.

From the above studies one can conclude that the structure-making ability of various ions in aqueous $DC_8NO$ solution is of the order $Na^+ > K^+ > Cl^- > Br^- > I^-$. Also these effects are more pronounced at higher concentrations of $DC_8NO$, which may be attributed (1) to the slight decrease in structure-making ability of the $DC_8NO$ in aqueous solutions at higher concentrations, and (2) to the differences in the strength of interaction between the ions with $DC_8NO$ dipoles in the micelles and monomers.

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## Glossary

| | |
|---|---|
| $B$, $D$ | viscosity coefficients |
| $V$, $E$ | adjustable parameters characteristic of the electrolyte in Goldsack-Franchetto's equation |
| $\bar{V}_e$ | average reduced volume in Breslau-Miller's equation |
| $B_\pm$ | ionic viscosity coefficient |
| $\bar{V}_\pm$ | ionic molar volume in the solutions |
| $\bar{V}^0{}_s$ | molar volume of the solvent |
| $\bar{V}^0{}_{ion}$ | free ionic molar volume |
| $N_B$ | hydration number |
| $\Delta G^\ddagger{}_{vis}$ | Gibbs energy of activation for viscous flow |
| $\Delta H^\ddagger{}_{vis}$ | enthalpy of activation for viscous flow |
| $\Delta S^\ddagger{}_{vis}$ | entropy of activation for viscous flow |
| $\Delta Y^\ddagger{}_{vis}$ | activation parameter of the solution |
| $\Delta Y^0{}_{vis}$ | activation parameter of the solvent |
| $X$ | mole fraction |
| $v$ | molar volume of the solution |
| $h$ | Planck's constant |
| $R$ | gas constant |
| $N$ | Avogadro's number |

### *Greek Letters*

| | |
|---|---|
| $\eta$ | viscosity of the solution |
| $\Delta\mu^0{}_2{}^\ddagger$ | free energy change of the activated complex for the viscous flow of the solution at infinite dilution |
| $\Delta\mu^0{}_1{}^\ddagger$ | free energy change of the activated complex for the viscous flow of the pure solvent |
| $\beta_y$, $\gamma_y$ | coefficients of the polynomial eq 11 |

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# High-Temperature Diffusion, Viscosity, and Density Measurements in *n*-Hexadecane

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**Mutual diffusion coefficients at infinite dilution have been measured for *n*-octane, *n*-decane, *n*-dodecane, and *n*-tetradecane in the solvent *n*-hexadecane. The data cover the elevated temperature range 50–291 °C at pressures of 1415 and 3450 kPa (205 and 500 psia). Viscosity and density of the solvent were also measured at all conditions. The Taylor dispersion method was used for diffusion measurements, and a capillary tube viscometer for viscosity measurements. Densities were measured by using a new technique based on retention times observed in the Taylor dispersion experiment. A free-volume expression represents the diffusion data well across the entire temperature range.**

## Introduction

Mutual diffusion, viscosity, and density are the thermophysical properties needed in evaluation of mass transport phenomena. For high-temperature applications such as multiphase chemical reactors the need for data, particularly on diffusion, is acute. The objective of this work was to measure these three properties at temperatures to 291 °C and pressures to 3450 kPa, the range of conditions useful for many chemical processes. The *n*-hexadecane/alkane systems studied are important from a fundamental standpoint and also because of the industrial importance of hydrocarbon processing.

## Experimental Techniques

Mutual diffusion coefficients of four *n*-alkane solutes (octane, decane, dodecane, and tetradecane) were measured by using the Taylor dispersion method (*1*). In this method, a narrow pulse of solute (A) diluted in the solvent (B) is injected into a tube in which the solvent is moving in slow laminar flow. The pulse ultimately assumes a Gaussian distribution whose temporal variance $\sigma^2$ is dependent on the average flow velocity $\bar{u}$ and molecular diffusivity $D_{AB}$. At the end of the diffusion tube one records concentration $C(t)$ vs. time data as the peak elutes. The normalized first and second temporal moments ($\bar{t}$ and $\sigma^2$) are calculated by finite summation, and then the diffusion coefficient is calculated from eq 1

$$D_{AB} = \tfrac{1}{2}\left[\bar{u}L\zeta_0 - \left[(\bar{u}L\zeta_0)^2 - \left(\frac{\bar{u}^2R^2}{12}\right)\right]^{1/2}\right] \qquad (1)$$

where

$$\bar{u} = (L/\bar{t})\,(1 + 2\zeta_0) \qquad (2)$$

$$\zeta_0 = \frac{2\sigma^2 - \bar{t}^2 + [\bar{t}^4 + 4\bar{t}^2\sigma^2]^{1/2}}{(8t^2 - 4\sigma^2)} \qquad (3)$$

Equation 1 accounts for molecular diffusion in both axial and radial directions within the dispersion tube. The tube length $L$ and radius $R$ are corrected for thermal expansion effects which are significant at temperatures above 100 °C.

Viscosity is measured by using the standard capillary viscometer technique, which is based on the Hagen–Poiseuille equation. Density is measured by using a new technique based on the retention time of the solute peak (*2*, *3*). The retention time is just the first temporal moment $\bar{t}$ calculated from the Taylor dispersion experiment and it depends on the solvent density, dispersion tube volume $V_t$, and mass flow rate. We calibrated the tube volume using water at 30 °C (condition 1) and calculate the density of hexadecane at any other condition 2 as follows:

$$\rho_2 = \rho_1 \frac{\dot{m}^{(2)}}{\dot{m}^{(1)}} \frac{\bar{t}^{(2)}}{\bar{t}^{(1)}} \frac{V_t^{(1)}}{V_t^{(2)}} \qquad (4)$$

The tube volume $V_t^{(2)}$ is corrected for thermal expansion effects (*3*).

The apparatus is shown in Figure 1. The hexadecane solvent is sparged with helium and pumped through a capillary restrictor and backpressure regulator, which act to dampen pulses from the metering pump. The solvent flows into a heated enclosure which contains the stainless steel capillary viscometer. The capillary diameter was calibrated by using distilled, deionized water at 30 and 120 °C. The capillary length and diameter were corrected for thermal expansion. Pressure drop was measured with two strain gauge transducers which were calibrated against a Ruska Instruments dead-weight pressure gauge. With the aid of a valve manifold, each transducer was used to measure both upstream and downstream pressure, and pressure difference was calculated for each transducer. The pressure drop from the two transducers always agreed to 1% or less. The volumetric flow rate was determined by measuring the mass flow rate and density at each experimental condition.

After the viscometer, solvent flows through the reference side of the concentration detector (LDC/Milton Roy Refracto-

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