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Prediction of Kinematic Viscosities for Binary and Ternary Liquid Mixtures with an ASOG-VISCO Group Contribution Method[1]

K. Tochigi,[2,3] K. Yoshino,[2] and V. K. Rattan[4]

The kinematic viscosities for 273 binary and 11 ternary systems were predicted with a new model (ASOG-VISCO) developed by combining the ASOG group contribution method and Eyring's theory of absolute reaction rates. The ASOG-VISCO group pair parameters were determined from literature kinematic viscosity data for group pairs of CH_2, ArCH, CyCH, OH, H_2O, CO, COO, CCl_3, and CCl_4 in the temperature range of 283.15 to 333.15 K. The overall average deviations between experimental and predicted kinematic viscosities for the binary and ternary systems were 4.15 and 5.03%, respectively. The predicted results using ASOG-VISCO were better than those determined with the UNIFAC-VISCO group contribution method.

KEY WORDS: ASOG; group contribution method; kinematic viscosity; prediction.

1. INTRODUCTION

The kinematic viscosity of a liquid system is an important physicochemical property required for fluid transport calculations in chemical processes. Although the correlation and prediction of viscosity has been carried out by many researchers [1], the database for liquid mixtures is relatively small

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[2] Department of Materials and Applied Chemistry, Nihon University, 1-8 Kanda-Surugadai, Chiyoda, Tokyo 101-8308, Japan.

[3] To whom correspondence should be addressed. E-mail: tochigi@chem.cst.nihon-u.ac.jp

[4] Department of Chemical Engineering and Technology, Panjab University, Chandigarh 160-014, India.

and so it is of interest to develop predictive methods. The absolute reaction rate theory of Eyring et al. [2] applicable to liquids could possibly be effective from a practical point of view, because it makes use of the excess Gibbs free energy [3–6], which can be combined with solution theory.

This paper proposes a group contribution method called ASOG-VISCO that combines the Eyring's model with the ASOG group contribution model [7]. By using ASOG-VISCO, the mixture kinematic viscosity can be evaluated from the known viscosity data of pure components and group pair parameters. Predictions were performed for 273 binary and 11 ternary data sets. The predicted results are compared with those by UNIFAC-VISCO [4].

2. EQUATIONS FOR CALCULATING KINEMATIC VISCOSITY

From Eyring's theory of absolute reaction rate [2–4], the kinematic viscosity ν is given as

$$\nu = \frac{hN_A}{M} \exp\left(\frac{\Delta^* \mathrm{G}}{RT}\right) \tag{1}$$

where $\Delta^* G$ is the activation free energy in the flowing state, R is the universal gas constant, T is the absolute temperature, h is Plank's constant, N_A is Avogadro's number, and M is the molar mass. $\Delta^* G$ is obtained from the ideal free energy of solution, $\Delta^* G^{\mathrm{id}}$, and the excess free energy $\Delta^* G^{\mathrm{E}}$ at the activation state as follows;

$$\Delta^* G = \Delta^* G^{\mathrm{id}} + \Delta^* G^{\mathrm{E}} \tag{2}$$

From Eqs. (1) and (2), the kinematic viscosity of a liquid mixture can be determined from the pure component values and the excess free energies of the activation,

$$\ln(\nu M) = \sum_i x_i \ln(\nu_i M_i) + \frac{\Delta^* G^{\mathrm{E}}}{RT} \tag{3}$$

where x_i is mole fraction of component i.

In order to calculte kinematic viscosity, we make use of the following equation similar to the relation [8] that is derived when the Eyring empirical constant [2] is set to 1.0;

$$\ln(\nu M) = \sum_i x_i \ln(\nu_i M_i) - \frac{\Delta G^{\mathrm{E}}}{RT} \tag{4}$$

Here ΔG^{E} is the excess Gibbs free energy at the equilibrium state.

3. DETERMINATION OF ASOG-VISCO GROUP PAIR PARAMETERS

In this work, ΔG^{E} was evaluated from the ASOG group contribution method, that is, a predictive method for the activity coefficient γ_i, given by the following equations [7]:

$$\frac{\Delta G^{\mathrm{E}}}{RT} = \sum_i x_i \ln \gamma_i = \sum_i x_i \left(\ln \gamma_i^{\mathrm{FH}} + \ln \gamma_i^{G}\right) \tag{5}$$

$$\ln \gamma_i^{\mathrm{FH}} = \ln \frac{\nu_i^{\mathrm{FH}}}{\sum_j \nu_j^{\mathrm{FH}} x_j} + 1 - \frac{\nu_i^{\mathrm{FH}}}{\sum_j \nu_j^{\mathrm{FH}} x_{\mathrm{j}}} \tag{6}$$

$$\ln \gamma_i^{G} = \sum_k \nu_{k,i} \left(\ln \Gamma_k - \ln \Gamma_k^{(i)}\right) \tag{7}$$

$$\ln \Gamma_k = -\ln \sum_l X_l a_{k,l} + 1 - \sum_l \frac{X_l a_{l,k}}{\sum_m X_m a_{l,m}} \tag{8}$$

$$X_l = \frac{\sum_i x_i \nu_{l,i}}{\sum_i x_i \sum_k \nu_{k,i}} \tag{9}$$

$$a_{k,l} = \exp\left(m_{k,l} + \frac{n_{k,l}}{T}\right) \tag{10}$$

Here, ν_i^{FH} and $\nu_{k,i}$ are the number of atoms (other than hydrogen atoms) in molecule i, and in group k of molecule i, respectively. The Γ_k and $\Gamma_k^{(i)}$ are group activity coefficients of group k in the mixture and standard state (pure component i), and $m_{k,l}$ and $n_{k,l}$ in Eq. (10) are ASOG-VISCO group pair parameters.

The systems discussed in this study contain n-paraffins, alcohols, water, ketones, esters, chloroform, and carbon tetrachloride. These systems are composed of CH_2, ArCH, CyCH, OH, H_2O, CO, COO, CCl_3, and CCl_4 groups.

The group pair parameters were determined from experimental kinematic viscosity data using the following objective function:

$$F_{\mathrm{obj.}} = \sum_{n=1}^{\mathrm{ND}} \left| \frac{\nu_{\mathrm{cal.}} - \nu_{\mathrm{exp.}}}{\nu_{\mathrm{exp.}}} \right|_n \tag{11}$$

Table I shows the group pair parameters. The temperature range is 283.15–333.15 K.

Table I. ASOG-VISCO Group Pair Parameters (283.15 – 333.15 K)

[*m*] *l k*	CH_2	ArCH	CyCH	OH	H_2O	CO	COO	CCl_3	CCl_4
(a) $m_{k,l}$									
CH_2	0	0.2779	0	−0.357	−9.006	0	0.3682	0	0
ArCH	1.2817	0	−1.565	0	–	−1.109	0.2418	0	0.1759
CyCH	0	−1.543	0	1.0616	–	3.4974	0	–	0.9018
OH	14.146	0	−4.676	0	−13.11	5.9432	−40.2	82.302	−3.874
H_2O	0.0879	–	–	0.204	0	0.2318	–	–	–
CO	0	3.7286	13.184	−11.32	−0.968	0	0	–	−0.451
COO	0.0952	−0.902	0	19.131	–	0	0	0	11.005
CCl_3	0	0	–	2.3089	–	–	0	0	–
CCl_4	0	0.3971	−2.335	1.3971	–	0.7525	−4.048	–	0
[*n*]*lk*									
(b) $n_{k,l}$									
CH_2	0	−418.5	0.1004	469.65	2216.5	265.39	112.59	−111.8	−177
ArCH	−187.4	0	510	280.63	–	678.02	140.35	91.432	−1.857
CyCH	1	368.21	0	0.9436	–	−765.5	−183.8	–	−130.2
OH	−6137	−1247	456.72	0	2964.1	−2071	11583	−27537	70.876
H_2O	528	–	–	537.65	0	94.521	–	–	–
CO	−460.5	−1922	−4657	3240.5	−0.968	0	−108.3	–	−270.9
COO	−383.6	−107.2	36.378	−5747	–	99.719	0	−277.9	−3780
CCl_3	84.034	−98.59	–	−306.4	–	–	231.03	0	–
CCl_4	128.78	−69.59	496.69	−16.11	–	31.126	1480.7	–	0

4. PREDICTED RESULTS

4.1. Binary Systems

The kinematic viscosities for binary systems were evaluated for 273 data sets as summarized in Table II. The overall average deviation between experimental [9, 10] and predicted kinematic viscosities was 4.15%. Table II shows the predicted results using ASOG-VLE [7] and UNIFAC-VISCO [4] parameters. The predictions using ASOG-VISCO were better than those made with UNIFAC-VISCO. Figure 1 shows predicted results for acetone + ethanol system at 298.15 K. Figure 1 shows the results using ASOG-VLE parameters and UNIFAC-VISCO parameters. Figure 2 shows the results for ethanol + water system at 293.15 – 333.15 K.

4.2. Ternary Systems

The kinematic viscosities for ternary systems have been predicted for 11 datasets composed of hydrocarbons, alcohols, ketones, and esters. The

Table II. Predicted Results of Kinematic Viscosity for Binary Liquid Mixtures using ASOG-VISCO, ASOG-VLE, and UNIFAC-VISCO(283.15−333.15 K)

System		No. of data sets	No. of data points	ASOG-VISCO	ASOG-VLE	UNIFAC-VISCO
(1)	(2)			$\Delta\nu$(%)		
Alkanes	Alcohols	11	109	3.36	12.28	2.82
Alkanes	Esters	25	249	2.5	9.44	0.73
Alkanes	Ketones	7	92	1.05	19.37	1.68
Alkanes	Cycloalkanes	5	28	10.42	10.5	4.73
Alkanes	Aromatics	24	254	4.15	7.7	9.63
Alcohols	Ketones	18	154	4.04	10.66	6.8
Alcohols	Esters	4	36	3.53	8.47	4.34
Alcohols	Cycloalkane	21	187	2.13	16.42	2.36
Alcohols	Aromatics	3	24	7.67	36.42	7.2
Alcohols	Water	24	227	4.52	45.53	unavailable
Aromatics	Esters	10	62	2.79	2.83	1.21
Aromatics	Ketones	17	170	4.39	15.93	5.71
Aromatics	Cycloalkanes	7	49	2.67	4.32	3.03
Cycloalkanes	Esters	4	36	2.19	7.84	12.09
Cycloalkanes	Ketones	3	26	3.95	46.83	5.61
Esters	Ketones	4	36	2.77	7.27	3.23
Ketones	Water	6	49	13.51	56.53	unavailable
Chloroform	Aromatics	2	16	3.07	–	unavailable
Chloroform	Alkanes	1	8	0.36	–	unavailable
Chloroform	Esters	1	7	2.21	–	unavailable
Chloroform	Alcohols	14	91	6.98	–	unavailable
CCl_4	Aromatics	5	38	1.84	–	unavailable
CCl_4	Ketones	4	46	0.84	–	unavailable
CCl_4	Esters	9	64	1.34	–	unavailable
CCl_4	Cycloalkanes	3	21	1.54	–	unavailable
CCl_4	Alcohols	41	394	6.45	–	unavailable
Overall (including water)		273	2473	4.15	17.27	- - - - - -
Overall		243	2197	3.90	11.76	4.59

overall average deviation between experimental [9] and predicted kinematic viscosity as shown in Table III is 5.03%.

5. CONCLUSIONS

A predictive model was developed based on the ASOG group contribution method and Eyring's absolute reaction rate theory. Calculations made with the model show that kinematic viscosities can be predicted

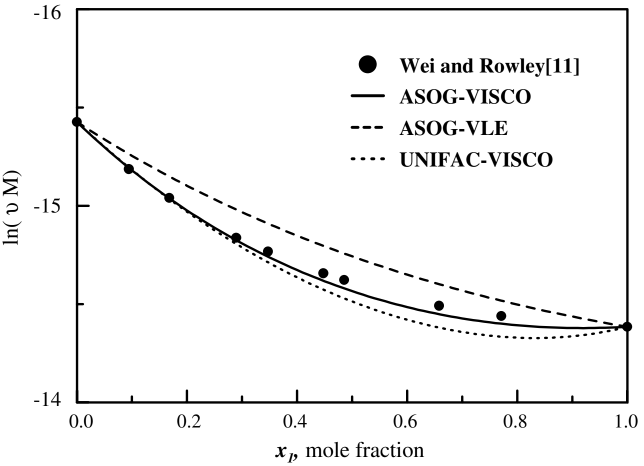

Fig. 1. Kinematic viscosity for acetone (1) + ethanol (2) system at 298.15 K.

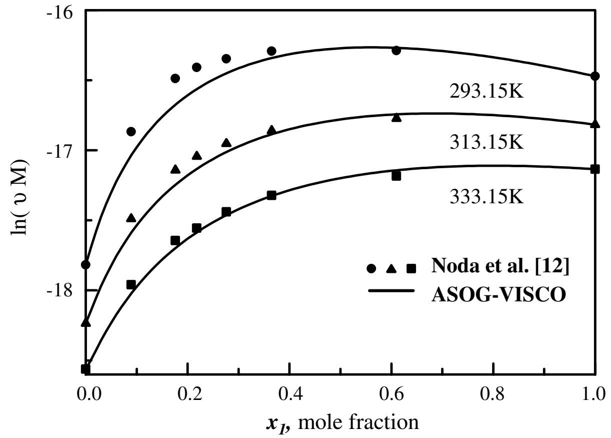

Fig. 2. Kinematic viscosity for ethanol (1) + water (2) system at 293.15, 313.15, and 333.15 K.

to within 4.2% for binary mixtures and 5.0% for ternary mixtures for the literature data studied. The model requires only pure component kinematic viscosities and molecular structure.

Table III. Predicted Results of Kinematic Viscosity for Ternary Liquid Mixtures using ASOG-VISCO

System			No of data points	ASOG-VISCO $\Delta\nu(\%)$
(1)	(2)	(3)		
Ethanol	Acetone	Cyclohexane	12	4.73
Acetone	Hexane	Ethanol	12	1.99
Acetone	Ethanol	Methanol	12	12.09
Acetone	Hexane	Cyclohexane	12	1.75
Hexane	Cyclohexane	Ethanol	12	4.29
Methanol	Ethanol	2-Propanol	12	2.83
Acetone	Ethanol	2-Propanol	12	8.63
Ethanol	Cyclohexane	2-Propanol	12	2.43
Methyl acetate	Cyclohexane	Ethanol	12	1.67
Methanol	Ethanol	1-Propanol	12	1.61
Toluene	1-Hexanol	Benzyl alcohol	24	7.51
Overall			136	5.03

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