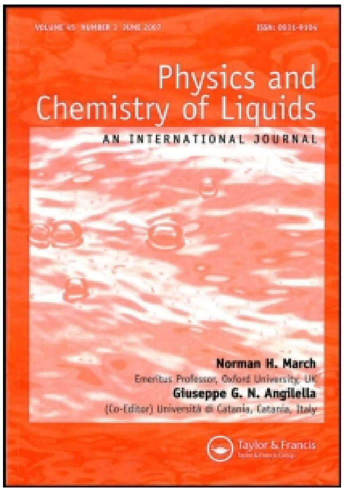

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DYNAMIC VISCOSITIES OF NON-ELECTROLYTE MIXTURES

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Viscosities have been obtained for some non-electrolyte mixtures at 298.15 K, over the whole concentration range. The viscosity data have been analysed in the light of the models of McAllister, Teja and Rice, Wei and Rowley and finally of Schrodt and Akel. The last method was found to give the best agreement with the experimental data.

KEY WORDS: Viscosities, binary mixtures of non-electrolytes.

1 INTRODUCTION

There is no method to predict viscosity coefficients for mixtures, because there is not a theory that can explain the intermolecular interactions and their influence in transport phenomena in liquids.

We report here experimental data of viscosities of the following systems: *n*-butylamine (BA) + 1,4-dioxane (D); propan-1-ol (1-PR) + dichloromethane (DCM); propan-2-ol (2-PR) + dichloromethane (DCM); *n*-pentane (P) + dichloromethane (DCM) and *n*-pentane (P) + methyl-acetate (MA) at 298.15 K. Further, the data have been analyzed in terms of the McAllister[1] method, the Teja and Rice[2] corresponding states argument, the Wei and Rowley[3] method, which obtain information from equilibrium vapor-liquid data, and the Schrodt and Akel[4] model, which is based on Eyring's concept of viscosity.

2 EXPERIMENTAL SECTION

The method used in our laboratory have been described previously[5,6]. Densities were determined with a digital densimeter AP, model DMA 45. A thermostatically controlled bath (constant to 0.01 K) was used. Calibration was carried out with air

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and doubly distilled water with an error of ± 0.1 kg m^{-3}. All weighings were made on a Mettler H315 balance. Temperatures were read from calibrated thermometers.

Viscosities of the pure components and of the mixtures were determined with a Cannon-Fenske viscosimeter calibrated with doubly distilled water and benzene. Kinetic energy corrections were applied to the viscosity data. The estimated error was ± 0.005 mPa s.

n-Butylamine (Fluka) was purified by the method described by Sreenivasulu and Naidu[7]; propan-1-ol, propan-2-ol and dichloromethane (Merck) were fractionally distilled over calcium chloride; methyl-acetate (Mallinckrodt) was heated at reflux with acetic anhydride and then distilled over potassium carbonate; 1,4-dioxane (Fluka) was distilled over phosphorous pentoxide. In all distillations, only the middle fraction was collected. The binary mixtures were prepared by mixing weighed amounts of the pure liquids. Caution was taken to prevent evaporation.

3 RESULTS

The experimental results for the pure liquids are reported in Table 1, together with literature values for comparison. The values of densities and viscosities of the following mixtures: BA(1) + D(2); 1-PR(1) + DCM(2); 2-PR(1) + DCM(2); P(1) + DCM(2) and P(1) + MA(2) were reported previously[13-17].

Densities and viscosities could be calculated, using an equation of the Redlich-Kister type:

$$P = x_1 P_1 + x_2 P_2 + x_1 x_2 \sum_{j=1}^{n} a_j (1 - 2x_1)^{j-1} \qquad (1)$$

where ν represents the kinematic viscosity (η/ρ) and ν_{12} and ν_{21} are the interaction parameters obtained by a computation program. Table 3 gives these values at 298.15 K with their percent error.

Table 1 Properties of the pure components at 298.15 K.

Substance	$\rho \times 10^{-3}$/kg m^{-3}		η/mPa s	
	Exp.	*Lit.*	*Exp.*	*Lit.*
n-Butylamine	0.7325	0.73308[a]	0.474	0.470[b]
1,4-Dioxane	1.0283	1.02687[c]	1.181	1.204[c]
Propan-1-ol	0.7995	0.7987[d]	1.922	2.004[c]
Propan-2-ol	0.7800	0.7807[e]	1.995	1.990[b]
Dichloromethane	1.3163	1.3168[f]	0.420	0.412[f]
n-Pentane	0.6214	0.62129[f]	0.214	0.225[f]
Methyl acetate	0.9273	0.9274[f]	0.363	0.364[f]

[a] Ref. (7); [b] Ref. (8); [c] Ref. (9); [d] Ref. (10); [e] Ref. (11); [f] Ref. (12).

tion of the change of standard error estimate with n:

$$\sigma = [\sum (P_{\mathrm{exp}} - P_{\mathrm{cal}})^2/(n_{\mathrm{obs}} - n)]^{1/2} \tag{2}$$

The values adopted for the coefficients a_j and the standard error of estimates associated with the use of Eq. (2) are summarized in Table 2.

4 DISCUSSION

Different equations in the literature can predict mixtures viscosities. The McAllister[1] correlation is based on a model proposed by Eyring, which considers that interaction occurs between three bodies:

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

where ν represents the kinematic viscosity (η/ρ) and ν_{12} and ν_{21} are the interaction parameters obtained by a computation program. Table 3 gives these values at 298.15 K with their percent error.

Table 2 Coefficients a_j and standard deviations σ determined by the method of least squares, at 298.15 K.

System	a_1	a_2	a_3	a_4	a_5	a_6	σ
BA(1) + D(2)							
$\rho \times 10^{-3}$/kg m^{-3}	−0.051031	−0.006097	—	—	—	—	1×10^{-4}
η/mPa s	−0.66310	−0.25981	−0.1629	−0.081566	—	—	2×10^{-3}
H^E/J mol^{-1}	1604	25	−530	45	716	—	3
1-PR(1) + DCM(2)							
$\rho \times 10^{-3}$/kg m^{-3}	−0.0817	−0.0383	0.0027	−0.0386	0.0246	—	2×10^{-4}
η/mPa s	−0.821	0.443	0.122	—	—	—	4×10^{-5}
H^E/J mol^{-1}	3319	3851	−3397	8564	8410	−13075	62
2-PR(1) + DCM(2)							
$\rho \times 10^{-3}$/kg m^{-3}	−0.09926	−0.0512	−0.04443	0.05871	0.12014	−0.1921	4×10^{-4}
η/mPa s	−2.3254	1.2285	−0.40573	—	—	—	5×10^{-3}
H^E/J mol^{-1}	4920	3200	3200	1100	600	2000	57
P(1) + DCM(2)							
$\rho \times 10^{-3}$/kg m^{-3}	−0.42215	−0.125834	−0.02903	−0.01473	−0.00811	—	7×10^{-5}
η/mPa s	−0.18736	−0.05833	0.05508	0.06051	—	—	8×10^{-4}
H^E/J mol^{-1}	5589	2343	−460	−4630	1095	5754	13
P(1) + MA(2)							
$\rho \times 10^{-3}$/kg m^{-3}	−0.139315	−0.025222	0.00418	−0.01334	—	—	6×10^{-5}
η/mPa s	−0.18174	−0.04216	−0.03981	−0.04816	—	—	6×10^{-4}
H^E/J mol^{-1}	5547	767	−4521	−4506	5204	4424	5

Table 3 Parameters of Eqs. (3), (4), (13) and (28) and average deviation % for the five systems at 298.15 K.

System	*McAllister*			*Teja and Rice*		*Wei and Rowley*		*Schrodt-Akel*	
	ν_{12}	ν_{21}	*AD%*	ψ	*AD%*	A_{12}	A_{21}	*AD%*	*AD%*
BA(1) + D(2)	0.3110	0.4817	0.33	0.975	0.49	0.0874	0.2423	1.88	0.41
1-PR(1) + DCM(2)	0.4657	0.2728	0.88	0.951	3.44	−1.5278	−1.2448	30.7	0.59
2-PR(1) + DCM(2)	0.3542	0.2649	1.22	0.884	3.27	1.1913	0.5858	29.2	0.66
P(1) + DCM(2)	0.1372	0.1954	0.19	0.950	0.88	0.00016	1.2441	2.03	0.17
P(1) + MA(2)	0.1193	0.1951	0.67	0.952	0.64	0.19724	2.3146	0.71	0.56

Teja and Rice[2] applied corresponding states theory to calculate mixtures viscosities. These authors proposed the relation:

$$\ln(\eta\xi) = \ln(\eta\xi)^{(r_1)} + \frac{\omega - \omega^{(r_1)}}{\omega^{(r_2)} - \omega^{(r_1)}}\left[\ln(\eta\xi)^{(r_2)} - \ln(\eta\xi)^{(r_1)}\right] \tag{4}$$

where r_1 and r_2 refer to the properties of two reference fluids (in this case, the pure components) and ω is the acentric factor. For mixtures, the pseudo properties T_{cm}, V_{cm} and ω_m of an hypothetical substance replacing the pure fluids, are defined as:

$$T_{cm}V_{cm} = \sum_i \sum_j x_i x_j T_{cij} V_{cij} \tag{5}$$

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \tag{6}$$

$$\omega_m = \sum_i x_i \omega_i \tag{7}$$

$$M_m = \sum_i x_i M_i \tag{8}$$

$$T_{cij} V_{cij} = \psi_{ij}(T_{cii} V_{cii} T_{cjj} V_{cjj})^{1/2} \tag{9}$$

$$V_{cij} = (V_{cii}^{1/3} + V_{cjj}^{1/3})^3/8 \tag{10}$$

where ψ_{ij} is a binary interaction coefficient which must be evaluated from experimental data. The values of ξ from Eq. (4) is obtained as:

$$\xi = V_c^{2/3}/(T_c M)^{1/2} \tag{11}$$

The two reference fluids contribution should be at the same reduced temperature of the mixtures. Using values of η from literature and our own values, we calculated constants A and B from the equation:

$$\ln(\eta\xi) = A + B/T_R \tag{12}$$

Next, values of $\ln(\eta\xi)^{(r_1)}$ and $\ln(\eta\xi)^{(r_2)}$ at the same T_R of the mixtures were calculated. Values of ψ are shown in Table 3 together with the average deviation in %.

Table 4 gives the parameters used to calculate viscosities.

Wei and Rowley[3] developed a local composition model which predicts viscosity, knowing excess enthalpies and NRTL model parameters for excess free energies. The Eyring[18] theory for shear viscosity gives:

$$\eta V = hN_A \exp(\Delta G^*/RT) \tag{13}$$

where V is the molar volume, h is Planck's constant, N_A is Avogadro's number and ΔG^* is the free energy of activation. However, for mixtures ΔG^* is an average of the activation energies of the individual molecular species and can therefore be related only to G^E through a proportionality factor. Thus:

$$\Delta G^* = \Delta G^*_{\mathrm{id}} - \sigma G^E \tag{14}$$

where ΔG^*_{id} is the activation energy for an hypothetical ideal mixture of the components and σ is a proportionality constant. Substitution of Eq. (14) into Eq. (13) and rearranging of G^E in terms of S^E and H^E yields:

$$\eta V = (\eta V)_{\mathrm{id}} \cdot e^{\sigma S^E/RT} \cdot e^{-\sigma H^E/RT} \tag{15}$$

where $(\eta V)_{\mathrm{id}}$ represents the volume viscosity product for an hypothetical ideal mixture of the constituent components and is defined as:

$$(\eta V)_{\mathrm{id}} = hN_A \cdot \exp(\Delta G^*_{\mathrm{id}}/RT) \tag{16}$$

A nonzero excess entropy is indicative of nonrandom mixing by the fluid components and can be grouped with $(\eta V)_{\mathrm{id}}$ to yield a local shear viscosity including nonrandom mixing effects. It is this term for which the local composition model is applicable. The mixture viscosity is therefore composed of one contribution due to non random mixing on the local level and another energetic portion related to the strength of intermolecular interaction which inhibit molecules from being removed

Table 4 Parameters for pure components at 298.15 K[a].

Substance	*M*	T_c/K	$V_c \times 10^6$ ($m^3\ mol^{-1}$)	ω	T_R	ξ
n-Butylamine	73.138	524	288	0.396	0.5690	0.2228
1,4-Dioxane	88.016	587	238	0.288	0.5079	0.1689
Propan-1-ol	60.096	537	218.5	0.624	0.5555	0.2020
Propan-2-ol	60.096	508.3	220	0.665	0.5866	0.2985
Dichloromethane	84.930	510	193	0.193	0.5846	0.1605
n-Pentane	72.150	469.6	304	0.251	0.6349	0.2456
Methyl acetate	74.079	506.8	228	0.324	0.5883	0.1926

[a] Ref. (8).

from their most favorable equilibrium position in the mixture. Then, the former portion is $(\eta V)_{\mathrm{loc}}$. Thus:

$$(\eta V) = (\eta V)_{\mathrm{loc}} \cdot \exp(-\sigma H^E/RT) \tag{17}$$

or defining a property as:

$$\xi = \ln(\eta V) \tag{18}$$

then

$$\xi = \xi_{\mathrm{loc}} - \sigma H^E/RT \tag{19}$$

Applying the two fluid theories[19,20] yields:

$$\xi_{\mathrm{loc}} = \sum_{j=1}^{n} \phi_j \sum_{i=1}^{n} \phi_i G_{ij} \xi_{ij} \bigg/ \sum_{i=1}^{n} \phi_i G_{ij} \tag{20}$$

Taking into account Eq. (17) the following expression is obtained for a binary system:

$$\xi_{21} = \frac{\phi_1^* \phi_1^* \xi_1^0 + \phi_2^* \phi_{22}^* \xi_2^0}{\phi_1^* \phi_{11}^* + \phi_2^* \phi_{22}^*} \tag{21}$$

where

$$\phi_j^* = 1/(1 + \Gamma_{ji}); \qquad \phi_{11}^* = 1 \bigg/ \left(1 + \frac{\phi_j^* G_{ij}}{\phi_i^*}\right); \qquad \Gamma_{ji} = \frac{V_i}{V_j} \left(\frac{G_{ij}}{G_{ji}}\right)^{1/2} \cdot \exp\left(\frac{\xi_i^0 - \xi_j^0}{2}\right) \tag{22}$$

and

$$G_{ij} = \exp(-\alpha A_{ij}/RT); \qquad G_{ji} = \exp(-\alpha A_{ji}/RT) \tag{23}$$

where

$$\xi_{jj} = \xi_j^0 \quad \text{and} \quad G_{11} = G_{22} = 1 \tag{24}$$

Values of A_{ij}, A_{ji} of NRTL equation are summarized in Table 3. We take $\alpha = 0.25$ and H^E values of the systems are calculated with the polynomial coefficients of Table 2.

Following the Schrodt and Akel[4] model, which is based upon Eyring's concept of dilute viscosity, for a pure component, Eq. (13) applies for mixtures:

$$\eta_m = \frac{hN_A}{V_M} \exp\left[\sum x_i \Delta G_i^* + \frac{\Delta G^{*E}}{A} \bigg/ RT\right] \tag{25}$$

where $V_M = (x_1 M_1 + x_2 M_2)/\rho$ is the molar volume of the solution and ΔG^{*E} is the excess free energy of activation and A an empirical factor (in this case = 1).

Note that for an ideal system

$$\frac{x_i \Delta G_i^*}{RT} = \frac{x_1 \Delta G_1^* + x_2 \Delta G_2^*}{RT} = x_1 \ln \frac{\eta_1 V_1}{hN_A} + x_2 \ln \frac{\eta_2 V_2}{hN_A} = \sum x_i \ln \eta_i^0 \tag{26}$$

which is the dimensionless viscosity. The excess free energy of activation can be expressed in a similar form with the Gibbs free energy in vapor-liquid equilibrium, by the following equation:

$$\frac{\Delta G^{*E}}{RT} = \sum x_i \ln \gamma_i^v \tag{27}$$

where γ_i^v is the viscosity activity coefficient (to be distinguished from the activity coefficient of VLE). Then, the expression (25) will be:

$$\ln \eta_m = \ln \frac{hN_A}{V_M} + \sum x_i \ln \eta_i^0 + \sum x_i \ln \gamma_i^v \tag{28}$$

With a set of binary viscosity data, we find ΔG^{*E} values, and the viscosity activity coefficients are determined in this case from predictive equations like NRTL and related to ΔG^{*E} as shown in Eq. (27). This coefficient in a binary solution should obey the Gibbs–Duhem relation. The parameters of NRTL equation are also given in Table 3. Next, we applied Eq. (28) to obtain mixtures viscosities and the average deviation in all cases (or percent error) are defined by:

$$AD = \left[\frac{\sum (\eta_{\text{exp}} - \eta_{\text{cal}})^2}{n}\right]^{1/2} \times 100 \tag{29}$$

are shown in Table 3.

An analysis of each of the four contributions to viscosity to our mixtures shows that the Schrodt and Akel equation gives the best agreement with the experimental results.

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References

1. R. A. McAllister, *A.I.Ch.E. J.*, **6**, 427 (1960).
2. A. S. Teja and P. Rice, *Ind. Eng. Chem. Fundamentals*, **20**, 77 (1981).
3. I. C. Wei and R. L. Rowley, *J. Chem. Eng. Data*, **29**, 332 (1983).
4. J. T. Schrodt and R. M. Akel, *J. Chem. Eng. Data*, **34**, 8 (1989).
5. I. L. Acevedo and M. Katz, *J. Sol. Chem.*, **19**, 1041 (1990).
6. G. C. Pedrosa, J. A. Salas and M. Katz, *Thermochim. Acta*, **160**, 243 (1990).
7. M. Sreenivasulu and R. P. Naidu, *J. Chem. Thermodynamics*, **10**, 731 (1978).

8. R. C. Reid, J. M. Prausnitz and T. K. Sherwood, *The properties of Gases and Liquids*, 3rd. Ed. Interscience Publ. New York (1977).
9. A. Weissberger, *Technique of Organic Chemistry*, Vol. VII, Organic Solvents, 2nd. Ed. Interscience Publ. New York (1955).
10. S. C. Hwang and A. L. Robinson, *J. Chem. Eng. Data*, **22**, 319 (1977).
11. G. N. Eduijee and A. P. Boyes, *J. Chem. Eng. Data*, **25**, 249 (1980).
12. J. A. Riddich, W. B. Bunger and T. K. Sakano, *Organic Solvents*, 4th Ed. J. Wiley & Sons, New York (1986).
13. I. L. Acevedo, M. A. Postigo and M. Katz, *J. Sol. Chem.*, **17**, 977 (1988).
14. G. C. Pedrosa, F. Davolio, M. de Japaze and M. Katz, *Lat. Am. J. Chem. Eng. Appl. Chem.*, **14**, 103 (1984).
15. J. L. Zurita, M. L. G. de Soria, M. A. Postigo and M. Katz, *J. Sol. Chem.*, **16**, 163 (1987).
16. M. A. Postigo, J. L. Zurita, M. L. G. de Soria and M. Katz, *Can. J, Chem.*, **64**, 1966 (1986).
17. M. L. G. de Soria, J. L. Zurita, M. A. Postigo and M. Katz, *Thermochim. Acta*, **130**, 258 (1988).
18. S. Glasstone, M. J. Laidler and H. Eyring, The theory of rate processes, McGraw-Hill Book Co., New York (1941).
19. I. C. Wei and R. L. Rowley, *Chem. Eng. Sci.*, **40**, 401 (1985).
20. H. Renon and J. M. Prausnitz, *A.I.Ch.E.J.*, **14**, 135 (1968).