

Viscosity and surface tension of aqueous mixtures

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Abstract

The viscosity and surface tension of aqueous mixtures of interest to the inkjet printer designer are estimated using the corresponding states principle and the universal quasi-chemical functional-group activity coefficient method. The former method performs best for estimating viscosity, whilst the latter method works best for surface tension, for the mixtures considered.

Introduction

Viscosity and surface tension are key physical parameters in a variety of flow phenomena, including bubble and droplet break-up and capillary wetting. In many instances, the liquid will be a mixture of one or more components. It is therefore important for the design of systems using these liquids to have methods for estimating the viscosity and surface tension of the mixtures. Here, we present methods for estimating the viscosity and surface tension of some typical aqueous mixtures of interest to the inkjet printer designer [5]: glycerol, ethylene glycol, and 1-propanol.

Theory

Corresponding States Principle (CSP)

The corresponding states principle [27] is that any two fluids at the same reduced pressure, P_r and temperature, T_r , will behave similarly. For example, they will have approximately the same compressibility factor, $Z = P V / (R T)$, where V is molar volume, R is the universal gas constant and the subscript ' r ' indicates normalization by the critical values. This principle is strictly valid only for molecules obeying the same two-parameter equation of state [11]. Pitzer et al [19] showed that the expression for the compressibility can be expanded as a Taylor series, with:

$$Z = Z^{(0)} + \omega Z^{(1)} \quad (1)$$

where $Z^{(0)}$ is the compressibility factor of a spherical reference fluid, $Z^{(1)}$ is a factor characterizing the deviation from the spherical molecule assumption [20] and ω is the acentric factor which characterizes the deviation from sphericity of the molecules and is a function of the reduced pressure at a reduced temperature value of 0.7. Lee and Kesler [14] modified Pitzer's expression to include a heavy, non-spherical reference fluid. Teja [25] generalized this expression, eliminating the spherical reference fluid and instead using two non-spherical reference fluids, denoted ($r1$) and ($r2$), respectively, giving:

$$Z = Z^{(r1)} + \frac{\omega - \omega^{(r1)}}{\omega^{(r2)} - \omega^{(r1)}} [Z^{(r2)} - Z^{(r1)}] \quad (2)$$

The compressibility factor can be replaced by any suitably non-dimensionalized property. The original application of this method was for prediction of pure component properties based on measured values of the same property for closely related molecules.

CSP: Viscosity

Letsou and Stiel [15] extended [19] to viscosity, μ , with:

$$\ln(\mu\xi) = \ln(\mu\xi)^{(0)} + \omega \ln(\mu\xi)^{(1)} \quad (3)$$

where

$$\xi = \frac{N_A}{R^{1/2}} \frac{V_c^{2/3}}{(T_c M)^{1/2}} \quad (4)$$

is the critical fluidity, N_A is Avogadro's number, M is molecular weight and the subscript ' c ' refers to critical parameters. Teja and Rice [26] applied the Generalized Corresponding States Principle (GCSP) [25] to modify the formula of Letsou and Stiel to the following:

$$\ln(\mu\xi) = \ln(\mu\xi)^{(r1)} + \frac{\omega - \omega^{(r1)}}{\omega^{(r2)} - \omega^{(r1)}} [\ln(\mu\xi)^{(r2)} - \ln(\mu\xi)^{(r1)}] \quad (5)$$

Teja and Rice extended the above expression to mixtures of liquids by replacing the values of T_c , V_c , M and ω with the so-called mixture 'pseudo-critical' values of a hypothetical equivalent substance, denoted by the subscript ' m ', where:

$$T_{c,m} V_{c,m} = \sum \sum_{ij} x_i x_j T_{c,ij} V_{c,ij} \quad (6)$$

$$V_{c,m} = \sum \sum_{ij} x_i x_j V_{c,ij} \quad (7)$$

$$\omega_m = \sum_i x_i \omega_i \quad M_m = \sum_i x_i M_i \quad (8)$$

In the above expressions, values of the cross-terms $T_{c,ij}$, $V_{c,ij}$, $i \neq j$ are obtained from the following expressions suggested by Teja and Rice:

$$T_{c,ij} V_{c,ij} = \psi_{ij} (T_{c,ii} T_{c,jj} V_{c,ii} V_{c,jj})^{\frac{1}{2}} \quad (9)$$

$$V_{c,ij} = \frac{1}{8} (V_{c,ii}^{1/3} + V_{c,jj}^{1/3})^3 \quad (10)$$

where repeated indices indicate pure (single component) values and ψ_{ij} is a binary interaction parameter which must be evaluated from experimental data.

CSP: Surface Tension

In a similar manner to mixture viscosity, Rice and Teja [22] presented a method to estimate mixture static surface tension, σ , using the GCSP [25]. In summary, the expression used to estimate mixture static surface tension for an n -component mixture is:

$$\sigma_m \phi_m = \sum_i^n x_i \sigma_i \phi_i \quad (11)$$

where

$$\phi = \frac{N_A V_c^{2/3}}{R T_c} \quad (12)$$

and the subscript ' i ' refers to the i^{th} molecule, and the critical properties are determined as per equations (6-8).

Universal Functional-Group Activity Coefficients (UNIFAC)

Thermodynamic properties of liquid mixtures are often estimated by assuming that it is valid to sum the contributions from each of the molecules' functional groups. Functional groups are assemblies of atoms, molecules and bonds that have similar properties whenever they occur in different compounds, for example OH, CH₃, H₂O. Thus properties of a wide range of chemical compounds can be obtained from a smaller number of parameters which

characterise the groups. The main limitation of the method is the fact that the contribution of a group in one molecule may not be the same as in another. One widely used group contribution method is UNIFAC [6].

In the UNIFAC method, the functional group sizes and interaction surface areas are obtained from pure-component molecular structure data. The activity coefficient, γ_i , is composed of two parts: a combinatorial part due to differences in the shape and size of the molecules in the mixture, and a residual part due to energy interactions. They are denoted by the superscripts 'C' and 'R', respectively:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (13)$$

For the combinatorial term:

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j \quad (14)$$

where x_i is the mole fraction, θ_i is the area fraction:

$$\theta_i = \frac{q_i x_i}{\sum_j r_j x_j} \quad (15)$$

Φ_i is the segment fraction (similar to the volume fraction):

$$\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad (16)$$

$z = 10$ is the coordination number, r_i is the molecular van der Waals volume, q_i is the molecular surface area, and

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad (17)$$

The values of r_i and q_i are obtained as the sum of the group values, R_k and Q_k :

$$r_i = \sum_k g_k^{(i)} R_k \quad \text{and} \quad q_i = \sum_k g_k^{(i)} Q_k \quad (18)$$

where $g_k^{(i)}$ is the number of groups of type k in molecule i , and the values of R_k and Q_k can be obtained from tables, for example [20].

For the residual term:

$$\ln \gamma_i^R = \sum_k g_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad (19)$$

where Γ_k is the group residual activity coefficient, $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i . Both of these coefficients can be calculated using:

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \Theta_m \Psi_{mk} \right) - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right] \quad (20)$$

where the area fraction for group m , Θ_m , is given by:

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad (21)$$

and X_m is the mole fraction of group m in the mixture. The group interaction parameter, Ψ_{mn} , is:

$$\Psi_{mn} = \exp \left(-\frac{a_{mn}}{T} \right) \quad (22)$$

where the group interaction temperature parameter, a_{mn} , is evaluated from experimental data; a table of common molecular groups is given in [20].

UNIFAC: Viscosity

The UNIFAC-VISCO method [7] is based on the original UNIFAC model [6] and the Eyring absolute reaction rate theory

[8]. The latter relates the kinematic viscosity, $\nu = \mu / \rho$, where ρ = density, of a pure fluid to the activation energy for viscous flow, Δ^*G :

$$\nu = \frac{h N_A}{M} \exp \left(\frac{\Delta^*G}{R T} \right) \quad (23)$$

where h = Planck's constant. For a mixture of liquids, the activation energy is split into ideal and non-ideal parts and the result is:

$$\ln(\nu M) = \sum_i x_i \ln(\nu_i M_i) + \frac{\Delta^*G_E}{R T} \quad (24)$$

where Δ^*G_E is the excess activation energy for viscous flow. The value of Δ^*G_E was obtained using the UNIFAC model, splitting into combinatorial and residual parts. For the former, the expression is:

$$\frac{\Delta^*G_E^C}{R T} = \sum_i x_i \ln \frac{\Phi_i}{x_i} + \frac{z}{2} \sum_i x_i q_i \ln \frac{\theta_i}{\Phi_i} \quad (25)$$

whilst for the latter:

$$\frac{\Delta^*G_E^R}{R T} = -\sum_i x_i \ln \Gamma_i \quad (26)$$

UNIFAC: Surface Tension

Suarez et al [24] developed a method for estimating the surface tension of mixtures based on UNIFAC with modifications proposed by Larsen et al [12]. The main assumption used in the analysis is that the surface layer can be treated as a distinct phase situated between the vapour and bulk liquid phases. Then, the surface tension of the mixture, σ_m , is given by:

$$\sigma_m A_i' = \sigma_i A_i + R T \ln \frac{x_{i,s} \gamma_{i,s}}{x_{i,b} \gamma_{i,b}} \quad (27)$$

where σ_i is the surface tension of mixture component i , A_i' is the partial molar area of component i in the mixture, A_i is the molar surface area of the pure component i and the subscripts 'i,s' and 'i,b' refer to the surface and bulk values for component i , respectively. Suarez et al assumed that $A_i' = A_i$ for all components, giving:

$$\sigma_m = \sigma_i + \frac{R T}{A_i} \ln \frac{x_{i,s} \gamma_{i,s}}{x_{i,b} \gamma_{i,b}} \quad (28)$$

To use this equation requires values of the pure component surface tensions, molar surface areas and the individual component activity coefficients in the bulk and surface phases. Note that the mole fraction sums, in the bulk and at the surface, both equal one.

The main difference between the original and Larsen et al UNIFAC model is in the determination of the combinatorial part of the activity coefficient, which instead is given by:

$$\ln \gamma_i^C = \ln \frac{\Phi_i^*}{x_i} + 1 - \frac{\Phi_i^*}{x_i} \quad (29)$$

where

$$\Phi_i^* = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}} \quad (30)$$

Larsen et al also re-evaluated the group interaction parameters, a_{mn} , and included temperature dependence for these parameters in the following form:

$$a_{mn}(T) = a_{mn,1} + a_{mn,2} (T - T_0) + a_{mn,3} \left(T \ln \frac{T_0}{T} + T - T_0 \right) \quad (31)$$

where the $a_{mn,i}$ parameters are presented in Table VII of [12], and $T_0 = 298.15$ K is a reference temperature.

Method

Pure Component Values

All of the models require the pure component values for each of the components considered. Here we present curve fits to data from the literature together with some viscosity data for glycerol

and ethylene glycol which were collected in-house using a Brookfield spindle viscometer.

Pure component viscosity data were curve fit to the following form as a function of reduced temperature $T_r = T / T_c$:

$$\mu \text{ (mPa s)} = \exp\left(\sum_{i=1}^5 C_i T_r^{i-1}\right) \quad (32)$$

Pure component surface tension data for all of the liquids apart from water were curve fit in a form suggested by Yaws *et al* [31]:

$$\sigma \text{ (mPa m)} = \sigma_0 (1 - T_r)^\beta \quad (33)$$

For water, the IAPWS recommended formula [9] was used:

$$\sigma \text{ (mPa m)} = B \tau^m (1 + b\tau) \quad (34)$$

where $B = 235.8 \text{ mPa m}$, $\tau = 1 - T_r$, $m = 1.256$ and $b = -0.625$. The values of the curve fit parameters are presented in Tables 1 and 2. The calculations also require values of critical temperature, volume and acentric factor, which are summarized in Table 3

	water	glycerol	ethylene glycol	1-propanol
C_1	84.517	-81.406	80.11	25.924
C_2	562.683	1281.65	1022.59	-84.636
C_3	1436.12	-5455.31	-4136.0	72.134
C_4	-1673.40	9257.69	6934.37	18.965
C_5	741.815	-5594.70	-4207.5	-39.106
Source data	[3]	[1,4], *	[1, 2, 13, 29], *	[2]

Table 1. Pure component viscosity-temperature curve fit parameters * = present study.

	glycerol	ethylene glycol	1-propanol
σ_0 (mPa m)	87.80	71.80	45.12
β	0.755	0.770	0.811
Source data	[32]	[10, 17, 32]	[10, 32]

Table 2. Pure component surface tension-temperature curve fit parameters.

Component	T_c (K)	V_c (m ³ /mol)	ω
water	647	5.60×10^{-5}	0.345
glycerol	850	2.64×10^{-4}	1.320
ethylene glycol	720	1.91×10^{-4}	0.487
1-propanol	537	2.18×10^{-4}	0.629

Table 3. Pure component critical temperature and volume and acentric factor. For water, values from IAPWS. For glycerol and ethylene glycol, the critical temperature comes from [18] whilst the critical volume and acentric factor come from [30]. For 1-propanol, see [20].

Outline of Calculation Procedure

For the GCSP methods, experimental data for each mixture are used to determine the value of ψ_{ij} . The procedure starts with calculation of the pseudo-critical values. Next component property values are estimated at the mixture reduced temperature (not the true experimental reduced temperature). Finally, the mixture property is evaluated using the combination rules above.

For the UNIFAC methods, firstly the molecular groups are identified, then the parameters for each group are taken from the references, and finally the calculation loops over all the groups. A summary of the method is given in [20, 21].

Results

Viscosity

Figure 1 compares the experimental viscosity data of Dean [1] (for aqueous glycerol mixtures) and Dizzechi & Marshall [2] (for aqueous ethylene glycol and 1-propanol mixtures) with the GCSP

and UNIFAC-VISCO methods. For the glycerol and ethylene glycol mixtures, the GCSP method fits the data well, whilst the UNIFAC-VISCO method does not. For the 1-propanol mixtures, the GCSP fits the data better than the UNIFAC-VISCO method, but the fit is not entirely satisfactory.

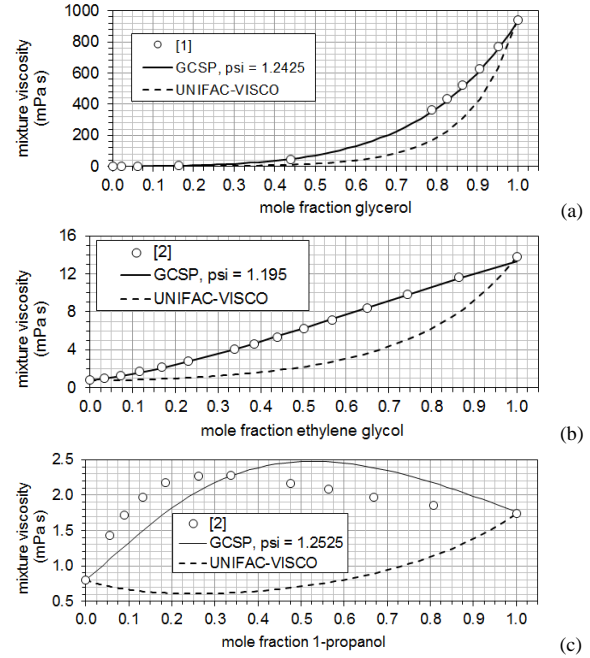


Figure 1. Comparison of experimental aqueous mixture viscosity data with GCSP and UNIFAC-VISCO methods. (a) glycerol, $T = 25 \text{ }^\circ\text{C}$; (b) ethylene glycol, $T = 30 \text{ }^\circ\text{C}$; (c) 1-propanol, $T = 30 \text{ }^\circ\text{C}$.

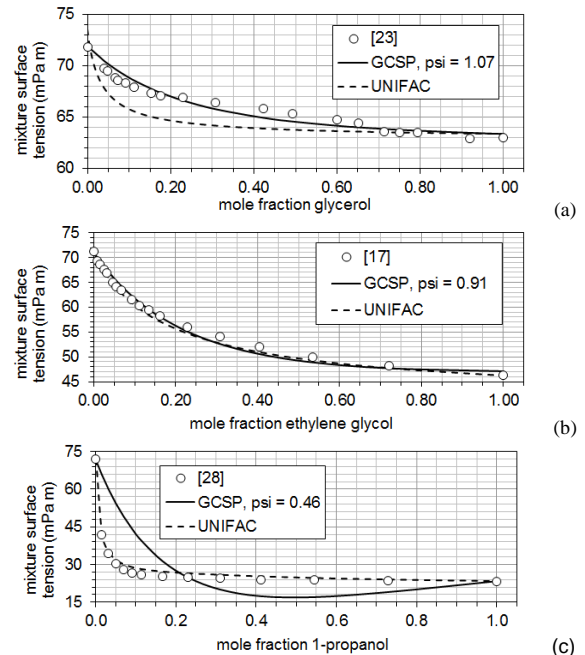


Figure 2. Comparison of experimental aqueous mixture surface tension data with GCSP and UNIFAC methods. (a) glycerol, $T = 25 \text{ }^\circ\text{C}$; (b) ethylene glycol, $T = 30 \text{ }^\circ\text{C}$; (c) 1-propanol, $T = 25 \text{ }^\circ\text{C}$.

Surface Tension

Figure 2 compares the experimental surface tension data of Romero & Paéz [23] (for aqueous glycerol mixtures) Nakanishi *et al* [17] (for aqueous ethylene glycol mixtures) and Vázquez *et al* [28] (for aqueous 1-propanol mixtures) with the GCSP and

UNIFAC methods. For the ethylene glycol mixtures, the GCSP and UNIFAC methods compare well with each other and with the data. For the glycerol mixtures, the GSCP method fits the data well, whilst the UNIFAC method does not; on the other hand, for 1-propanol mixtures, the UNIFAC method compares very well with the data whilst the GSCP does not.

Conclusions

The viscosity and surface tension of aqueous mixtures with glycerol, ethylene glycol and 1-propanol have been compared with calculated values using both the GCSP and UNIFAC methods. Overall, the GCSP compares best with the viscosity data, whilst the UNIFAC method compares best with the surface tension data. In reality, both of these methods are not predictive, rather they rely on curve-fitting: in the GCSP, the fitting parameter, ψ_{ij} , is varied until the average difference between the data and model is minimized; whereas in the UNIFAC method, mixture activity data from a large database are curve fit in terms of their constituent groups, and the activity values are used in the subsequent property estimations. Nonetheless, these models are useful for characterizing mixture properties and can aid the inkjet printer designer in estimating performance over a range of compositions and temperatures.

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