UNIVERSIDAD DE VALLADOLID

ESCUELA DE INGENIERIAS INDUSTRIALES

International Semester

Prediction of the viscosity of mixtures from VLE correlation parameters

Autor:

Ndebele, Mthobisi Sbonelo

Tutor:

MATO CHAÍN, Rafael
Departamento de Ingeniería
Química y TMA

Valladolid, July 5, 2017

ABSTRACT

Viscosity properties of liquid and liquid mixtures are important to understand molecular interactions between the components of mixtures and for engineering process involving mass transfer, heat transfer and fluid flow. Thus, it is necessary to have reliable and accurate methods of obtaining viscosities of liquid mixtures rather than being dependent on experimental data.

A study between activity coefficient and viscosity parameters was conducted in an attempt to determine if there is any correlation between these variables. A total number of 40 binary liquid mixtures were used to regress viscosity binary interactions parameters. Viscosity parameters were regressed from infinite dilution activity coefficients, using excel solver. The viscosity deviations were reduced from 9.44 to 8.05 using a polynomial equation, while regression of Andrade parameters using Aspen Plus reduced it to 3.61. Thus, this attempt to predict viscosity parameters from VLE correlations was not as successful as expected..

Keywords: Viscosity, NRTL, Andrade, Estimation, Aspen Plus

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

η^l	Viscosity of liquid
A	Area
F	Force
τ	Binary Parameter
u	Velocity
y	Vertical direction
n	number of components in a mixture
a_{ij}	Adjustable parameter
b_{ij}	Adjustable parameter
T	Temperature
i	Component i
j	Component j
f	An adjustable parameter
m_{ij}	An adjustable parameter
d_{ij}	An adjustable parameter
c_{ij}	An adjustable parameter
V_{mn}^l	API liquid volume
X	Mole fraction or weight fraction of component
k_{ij}	Symmetric binary parameter
l_{ij}	Antisymmetric binary parameter
T_r	Reference Temperature
μ_m	Absolute viscosity of the mixture
μ_i	Absolute viscosity of component
w_i	Weight fraction of component i

INTRODUCTION

Viscosity is a very important property which can be defined as the resistance of a fluid to deformation; it can also be considered as a measure of the effect of internal friction in the fluid flow where momentum is transferred between molecules. Consider a thin layer of fluid between two parallel plates separated by a distance Y, with the lower plane fixed and a shearing force F applied to the other (Sinnott 2005) as shown in figure 1.
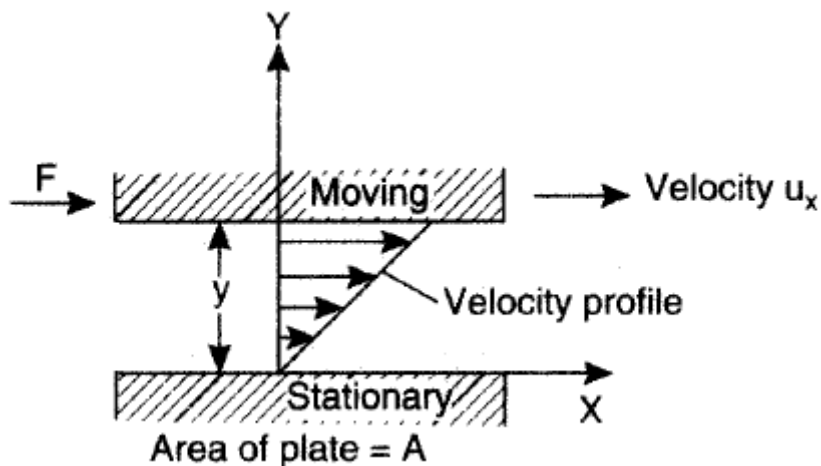
Figure 1: Viscosity profile of a fluid between two plates (Sinnott 2005)

Since fluids deform continuously under shear, the upper plane moves at a steady velocity u_x relative to the fixed lower plane. When conditions are steady, the force F is balanced by an internal force in the fluid which is influenced by its viscosity (η) and the shear force per unit area (A) is proportional to the velocity gradient in the fluid (Viswanath *et al.* 2007). This can be demonstrated by the following equation:

$$\frac{F}{A} = \tau \, \alpha \frac{u_x}{y} \propto \frac{du_x}{dy}$$

1

Whereas α is the shear stress in the fluid and du_x/dy is the velocity gradient or the rate of shear.

Viscosity is one of the important properties required in chemical engineering, especially for plant designs and process optimisation through simulations (Al-Jimaz, Al-Kandary and Abdul-Latif 2004). These engineering designs and processes involve mass transfer, heat transfer and fluid flow such as distillation columns, heat exchangers and pumps respectively. Viscosity is vital in calculations of dimensionless groups such as Reynolds, Prandtl and Sherwood numbers, which are mostly used to correlate heat and mass transfer coefficients during designs. On the other hand, Reynolds number is popularly used in pressure drop calculations.

Since viscosity is important in such a wide range of areas, there is a need of seeking convenient ways of obtaining viscosity values (Al-Jimaz, Al-Kandary and Abdul-Latif 2004; Lin, Hassein-bey-Larouci et al. 2014). Viscosities of liquids, both pure components and mixtures, are available in an ideal form in commercial simulators; however, these show large deviations for mixtures due to molecular interactions and unavailability of binary interaction parameters. Also, it is not feasible to be utterly dependent on experimental viscosity data alone available in different sources as the amount and variety of data needed increases. However, a number of equations are available for calculating other thermodynamic properties as excess volume, excess enthalpy, and excess free energy of multicomponent systems, with available parameters regressed from experimental values. Such methods are rarely used for viscosity (Domínguez et al. 2000). Therefore, to overcome these challenges, the viscosity molecular interactions between the components of mixtures and correlations of excess thermodynamic properties are worth investigating.

Research Objective
In this report, correlations between binary interactions of viscosity and vapour liquid equilibrium which may be used to predict viscosity parameters for liquid mixtures using NRTL parameters to improve non-ideal viscosity systems were studied. The viscosity data from NIST have been used to calculate the viscosity deviations, and

calculations of infinity dilution activity coefficients were done using available NRTL parameters in Aspen Plus software..

Viscosity Models

Viscosity models describe the change in the viscosity of the fluid as the pressure, temperature and composition change. There are a number of models available in Aspen to predict the viscosity of pure components and mixtures such as Andrade Liquid Mixture Viscosity, API liquid viscosity, API 1997 liquid viscosity, Chung-Lee-Starling, Letsou-Stiel, TRAPP viscosity, Aspen Liquid Mixture Viscosity, ASTM Liquid Mixture Viscosity, Twu liquid Viscosity and Viscosity quadratic mixing rule. However, there is no widely accepted simple theoretical model for the viscosity of liquids. Instead, empirical viscosity models are developed to describe the behaviour of the viscosity of the liquids with temperature.

It is generally known that for most liquids, the logarithm of the viscosity varies almost linearly with the inverse of temperature (Joback and Reid 1987) from the freezing point to the normal boiling point. Above the normal boiling point, this observation is not valid as the viscosity of the liquid tends to merge to the viscosity of the gas at the critical point (Viswanath *et al.* 2007).

Andrade Model

The Andrade equation can be considered as the most well-known empirical correlation for the viscosity of the liquids. The Andrade correlation is the commonly used correlation for regression of the constants to experimental liquid viscosity data. Alternatives to the Andrade equation are also available which simply add extra parameters to the same basic functional form to more accurately regress the available viscosity data over a broader range of temperature. The liquid viscosity is calculated by the modified Andrade equation (Reid, Prausnitz and Poling 1987):

$$ln\eta^l = \sum_{i=1}^{n} f_i ln\ \eta_i^{*,l} + \sum_{i=1}^{n}\sum_{j=1}^{n}\left(k_{ij}f_if_j + m_{ij}f_i^2f_j^2\right)$$

Where:

$$k_{ij} = a_{ij} + \frac{b_{ij}}{T}$$

$$m_{ij} = c_{ij} + \frac{d_{ij}}{T}$$

n = **number of components in a mixture**

f_i = **depends on the option code for the model MUL2ANDR** (mole fraction in all considered cases)

API liquid viscosity

The liquid mixture viscosity is calculated using a combination of the API and General equations such as Andrade Liquid Viscosity, DIPPR Liquid Viscosity, PPDS, NIST PPDS9 Equation and Polynomial. This model (MUL2API) is used for petroleum and petrochemical applications (Reid, Prausnitz and Poling 1987)

$$\eta^l = fcn\left(T, \, x, \, T_{bt} \, API_t \, V_{mn}^l \right)$$

Where:

V_m^l **is obtained from the API liquid volume model**

Aspen Liquid Mixture Viscosity

Aspen Liquid Mixture Viscosity Model (MUASPEN) is a correlative model and it is essentially a new mixing rule for calculating the mixture viscosity from the pure component viscosities. It requires the pure component liquid viscosities being calculated by another model before the mixture liquid viscosity can be calculated (Reid, Prausnitz and Poling 1987).

$$ln\eta^l = \sum_i X_i \, ln\eta_i^{*,l} + \sum_{j>i} k_{ij} X_i X_j ln\eta_{ij} + \sum_i X_i \left[\sum_{j \neq i} X_j \left(l_{ij} ln\eta_{ij}\right)^{1/3} \right]^3$$

$$ln\eta_{ij} = \frac{\left| in\eta_i^{*,l} - ln\eta_j^{*,l} \right|}{2}$$

Where:

X_i = **Mole fraction or weight fraction of component** i

k_{ij} = **Symmetric binary parameter** $(k_{ij} = k_{ji})$

l_{ij} = **Antisymmetric binary parameter** $(l_{ij} = -l_{ji})$

The pure component liquid viscosity $\eta_i^{*,l}$ is calculated by the General Pure Component Liquid model. The binary parameters k_{ij} and l_{ij} allow accurate representation of complex liquid mixture viscosity temperature dependence. Both binary parameters default to zero. These parameters are specified by the following equation:

$$k_{ij} = a_{ij} + b_{ij}/T_r + c_{ij}inT_r + d_{ij}T_r + e_{ij}T_r^2$$

$$l_{ij} = \acute{a}_{ij} + \acute{b}_{ij}/T_r + \acute{c}_{ij}\,inT_r + \acute{d}_{ij}T_r + \acute{e}_{ij}T_r^2$$

With

$$T_r = \frac{T}{T_{ref}},$$

Where T_{ref} is the reference temperature and the default value is 298.15 K

ASTM Liquid Mixture Viscosity

It is generally difficult to predict the viscosity of a mixture of viscous components. For hydrocarbons, the following weighting method (ASTM †, model MUL2ASTM) is known to give satisfactory results (Reid, Prausnitz and Poling 1987):

$$log\big(log(1000\mu_m + f)\big) = \sum_i w_i log\big(log(1000\mu_i + f)\big)$$

Where

$w_i = $ **Weight fraction of component i**

$\mu_m = $ **Absolute viscosity of the mixture $(N - sec/m^2)$**

$\mu_i = $ **Absolute viscosity of component i $(N - sec/m^2)$**

$log = $ **Common logarithm (base 10)**

$f = $ **An adjustable paramter, typically in the range of 0.5 to 1.0**

Viscosity quadratic mixing rule

With i and j being components, and n the number of component in the mixture, the viscosity quadratic mixing rule is

$$ln\eta^l = \sum_{i=1}^{n} x_i in\eta_i^{*,l} + \sum_{i=1}^{n} x_i \sum_{j=i}^{n} x_j K_{ij}\big(in\eta_i^{*,l} + ln\eta_j^{*,l}\big)$$

Other than mentioned model equations, there are a number of models available in the literature. Al Jimez (2004) estimated binary interaction parameters by fitting viscosity data with equations of Grunberg and Nissan (1949), Hind, McLaughlin and

Ubbelohde (1960), Frenkel (1946) and McAllister (1960). It was reported that the Grunberg and Nissan, Frenkel, and McAllister were suitable for representing the viscosities of phenetole + 1-alkanols binary mixtures.

Hind et al (1960) was found to be the worse correlation equations amongst all, while McAllister produced the best correlation (Al-Jimaz, Al-Kandary and Abdul-Latif 2004). McAllister equation performed worse fit with high deviation during correlation of cyclopentane + propanol binary mixtures while Heric (1966) equation produced the best fit with lower deviation as reported by Kumar *et al.* (2011).

METHODS

Data survey and selection

It was necessary to obtain extensive accurate and reliable experimental viscosity data of binary mixtures in order to conduct this research. NIST (*National Institute of Standards and Technology*) was selected as a source of binary viscosity data, which is available in Aspen Plus. The total number of 40 liquid mixtures has been selected and compiled representing a wide range of chemical families as listed in Table 1.

Table 1: List of Liquid binary mixtures selected

Component A	Component B	Number of Viscosity Data Set	Temperature Range (K)
1,2-DICHLOROETHANE	1-PROPANOL	2	288 - 313
N-BUTANOL	ACETONITRILE	3	298 - 0323
1,2-DICHLOROETHANE	N-BUTANOL	1	303 - 303
N-HEPTANE	1-PROPANOL	2	278- - 308
STYRENE	BENZENE	1	298 - 313
1,2-DICHLOROETHANE	1-PENTANOL	1	303 - 303
BENZENE	BUTYL-ETHER	1	298 - 308
METHANOL	CARBON-TETRACHLORIDE	10	297 - 323
TOLUENE	N-OCTANE	2	303 - 423
P-XYLENE	ACETONITRILE	1	308 - 308
N-OCTANE	N-BUTANOL	3	293 - 323
BENZENE	1,2-DICHLOROETHANE	4	273 - 333
CARBON-TETRACHLORIDE	N-HEXANE	2	298 - 298
BENZENE	CHLOROFORM	10	273 - 343
CHLOROBENZENE	CARBON-TETRACHLORIDE	2	298 - 298
ACETONITRILE	CARBON-TETRACHLORIDE	1	288 - 343
ETHYL-ACETATE	CARBON-TETRACHLORIDE	4	292 - 317
N-HEXANE	BENZENE	19	283 - 465
METHANOL	BENZENE	7	283 - 352

TRICHLOROETHYLENE	METHANOL	3	288 - 323
N-HEPTANE	BENZENE	7	291 - 524
TOLUENE	N-HEPTANE	2	298 - 313
TOLUENE	ETHANOL	5	223 - 253
METHANOL	ACETONE	5	273 - 323
METHANOL	TOLUENE	10	293 - 383
CYCLOHEXANE	METHANOL	1	321 - 325
CHLOROFORM	ACETONE	10	273 - 336
N-HEXANE	TOLUENE	10	298 - 333
1,4-DIOXANE	METHANOL	7	283 - 423
ETHYL-ACETATE	CYCLOHEXANE	4	292 - 308
METHANOL	ISOPROPYL-ALCOHOL	1	298 - 298
P-XYLENE	M-XYLENE	2	285 - 337
1,4-DIOXANE	CHLOROFORM	4	293 - 303
ETHANOL	CYCLOHEXANE	9	288 - 508
METHYL-TERT-BUTYL-ETHER	METHANOL	2	298 - 298
DIMETHYL-SULFOXIDE	METHANOL	8	298 - 318
BENZENE	CARBON-TETRACHLORIDE	19	273 - 352
1,2-DICHLOROETHANE	ETHANOL	2	303 - 333
1-PROPANOL	ISOPROPYL-ALCOHOL	1	293 - 333
BENZENE	CYCLOHEXANE	31	283 - 393
METHYL-ACETATE	ETHANOL	3	273 - 328

NRTL Parameters

The NRTL model can describe VLE and LLE of strongly non-ideal solutions. The model requires binary parameters. Many binary parameters for VLE and LLE, from literature and from a regression of experimental data, are included in the Aspen Physical Property System databanks. The property methods with a vapour phase model that can be used up to moderate pressures have the Poynting correction included in the liquid fugacity coefficient calculation. NRTL model is reliable in a sense that it can

handle any combination of polar and non-polar compounds, up to very strong non-ideality.

The NRTL model calculates liquid activity coefficients and can be used for VLE and LLE applications. The model can also be used in the advanced equation-of-state mixing rules. The equation for NRTL model can be represented as follows:

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ij}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right)_{\text{for } T_{lower} \leq T \leq T_{upper}}$$

Where:

$$G_{ij} = exp\left(-\alpha_{ij}\tau_{ij}\right)$$

$$\tau_{ij} = a_{ij} + {b_{ij}}/{T} + e_{ij} in\, T + f_{ij} T$$

$$\alpha_{ij} = c_{ij} + d_{ij}(T - 273.15K)$$

$$\tau_{ii} = 0$$

$$G_{ii} = 1$$

$$a_{ij}, b_{ij}, and f_{ij} \text{ are unsymmetrica. That is} - a_{ij} \text{ may not be equal to } a_{ji}, \text{etc}$$

Parameters usually available in Aspen Plus are: $a_{ij}, b_{ij}, and c_{ij}$

Evaluation, Regression and correlations of viscosity data
After selecting viscosities of binary liquid mixtures, these data were evaluated with zero parameters of KIJ and MIJ values to determine viscosity deviations. The model in Aspen was used to reduce these deviations by applying its parameters of KIJ and MIJ. Eventually, parameters were correlated for prediction of viscosity parameters by a proposed mathematic expression.

Statistical Tools
Calculated values of parameters were analysed using software R statistic and Excel.

RESULTS AND DISCUSSION

Five NRTL parameters AIJ, AJI, BIJ, BJI and CIJ were successfully obtained from Aspen after evaluation and regression experimental data of binary liquid viscosities. These parameters were recorded on Excel, as shown in Table 5 in the annexure. Binary parameters Tau and G were calculated based on the following equation:

$$\tau_{ij} = a_{ij} + {b_{ij}}/{T} + e_{ij} in\ T + f_{ij}T, \qquad G_{ij} = exp(-\alpha_{ij}\tau_{ij}),$$

This follows the calculations of infinite dilution activity coefficient of both components i and j. These values of infinite dilution activity coefficient are presented in Table 2. It can be seen that majority of liquid binary mixtures shows positive deviation as activity coefficients are greater than one.

Table 2: Infinite dilution activity coefficients for component i and j

Component i	Component j	γ_i	γ_j
1,2-DICHLOROETHANE	1-PROPANOL	3.270	6.602
N-BUTANOL	ACETONITRILE	2.432	6.314
1,2-DICHLOROETHANE	N-BUTANOL	2.753	6.479
N-HEPTANE	1-PROPANOL	7.244	13.444
STYRENE	BENZENE	1.022	1.205
1,2-DICHLOROETHANE	1-PENTANOL	2.280	6.379
BENZENE	BUTYL-ETHER	1.029	1.076
METHANOL	CARBON-TETRACHLORIDE	15.631	5.668
TOLUENE	N-OCTANE	1.216	1.337
P-XYLENE	ACETONITRILE	10.227	1.243
N-OCTANE	N-BUTANOL	5.998	6.820
BENZENE	1,2-DICHLOROETHANE	1.030	1.031
CARBON-TETRACHLORIDE	N-HEXANE	1.232	1.199
BENZENE	CHLOROFORM	0.723	0.786

CHLOROBENZENE	CARBON-TETRACHLORIDE	1.313	1.109
ACETONITRILE	CARBON-TETRACHLORIDE	8.604	5.079
ETHYL-ACETATE	CARBON-TETRACHLORIDE	1.374	1.332
N-HEXANE	BENZENE	1.500	1.379
METHANOL	BENZENE	7.031	6.405
TRICHLOROETHYLENE	METHANOL	9.449	22.820
N-HEPTANE	BENZENE	1.559	1.265
TOLUENE	N-HEPTANE	1.410	1.751
TOLUENE	ETHANOL	6.321	20.016
METHANOL	ACETONE	1.980	1.997
METHANOL	TOLUENE	8.264	7.294
CYCLOHEXANE	METHANOL	18.880	25.209
CHLOROFORM	ACETONE	0.452	0.328
N-HEXANE	TOLUENE	1.877	1.481
1,4-DIOXANE	METHANOL	2.701	2.239
ETHYL-ACETATE	CYCLOHEXANE	3.911	3.347
METHANOL	ISOPROPYL-ALCOHOL	1.314	1.341
P-XYLENE	M-XYLENE	1.002	1.002
1,4-DIOXANE	CHLOROFORM	0.197	0.347
ETHANOL	CYCLOHEXANE	16.485	6.152
METHYL-TERT-BUTYL-ETHER	METHANOL	3.556	3.590
DIMETHYL-SULFOXIDE	METHANOL	0.250	0.376
BENZENE	CARBON-TETRACHLORIDE	1.112	1.124
1,2-DICHLOROETHANE	ETHANOL	4.505	7.338
1-PROPANOL	ISOPROPYL-ALCOHOL	0.870	1.097
BENZENE	CYCLOHEXANE	1.393	1.503
METHYL-ACETATE	ETHANOL	2.865	2.689

KIJ and MIJ viscosity parameters were obtained from experimental data using Aspen Plus. The relationship between KIJ parameters and infinite dilution activity coefficients was evaluated through R statistic in a form of 3D graphs to visualise if there are any apparent correlations between these variables.
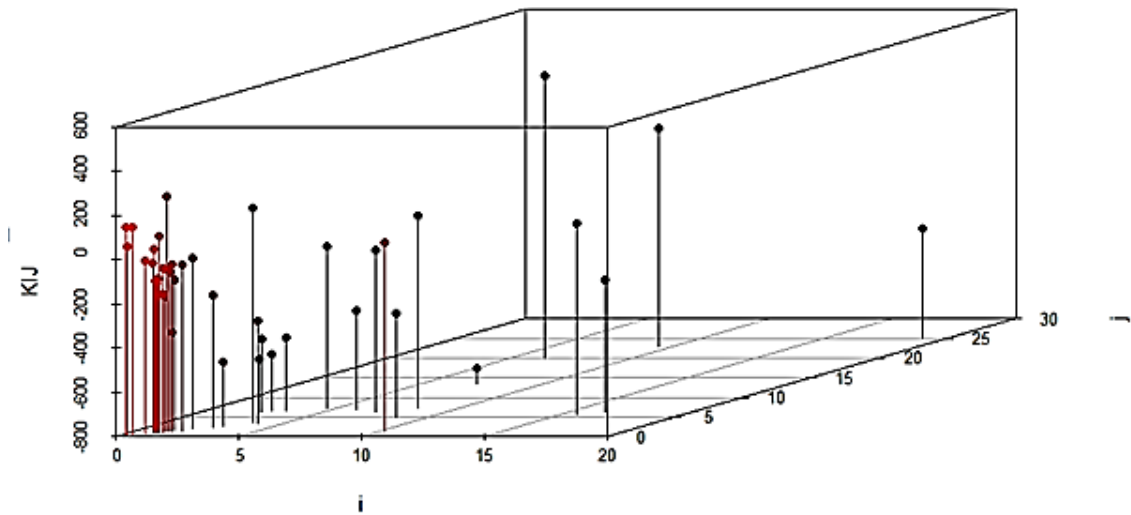
Figure 2: 3D Visualisation of KIJ parameter dependence on infinite dilution activity coefficients of component i and j.

As demonstrated by a 3D graph in figure 2, it can be seen that most of the activity coefficient of component i lies below the value of 5 as well as that of component j. with regard to KIJ parameter, most points lie between -200 to 200. Other points are scatted and distributed away from one another, which makes it difficult to determine any existing relationship. Further, rotated 3D graph was plotted to visualise all the angles as depicted in figure 3.

a   b
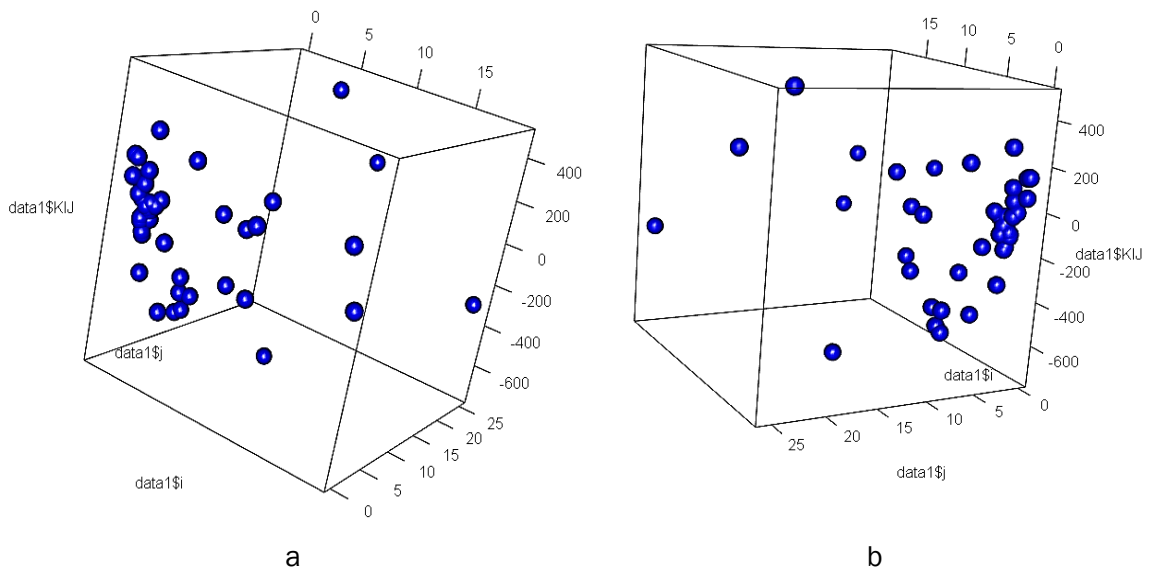
Figure 3: a) Left view rotated 3D graph of activity coefficients and KIJ parameter b) Right view rotated 3D graph of activity coefficient and KIJ parameter

With this visualisation, it is clear that points are packed on one side of the graph, and the distribution does not clearly show any correlation among the variables. However the model was developed to predict KIJ and MIJ parameters for viscosity calculations. These are presented in Table 3.

KIJ and MIJ parameters for obtaining predicted values were obtained by fitting the experimental data to the developed equation using excel solver, after an extensive trial with different functions:

$$KIJ = -28.54 + 150.40i - 177.28j - 6.64i^2 + 6.11j^2 - 0.98\left(\frac{i}{j}\right)^3 + 0.08\left(\frac{j}{i}\right)^8$$

$$MIJ = 360.66 + 256.17i - 91.57j - 6.47i^2 + 13.18j^2 - 273.33\left(\frac{i}{j}\right) - 181.12\left(\frac{j}{i}\right)$$

Table 3: Regressed and Predicted KIJ and MIJ parameters

Component A	Component B	ANDKIJ/2 Regressed (K)	ANDKIJ/2 Predicted (K)	ANDMIJ/2 Regressed (K)	ANDMIJ/2 Predicted (K)
1,2-DICHLOROETHANE	1-PROPANOL	-468	-490	318	110
N-BUTANOL	ACETONITRILE	-468	-411	751	-125
1,2-DICHLOROETHANE	N-BUTANOL	-543	-481	485	-33
N-HEPTANE	1-PROPANOL	-730	-555	885	339
STYRENE	BENZENE	-110	-87	170	76
1,2-DICHLOROETHANE	1-PENTANOL	-565	-298	554	-193
BENZENE	BUTYL-ETHER	-129	-65	293	82
METHANOL	CARBON-TETRACHLORIDE	60	-129	551	1520
TOLUENE	N-OCTANE	-188	-82	481	110
P-XYLENE	ACETONITRILE	52	57	108	-64

N-OCTANE	N-BUTANOL	-353	-291	-203	683
BENZENE	1,2-DICHLOROETHANE	-117	-58	-10	82
CARBON-TETRACHLORIDE	N-HEXANE	-175	-58	74	115
BENZENE	CHLOROFORM	-17	-59	-6	33
CHLOROBENZENE	CARBON-TETRACHLORIDE	-60	-33	66	122
ACETONITRILE	CARBON-TETRACHLORIDE	-334	26	6304	1118
ETHYL-ACETATE	CARBON-TETRACHLORIDE	-72	-61	141	138
N-HEXANE	BENZENE	-353	-52	744	158
METHANOL	BENZENE	-73	-185	203	875
TRICHLOROETHYLENE	METHANOL	184	30	-230	-136
N-HEPTANE	BENZENE	-44	-27	-141	161
TOLUENE	N-HEPTANE	-121	-122	65	127
TOLUENE	ETHANOL	473	377	-2158	-508
METHANOL	ACETONE	-27	-87	-96	232
METHANOL	TOLUENE	70	-209	-455	994
CYCLOHEXANE	METHANOL	-306	-142	1660	467
CHLOROFORM	ACETONE	138	-22	168	-58
N-HEXANE	TOLUENE	-50	-21	30	213
1,4-DIOXANE	METHANOL	-199	-39	355	350
ETHYL-ACETATE	CYCLOHEXANE	-334	-68	245	527
METHANOL	ISOPROPYL-ALCOHOL	262	-70	-486	128
P-XYLENE	M-XYLENE	30	-57	-94	78

1,4-DIOXANE	CHLOROFORM	142	-53	128	-91
ETHANOL	CYCLOHEXANE	-202	-232	189	1542
METHYL-TERT-BUTYL-ETHER	METHANOL	168	-136	-802	455
DIMETHYL-SULFOXIDE	METHANOL	52	-55	-117	-59
BENZENE	CARBON-TETRACHLORIDE	88	-62	-208	96
1,2-DICHLOROETHANE	ETHANOL	-69	-454	-74	345
1-PROPANOL	ISOPROPYL-ALCOHOL	-36	-90	143	48
BENZENE	CYCLOHEXANE	-84	-85	-276	138
METHYL-ACETATE	ETHANOL	-512	-86	809	369

Predicted parameters KIJ and MIJ was used to calculate viscosity deviations obtained values are presented in Table 4 together with evaluation and regression calculated by Aspen.

Table 4: Viscosity deviations from Experimental data and Predicted data

Component i	Component j	Evaluation Total Average%	Regression Total Average %	Evaluation calculated with predicted parameters
1,2-DICHLOROETHANE	1-PROPANOL	26.89	2.45	8.60
N-BUTANOL	ACETONITRILE	22.76	5.26	7.29
1,2-DICHLOROETHANE	N-BUTANOL	25.21	2.28	10.10
N-HEPTANE	1-PROPANOL	35.05	9.66	14.69
STYRENE	BENZENE	4.87	1.77	2.44
1,2-DICHLOROETHANE	1-PENTANOL	25.78	2.78	14.95
BENZENE	BUTYL-ETHER	4.03	1.075	2.45
METHANOL	CARBON-TETRACHLORIDE	9.65	4.67	5.97
TOLUENE	N-OCTANE	4.368	1.39	3.012
P-XYLENE	ACETONITRILE	3.72	0.38	2.57
N-OCTANE	N-BUTANOL	24.35	1.18	18.43
BENZENE	1,2-DICHLORO ETHANE	5.61	1.24	4.42
CARBON-TETRACHLORIDE	N-HEXANE	8.46	1.09	7.37
BENZENE	CHLOROFORM	3.01	2.59	2.72
CHLOROBENZENE	CARBON-TETRACHLORIDE	2.40	0.68	2.21
ACETONITRILE	CARBON-TETRACHLORIDE	2.83	2.31	2.64

ETHYL-ACETATE	CARBON-TETRACHLORIDE	3.59	3.31	3.36
N-HEXANE	BENZENE	10.11	3.84	9.54
METHANOL	BENZENE	3.69	3.69	3.62
TRICHLOROETHYLENE	METHANOL	7.28	3.47	7.24
N-HEPTANE	BENZENE	19.57	19.65	19.57
TOLUENE	N-HEPTANE	4.086	4.518	4.113
TOLUENE	ETHANOL	18.12	17.99	18.28
METHANOL	ACETONE	7.94	6.87	8.05
METHANOL	TOLUENE	4.79	5.33	4.94
CYCLOHEXANE	METHANOL	4.02	1.88	4.16
CHLOROFORM	ACETONE	10.39	2.70	11.30
N-HEXANE	TOLUENE	3.321	3.002	3.663
1,4-DIOXANE	METHANOL	6.80	1.60	7.57
ETHYL-ACETATE	CYCLOHEXANE	12.26	4.82	13.68
METHANOL	ISOPROPYL-ALCOHOL	9.72	2.59	11.05
P-XYLENE	M-XYLENE	6.244	6.279	7.104
1,4-DIOXANE	CHLOROFORM	9.86	2.55	11.90
ETHANOL	CYCLOHEXANE	8.34	0.984	10.52
METHYL-TERT-BUTYL-ETHER	METHANOL	1.858	1.149	2.387
DIMETHYL-SULFOXIDE	METHANOL	4.61	3.95	6.24
BENZENE	CARBON-TETRACHLORIDE	3.15	2.12	4.28
1,2-DICHLOROETHANE	ETHANOL	7.65	7.99	10.67
1-PROPANOL	ISOPROPYL-ALCOHOL	1.95	1.99	3.11
BENZENE	CYCLOHEXANE	2.76	1.85	12.37
METHYL-ACETATE	ETHANOL	6	1.70	21.31

The average deviation of Evaluation by aspen, using default values KIJ = MIJ = 0, was determined to be 9.44. This value should be minimised and by using regression from Aspen plus it was reduced to 3.61. The model expression developed in this work slightly improved viscosity deviation from 9.44 to 8.05, far from the aspen regressed values (3.61).

CONCLUSION

Viscosity parameters were calculated by a developed model expression. The activity coefficients correlated with viscosity parameters did not show a clear relationship. Based on statistical analysis and calculations, there was not a clear correlation between infinite dilution activity coefficients and viscosity binary parameters. The attempt of employing a generalised developed model equation was unsuccessful in predicting viscosity parameters that improves the viscosity deviations from experimental data.

REFERENCES

Al-Jimaz, A. S., Al-Kandary, J. A. and Abdul-Latif, A.-H. M. 2004. Densities and viscosities for binary mixtures of phenetole with 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol at different temperatures. Fluid phase equilibria, 218 (2): 247-260.

Domínguez, M., Pardo, J. I., Gascón, I., Royo, F. M. and Urieta, J. S. 2000. Viscosities of the ternary mixture (2-butanol+n-hexane+ 1-butylamine) at 298.15 and 313.15 K. Fluid Phase Equilibria, 169 (2): 277-292.

Frenkel, J. 1946. Kinetic Theory of Liquids-Oxford Univ. Press-1946,

Grunberg, L. and Nissan, A. H. 1949. Mixture law for viscosity. Nature, 164 (4175): 799-800.

Hassein-bey-Larouci, A., Igoujilen, O., Aitkaci, A., Segovia, J. and Villamanan, M. 2014. Dynamic and kinematic viscosities, excess volumes and excess Gibbs energies of activation for viscous flow in the ternary mixture {1-propanol+ N, N-dimethylformamide+ chloroform} at temperatures between 293.15 K and 323.15 K. Thermochimica Acta, 589: 90-99.

Heric, E. 1966. On the Viscosity of Ternary Mixtures. Journal of Chemical and Engineering Data, 11 (1): 66-68.

Hind, R., McLaughlin, E. and Ubbelohde, A. 1960. Structure and viscosity of liquids. Camphor+ pyrene mixtures. Transactions of the Faraday Society, 56: 328-330.

Joback, K. G. and Reid, R. C. 1987. Estimation of pure-component properties from group-contributions. Chemical Engineering Communications, 57 (1-6): 233-243.

Kumar, H., Singla, M., Khosla, A. and Gaba, R. 2011. Viscometric studies of binary liquid mixtures of cyclopentane (1)+ 2-propanol (2),+ 1-butanol (2), and+ 2-butanol (2) at T=(298.15 and 308.15) K. Journal of Molecular Liquids, 158 (3): 182-186.

Lin, C.-F., Hsieh, H.-M. and Lee, L.-S. 2007. Estimations of the viscosities of binary mixtures with different equations of state and mixing rules. Journal of the Chinese Institute of Chemical Engineers, 38 (1): 1-19.

McAllister, R. 1960. The viscosity of liquid mixtures. AIChE Journal, 6 (3): 427-431.

Reid, R. C., Prausnitz, J. M. and Poling, B. E. 1987. The properties of gases and liquids. 4th. The Properties of Gases and Liquids, 4th,

Sinnott, R. 2005. Coulson's and Richardson's Chemical Engineering, Volume 6: Chemical Engineering Design: Elsevier Inc., UK.

Viswanath, D. S., Ghosh, T., Prasad, D. H., Dutt, N. V. and Rani, K. Y. 2007. Viscosity of liquids: theory, estimation, experiment, and data. Springer Science & Business Media.

ANNEXURE

Table 5: NRTL Parameters from Experimental Viscosity data

Component A	Component B	AIJ NRTL	AJI NRTL	BIJ NRTL (K)	BJI NRTL (K)	CIJ NRTL
1,2-DICHLOROETHANE	1-PROPANOL	0	0	523.671	45.5259	0.3
N-BUTANOL	ACETONITRILE	-6.4361	4.1663	2645.94	-1364.04	0.3
1,2-DICHLOROETHANE	N-BUTANOL	-2.2981	0.4576	1284.74	-160.426	0.3
N-HEPTANE	1-PROPANOL	0.3138	-0.4713	467.577	402.777	0.3
STYRENE	BENZENE	0	0	394.118	-260.938	0.3
1,2-DICHLOROETHANE	1-PENTANOL	-1.9855	-0.7362	1147.74	238.765	0.47
BENZENE	BUTYL-ETHER	0	0	226.264	-172.17	0.3
METHANOL	CARBON-TETRACHLORIDE	0.4194	0.7318	52.3334	472.565	0.3
TOLUENE	N-OCTANE	0	0	265.223	-142.116	0.3
P-XYLENE	ACETONITRILE	6.3174	-11.6647	-2254.44	4725.8	0.3
N-OCTANE	N-BUTANOL	0	0	370.919	293.306	0.3
BENZENE	1,2-DICHLOROETHANE	0	0	29.6038	-19.9036	0.3035
CARBON-TETRACHLORIDE	N-HEXANE	-1.1602	1.5763	310.836	-371.369	0.3
BENZENE	CHLOROFORM	0.6209	-1.0488	-480.842	607.006	0.3

CHLOROBENZENE	CARBON-TETRACHLORIDE	0.6777	-1.0116	-414.486	645.778	0.3
ACETONITRILE	CARBON-TETRACHLORIDE	-1.4646	1.5342	658.938	31.7484	0.3
ETHYL-ACETATE	CARBON-TETRACHLORIDE	0	0	-3.9616	100.646	0.3
N-HEXANE	BENZENE	0.4066	-1.554	-213.735	797.572	0.3
METHANOL	BENZENE	-1.7086	11.5801	892.24	-3282.55	0.4
TRICHLOROETHYLENE	METHANOL	0	0	730.502	448.696	0.47
N-HEPTANE	BENZENE	0	0	-226.282	448.199	0.3
TOLUENE	N-HEPTANE	2.1221	-1.6889	-335.644	390.858	0.3
TOLUENE	ETHANOL	-1.7221	1.1459	992.737	-113.466	0.3
METHANOL	ACETONE	0	0	114.135	101.886	0.3
METHANOL	TOLUENE	0	0	371.084	446.875	0.3
CYCLOHEXANE	METHANOL	-4.6753	1.3869	2277.79	224.76	0.43
CHLOROFORM	ACETONE	0.5382	0.9646	-106.422	-590.026	0.3
N-HEXANE	TOLUENE	1.5182	-2.9483	-595.67	1259.25	0.3
1,4-DIOXANE	METHANOL	-0.1302	0.6659	96.6612	67.1858	0.3
ETHYL-ACETATE	CYCLOHEXANE	-1.657	-0.3574	648.458	386.237	0.3
METHANOL	ISOPROPYL-ALCOHOL	0	0	79.5395	7.9115	0.3
P-XYLENE	M-XYLENE	0	0	-3.869	4.6301	0.3
1,4-DIOXANE	CHLOROFORM	0	0	-676.376	852.105	0.3
ETHANOL	CYCLOHEXANE	-0.156	1.6271	459.877	214.076	0.45
METHYL-TERT-BUTYL-ETHER	METHANOL	0	0	213.621	205.795	0.3
DIMETHYL-SULFOXIDE	METHANOL	0	0	-331.156	30.5966	0.3

BENZENE	CARBON-TETRACHLORIDE	0	0	66.4584	-29.2278	0.3
1,2-DICHLOROETHANE	ETHANOL	0	0	488.674	170.45	0.3
1-PROPANOL	ISOPROPYL-ALCOHOL	0	0	556.304	-369.901	0.3
BENZENE	CYCLOHEXANE	0	0	182.755	-43.3406	0.3
METHYL-ACETATE	ETHANOL	0	0	134.162	198.971	0.3

Table 6: Binary parameters of liquid binary viscosity

Component A	Component B	τ_{ij}	τ_{ji}	G_{ij}	G_{ji}
1,2-DICHLOROETHANE	1-PROPANOL	1.743	0.152	0.593	0.956
N-BUTANOL	ACETONITRILE	2.085	-0.227	0.535	1.070
1,2-DICHLOROETHANE	N-BUTANOL	1.942	-0.072	0.558	1.022
N-HEPTANE	1-PROPANOL	1.910	0.903	0.564	0.763
STYRENE	BENZENE	1.290	-0.854	0.679	1.292
1,2-DICHLOROETHANE	1-PENTANOL	1.802	0.052	0.429	0.976
BENZENE	BUTYL-ETHER	0.747	-0.568	0.799	1.186
METHANOL	CARBON-TETRACHLORIDE	0.588	2.256	0.838	0.508
TOLUENE	N-OCTANE	0.731	-0.392	0.803	1.125
P-XYLENE	ACETONITRILE	-1.002	3.679	1.351	0.332
N-OCTANE	N-BUTANOL	1.204	0.952	0.697	0.751
BENZENE	1,2-DICHLOROETHANE	0.098	-0.066	0.971	1.020
CARBON-TETRACHLORIDE	N-HEXANE	-0.117	0.330	1.036	0.906

BENZENE	CHLOROFORM	-0.940	0.922	1.326	0.758
CHLOROBENZENE	CARBON-TETRACHLORIDE	-0.713	1.155	1.239	0.707
ACETONITRILE	CARBON-TETRACHLORIDE	0.624	1.635	0.829	0.612
ETHYL-ACETATE	CARBON-TETRACHLORIDE	-0.013	0.331	1.004	0.906
N-HEXANE	BENZENE	-0.165	0.579	1.051	0.841
METHANOL	BENZENE	1.102	1.241	0.644	0.609
TRICHLOROETHYLENE	METHANOL	2.391	1.469	0.325	0.501
N-HEPTANE	BENZENE	-0.555	1.100	1.181	0.719
TOLUENE	N-HEPTANE	1.023	-0.409	0.736	1.131
TOLUENE	ETHANOL	2.449	0.669	0.480	0.818
METHANOL	ACETONE	0.383	0.342	0.891	0.903
METHANOL	TOLUENE	1.098	1.322	0.719	0.673
CYCLOHEXANE	METHANOL	2.377	2.083	0.360	0.408
CHLOROFORM	ACETONE	0.189	-0.973	0.945	1.339
N-HEXANE	TOLUENE	-0.370	1.043	1.117	0.731
1,4-DIOXANE	METHANOL	0.144	0.856	0.958	0.773
ETHYL-ACETATE	CYCLOHEXANE	0.505	0.930	0.860	0.757
METHANOL	ISOPROPYL-ALCOHOL	0.267	0.027	0.923	0.992
P-XYLENE	M-XYLENE	-0.012	0.015	1.004	0.996
1,4-DIOXANE	CHLOROFORM	-2.270	2.859	1.976	0.424

ETHANOL	CYCLOHEXANE	0.999	2.165	0.638	0.377
METHYL-TERT-BUTYL-ETHER	METHANOL	0.717	0.691	0.806	0.813
DIMETHYL-SULFOXIDE	METHANOL	-1.075	0.099	1.381	0.971
BENZENE	CARBON-TETRACHLORIDE	0.213	-0.094	0.938	1.028
1,2-DICHLOROETHANE	ETHANOL	1.537	0.536	0.631	0.851
1-PROPANOL	ISOPROPYL-ALCOHOL	1.777	-1.182	0.587	1.426
BENZENE	CYCLOHEXANE	0.541	-0.128	0.850	1.039
METHYL-ACETATE	ETHANOL	0.446	0.662	0.875	0.820