

Liquid viscosities of binary mixtures and some hydrocarbons in the high pressure range with applications of the significant structure theory

by

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(Received Apr. 29, 1970)

ABSTRACT

Further validity of the significant structure theory has been tested by calculating the viscosities of binary mixtures—three pairs of $C_6H_6(1)+C_6H_{12}(2)$, $CCl_4(1)+C_6H_6(2)$ and $CCl_4(1)+C_6H_{12}(2)$ —and also by calculating the viscosities of $n-C_5H_{12}$ and $n-C_6H_{14}$ in the pressure range of 1 bar to 4000 bars.

The results are quite satisfactory for both cases and provide another evidence for the validity of the significant structure theory.

1. LIQUID VISCOSITIES OF BINARY MIXTURES

A. Introduction

Numerous attempts have been made to derive an equation relating the viscosities of a mixture to its composition and the viscosities of its constituents but none can be regarded as satisfactory, especially for liquid systems exhibiting appreciable departure from ideal behavior.

One of them was formulated, considering the deviations of the observed free energies of activation for flow in mixtures from the linear additive law, as follows (1);

$$\zeta = \frac{V_{1,2}}{hN} \exp \left\{ - \left[(X_1 \Delta F_1^\ddagger + X_2 \Delta F_2^\ddagger) \right. \right.$$

$$\left. \left. - \Delta F_m^\ddagger \right] / RT \right\}$$

here ΔF_m^\ddagger is the so called "excess free energy of mixing", ΔF^\ddagger free energy change of activation, $V_{1,2}$ the mean value of the liquid volume of two constituents, X the mole fraction and subscripts 1 and 2 indicate the two constituents. Since ΔF_m^\ddagger was calculated empirically, the relation gave very excellent results over wide varieties of materials.

Here, with the use of significant structure theory of liquid mixture(2) in conjunction with the theory of rate process, (1) one can predict the viscosity-mole fraction relation more fundamentally and explicitly. Tested materials are Benzene-Cyclohexane, Carbontetrachloride-Cyclohexane,

xane and Carbontetrachloride-Benzene. All gave very good agreement between experiment and theory.

B. Theory

According to the significant structure theory, the partition function for a mixture takes the following form (2);

$$f_{mix} = \frac{N!}{N_1!N_2!} [f_{s_1}^{N_1} f_{s_2}^{N_2}]^{V_s/V} [f_{deg} e^{E_s/RT}]^{\frac{(N_1+N_2)V_s}{V}} \times [f_{g_1}^{N_1} f_{g_2}^{N_2}]^{(V-V_s)/V}$$

where

$$f_{s_1} = \frac{1}{(1 - e^{-\theta_1/T})^3} f_{rot_1}^{(s)} f_{vib_1}^{(s)}$$

Here we assume that the solid-like molecule rotates:

$$f_{g_1} = \frac{(2\pi mkT)^{3/2}}{h^3} f_{rot_1}^{(g)} f_{vib_1} \frac{e}{N_1 + N_2}$$

with similar equations for component 2, and

$$f_{deg} = 1 + Z \frac{V - V_s}{V_s} \exp\left[\frac{-bE_s V_s}{(V - V_s)RT}\right]$$

$$E_s = X_1^2 E_{s_1} + X_2^2 E_{s_2} + 2(1 + \delta E_s) \sqrt{E_{s_1} E_{s_2}} \quad [3, 4]$$

$$V_s = X_1 V_{s_1} + X_2 V_{s_2} + (\delta V_s) X_1 X_2 \sqrt{V_{s_1} V_{s_2}}$$

$$Z = X_1 Z_1 + X_2 Z_2 \quad b = X_1 b_1 + X_2 b_2$$

where Z denotes the number of molecules nearest the hole and b the ratio between the hole energy and $E_s V_s / (V - V_s)$.

Using the rate equation (1, 2),

$$k' = n' \kappa \frac{kT}{h} \frac{F^\ddagger}{F} \exp(-\epsilon_o/kT)$$

where

$$n' = Z \frac{V - V_s}{V_s}, \quad \epsilon_o/kT = bE_s V_s / (V - V_s) RT, \quad \frac{F^\ddagger}{F} = \frac{1}{(f_{E1})^{X_1}} \frac{1}{(f_{E2})^{X_2}}$$

where f_s indicates the one dimensional Einstein partition function related. Using the above relations, the equation for viscosity of liquid mixtures will be derived in the similar procedure (2);

$$\eta = \frac{hN}{r} \frac{6}{\sqrt{2}} \frac{1}{(1 - e^{-\theta_1/T})^{X_1}} \frac{1}{(1 - e^{-\theta_2/T})^{X_2}} \frac{1}{V - V_s} \times \exp\left[\frac{bE_s V_s}{(V - V_s)RT} + \frac{V - V_s}{V} \sum_{i=1}^2 \frac{2}{3d_i^2} \left[\frac{m_i kT}{\pi^3}\right]^{1/2} X_i\right]$$

Here $r = Z\kappa$, $m_1 = M_1/N$ and $m_2 = M_2/N$ with $r = r_1 X_1 + r_2 X_2$. M denotes the molecular weight. For derivation of above equation, the interaction between the viscosities of the gas-like degree of freedom

of species 1 and 2 is neglected. It is further assumed that the parametric values r , V_s , E_s and b are only concentration-dependent.

The quantities δE_s and δV_s are the only

parameters in the mixture partition function which can't be evaluated from the pure liquids. In general, these values are very small (5), and reasonable results have been obtained when they are taken to be zero.

C. Results and Discussions

The calculated results are presented in

Table 2 and Fig. 1, 2 and 3. One sees that the agreement is quite satisfactory. However, as the dissimilarity of molecules increases, the agreement becomes a little poorer. Further more, the addition of δE_s causes no appreciable effects upon viscosities. ($\delta E_s = 0.01 \sim 0.02$ tried). So the secondary effect in E_s may be concluded to be negligible.

TABLE 1. Parameters used.

	CCl ₄	C ₆ H ₆	C ₆ H ₁₂
$r = Z\kappa$	1.818	3.164	1.2295
b	9.736×10^{-4}	8.217×10^{-4}	15.4035×10^{-4}
E_s (cal/mole)	8613.4	9636.1	8748.7
V_s (cc/mole)	89.39	82.826	99.81
θ (°K)	53.53	44.36	77.827

From: K. Liang, H. Eyring and R. P. Marchi, Proc. Natl. Acad. Sci. (U. S.), 52, pp. 1107-1114 (1964).

S. M. Ma and H. Eyring, J. Chem. Phys., 42, pp. 1920-1926 (1965).

The values in the row of r and b are adjusted for the viscosity data (Partington; An Advanced Treatise on Physical Chemistry vol. 2 p. 109 & International Critical Table).

TABLE 2. Results

C₆H₆(1) + C₆H₁₂(2) system:

X_1 (mole fraction)	0	0.2	0.4	0.6	0.8	1.0
$100V^M / V^{\circ(a)}$	0	0.435	0.640	0.625	0.405	0
$\eta_{\text{obs}}(\text{cp})^{(b)}$	0.892	0.734	0.641	0.593	0.587	0.602
$\eta_{\text{calc}}(\text{cp})$	0.8715	0.6947	0.6096	0.5729	0.5681	0.5889
%(η_c / η_o)	97.70	94.64	95.10	96.61	96.78	97.82

CCl₄(1) + C₆H₆(2) system:

X_1	0	0.2	0.4	0.6	0.8	1.0
$100V^M / V^{\circ(a)}$	0	0.013	0.01	0.01	0.013	0
$\eta_{\text{obs}}(\text{cp})^{(d)}$	0.602	0.658	0.714	0.773	0.832	0.893
$\eta_{\text{calc}}(\text{cp})$	0.5889	0.6208	0.6615	0.7120	0.7761	0.8621

$\%(\eta_c/\eta_o)$ 97.82 94.34 92.65 92.11 93.28 96.54

CCl₄(1)+C₆H₁₂(2) system:

X_1	0	0.272	0.5295	0.7707	1.0
$100V^M/V^o(c)$	0	0.122	0.158	0.1216	0
$\eta_{obs}(cp)^{(d)}$	0.8856	0.858	0.8658	0.8670	0.9019
$\eta_{calc}(cp)$	0.8715	0.7552	0.7519	0.8370	0.8621
$\%(\eta_c/\eta_o)$	98.40	88.02	87.76	96.54	95.59

(a) S.M. Ma and H. Eyring, *J. Chem. Phys.*, **42**, pp. 1920-1926 (1965).

(b) R.J. Fort and W.R. Moore, *Trans. Farad. Soc.*, **62** 1112 (1966).

(c) K. Liang, H. Eyring and R.P. Marchi, *Proc Natl Acad. Sci.*, **52**, pp. 1107-1114(1964).

(d) L. Grunberg, *Trans. Farad. Soc.*, **50**, 1297 (1954).

Here V^M and V^o means the excess volume of mixing and the sum of volume of pure components in ideal mixing.

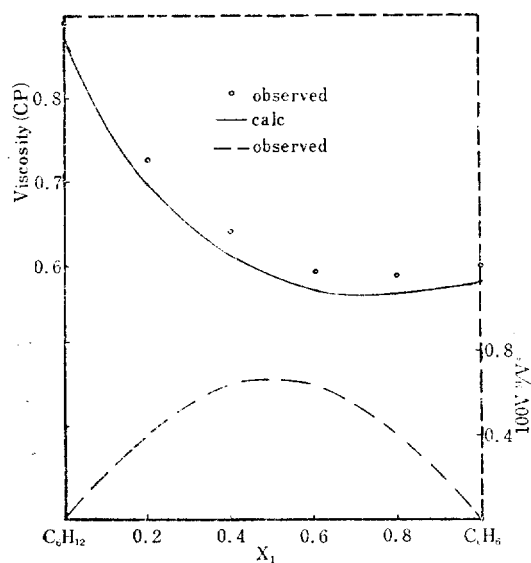


Figure 1. System C₆H₁₂-C₆H₆, Viscosity-mole fraction relation

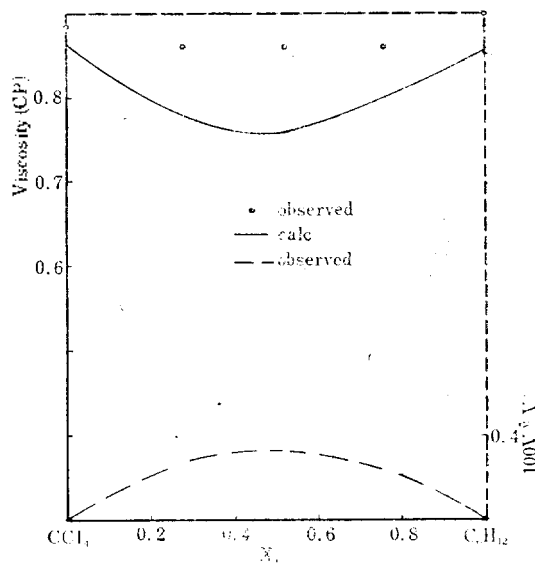


Figure 2. System CCl₄-C₆H₁₂ Viscosity-mole fraction relation

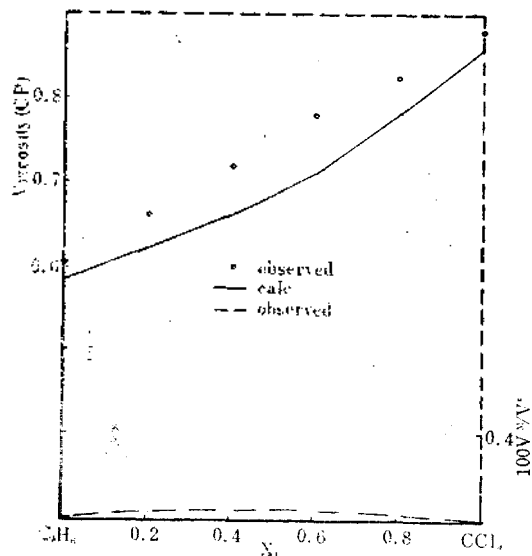


Figure 3. System C₆H₆-CCl₄, Viscosity-mole fraction relation

II. LIQUID VISCOSITIES OF HYDROCARBONS IN THE HIGH PRESSURE RANGE

A. Introduction

Recently, Hogenboom, Webb and Dixon(6) analyzed the data on the viscosity-pressure-temperature relations for the pure hydrocarbon liquids investigated by the High Pressure Laboratory at the Pennsylvania State University. They employed the Eyring significant structure theory, the Cohen-Turbull free volume model (7), and the empirical Doolittle equation(8, 9) at atmospheric pressure with success.

The extension of the significant structure theory of viscosity to high pressure was

made feasible by Jhon *et al.* (10). In the similar way, n-C₅H₁₂ and n-C₆H₁₄ were calculated and the procedure used was found more reasonable for the simpler hydrocarbons by comparing implicit parameters, the transmission coefficient κ and bZ.

B. Theory

The equation for shear viscosity η has the form (2)

$$\eta = \frac{V_s}{V} \eta_s + \frac{V - V_s}{V} \eta_g$$

where V denotes the liquid molar volume, V_s the solid molar volume, and the subscript g and s indicate gas and solid respectively. The contribution of the gas-like portion is approximately less than 2% of the total viscosity and so is within the uncertainty of the experimental data and has been neglected.

The theoretical equation (10) used to calculate the viscosity of simple liquids is

$$\eta = \frac{(\pi mkT)^{\frac{1}{2}} N l_f}{2(V - V_s) \kappa} \exp \frac{b V_s Z \phi(a)}{2(V - V_s) k T}$$

where k denotes the Boltzmann constant, l_f the free length, m the mass of one molecule, N the Avogadro number, Z the number of molecules nearest the hole and $\phi(a)$ the potential energy function.

Above equation can be written in the form

$$\ln \eta \frac{V - V_s}{\sqrt{T}} = A + B \frac{V_s}{(V - V_s) T}$$

where

$$A = l_n \frac{(\pi mk)^{\frac{1}{2}} N}{2\kappa} l_f = A_0 + l_n (l_f / l_{f0})$$

$$l_f \approx 2 \left(\left(\frac{\sqrt{2} V_s}{N} \right)^{\frac{1}{3}} - \left(\frac{V_c}{12N} \right)^{\frac{1}{3}} \right)$$

$$B = bZ\phi(a)/2k = B_0[\phi(a)/\phi_0(a)]$$

$$\phi(a) = \epsilon[1.0109(N\sigma^3/V_c)^4 - 2.4090(N\sigma^3/V_c)^2]$$

Here subscript 0 denotes the value at 1 atmosphere pressure, V_c the critical volume of liquid, ϵ the constant of Lennard-Jones parameters and σ the collision diameter.

To extend the viscosity equation to high pressures, the effect of pressure on the solid-like volume V_s must be consid-

ered, i. e.,

$$V_s = V_{s0}(1 - \beta\Delta P)$$

Here β the compressibility coefficient.

C. Results and Discussions

The physical constants used in these calculations are listed in Table 3. The calculated results are compared with the experimental values in Table 4 and Table 5. The agreements between experiment and theory are quite good.

TABLE 3. Physical constants used in Calculation:

	A_0	B_0	V_c (cc/mole)	V_{s0} (cc/mole)	β (bar ⁻¹)	β_s (bar ⁻¹)
n-Pentane	-6.04445	73.9924	311	82.7(b)	1.42×10^{-5}	1.93×10^{-5}
n-Hexane	-5.73030	41.1944	368	102.30	1.57×10^{-5}	

TABLE 4. Calculated Results for n-Pentane:

P(bars)	1	500	1000	1500	2000	2500	3000	3500	4000
$\eta_{\text{obs}}(a)$ (cp)	0.216	0.3305	0.4493	0.5897	0.7495	0.9007	1.080	1.281	1.501
η_{calc} (cp)	0.216	0.3448	0.4346	0.621	0.791	0.925	1.145	1.347	1.6156
%(η_c/η_0)	100	104.33	96.73	105.31	105.54	102.70	106.19	105.15	107.63

(a) D. W. Brazier and T. R. Freeman, *Canadian J. Chem.*, **47**, 893 (1969).

TABLE 5. Calculated results for n-Hexane:

P(bars)	1	500	1000	1500	2000	2500	3000	3500	4000
$\eta_{\text{obs}}(a)$ (cp)	0.285	2.4503	0.6213	0.80085	0.9804	1.23975	1.5105	1.844	2.2088
η_{calc} (cp)	0.285	0.4442	0.6067	0.81505	1.0099	51.2518	1.538	1.7997	2.1844
%(η_c/η_0)	100	98.64	97.65	101.773	103.01	100.97	101.82	97.60	98.90

(a) D. W. Brazier and T. R. Freeman, *Canadian J. Chem.*, **47**, 893 (1969).

To test the validity of theoretical formulation, the transmission coefficient κ and bZ are calculated. For n-C₁₂H₂₆, κ is approximately equal to 1.6837 and bZ = 2.010.

For n-C₅H₁₂ and n-C₆H₁₄, κ is approximately 1.26 and 1.16. Less discrepancies are noted as anticipated. bZ is 1.89 10 for n-C₅H₁₄ and 0.2394 for n-C₆H₁₄. More refined results indicate the formulat-

ion was more suitable for simpler molecules.

The value of V_{s0} for $n\text{-C}_5\text{H}_{12}$ is obtained from the solid volume data (11) and gave good results. V_{s0} for $n\text{-C}_6\text{H}_{14}$ is guessed from the density data at the high pressure, assuming the compression ratio equal to that found for lower hydrocarbon. Then trial-error procedure is adopted to find the best fitting values of three unknowns V_{s0} , A_0 and B_0 for the five equations chosen from the experimental data of viscosity-temperature at 1 atmosphere pressure (12), adjusting with least square method. so, V_{s0} can be assured to be calculated reasonably around 100.

100% fitting values of β calculated indicate somewhat interesting facts. β -values for $n\text{-C}_5\text{H}_{12}$ increases from $1.19 \times 10^{-5} \text{ bar}^{-1}$ to $1.459 \times 10^{-5} \text{ bar}^{-1}$ but always smaller than $\beta_s = 1.93 \times 10^{-5} \text{ bar}^{-1}$, the compressibility coefficient for solid.

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