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SHORT COMMUNICATION

UDC 532.13+66.06:547

VISCOSITY OF BINARY NON-ELECTROLYTE LIQUID MIXTURES: PREDICTION AND CORRELATION

The viscosity of 31 binary liquid mixtures containing diverse groups of organic compounds, determined at atmospheric pressure: alcohols, alkanes (cyclo and aliphatic), esters, aromatics, ketones etc., were calculated using two different approaches, correlative (with Teja-Rice and McAllister models) and predictive by group contribution models (UNIFAC-VISCO, ASOG-VISCO and Grunberg-Nissan). The obtained results were analysed in terms of the applied approach and model, the structure of the investigated mixtures, the nature of components of the mixtures and the influence of alkyl chain length of the alcohol molecule.

Key words: liquid mixtures; viscosity; prediction; correlation.

The knowledge of thermophysical properties of multicomponent liquid mixtures is very important in applied areas of the research in huge number of design processes and has a theoretical significance in a better insight into the liquid state theory. The viscosity of binary non-electrolyte mixtures is one of the properties widely used in numerous chemical-engineering correlations regarding the fluid flow, mass and heat transfer calculations, but it is also a very often used property for pure substance(s) characterizations.

In this work, the estimation of the viscosity of binary non-electrolyte mixtures, determined at atmospheric pressure, was performed using two approaches: (i) predictive models (UNIFAC-VISCO [1,2], ASOG-VISCO [3] and Grunberg-Nissan [4]) and (ii) correlative models (Teja-Rice [5,6] and McAllister [7]).

The significance of the predictive approach utilization is that the mixture viscosity could be calculated requiring only pure component data and the relating functional groups parameters. The requirement of the very precise determination of universal group parameters sometimes could be a disadvantage of the applied approach. On the other hand, correlative models usually lead to better results, but for the determination of the interaction parameters (one or more), some optimization technique should be involved.

In order to get general conclusions for the investigated type of mixtures, both of the above mentioned procedures were applied in the viscosity estimation of 31 binary mixtures of organic compounds. Very important industrial mixtures, e.g. alcohols with aliphatic and cyclic alkanes, chlorinated hydrocarbons, ketons, aromatics etc., are chosen.

CORRELATION AND PREDICTION

Predictive approach

Group contribution based property estimation models are suitable for obtaining quick evaluations of thermophysical properties under different conditions of temperature, pressure and composition.

These models use the functional groups present in the molecules that make up the liquid mixture to calculate different properties. They are mainly developed for the activity coefficients or phase equilibrium (VLE) calculations. Later, this approach has been applied for other properties, such as viscosity calculations.

Some of the best known and most successful group contribution based models for the prediction of viscosities of mixtures of organic compounds are the UNIFAC-VISCO, ASOG-VISCO and Grunberg-Nissan model.

UNIFAC-VISCO model

Gaston-Bonhomme, Petrino and Chevalier [1,2] have modified the UNIFAC (Universal Functional Activity Coefficient) model to predict viscosities. Using this model, viscosity is calculated by:

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Paper received: October 10, 2008.

Paper accepted: October 21, 2008.

$$\ln \eta_m = \sum_i x_i \ln(\eta_i V_i) - \ln V_m + \frac{\Delta^* g^{EC}}{RT} + \frac{\Delta^* g^{ER}}{RT} \quad (1)$$

This approach includes calculation using viscosity (η) and volume (V) of pure substances and mixture volumes (V_m), as well as liquid mole fraction (x_i). Combinatorial part ($\Delta^* g^{EC}/RT$ - depends on the molecular structure of the components) and the residual part ($\Delta^* g^{ER}/RT$ - depends on the interaction of the functional group within the mixture) are defined by the procedure described in literature [1,2].

ASOG-VISCO model

ASOG (Analytical Solution of Groups) model [3] is also the group contribution based estimation model, previously developed for an activity coefficient and VLE prediction and correlation. Viscosity of liquid mixtures of organic compounds could be calculated using:

$$\ln(\nu M) = \sum_i x_i \ln(\nu_i V_i) - \Delta G^E / RT \quad (2)$$

where ν is kinematic viscosity. Excess Gibbs free energy (ΔG^E) could be calculated as sum of combinatorial and residual contributions [3], defined on the similar manner as in the UNIFAC-VISCO model.

Grunberg-Nissan model

The liquid mixture viscosity using Grunberg-Nissan model [4], could be determined by the following equation:

$$\ln \eta_m = \sum_i x_i \ln \eta_i + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n x_i x_j G_{ij} \quad (3)$$

where G_{ij} is an interaction parameter ($G_{ii} = G_{jj} = 0$), proportional to the interchange energy. The interaction parameters could be defined based on the group contribution models [4] and that procedure was used in this paper.

Correlative approach

Correlative models involve interaction parameters (one or more) generally obtained by employing some optimization technique. These models require some experimental data in order to establish the value of an interaction parameter specific for each binary pair, and according to that, they have specific values for each mixture for the defined temperature and pressure.

In this paper, one-parameter Teja and Rice [5,6], two-parameter Three-body McAllister [7] and three-parameter Four-body McAllister [7] models were used for viscosity determination.

Teja and Rice model

Teja and Rice model [5,6] is based on a corresponding-states treatment for the mixture compressi-

bility factors. Teja and Rice proposed an analogous form for the liquid mixture viscosity. According to the proposed procedure, the viscosity could be determined using the following expression:

$$\ln(\eta_m \varepsilon_m) = \ln(\eta \varepsilon)^{(R1)} + (\ln(\eta \varepsilon)^{(R2)} - \ln(\eta \varepsilon)^{(R1)}) \frac{\omega_m - \omega^{(R1)}}{\omega^{(R2)} - \omega^{(R1)}} \quad (4)$$

where the superscripts (R1) and (R2) refer to two reference fluids. η is the viscosity, ω the acentric factor, and ε is a mixture parameter. ε could be obtained by the procedure given in literature [5,6] from critical mixture parameters and the interaction parameter, ψ_{12} , which must be found from experimental data.

McAllister models

The equation developed by McAllister [7] has been used successfully to correlate data for binary mixtures. The equation has been written to contain either two or three adjustable parameters.

Three-body McAllister (McAllister-3) [6] is two-parameter model, based on Eyring's theory of absolute reaction rates. Three-body interaction model is as follows

$$\begin{aligned} \ln \nu = & x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \\ & - \ln(x_1 + x_2 \frac{M_2}{M_1}) + 3x_1^2 x_2 \ln(\frac{2 + M_2/M_1}{3}) + \\ & + 3x_1 x_2^2 \ln(\frac{1 + 2M_2/M_1}{3}) + x_2^3 \ln \frac{M_2}{M_1} \end{aligned} \quad (5)$$

where ν_{12} and ν_{21} are interaction parameters obtained by data regression, and M_i and ν_i are molecular mass and kinematic viscosity of the pure component i , respectively.

Four-body McAllister (McAllister-4) [7] is three-parameter model, given by the equation:

$$\begin{aligned} \ln \nu_m = & x_1^4 \ln \nu_1 + 4x_1^3 x_2 \ln \nu_{1112} + 6x_1^2 x_2^2 \ln \nu_{1122} + \\ & + 4x_1 x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln(x_1 + x_2 \frac{M_2}{M_1}) + \\ & + 4x_1^3 x_2 \ln(\frac{3 + M_2/M_1}{4}) + 6x_1^2 x_2^2 \ln(\frac{1 + M_2/M_1}{2}) + \\ & + 4x_1 x_2^3 \ln(\frac{1 + 3M_2/M_1}{4}) + x_2^4 \ln \frac{M_2}{M_1} \end{aligned} \quad (6)$$

where ν_{1112} , ν_{1122} and ν_{2221} are binary interaction parameters also obtained by data regression.

RESULTS AND DISCUSSION

The estimating ability of each of the presented models, was tested by calculating the percentage deviations PD_{max} , between the experimental and the calculated viscosity as:

$$PD_{\max} = \frac{100}{N} \sum_{i=1}^N \left| \frac{\eta_{\text{exp}} - \eta_{\text{cal}}}{\eta_{\text{exp,max}}} \right| \quad (7)$$

where $\eta_{\text{exp,max}}$ denotes the maximum absolute value of experimental points, and N is the number of experimental data. The results of the calculation are presented in Table 1 and Figure 1.

the influence on the quality of the obtained results. In this paper it was shown that liquid mixtures viscosities are also very sensitive to the structure of the constituent molecules and that even weak association effects between components can often significantly affect the viscosity. For liquid mixtures, the shape of the curve of the viscosity as a function of the composition

Table 1. Results of viscosity prediction and correlation of binary liquid mixtures

System	T / K	PD_{\max}					
		Predictive models			Correlative models		
		UNIFAC-VISCO	ASOG-VISCO	Grunberg-Nissan	Teja-Rice	McAllister	
					-3	-4	
Chloroform + 1-propanol [10]	303.15	13.24	1.90	4.66	1.98	1.00	0.30
Chloroform + 1-butanol [10]	303.15	9.72	1.45	3.94	1.73	0.66	0.30
Chloroform + Methanol [11]	298.15	48.17	21.70	3.12	1.71	1.35	0.38
Acetone + Ethanol [11]	298.15	6.56	4.77	10.05	0.76	0.36	0.20
Acetone + Methanol [11]	298.15	16.13	14.31	3.47	1.78	0.37	0.27
Acetone + Hexane [11]	298.15	3.22	3.45	6.35	0.78	0.61	0.21
Acetone + Cyclohexane [11]	298.15	7.83	1.71	7.82	2.90	0.60	0.33
Hexane + Ethanol [11]	298.15	12.75	10.08	1.17	1.16	0.83	0.33
Hexane + Chloroform [11]	298.15	7.75	1.74	0.72	0.76	0.37	0.33
Hexane + Cyclohexane [11]	298.15	2.11	6.64	11.74	0.77	0.24	0.23
Ethanol + Cyclohexane [11]	298.15	3.24	7.01	16.07	2.01	0.85	0.33
Methanol + Ethanol [11]	298.15	3.15	3.28	10.46	0.46	0.25	0.17
Methanol + 2-propanol [11]	298.15	1.48	8.90	17.74	1.44	0.50	0.28
Ethanol + 2-propanol [11]	298.15	1.81	1.42	4.72	0.28	0.30	0.26
Cyclohexane + 2-propanol [11]	298.15	12.87	1.10	27.49	2.94	0.94	0.38
Acetone + 2-propanol [11]	298.15	11.35	8.16	39.9	3.72	0.86	0.21
Methylcyclohexane + Ethanol [12]	298.15	1.36	5.86	13.55	1.56	0.29	0.28
Methylcyclohexane + 1-propanol [12]	298.15	3.72	7.08	10.55	3.69	1.87	1.05
Methylcyclohexane + 1-butanol [12]	298.15	19.26	21.53	7.83	1.25	1.62	0.73
Methylcyclohexane + 2-propanol [12]	298.15	18.63	4.18	23.51	1.72	0.50	0.43
Methylcyclohexane + 3-methyl-1-butanol [12]	298.15	12.36	17.39	3.67	2.13	0.38	0.19
Methylcyclohexane + 2-methyl-1-propanol [12]	298.15	8.78	0.68	16.16	1.31	0.52	0.37
Ethylbenzene + Ethanol [13]	298.15	0.90	2.93	13.33	2.45	0.59	0.45
Ethylbenzene + 1-propanol [13]	298.15	2.60	1.45	15.69	4.16	0.98	0.89
Ethylbenzene + 1-butanol [13]	298.15	1.80	2.21	16.06	2.51	1.36	0.64
Cyclohexane + Acetone [14]	298.15	1.03	1.38	5.86	0.78	0.47	0.24
Cyclohexane + Butanone [14]	298.15	2.44	0.37	7.54	1.17	0.43	0.25
Cyclohexane + 2-pentanone [14]	298.15	3.33	0.62	8.60	1.01	0.32	0.25
Cyclopentane + Acetone [14]	298.15	0.97	3.28	7.91	0.63	0.48	0.38
Cyclopentane + butanone [14]	298.15	0.83	4.03	7.81	0.72	0.32	0.27
Cyclopentane + 2-pentanone [14]	298.15	1.37	3.79	7.70	0.50	0.44	0.28

In our previous papers [8,9] dealing with determination and modelling of volumetric properties, it was shown that besides the complexity of the chosen model, structural parameters such as: the chain length of the alcohol molecule, the position of the OH group, size and the shape of the molecules and others, have

can be nearly linear (Figure 1a) for so-called ideal mixtures. Similar to the excess molar volumes, the viscosity is related to the molecular interaction between the components of the mixtures, as well as to the size and shape of molecules. Positive values of the viscosity deviation ($\Delta\eta$) are indicative of stronger

interactions whereas negative values indicate weaker interactions. The negative values of $\Delta\eta$ support the main factor of breaking of the self-associated alcohols and weak interactions between unlike molecules.

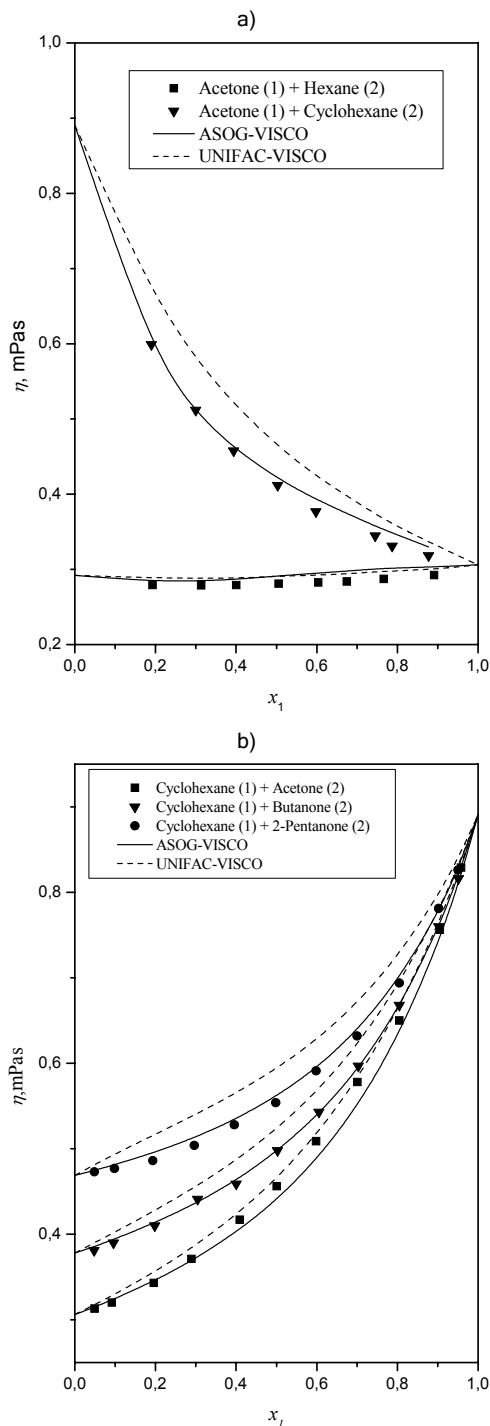


Figure 1. Results of the prediction and correlation of binary liquid mixture viscosity: a) acetone + hexane or +cyclohexane [11] at 298.15 K and b) cyclohexane + acetone, or +butanone + 2-pentanone [14] at 298.15 K. Symbols refer to experimental points and lines represent the results calculated by considered models.

As it can be seen from Table 1, the results obtained by correlative models are generally very good, especially those obtained with McAllisters' models. Also, predictive models gave good results, in some cases (ethanol + 2-propanol, systems with cyclopentane, *etc.*) of the same quality as correlative models. Commonly, the estimated results using ASOG-VISCO and UNIFAC-VISCO models were better than those determined with the Grunberg-Nissan. For the systems Cyclohexane + acetone, or + butanone, + 2-pentanone (Figure 1b) the predictive results are very good, especially those obtained with ASOG-VISCO model.

Acknowledgement

This work was supported by a grant from the Research Fund of Ministry of Science and Technological Development, Serbia, and the Faculty of Technology and Metallurgy, University of Belgrade (Project No 142064).

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