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Excess viscosities and thermodynamics of viscous flow of *n*-butyl-1-butanamine with chloroalkanes at 298.15 K

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Abstract

Viscosities of three non-electrolyte binary mixtures have been determined at 298.15 K over the whole concentration range. Excess molar viscosities and excess molar energies of activation for viscous flow for n-butyl-1-butanamine + dichloromethane, trichloromethane and tetrachloromethane systems have been calculated. The predictive abilities of some equations for viscosities of mixtures are examined.

INTRODUCTION

In this work, viscosities of three non-electrolyte binary mixtures at 298.15 K have been measured. These mixtures were composed of n-butyl-1-butanamine, which is associated in its pure state by hydrogen bonds, and three chloroalkanes with different polarities. Information can be obtained concerning the interaction between the mixed chemical species. Excess molar viscosities and the energies of activation for viscous flow have been used to calculate some thermodynamic activation parameters. A few existing equations which predict viscosities, such as those of Grunberg and Nissan [1], McAllister [2], Teja and Rice [3] and Schrodt and Akel [4] have been compared, and the last one showed the best agreement with experimental data.

EXPERIMENTAL

The methods 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 ° C) was used. Calibrations were carried out with air and doubly distilled water with an error of

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TABLE 1

Properties characterizing the pure components at 298.15 K

Substance	$\rho \times 10^{-3}$ (kg m^{-3})		η (mPa s)	
	Exp.	Lit.	Exp.	Lit.
n-Butyl-1-butanamine	0.7555	0.7577 [a]	0.798	0.833 [c]
Dichloromethane	1.3151	1.31678 [b]	0.413	0.406 [c]
Trichloromethane	1.4788	1.4797 [a]	0.542	0.542 [d]
Tetrachloromethane	1.5840	1.58401 [c]	0.905	0.9004 [a]

[a] Ref. 7.
[b] Ref. 8.
[c] Ref. 9.
[d] Ref. 10.

±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 using an Ubbelhode viscosimeter, with a Schott-Geräte viscosimeter, model AVS 400, and a CT 1450 thermostat. The estimated error was ±0.005 mPa s.

n-Butyl-1-butanamine or dibutylamine (DBA) (Merck, puriss.) was dried over sodium hydroxide and fractionally distilled. Dichloromethane (DCM) (Merck, puriss.) was distilled over calcium oxide. Trichloromethane (TCM) (Merck, puriss.) was washed with distilled water, dried over calcium chloride and distilled. Finally, tetrachloromethane (TC) (Merck, puriss.) was used without further purification.

Mixtures were prepared by mixing weighed amounts of the pure liquids. Caution was taken to prevent evaporation.

RESULTS AND DISCUSSION

The experimental results for the pure liquids are reported in Table 1, together with literature values for comparison.

Table 2 shows the experimental densities and viscosities of the solutions at 298.15 K.

Different equations exist in the literature which can predict viscosity coefficients of mixtures. Grunberg and Nissan [1] have proposed an empirical equation to describe viscosities of real mixtures

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 \delta \qquad (1)$$

where δ is taken to reflect the nonideality of the system. The parameter δ has usually been regarded as an approximate measurement of the strength of the interaction between both components [11]. However, it has been shown that in certain cases δ can also be correlated with the difference in

TABLE 2

Densities and viscosities of the DBA(1)+DCM(2), DBA(1)+TCM(2) and DBA(1)+TC(2) systems at 298.15 K.

DBA(1)+DCM(2)			DBA(1)+TCM(2)			DBA(1)+TC(2)		
x_1	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPa s)	x_1	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPa s)	x_1	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPa s)
0.0995	1.1869	0.494	0.1020	1.3410	0.639	0.0922	1.4593	0.898
0.2125	1.0799	0.550	0.1990	1.2340	0.717	0.1730	1.3625	0.894
0.2990	1.0166	0.590	0.3088	1.1330	0.803	0.3108	1.2194	0.887
0.3913	0.9614	0.633	0.3714	1.0831	0.845	0.4089	1.1315	0.881
0.4338	0.9394	0.650	0.4997	0.9939	0.904	0.5011	1.0575	0.877
0.6097	0.8644	0.719	0.6082	0.9300	0.925	0.5964	0.9886	0.872
0.6782	0.8047	0.740	0.6980	0.8831	0.907	0.7077	0.9160	0.864
0.8070	0.8021	0.768	0.7719	0.8481	0.890	0.7916	0.8661	0.848
0.8865	0.7815	0.787	0.9007	0.7935	0.852	0.9034	0.8048	0.823

molecular volumes of the components and with the entropies of mixing [12]. The values obtained for δ at 298.15 K for the three systems are summarized in Table 3 with their percent error.

The McAllister [2] correlation is based on a model proposed by Eyring which considers that interaction occurs between three bodies

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

where ν represents the kinematic viscosity (η/ρ), M_1 and M_2 are the molecular weights and ν_{12}, ν_{21} are the interaction parameters obtained by a computation program. Table 3 gives these values at 298.15 K with the percent error.

We also applied the corresponding states method of Teja and Rice [3] to calculate viscosities of mixtures. These authors proposed the relation

$$\ln(\eta\xi) = \ln(\eta\xi)^{(r_1)} + \frac{\omega - \omega^{(r_1)}}{\omega^{(r_2)} - \omega^{(r_1)}}\left[\ln(\eta\xi)^{(r_2)} - \ln(\eta\xi)^{(r_1)}\right] \qquad (3)$$

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 pseudocritical properties T_{cm}, V_{cm} and ω_m of a hypothetical equivalent substance replacing the pure fluids can be

$$T_{cm} V_{cm} = \sum_i \sum_j x_i x_j T_{cij} V_{cij} \qquad (4)$$

TABLE 3

Parameters from eqns. (1), (2), (3) and (17)

System	Eqn. (1)		Eqn. (2)			Eqn. (3)		Eqn. (17)		
	δ	AD (%)	ν_{12}	ν_{21}	AD (%)	ψ	AD (%)	τ_{12}	τ_{21}	AD (%)
DBA(1)+DCM(2)	0.749	1.5	0.3018	0.4834	2.6	1.135	0.8	−0.2954	2.0804	0.7
DBA(1)+TCM(2)	1.242	1.0	0.4750	0.5441	0.6	1.185	0.9	0.4256	1.3685	0.6
DBA(1)+TC(2)	1.135	0.8	0.4277	0.4712	0.2	1.023	0.5	1.0311	−0.5487	0.6

$$V_{\mathrm{cm}} = \sum_i \sum_j x_i x_j V_{\mathrm{c}ij} \tag{5}$$

$$\omega_{\mathrm{m}} = \sum_i x_i \omega_i \tag{6}$$

$$M_{\mathrm{m}} = \sum_i x_i M_i \tag{7}$$

$$T_{\mathrm{c}ij} V_{\mathrm{c}ij} = \psi_{ij} \left(T_{\mathrm{c}ii} V_{\mathrm{c}ii} T_{\mathrm{c}jj} V_{\mathrm{c}jj} \right)^{1/2} \tag{8}$$

$$V_{\mathrm{c}ij} = \left(V_{\mathrm{c}ii}^{1/3} - V_{\mathrm{c}jj}^{1/3} \right)^3 / 8 \tag{9}$$

where ψ_{ij} is a binary interaction coefficient which must be evaluated from experimental data. The values of ξ from eqn. (3) have been obtained by

$$\xi = V_{\mathrm{c}}^{2/3} / (T_{\mathrm{c}} M)^{1/2} \tag{10}$$

V_{c} and T_{c} of the mixtures (V_{cm}, T_{cm}) are obtained from eqns. (4)–(9). The two reference fluid contributions should be at the same reduced temperature of the mixtures. Using values of η from the literature and our own values we can calculate constants A and B from the equation

$$\ln(\eta\xi) = A + B/T_{\mathrm{R}} \tag{11}$$

A and B are determined by the method of least squares. Next, values of $(\eta\xi)^{(r_1)}$ and $(\eta\xi)^{(r_2)}$ at the T_{R} of the mixture are calculated with ψ values indicated in Table 3 and we have determined the values of viscosities for the three systems.

Following the Schrodt and Akel [4] model, which is based upon Eyring's concept of fluid viscosity, for a pure component

$$\eta = \frac{hN_{\mathrm{A}}}{V} \exp(\Delta G^*/RT) \tag{12}$$

where h is Planck's constant, N_{A} is Avogadro's number, V is the molar volume and ΔG^* is the free energy of activation for viscous flow. For mixtures

$$\eta_{\mathrm{m}} = \frac{hN_{\mathrm{A}}}{V_{\mathrm{m}}} \exp\left[\left(\sum x_i \, \Delta G_1^* + \frac{\Delta G^{*\mathrm{E}}}{A} \right) / RT \right] \tag{13}$$

where $V_{\mathrm{m}} = (x_1 M_1 + x_2 M_2)\rho$ is the molar volume of the solution and $\Delta G^{*\mathrm{E}}$ is the excess free energy of activation and A is an empirical factor (in this case equal to 1).

Note that for an ideal system

$$\frac{x_i \, \Delta G_i^*}{RT} = \frac{x_1 \Delta G_1^* + x_2 \Delta G_2^*}{RT} = x_1 \ln \frac{\eta_1 V_1}{hN_{\mathrm{A}}} + x_2 \ln \frac{\eta_2 V_2}{hN_{\mathrm{a}}} = \sum x_i \ln \eta_i^0 \tag{14}$$

where

$$\eta_i^0 = \frac{\eta_i V_i}{h N_A} \tag{15}$$

which is the dimensionless viscosity. The excess free energy of activation can be expressed in a similar form to that of the free energy of Gibbs in vapor–liquid equilibrium (VLE) by the equation

$$\frac{\Delta G^{*E}}{RT} = \sum x_i \ln \gamma_i^v \tag{16}$$

where γ_i^v is the viscosity activity coefficient to be distinguished from the activity coefficient of VLE. Then, expression (13) will be

$$\ln \eta_m = \ln \frac{h N_A}{V_m} + \sum x_i \ln \eta_i^0 + \sum x_i \ln \gamma_i^v \tag{17}$$

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 such as non-random two liquids (NRTL) and related to $\Delta G^{*E}/RT$ as shown in eqn. (16). These viscosity coefficients in a binary solution should obey the Gibbs–Duhem relation.

The parameters of the NRTL equation are also given in Table 3. Next, we applied eqn. (17) to obtain viscosities of mixtures and the average deviation (AD) in all cases, or percent error, is given by

$$\mathrm{AD} = \left[\frac{\sum (\eta_{\mathrm{exp}} - \eta_{\mathrm{cal}})^2}{n} \right]^{1/2} \times 100 \tag{18}$$

Values are shown in Table 3.

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

The excess energies of activation for viscous flow have been obtained by using the equation

$$\Delta G^{*E} = RT(\ln \eta V - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2) \tag{19}$$

Each set of results has been fitted with a Redlich–Kister equation of the type

$$X^E = x_1(1 - x_1) \sum_{j=1}^{n} a_j (1 - 2x_1)^{j-1} \tag{20}$$

where X^E is η^E or ΔG^{*E}, and a_j are the polynomial coefficients obtained by a linear least squares fitting procedure. In each case the optimum

TABLE 4

Coefficients a_j and standard deviations σ by the method of least squares at 298.15 K

System		a_1	a_2	a_3	a_4	a_5	a_6	σ
DBA(1)	η^E	0.107	−0.12	0.12	0.07	−0.20	-	0.01
+DCM(2)	ΔG^{*E}	2815	654	−70	1180	1890	-	5
DBA(1)	η^E	0.996	−0.12	−0.60	0.40	0.64	−0.53	0.003
+TCM(2)	ΔG^{*E}	3810	500	−1300	100	1900	-	9
DBA(1)	η^E	0.329	−0.135	−0.106	0.32	0.15	−0.43	0.001
+TC(2)	ΔG^{*E}	680	−280	300	200	−500	-	3

number of coefficients was ascertained from an examination of the standard error estimated with n

$$\sigma = \left[\sum \left(X^E_{\text{obs}} - X^E_{\text{cal}} \right)^2 / \left(n_{\text{obs}} - n \right) \right]^{1/2} \tag{21}$$

The values adopted for the coefficients a_j and the standard deviations are summarized in Table 4.

Figure 1 shows the experimental values of η^E as a function of x_1 for our three systems at 298.15 K. The continuous curves are obtained using eqn. (20) with the coefficients adopted in Table 4.

Figure 2 shows the experimental values of ΔG^{*E}. The continuous curves are obtained using eqn. (20).

Figure 1 shows η^E positive for the three systems and the values obtained are greater than for n-butylamine with the same substances [5]. The n-butyl-1-butanamine is an associated liquid through hydrogen bondings and the addition of the three halogenated hydrocarbons, which are polar molecules, except carbon tetrachloride, produce the ruptures of the hydrogen bonds and an interaction is produced between monomers of DBA and the halogenated hydrocarbons, by hydrogen bonding N–H $\cdots$ Cl which causes a positive η^E. This is corroborated by excess molar volumes which

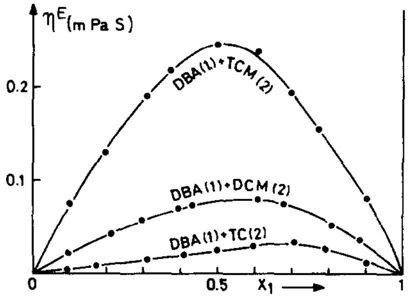

Fig. 1. Excess molar viscosities for the DBA(1)+DCM(2), DBA(1)+TCM(2) and DBA(1)+TC(2) systems at 298.15 K; ●, experimental results; continuous curves calculated using eqn. (20).

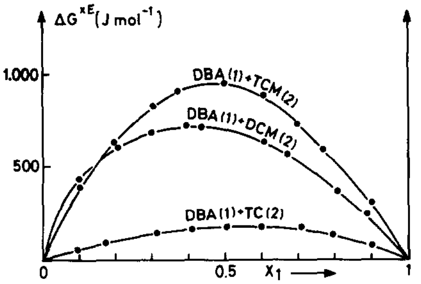

Fig. 2. Excess molar energies of activation for viscous flow for the three systems at 298.15 K; ●, experimental results; continuous curves calculated using eqn. (20).

are negative, and with dichloromethane a sigmoid curve is obtained. With trichloromethane the η^E value is more positive than the other two, showing a specific and stronger interaction.

These explanations are in agreement with the work of Reed and Taylor [13] and Meyer et al. [14] concerning the parameter ΔG^{*E}, which, when positive, implies the existence of specific interactions between the molecules. In the three systems ΔG^{*E} is positive, with greater values for DBA + TCM.

Fort and Moore [11] and Nigam and Mahl [15] have reported that specific interactions are stronger in binary mixtures where η^E and δ are large and positive, as in these systems.

In conclusion, this study indicates that the strength of specific interactions between DBA and TCM is greater than between DBA and the other two compounds, and between n-butylamine and these three halogenated hydrocarbons. The DBA + TCM system has a viscosity maximum which is not observed in the other two systems.

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