Journal of Molecular Liquids 191 (2014) 156–160

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Viscosities and deviations in viscosity of tert-butanol with n-butylamine, di-n-butylamine and tri-n-butylamine

Faisal Islam Chowdhury *, M.A. Saleh [1]

Department of Chemistry, University of Chittagong, Chittagong 4331, Bangladesh

ARTICLE INFO

Article history:
Received 1 September 2013
Received in revised form 8 November 2013
Accepted 13 November 2013
Available online 2 December 2013

Keywords:
Viscosity
Viscosity deviation
Dispersive force
tert-Butanol
n-Butylamine
di-n-Butylamine
tri-n-Butylamine

ABSTRACT

Viscosities of the systems of tert-butanol (TB) + n-butylamine (NBA), TB + di-n-butylamine (DBA) and TB + tri-n-butylamine (TBA) were determined at the temperatures ranging from 303.l5 to 323.15 K within the composition range $0 \leq x_2 \leq 1$, where x_2 is the mole fraction of TB. The viscosity, η increases slowly up to $x_2 \sim 0.7$, beyond which the values increase sharply until that of pure TB is reached. In all systems, deviations in viscosity, $\Delta\eta$ show negative values throughout the whole range of composition with minima in the TB-rich region. The magnitudes of the negative values of $\Delta\eta$ at the minimum are in the order TB + TBA > TB + DBA > TB + NBA. The negative $\Delta\eta$ has been accounted for dispersive force.

1. Introduction

As a continuation of our research program on molecular interactions through measurement of volumetric and viscometric properties of binary liquid systems consisting of alcohols and amines, here we present the viscosities and deviations in viscosity of tert-butanol with some alkylamines (n-butylamine, di-n-butylamine and tri-n-butylamine) at different temperatures between 303.15 and 323.15 K under the atmospheric pressure. Present literature survey shows that a number of volumetric and viscometric works are performed on binary liquid systems comprising of either different types of alcohols or amines on both aqueous and non-aqueous media, other than water + amines, and amines + aromatic and aliphatic hydrocarbons. Reinmann and Heintz [1], Papaioannov et al. [2], Pikkarainen [3] and Panayiotou [4] carried out volumetric, viscometric, enthalpic and thermodynamic properties of alcohols + amines and suggested for strong interactions between amines and alcohols through H-bond. However, no reports are available yet on tert-butanol + butylamines.

In our previous publications we have reported the volumetric and viscometric properties of aqueous solutions of n-butylamine, sec-butylamine and tert-butylamine [5] and of aqueous solutions of ethylenediamine, trimethylenediamine and N, N-dimethyltrimethylenediamine at the dilute regions [6]. Similarly, Kipkemboi and Easteal [7] have reported on volumetric and viscometric work of aqueous solutions of tert-butanol and tert-butylamine. Recently, further investigations by Oswal and Desai are made on the systems of alkylamines + 1-alkanols [8,9]. In order to get new data as well as further information about the nature of interactions we made a systematic attempt to investigate the volumetric and viscometric properties of the systems of tert-butanol with some butylamines over a wide range of temperature, 303.15 to 323.15 K and in the entire range of composition. The present aim would provide us with an opportunity of examining the effect of the number of butyl groups attached to the amine group of different types of alcohols and amines, other than water + amines, and amines + aromatic and aliphatic hydrocarbons. A volumetric part of these systems has already been published [10] in which we have suggested strong interaction.

2. Experimental

Chemicals used for the present experiments are: tert-butanol (Aldrich, 99.5%), n-butylamine (Aldrich, 99%), di-n-butylamine (Aldrich, 99%), and tri-n-butylamine (Aldrich, 99%). These were used without further purification except that each of the amines was kept over a molecular sieve (4 Å) for at least three weeks prior to use. For the purity check, densities and viscosities of pure liquids are compared with the available literature values [5,8,9,11–30], which show satisfactory agreements as in Table 1. The density was measured by a 25 ml specific gravity bottle previously calibrated by thrice-distilled water. An Ostwald viscometer (British Standard Institution) with sufficient efflux time was used so that no kinetic energy correction was necessary in the viscosity measurement. The time of flow was

* Corresponding author.
E-mail address: faisal.cubd@yahoo.com (F.I. Chowdhury).
[1] Deceased.

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http://dx.doi.org/10.1016/j.molliq.2013.11.013

Table 1
Experimental and literature values of densities, ρ/g cm^{-3} and viscosities, η/mPa · s of pure tert-butanol (TB), n-butylamine (NBA), di-n-butylamine (DBA) and tri-n-butylamine (TBA) at different temperatures.

T/K	TB		NBA		DBA		TBA	
	ρ	η	ρ	η	ρ	η	ρ	η
303.15	0.7752	3.392	0.7277	0.4434	0.7523	0.7734	0.7705	1.166
	0.77521[a]	3.378[b]	0.7273[c]	0.464[d]	0.75424[e]		0.77037[f]	
	0.7754[g]	3.381[h]	0.72865[i]	0.4442[i]	0.75248[j]		0.77046[o]	
	0.7755[k]	3.378[l]	0.7276[m]	0.458[n]	0.75194[o]			
	0.77524[p]	3.390[q]	0.7321[d]					
	0.77629[b]	3.372[g]						
	0.7753[h]	3.3873[s]						
	0.7752[l]							
	0.7757[q]							
308.15	0.7698	2.644	0.7229	0.4170	0.7481	0.7184	0.7667	1.069
	0.76997[a]	2.563[r]	0.7226[c]		0.74791[o]		0.76695[o]	
	0.76836[t]	2.47333[t]	0.7228[m]					
	0.76975[u]	2.623[u]						
313.15	0.7644	2.108	0.7180	0.3922	0.7440	0.6692	0.7626	0.9845
	0.76469[a]	2.106[h]	0.7176[c]	0.397[d]	0.74284[e]		0.76337[o]	
	0.7648[h]	2.1037[q]	0.71917[i]	0.3927[i]	0.74393[o]			
	0.7649[g]	2.063[r]	0.7192[v]	0.398[n]				
			0.7182[w]					
318.15	0.7590	1.712	0.7131	0.3695	0.7399	0.6249	0.7591	0.9086
	0.75937[a]	1.690[r]	0.7127[c]		0.7399[o]		0.75974[o]	
323.15	0.7536	1.421	0.7082	0.3491	0.7358	0.5859	0.7563	0.8422
	0.75401[a]	1.409[h]	0.7078[c]	0.355[d]	0.73591[o]		0.75604[o]	
	0.7538[h]	1.407[q]		0.353[n]				
	0.7540[q]							

[a] Kim and Marsh [11].
[b] Manukonda et al. [21].
[c] Saleh et al. [5].
[d] Weng [28].
[e] Oswal and Desai [9].
[f] Oswal and Desai [12].
[g] Nikam et al. [14].
[h] Weng [24].
[i] Oswal and Desai [13].
[j] Oswal and Desai [8].
[k] Aminabhavi and Gopalkrishna [16].
[l] Nikam et al. [25].
[m] Acevedo and Katz [15].
[n] Lee et al. [29].
[o] Oswal et al. [20].
[p] Brown and Smith [17].
[q] TRC thermodynamic tables, non-hydrocarbons [26].
[r] Bravo-Sánchez et al. [27].
[s] Saleh et al. [30].
[t] Bachu et al. [22].
[u] Nikam et al. [23].
[v] de Schaefer et al. [18].
[w] Dominguez et al. [19].

recorded by a timer accurate up-to 0.1 s. An analytical balance (Mettler Toledo B-S) weighing up-to the accuracy of ±0.0001 g was used in the measurement. Temperature was controlled by a circulator temperature controller (HAAKE DC 10) with the fluctuation of ±0.05 K. The average uncertainty in the measured viscosity was estimated to be $\pm 5 \times 10^{-4}$ mPa · s.

The viscosities of the systems are represented by a polynomial equation of the form,

$$\eta/\mathrm{mPa\cdot s} = \sum_{i=0}^{n} a_i x_2^i \quad (1)$$

where, x_2 is the mole fraction of TB, a_i is the regression coefficient and n is the degree of polynomial. The values of η fit to Eq. (1) well for n = 4. The coefficients a_i of Eq. (1) and relevant values of r^2 are listed in Table 3.

Viscosity deviation, Δη, was calculated by the following equation,

$$\Delta\eta = \ln\eta - (x_1 \ln\eta_1 + x_2 \ln\eta_2). \quad 2)$$

Here, η is the measured viscosity of a particular solution, η_1 and η_2 are the viscosities and x_1 and x_2 are the mole fractions of pure components 1 (amines) and 2 (tert-butanol), respectively. The viscosity deviation, Δη, was fitted to the Redlich–Kister polynomial equation of the form,

$$\Delta\eta/\mathrm{mPa\cdot s} = x_2(1-x_2)\sum_{i=1}^{n} A_i(1-2x_2)^{i-1} \quad (3)$$

where, A_i is the ith fitting coefficient of the Redlich–Kister polynomial equation and all the other terms have their usual significance. Using n = 4, four different A_i values and the relevant standard deviations, σ were obtained through the least squares method. All the coefficients A_i of Eq. (3) and their relevant σ values are listed in Table 4.

3. Results and discussion

The coefficient of viscosity, η, of the pure tert-butanol (TB) and amines: n-butylamine (NBA), di-n-butylamine (DBA) and tri-n-butylamine (TBA) are shown in Table 1 at different temperatures