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A NEW VISCOSITY EQUATION FOR BIN AQUEOUS SOLUTIONS

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ABSTRACT

An equation for the viscosity of binary aqueous solutions has been derived based on the Power law equation and Erying's absolute rate theory. The concentration dependent equation for viscosities of binary aqueous systems is derived using additive contribution from water and solute component. The equation has sufficient degree of freedom to represent the whole range of concentration. The equation has been applied to 12 non-electrolyte aqueous systems and 10 electrolyte systems at various temperatures. An average absolute deviation percentage error (AAD%) of 0.2856% is reported for electrolyte systems. For non-electrolyte systems an average AAD% of 0.7843% is reported. Overall, the equation is found to have yielded an AAD% of 0.5576%.

Keywords: Viscosity Equation; Binary Aqueous Solutions.

1 INTRODUCTION

The viscosity of aqueous solution plays a very important role in many fields of chemical engineering like separation process, wastewater treatment and chemical transport. There are many experimental measurements of aqueous solution viscosities reported in literature. Equally important are the many correlations proposed to interpolate the measured data.

There are many equations proposed to represent aqueous electrolyte systems. For aqueous non-electrolyte systems, mostly polynomial-type equations are used. Therefore, it is desirable to obtain an equation, which has the capability to represent the viscosity of aqueous binary electrolyte and also aqueous binary non-electrolyte systems for the whole range of concentration accurately. However modeling studies of viscosities of aqueous solution over the whole concentration ranges are rather difficult (Hu, 2004).

An equation based on Erying's absolute rate theory (Glasstone et al., 1941) to represent aqueous solution viscosity is proposed in this paper. The equation has 6 parameters. The equation also utilizes some physical chemical data of the aqueous solution's component, which is easily available.

2 MODEL

The new proposed equation is derived using a novel approach by utilizing the Power Law equation and Erying's method, based on the absolute rate theory. The Power Law or Ostwald-de Waele equation is used to describe viscosity for non-Newtonian fluids (Bird, 1960).

$$\tau = K \cdot \left(\frac{dv_x}{\lambda}\right)^{\psi} \tag{1}$$

where $\frac{dv_x}{\lambda}$ is the local velocity gradient, ψ dimensionless constant representing deviation of system from Newtonian, τ is the shear stress, K is the apparent viscosity and λ is distance of molecule movement.

The theory of rate process states that flow of a liquid is considered a type rate process. Therefore, viscosity, which is a measurement of flow, can be described using the theory of rate process. The theory of rate process assumes that liquid consist of void holes moving about in a matter of compact molecules. In order for the liquid to flow, holes have to be created so that the liquid molecule can move to its new position. From the equation of state, a relationship between molecular velocity and the energy required has been established. The relationship is described in Equation (2) below. The assumption made to simplify the model is that the void hole is of cubical dimension with a symmetrical length of λ (Glasstone et al., 1941).

$$dv_x = \frac{\tau \overline{V} \lambda}{Nh} e^{-\Delta G^*/RT} \tag{2}$$

where, N is Avogadro's constant, h is Plank's constant, R is gas constant, T is temperature, $\overline{V}$ is the molar volume of hole in the liquid, ΔG^* is the molar free energy of activation. The apparent viscosity, K is defined as a multiplication of absolute viscosity, η with constant, sigma, σ. Equation (1) is rearranged to represent viscosity (Glasstone et al., 1941).

$$\eta = \frac{\tau}{\sigma} \cdot \left(\frac{\lambda}{dv_x} \right)^{\psi} \tag{3}$$

Applying Equation (2) into Equation (3), a viscosity equation based on the Power Law and the theory of rates is obtained.

$$\eta = \frac{\tau}{\sigma} \cdot \left(\frac{N h}{\tau \overline{V}} \cdot e^{\Delta G^* / RT} \right)^{\psi} \tag{4}$$

The above equation is used for representing pure liquids. For binary aqueous solutions, it is assumed that the system consists of two components, which is completely soluble in each other. The component term is used because the equation represents the viscosity for the whole range of concentration. Therefore, either component will represents 'solvents' in the extreme ends of the range.

In aqueous system, one of the components is water. The other component is a liquid, which is completely soluble in water. In aqueous electrolyte systems, the other component is the saturated salt liquor. Equation (4) is rewritten to represent the binary equation.

$$\eta_C = \frac{\tau_C^{1-\psi_C}}{\sigma_c} \cdot \left(\frac{Nh}{\overline{V}_C} e^{\Delta G_C^* / RT} \right)^{\psi_C} \tag{5}$$

More assumptions are made to simplify the model. The first assumption is that the term molecule in the absolute rates theory is assumed to be the complete molecule of the component, together with its hydration. All molecules regardless of its size and shape occupy an imaginary hard spherical volume, where the molecule rotates and vibrates freely in any orientation in the confined spherical volume. The molecules in the system are assumed to be pack layer by layer in an orderly manner. All components in the system are evenly distributed.

There are five parameters namely, ΔG_c^*, $\overline{V}_c$, τ_c, σ_c and ψ_c. Each parameter has a corresponding equation to correlate with the pure component's parameter or the pure component's physical properties. Additive correlation is used to correlate the first two parameters, the molar volume of holes, $\overline{V}_c$ and total free activation energy constants for the binary liquids, ΔG_c^*. The parameter, ψ_c is correlated using a non-linear correlation similar to Grunberg-Nissan's (1949). The apparent viscosity rates, σ_c describes the anomalies of the shear rates of the non-Newtonian liquids. This parameter varies with ψ_c.

$$\Delta G_c^* = (1-x)\Delta G_1^* + x\Delta G_2^* \tag{6}$$

$$\overline{V}_c = (1-x)\overline{V}_1 + x\overline{V}_2 \tag{7}$$

$$\psi_C = (1-x^\beta)\psi_1 + x^\beta(1-x^\beta)\psi_{12} + x^\beta\psi_2 \tag{8}$$

$$\sigma_c = \sigma^{\psi_c - 1} \tag{9}$$

where subscripts 1 and 2 denotes the component 1 and 2 in the binary system, subscript 12 denotes non-linear constant for the binary system and β is a non-linear adjustable constant for the mole fraction, x.

The shear stress, τ_c is defined as force per unit area (Bird, 1960). The molar force acting on the each other depends on the molecule mass. The molar unit area depends on the estimate molecule size. As both parameters are indirectly related to the make-up of the molecules in the system, therefore, the shear stress is assumed to vary with concentration. Therefore, the estimate shear stress is calculated as follows:

$$\tau_c = \frac{4g(\rho_1\rho_2)^{2/3}}{\pi N^{1/3}} \cdot \frac{((1-x)M_1 + xM_2)}{\left((1-x)(M_1\rho_2)^{2/3} + x(M_2\rho_1)^{2/3}\right)} \tag{10}$$

where, ρ is density, M is the molar mass and g is gravity acceleration. Inserting Equation (6) and Equation (7) into Equation (5),

$$\eta_C = \frac{\tau_c^{1-\psi_C}}{\sigma_c} \cdot \left(\frac{hN}{(1-x)\overline{V}_1 + x\overline{V}_2} e^{\left((1-x)\Delta G_1^* + x\Delta G_2^*\right)/RT} \right)^{\psi_C} \tag{11}$$

$$\eta_C = \frac{\tau_c^{1-\psi_C}}{\sigma_c} \cdot \left(\frac{hNe^{\Delta G_1^*/RT}}{\overline{V}_1} \cdot \frac{e^{x\left(\Delta G_2^* - \Delta G_1^*\right)/RT}}{1 + x\left(\frac{\overline{V}_2 - \overline{V}_1}{\overline{V}_1}\right)} \right)^{\psi_C} \tag{12}$$

$$\eta_C = \frac{\tau_c^{1-\psi_C}}{\sigma_c} \cdot \left(\left(\frac{\tau_1}{\sigma_1} \cdot \frac{\sigma_1}{\tau_1}\right)^{\frac{1}{\psi_1}} \cdot \left(\frac{\tau_1}{\tau_1}\right)^{\frac{\psi_1}{\psi_1}} \cdot \left(\frac{hNe^{\Delta G_1^*/RT}}{\overline{V}_1}\right)^{\frac{\psi_1}{\psi_1}} \cdot \frac{e^{x\left(\Delta G_2^* - \Delta G_1^*\right)/RT}}{1 + x\left(\frac{\overline{V}_2 - \overline{V}_1}{\overline{V}_1}\right)} \right)^{\psi_C} \tag{13}$$

Defining,

$$E = \frac{\Delta G_2^* - \Delta G_1^*}{RT} \tag{14}$$

$$V = \frac{\overline{V}_2 - \overline{V}_1}{\overline{V}_1} \tag{15}$$

$$\eta_1 = \frac{\tau_1}{\sigma_1} \cdot \left(\frac{N h}{\tau_1 \overline{V}_1} \cdot e^{\Delta G_1^* / RT} \right)^{\psi_1} \tag{16}$$

Using Equations (14), (15) and (16), Equation (13) is simplified.

$$\eta_C = \frac{\tau_c}{\sigma_c} \cdot \left(\frac{\tau_1}{\tau_c} \left(\frac{\eta_1 \sigma_1}{\tau_1} \right)^{\frac{1}{\psi_1}} \cdot \frac{e^{xE}}{1 + xV} \right)^{\psi_C} \tag{17}$$

A further simplification is done to Equation (17) for aqueous systems as water; component 1 is a known Newtonian fluid (Bird, 1960).

$$\eta_C = \frac{\tau_c}{\sigma_c} \cdot \left(\frac{\eta_1}{\tau_c} \cdot \frac{e^{xE}}{1 + xV} \right)^{\psi_C} \tag{18}$$

where, $\psi_C = 1 - x^{\beta} + x^{\beta}(1 - x^{\beta})\psi_{12} + x^{\beta}\psi_2$.

3 METHODOLOGY

Non-electrolyte viscosity data of Methanol, n-Propanol, Diethanolamine (DEA), N-Methyldiethanolamine (MDEA), Diglycolamine (DGA), Formamide, N, N-dimethylformamide (DMF), 2-Picoline, Propylene Glycol Monomethyl Ether (PGME), Dimethyl Sulphoxide (DMSO), Ethylene Glycol (EG) and Diethylene Glycol (DEG) from experimental data and literature are treated and arranged in the form of mole fraction and absolute viscosity. Electrolyte systems of Sodium Fluoride (NaF), Sodium Chloride (NaCl), Sodium Bromide (NaBr), Sodium Nitrate ($NaNO_3$), Potassium Chloride (KCl), Magnesium Chloride ($MgCl_2$), Calcium Chloride ($CaCl_2$), Copper Sulphate ($CuSO_4$), Zinc Sulphate ($ZnSO_4$) and Ammonium Bromide (NH_4Br) from literature are treated and arranged in a similar manner. References to all the data used are listed in Tables 1 and 2.

There are 6 unknown parameters for every set of system. It is noted all parameters are dimensionless parameter except for σ which has a dimension of seconds (s). Each parameter is estimated for its closest guess value. Using non-linear regression method (Marquardt, 1963), Equation (18) is fitted to obtain the best parameter values. The overall regression results are measured using average absolute percent deviation (AAD%) (Monnery et al., 1995),

$$AAD\% = \frac{1}{N_D} \sum \sqrt{\left(\frac{\eta_{exp} - \eta_{calc}}{\eta_{exp}} \right)^2} \times 100\% \tag{19}$$

where N_D is the total number of data in the sample, subscript *exp* denotes experimental data and subscript *calc* denotes calculated data.

4 RESULTS AND DISCUSSION

An average AAD% of 0.2856% is reported for 10 electrolyte systems. The results for electrolyte systems are comparable or better with those reported by other equations like Kumar's equation, AAD% of 0.71% (Kumar, 1993), Debye-Hückel based equation, AAD% of 0.98% (Esteves et al., 2002), Kaminsky equation, AAD% of 0.81% and Jiang's equation, AAD% of 0.29% (Jiang, 2003). In Table 1, higher error recorded for $MgCl_2$ and $ZnSO_4$ systems could be due to bad experimental data points at lower temperature sets from literature. Equation (18) gives an AAD% of less than 0.1% for NaF, KCl and NH_4Br systems.

Table 2 shows that Equation (18) gives a good data fitting regardless of viscosity range of non-electrolyte systems. An Average Absolute Deviation percentage error (AAD%) of 0.7843% is reported. High ADD% values are reported for MDEA, PGME and DMSO could be due to bad experimental data points reported by the literature. However the results are comparable or better than if fitted using polynomial equations. From Table 2, Equation (18) gives an AAD% of less than 0.5% for Methanol, Formamide and DMF systems. The equation overall is found to have yielded an AAD% of 0.5576%.

TABLE 1. Application of Equation (18) on various binary aqueous electrolyte systems

System	Reference	Total no. of data	Max. η	Max. x	Temperature Range, (°C)	Average AAD%
NaF	(Goldsack and Franchetto, 1977)	54	1.801	0.0142	5 – 55	0.0553
NaCl	(Afzal et al., 1989)	70	1.555	0.0680	20 – 50	0.1005
NaBr	(Goldsack and Franchetto, 1977)	54	3.084	0.0125	5 – 55	0.2465
$NaNO_3$	(Isono, 1984)	70	2.532	0.1260	15 – 50	0.2121
KCl	(Afzal et al., 1989)	54	0.913	0.0821	30 – 55	0.0734
$MgCl_2$	(Afzal et al., 1989)	77	12.94	0.0836	20 – 50	0.6895
$CaCl_2$	(Afzal et al., 1989)	77	8.507	0.0836	20 – 50	0.2225
$CuSO_4$	(Stokes and Mills, 1965)	119	1.724	0.0265	30 – 60	0.3921
$ZnSO_4$	(Stokes and Mills, 1965)	105	8.875	0.0644	30 – 60	0.7868
NH_4Br	(Stokes and Mills, 1965)	54	1.516	0.0125	5 – 55	0.0777

TABLE 2. Application of Equation (18) on various binary aqueous non-electrolyte systems

System	Reference	Total no. of data	Max. η	Temperature Range, (°C)	Average AAD%
Methanol	(Mikhail and Kimel, 1961)	66	2.5067	10 – 50	0.2812
n-Propanol	(Tan et al.)	135	3.1741	20 – 60	0.7715
DEA	(Teng et al., 1994)	70	566.3	25 – 80	0.8485
MDEA	(Teng et al., 1994)	80	82.37	25 – 80	1.2969
DGA	(Henni et al., 2001)	58	27.716	25 – 70	0.8808
Formamide	(Osinska et al., 1983)	55	6.0338	5 – 45	0.2602
DMF	(Osinska et al., 1983)	75	5.0641	5 – 45	0.4782
2-picoline	(Lee and Wei, 1992)	33	2.5945	30 – 50	0.7600
PGME	(Krishnaiah et al., 1993)	52	3.8641	25 – 55	1.0654
DMSO	(Palaiologou et al., 2002)	38	7.3300	5 – 20	1.1585
EG	(Pai and Singh, 1997)	36	13.349	30 – 35	0.6894
DEG	(Pai and Singh, 1997)	34	21.030	30 – 35	0.9211

4 CONCLUSION

A new viscosity equation has been proposed to correlate the viscosity of aqueous solutions. The equation is derived from Power-law equation using the absolute rate theory. The equation is capable of correlating the whole range of mole fractions of the binary aqueous systems. An overall average AAD% of 0.5576 has been obtained for 22 different aqueous systems of various electrolytes and non-electrolytes.

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