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Viscosity and excess molar volume of binary mixtures of methanol with *n*-butylamine and di-*n*-butylamine at 303.15, 313.15 and 323.15 K. Characterization in terms of ERAS model

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ABSTRACT

The excess molar volume V_m^E, viscosity deviation $\Delta\eta$, and excess Gibbs energy of activation ΔG^{*E} of viscous flow have been investigated from the density ρ and viscosity η measurements of binary mixtures of methanol with *n*-butylamine and di-*n*-butylamine over the entire range of mole fractions at 303.15, 313.15, and 323.15 K. The systems studied exhibit very strong cross association through strong O–H…N bonding between –OH and –NH– groups. As a consequence of this strong intermolecular association, both the systems have very large negative V_m^E and positive $\Delta\eta$ and ΔG^{*E} over entire range of composition and at all the temperatures of investigation. V_m^E of the studied mixtures is consistently described by the ERAS model. The values of cross association constants K_{AB} illustrate that cross-associates are more pronounced in primary amine mixtures than that in secondary amine.

1. Introduction

The increasing use of the alkylamine and alkanol in many industrial processes has greatly stimulated the need for extensive information on the thermodynamic and transport properties of their mixtures [1–11]. The systems of alkanol with alkylamine are of considerable interest from the two counts: (i) breaking of H-bonded structures and disruption of dipolar order in alkanols and amines, and (ii) formation of new H-bonded molecular complexes between alkanol and alkylamine. The primary and secondary amine and the alkanol have both a proton acceptor and a proton donor groups. Besides AB, and A_iB mixed associates, the species of type A_iB_j also exist [12]. The latter species that contain many monomers can be formed with/without the breaking of the H-bonds present in the pure liquids.

The thermodynamic and transport properties of liquid mixtures are required in several industrial computations and also in analytical sciences and pharmaceutical formulation processes. As a part of our systematic studies on the thermodynamic and transport properties of liquid mixtures of alkanol+alkylamine, in previous paper [13], the excess molar volume V_m^E, viscosity deviation $\Delta\eta$, and excess Gibbs energy of activation ΔG^{*E} of viscous flow have been reported for binary mixtures of methanol and ethanol with triethylamine and tri-*n*-butylamine at 303.15, 313.15, and 323.15 K. As an extension, in this paper we report the same properties of methanol (MeOH) with *n*-butylamine (BA) and di-*n*-butylamine (DBA) mixtures at same temperatures. The study will shed some more light on the formation of mixed species and their influence on properties of the mixtures. In addition, this work will also provide a test of the ERAS model [14,15] to characterize excess molar volumes.

2. Experimental procedure

BA and DBA from National Chemicals (Vadodara) and MeOH from Alembic Limited (Vadodara) were used after further purification and drying by the standard procedures [16]. BA and DBA were stored over sodium hydroxide pellets and fractionally distilled twice [17]. MeOH was dried over molecular sieve type 4A (Fluka) and fractionally distilled twice, just before use. The purities of the liquid samples were checked by gas–liquid chromatography and boiling point measurements. The estimated purity was better then 99 mol% for methanol and amines. The measured values of densities ρ and viscosities η are compared with the literature values in Table 1.

The measurements of the kinematic viscosity η/ρ were obtained with a modified Cannon–Fenske viscometer [33]. The viscometer has been calibrated so as to determine the two constants C and B in the equation $\eta/\rho = Ct - B/t$, obtained by measuring the flow time t with pure water, benzene and cyclohexane [16]. The flow time of a definite volume of liquid through the capillary was measured with an accurate stop watch with a resolution of 0.1 s. Four to five sets of readings for

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the flow times were taken for each pure liquid or liquid mixture and the arithmetic mean was taken for the calculations. The densities ρ of pure components and mixtures were measured with a single stem calibrated pycnometer with a capacity of 12.3 cm^3 and graduated capillary of internal diameter 0.1 cm. The pycnometer and viscometer were submerged in a thermostatic bath at predetermined temperature with a resolution of ±0.05 K. The details of the methods and techniques used to determine viscosity and density have been described in previous publication [13].

The mixtures were prepared by mixing known masses of pure liquids in air tight, narrow-mouth ground stoppered bottles taking due precautions to minimize the evaporation losses. All the mass measurements were performed on an electronic balance (Mettler AE 163, Switzerland) accurate to 0.01 mg. The possible error in the mole fraction is estimated to be less than $\pm 1 \times 10^{-4}$. The viscosity η and the density ρ were reproducible to within $\pm 2 \times 10^{-3}$ mPa s and $\pm 1 \times 10^{-4}$ g cm^{-3}, respectively.

Table 1
Comparison of densities and viscosities of pure liquids

Liquids		Density (g cm^{-3})		Viscosity (mPa s)	
		Expt.	Lit.	Expt.	Lit.
Methanol	303.15	0.7811	0.7816[a,b]	0.505	0.506[c]
	313.15	0.7715	0.7720[b], 0.77232[d]	0.448	0.448[e]
	323.15	0.7615	0.7622[b]	0.396	0.3975[e]
n-butylamine	303.15	0.7285	0.7282[f], 72849[g],	0.444	0.443[h],0.456[i]
	313.15	0.7192	0.7182[j] 0.7192[k],	0.393	0.3852[a], 0.398[l]
	323.15	0.7130	0.7127[k], 0.7132[l]	0.333	0.353[l]
Di-*n*-butylamine	303.15	0.7524	0.75248[m], 0.7513[a]	0.759	0.734[n], 0.7593[o]
	313.15	0.7428	0.74284[n], 0.7431[a]	0.657	0.64[n] , 6567[o]
	323.15	0.7360	0.73515[m]	0.557	0.55[p]

[a] Ref. [18].
[b] Ref. [19].
[c] Ref. [20].
[d] Ref. [21].
[e] Ref. [22].
[f] Ref. [23].
[g] Ref. [24]
[h] Ref. [25].
[i] Ref. [16].
[j] Ref. [26].
[k] Ref. [27].
[l] Ref. [28].
[m] Ref. [29].
[n] Ref. [30].
[o] Ref. [31].
[p] Ref. [32].

3. The ERAS model

The Extended Real Associated Solution (ERAS) model [14,15] for mixtures consisting of associating components (A, alkanol) and (B, amine), which can form cross-association complex (A_iB_j) provides a quantitative treatment which accounts for the competing effects present in the mixtures. The ERAS model combines the effect of association with non-associative intermolecular interaction occurring in liquid mixtures based on equation of state developed originally by Flory et al. [34]. In the frame work of the ERAS model, the thermodynamic excess properties of binary mixtures can be expressed as the addition of a physical, and a chemical contribution for excess molar enthalpies and excess molar volumes, as follows [15,35]

$$H^E_{chem} = x_A K_A \Delta h^*_A(\phi_{A1} - \phi^o_{A1}) + x_B K_B \Delta h^*_B(\phi_{B1} - \phi^o_{B1}) + x_A K_{AB} \Delta h^*_{AB} \frac{\phi_{B1}(1 - K_A\phi_{A1})}{(V_B/V_A)(1 - K_B\phi_{B1}) + K_{AB}\phi_{B1}} - \frac{P^*_M V^E_{chem}}{\tilde{v}^2_M} \tag{1}$$

$$H^E_{Phy} = (x_A V^*_A + x_B V^*_B)\left(\frac{\phi_A P^*_A}{\tilde{v}_A} + \frac{\phi_B P^*_B}{\tilde{v}_B} - \frac{P^*_M}{\tilde{v}_M}\right) \tag{2}$$

$$V^E_{chem} = \tilde{v}_M \left\{ x_A K_A \Delta_{V^*_A}(\phi_{A1} - \phi^o_{A1}) + x_B K_B \Delta_{V^*_B}(\phi_{B1} - \phi^o_{B1}) + x_A K_{AB} \Delta_{V^*_{AB}} \frac{\phi_{B1}(1 - K_A\phi_{A1})}{(V_B/V_A)(1 - K_B\phi_{B1}) + K_{AB}\phi_{B1}} \right\} \tag{3}$$

$$V^E_{phy} = (x_A V^*_A + x_B V^*_B)(\tilde{v}_M - \phi_A \tilde{v}_A - \phi_B \tilde{v}_B) \tag{4}$$

The association constants K_i (i=A, B and AB) in Eqs.(1) and (3) are assumed to be independent of the chain length. Their temperature dependence is given by

$$K_i = K_o \exp\left[-\left(\frac{\Delta h^*_i}{R}\right)\left(\frac{1}{T} - \frac{1}{T_o}\right)\right] \tag{5}$$

where K_o is the equilibrium constant at the standard temperature T_o (298.15 K), R the gas constant and Δh^*_i and Δv^*_i correspond to the hydrogen bonding energy and reaction volume of hydrogen bond formation. The chemical contributions H^E_{chem} and V^E_{chem} contain the cross terms K_{AB}, Δh^*_{AB}, and Δv^*_{AB}, the cross association constant, hydrogen bond energy, and reaction volume of hydrogen bond formation, respectively for O–H…N complex formation. The physical contributions H^E_{Phy} and V^E_{phy} contain the reduction and reduced parameters of the pure substances. Details to obtain all the parameters P^*_i, V^*_i, T^*_i and $\tilde{v}_i$ from pure component properties such as molar volume V, thermal expansion coefficient α, and isothermal compressibility κ_T and association parameters: association constant K_i, hydrogen bond energy Δh^*_i and hydrogen bond volume Δv^*_i can be found elsewhere [14,15,35]. ϕ_{Ai} and θ_i are hard-core volume fraction and the surface fraction of the component *i*. ϕ_{A1} and ϕ_{B1}, the hard core volume fraction of the monomeric alkanol and amine in the mixture, respectively are calculated numerically from the solution of the following coupled equations

$$\phi_A = \frac{\phi_{A1}}{(1 - K_A\phi_{A1})^2}\left[1 + \frac{V_A K_{AB}\phi_{B1}}{V_B(1 - K_B\phi_{B1})}\right] \tag{6}$$

$$\phi_B = \frac{\phi_{B1}}{(1 - K_B\phi_{B1})^2}\left[1 + \frac{K_{AB}\phi_{A1}}{(1 - K_A\phi_{A1})}\right] \tag{7}$$

Here ϕ_A and ϕ_B are the stoichiometric hard-core volume fractions of alkanol and amine, respectively. The values of unknown cross parameters: X_{AB} (the Flory's contact interaction parameter), K_{AB} (the cross-association constant), Δh^*_{AB}(the association energy per mole of hydrogen bonds due cross association) and Δv^*_{AB}(the reaction volume per mole of hydrogen bonds due to cross-association) appearing in Eqs.(1)–(4) were adjusted simultaneously to experimental H^E_m and V^E_m [15].

4. Results and discussion

The measured η and ρ for binary mixtures at number of mole fractions at 303.15, 313.15 and 323.15 K are given in Table 2. The excess molar volumes V^E_m were calculated from the molar masses M_i and the densities of pure liquids and the mixtures as

$$V^E_m = \sum_{i=A}^{B} x_i M_i (1/\rho - 1/\rho_i) \tag{8}$$

The viscosity deviations from linear dependence on mole fraction were calculated by

$$\Delta\eta = \eta - \sum_{i=A}^{B} x_i \eta_i \tag{9}$$

On the basis of the theory of absolute reaction rates [36], the excess Gibbs energy of activation ΔG^{*E} of viscous flow was calculated from

$$\Delta G^{*E} = RT[\ln \eta V/\eta_B V_B - x_A \ln \eta_A V_A/\eta_B V_B] \tag{10}$$