

*Marina GRINTCHAK**, *Georgi KURANOV***,
and *Ludmilla KUDRYAVTSEVA**

THE APPLICATION OF THE GROUP CONTRIBUTION METHOD TO PREDICTING AND CALCULATING THE KINEMATIC VISCOSITY OF BINARY SYSTEMS CONTAINING UNSATURATED HYDROCARBONS

Data on the viscosities of liquid mixtures are necessary in engineering calculations. At the same time they enable us to get a better understanding of the molecular interaction and behaviour of solutions. Very often experimental data on viscosities of liquid mixtures are not available. Therefore, attempts have been made to predict these transport properties on the basis of theory. However, a theory of predicting viscosities of liquid mixtures from those of pure components has not yet been developed. Some of the semi-empirical correlations proposed [1, 2] are based on the Eyring theory [3]. They give a good representation of the kinematic viscosity in binary systems. Others, for example those described in [4], have been established from Green radial distribution for a nonequilibrium fluid. All these semi-empirical models require preliminary determination of two or more parameters from experimental data.

The predictive models, such as the group contribution one, have also been applied to viscosity calculations. The advantage of such an approach is that a larger number of components may be represented by relatively few groups. For the determination of group interaction parameters binary viscosity data are needed. Prediction can be made for other binary systems presenting adequate group interactions, as well as for multicomponent systems, where the related binary data are either lacking or taken at different temperatures.

The lack of experimental data on the viscosity of binary systems containing unsaturated hydrocarbons prompted us to undertake this study. For several binary systems new experimental kinematic viscosity data have been obtained. The group contribution approach based on the well-known UNIFAC model [5] has been tested for its ability to correlate and predict the kinematic viscosity in binary systems.

Kinematic viscosity equations

The Eyring theory of absolute reaction rate presents the following equation for calculating the kinematic viscosity of a pure liquid, ν_i :

$$\nu_i = \frac{hN_A}{M_i} \exp \frac{\Delta^*G_i}{RT}, \quad (1)$$

where Δ^*G_i is the free energy of activation for the flow process, M_i is the molecular weight of the liquid i , h is the Planck constant, N_A is the Avogadro number, R is the gas constant.

* Eesti Teaduste Akadeemia Keemia Instituut (Institute of Chemistry, Estonian Academy of Sciences). Akadeemia tee 15, EE-0026 Tallinn, Estonia.

** Санкт-Петербургский университет (St. Petersburg University). Университетская наб., 7/9, 199164 Санкт-Петербург, Россия.

For the viscosity of a liquid mixture, ν , also the following expression holds:

$$\nu = \frac{hN_A}{M} \exp \frac{\Delta^*G}{RT}, \quad (2)$$

where Δ^*G and M are the free energy of activation for the flow process and the molecular weight of the mixture.

By a definition for an ideal mixture we get

$$\Delta^*G_{id} = \sum_i x_i \Delta^*G_i \quad (3)$$

while for a non-ideal mixture the following equation is obtained:

$$\Delta^*G = \Delta^*G_{id} + \Delta^*G^E, \quad (4)$$

where Δ^*G^E is the excess molar free energy of activation for the flow.

Then Δ^*G^E is related to the viscosity by means of the following equation:

$$\Delta^*G^E = RT[\ln^E(\nu M)] \quad (5)$$

with $M = \sum_i x_i M_i$.

In the same way,

$$\nu = \nu_{id} + \nu^E. \quad (6)$$

In [6] the representation of Δ^*G^E/RT is given by the UNIFAC group contribution method adapted to viscosities (UNIFAC—VISCO). The excess molar free energy of activation for the flow, Δ^*G^E , is assumed to be the sum of two contributions: a combinatorial part, essentially due to differences in size and shape of the molecules in the mixture, and a residual term, essentially due to the energy interaction between the structural groups contained in the mixture:

$$\Delta^*G^E = \Delta^*G^{EC} + \Delta^*G^{ER}. \quad (7)$$

Moreover,

$$\Delta^*G^E = RT \sum_i x_i \ln \gamma_i^*. \quad (8)$$

The activity coefficient γ_i^* is a function of the combinatorial (γ_i^{*C}) and residual (γ_i^{*R}) terms.

Table 1
Group volume and surface-area parameters

Group k	R_k	Q_k
CH ₂	0.6744	0.540
CH ₃	0.9011	0.848
OH	1.0000	1.200
CCl ₄	3.3900	2.910
CH ₂ =CH	1.3454	1.176
CH≡C	1.2920	1.088

Table 1 presents the volume and surface-area parameters of groups obtained from the atomic and molecular data [7] normalized by Abrams and Prausnitz [8].

The original UNIFAC [5] and UNIFAC—VISCO methods differ mainly in the determination of group interaction parameters. The viscosimetric parameters of UNIFAC—VISCO are fitted to the experimental kinematic viscosities measured for binary mixtures.

Experimental

In this work, the kinematic viscosities of unsaturated hydrocarbons (1-alkene, 1-alkyne) mixtures with n -alkanes (n -octane, n -decane, n -dodecane) and alcohols (1-propanol and 1-butanol) were measured. The viscosities of n -octane binaries with ethanol and 1-propanol, 1-butanol mixtures with tetrachlormethane were also determined.

The experimental data were obtained using calibrated Ubbelohde viscometers. The samples were temperature stabilized, and fluctuations of no more than $\pm 0.1^\circ\text{C}$ were observed with a thermometer. Over five measurements of viscosity with deviations of no more than 0.2% in the efflux time were made and averaged for each solution. Viscosities were measured over the whole composition range at several temperatures from 288.15 to 323.15 K.

For the determination of group interaction parameters the data on the binary systems with $\Delta^*G_{\text{max}}^E$ values higher than 100 J/mole were used. The experimental points which lay on the smooth curve $\Delta^*G^E(x)$ were selected. As a result, the following experimental points were taken into consideration:

Type of system	Number of systems	Number of points	Temperature range, K
Alkane-alkene	4	33	293.15—323.15
Alkane-alkyne	2	15	293.15—323.15
Alkane-alcohol	2	38	288.15—303.15
Alkene-alcohol	2	56	288.15—303.15
Alcohol- CCl_4	1	24	293.15—323.15

Calculations were done in two ways. In the first version it was assumed that the CH_3 and CH_2 groups are energetically identical, i. e. their group interaction parameters are equal. In the second version the interaction parameters for the CH_3 and CH_2 groups were adopted from [6]. Interaction parameters for the other groups were calculated from our experimental data and are presented in Table 2 (version 1) and Table 3 (version 2).

Table 2

UNIFAC—VISCO group interaction parameters (Version 1)

Group	CH_3 (CH_2)	$\text{CH}_2=\text{CH}$	$\text{CH}\equiv\text{C}$	OH	CCl_4
CH_3 (CH_2)	0	-3266.61	-153.95	654.30	892.05
$\text{CH}_2=\text{CH}$	57.85	0	—	3918.01	—
$\text{CH}\equiv\text{C}$	1610.95	—	0	—	—
OH	-300.08	-2818.90	—	0	-112.39
CCl_4	-30.09	—	—	-154.28	0

Table 3

UNIFAC—VISCO group interaction parameters (Version 2)

Group	CH_3	CH_2	$\text{CH}_2=\text{CH}$	$\text{CH}\equiv\text{C}$	OH	CCl_4
CH_3	0	-709.50	5.82	247.16	1490.65	580.45
CH_2	66.53	0	68.51	428.66	449.99	580.45
$\text{CH}_2=\text{CH}$	0.04	-588.98	0	—	3898.68	—
$\text{CH}\equiv\text{C}$	-149.18	-687.73	—	0	—	—
OH	4989.62	-632.62	214.77	—	0	580.41
CCl_4	-198.79	-303.30	—	—	-306.39	0

Results

Binary systems of unsaturated hydrocarbons with *n*-alkanes. A comparison of the experimental and calculated values of kinematic viscosities of 1-octene mixtures with *n*-dodecane and *n*-tetradecane, 1-dodecene binaries with *n*-octane and, finally, the 1-decene system with *n*-tetradecane (Table 4, Fig. 1) shows that version 2 describes the experimental curve $\nu^E(x)$ considerably better than version 1. The maximum deviation diminishes by a factor 7 if the CH₃ and CH₂ groups are considered not identical. The overall average absolute deviation between the experimental and calculated results is about 1.80 and 0.45% in the two versions, respectively.

The predicted kinematic viscosities for the binary systems *n*-octane-1-octene, *n*-tetradecane-1-dodecene and *n*-octane-1-decene over the whole temperature range are in good agreement with experiment in case of version 2. A comparison of the values of experimental and predicted kinematic viscosities shows (Fig. 1, Table 5) that the UNIFAC—VISCO model with the group interaction parameters for the CH₂=CH group determined in this work describes the $\nu^E(x)$ curves in the investigated systems quite well.

Table 4

A comparison of deviation of the experimental and calculated kinematic viscosity for *n*-alkane and 1-alkene binary systems

System	T, K	AAD*		$ E_v _{\max}^{**}$	
		Version 1	Version 2	Version 1	Version 2
<i>n</i> -Dodecane-1-octene	293.15	0.78	0.57	1.64	0.85
	303.15	0.68	0.44	1.30	0.93
	308.15	0.78	0.51	1.43	0.88
	313.15	0.64	0.39	1.15	0.78
	323.15	0.37	0.37	0.85	0.70
<i>n</i> -Tetradecane-1-octene	293.15	4.30	0.43	5.99	0.88
	303.15	4.16	0.45	5.86	0.77
	308.15	4.44	0.42	6.25	0.89
	313.15	4.44	0.47	6.36	1.05
	323.15	4.47	0.68	6.48	1.47
<i>n</i> -Octane-1-dodecene	293.15	1.49	0.49	1.74	0.65
	303.15	1.61	0.12	1.82	0.39
	308.15	1.60	0.23	1.90	0.43
	313.15	1.46	0.24	1.77	1.13
	323.15	1.69	0.73	2.14	1.17
<i>n</i> -Tetradecane-1-decene	293.15	0.47	0.60	0.92	0.74
	303.15	0.68	0.45	1.17	0.74
	308.15	0.46	0.64	0.86	0.89
	313.15	0.78	0.31	1.05	0.47
	323.15	0.60	0.38	1.07	0.92

$$* \text{ AAD} = \left[\frac{1}{N_p} \sum \frac{\nu_{\text{exp}} - \nu_{\text{calc}}}{\nu_{\text{exp}}} \right] \times 100; \text{ average absolute deviation, \%}$$

N_p — experimental points number

$$** |E_v|_{\max} = \left| \frac{|\nu_{\text{exp}} - \nu_{\text{calc}}|}{\nu_{\text{exp}}} \times 100 \right|_{\max}; \text{ maximum deviation, \%}$$

The validity of the model was proved in a wide temperature range. It can be concluded that the temperature dependence of kinematic viscosity in this type of systems can be described quite adequately (Fig. 2): with increasing temperature the deviations from ideality become less negative.

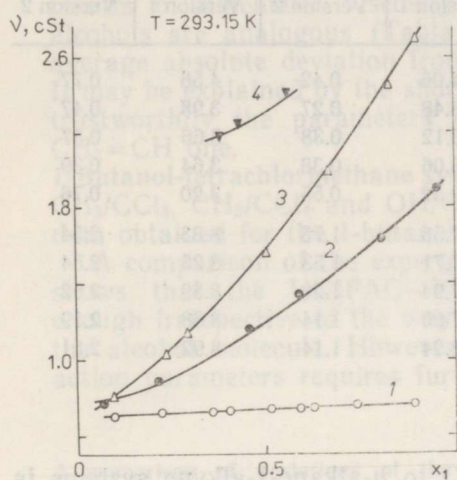


Fig. 1. The kinematic viscosity of *n*-alkane-1-alkene mixtures: 1 — *n*-octane-1-octene, 2 — *n*-dodecane-1-octene, 3 — *n*-tetradecane-1-octene, 4 — *n*-tetradecane-1-dodecene. Points — experiment, curves 2, 3 — correlation, curves 1, 4 — prediction.

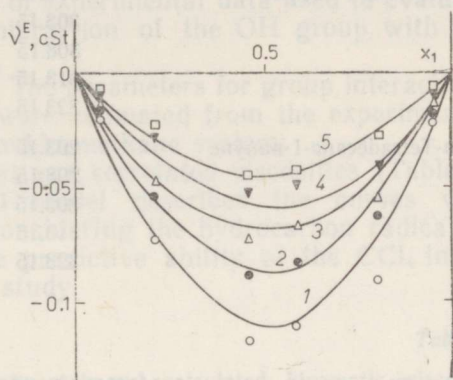


Fig. 2. The excess kinematic viscosity of the binary system *n*-dodecane-1-octene in the temperature range 293.15–323.15 K. 1 — 293.15 K, 2 — 303.15 K, 3 — 308.15 K, 4 — 313.15 K, 5 — 323.15 K. Points — experiment, curves — correlation.

Table 5

A comparison of deviation of the experimental and predicted kinematic viscosity for *n*-alkane and 1-alkene binary systems

System	T, K	AAD		E _v max	
		Version 1	Version 2	Version 1	Version 2
<i>n</i> -Octane-1-octene	293.15	6.92	0.23	9.15	0.40
	303.15	6.80	0.31	9.05	0.49
	308.15	6.69	0.30	9.02	0.41
	313.15	6.75	0.33	9.07	0.51
	323.15	6.60	0.38	9.08	0.85
<i>n</i> -Octane-1-decene	293.15	4.66	0.41	4.96	0.49
	303.15	4.59	0.23	5.14	0.37
	308.15	4.55	0.17	5.13	0.30
	313.15	4.54	0.22	5.18	0.29
	323.15	4.40	0.22	5.05	0.38
<i>n</i> -Tetradecane-1-dodecene	293.15	3.69	0.54	4.28	1.17
	303.15	3.82	0.45	4.35	1.03
	308.15	3.61	0.52	4.14	1.25
	313.15	3.13	0.84	4.22	1.28
	323.15	3.85	0.36	4.26	0.88

A comparison of deviation of the experimental and calculated kinematic viscosity for 1-nonyne binary mixtures with *n*-alkanes

System	<i>T</i> , K	AAD		E_v max	
		Version 1	Version 2	Version 1	Version 2
<i>n</i> -Octane-1-nonyne	293.15	4.06	0.42	4.56	0.77
	303.15	3.48	0.27	3.98	0.47
	308.15	3.12	0.38	3.66	0.57
	313.15	3.06	0.38	3.64	0.39
	323.15	2.52	0.55	3.20	0.76
<i>n</i> -Tetradecane-1-nonyne	293.15	7.55	1.78	8.33	2.54
	298.15	7.71	1.53	8.25	2.54
	303.15	7.94	1.28	8.59	2.52
	313.15	7.90	1.14	8.68	2.19
	323.15	8.24	1.14	8.92	2.51

The application of UNIFAC—VISCO to *n*-alkane-1-alkyne systems is shown in Table 6. For the *n*-octane-1-nonyne binary system the average absolute deviations were 3.25 and 0.4% in versions 1 and 2, respectively. For the *n*-tetradecane mixtures with 1-nonyne they were 7.87 and 1.37%. The description of the $v^E(x)$ curve for alkyne binaries is worse due to the insufficiency of experimental data used for the determination of interaction parameters of the $\text{CH}\equiv\text{C}$ group.

Table 7

A comparison of deviation of the experimental and calculated kinematic viscosity for alcohol binary systems with hydrocarbons

System	<i>T</i> , K	AAD		E_v max	
		Version 1	Version 2	Version 1	Version 2
Ethanol- <i>n</i> -octane	288.15	1.43	1.22	4.63	4.05
	293.15	2.61	2.30	9.00	8.98
	298.15	1.91	1.41	2.92	3.48
	303.15	1.75	1.07	3.18	3.38
1-Propanol- <i>n</i> -octane	288.15	10.37	2.73	15.32	5.24
	293.15	10.60	3.46	17.06	6.02
	298.15	9.81	3.19	16.18	5.97
	303.15	9.64	3.48	15.27	7.35
1-Propanol-1-octene	288.15	4.89	7.87	13.57	18.31
	293.15	4.54	8.31	10.80	15.91
	298.15	3.54	6.78	9.30	14.78
	303.15	3.28	6.67	8.04	13.85
1-Butanol-1-octene	288.15	6.76	5.37	15.61	12.07
	293.15	6.52	5.29	15.32	12.17
	298.15	6.04	4.94	14.68	11.90
	303.15	5.21	4.44	14.07	11.61

Alcohol-hydrocarbon binary mixtures. The parameters for CH_3/OH and CH_2/OH interactions were determined from the experimental data for *n*-octane binaries with ethanol and 1-propanol (Tables 2, 3). A more detailed consideration of the hydrocarbon molecule structure in version 2 gives only slightly better results in comparison with version 1 when the CH_3 and CH_2 groups have been assumed to be energetically identical; the results of kinematic viscosity calculation for 1-alkene mixtures with alcohols are analogous (Table 7). For 1-propanol-1-octene mixtures the average absolute deviation from experiment in version 2 is even greater. It may be explained by the shortage of experimental data used to evaluate trustworthily the parameters of interaction of the OH group with the $\text{CH}_2=\text{CH}$ one.

1-Butanol-tetrachlormethane system. The parameters for group interactions CH_3/CCl_4 , CH_2/CCl_4 and OH/CCl_4 were estimated from the experimental data obtained for the 1-butanol-tetrachlormethane system.

A comparison of the experimental and correlated viscosities (Table 8) shows that the UNIFAC—VISCO model describes the curves well enough irrespective of the way of considering the hydrocarbon radical of the alcohol molecule. However, the predictive ability of the CCl_4 interaction parameters requires further study.

Table 8

A comparison of deviations of the experimental and calculated kinematic viscosity values for the 1-butanol- CCl_4 system

T, K	AAD		$ E_v _{\max}$	
	Version 1	Version 2	Version 1	Version 2
293.15	0.72	0.66	2.13	1.60
298.15	0.76	0.76	1.67	2.12
303.15	0.82	0.82	2.31	2.69
308.15	0.62	0.64	1.85	2.17
313.15	0.38	0.33	0.80	0.55
318.15	0.56	0.46	1.46	0.73
323.15	0.65	0.48	1.74	1.30

Conclusions

In this work, which is a development of the group contribution model, the kinematic viscosities of liquid-phase mixtures containing saturated and unsaturated hydrocarbons, alcohols and tetrachlormethane were predicted from the known viscosities of pure components.

It can be concluded that the deviation from the ideality represented by the UNIFAC—VISCO method provides a sufficient estimation for predicting the kinematic viscosity.

For the first time the validity of the model was proved over a wide temperature range. It was shown that the model describes the temperature dependence of kinematic viscosity correctly.

To complete the matrix of group interaction parameters and to obtain more exactly the available ones, the study of other binary systems must be continued.

1. *Heric, E. L.* The viscosity of ternary mixtures. — *J. Chem. Eng. Data*, 1966, **11**, 66—68.
2. *McAllister, R. A.* The viscosity of liquid mixtures. — *AIChE Journal*, 1960, **6**, 3, 427—431.
3. *Глестон С., Лейдлер К., Эйринг Г.* Теория абсолютных скоростей реакций. Изд-во ИЛ, Москва, 1948.
4. *Harada, M., Tanigaki, M., Egughi, W.* Viscosity of liquid mixtures. — *J. Chem. Eng. Jap.*, 1975, **8**, 1—7.
5. *Fredenslund, Aa., Gmehling, J., Rasmussen, P.* Vapor-liquid equilibria using UNIFAC. Elsevier, Amsterdam—Oxford—New York, 1977.
6. *Chevalier, J. L., Petrino, P., Gaston-Bonhomme, Y.* Estimation method for the kinematic viscosity of a liquid-phase mixture. — *Chem. Eng. Sci.*, 1988, **43**, 6, 1303—1309.
7. *Bondi, A.* Physical properties of molecular crystals, liquids and glasses. J. Wiley, New York, 1968.
8. *Abrams, D. S., Prausnitz, J. M.* Statistical-thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. — *AIChE Journal*, 1975, **21**, 116—119.

Presented by U. Kirso

Received

December 1, 1992

Marina GRINTSAK, Georgi KURANOV, Ludmilla KUDRJAVTSEVA

GRUPIMUDELI RAKENDAMINE KINEMAATILISE VISKOOSUSE ARVUTAMISEKS JA ENNUSTAMISEKS KÜLLASTUMATA SÜSIVESINIKKE SISALDAVATE BINAARSETE SÜSTEEMIDE PUHUL

On kontrollitud võimalust kasutada UNIFAC—VISCO-mudelit nende binaarsete segude puhul, kus 1-alkeenidele või 1-alküünidele on lisatud *n*-alkaanide või alkohole. Arvutustes on kasutatud vastastikmõju parameetreid, mis on saadud eksperimentaalsete viskoossuste põhjal. Tulemused näitavad, et mudel kirjeldab liigviskoossuse kontsentratsiooni sõltuvusi piisavalt hästi. On saadud usaldusväärseid tulemusi ka 1-alkeenide ja *n*-alkaanide segude viskoossuse ennustamisel kogu temperatuurivahemikus.

Марина ГРИНЧАК, Георгий КУРАНОВ, Людмила КУДРЯВЦЕВА

ПРИМЕНЕНИЕ МЕТОДА ГРУППОВОГО ВЗАИМОДЕЙСТВИЯ ДЛЯ ПРЕДСКАЗАНИЯ И ОПИСАНИЯ КИНЕМАТИЧЕСКОЙ ВЯЗКОСТИ БИНАРНЫХ СИСТЕМ С НЕНАСЫЩЕННЫМИ УГЛЕВОДОРОДАМИ

Впервые получены параметры взаимодействия для расчетов кинематической вязкости бинарных систем *n*-алканов и спиртов с 1-алкенами и 1-алкинами по модели УНИФАК—ВИСКО. Показано, что модель довольно точно описывает концентрационные зависимости избыточной кинематической вязкости для всех экспериментально исследованных систем. Проверена и показана применимость модели для предсказания вязкости смесей *n*-алканов с 1-алкенами во всем температурном интервале исследования.