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Viscosity of binary mixtures of 1-alkanol+cyclohexane, 2-alkanol+cyclohexane and 1-alkanol+methylcyclohexane at 303.15 K

S.L. Oswal[a,*], K.D. Prajapati[b], P. Oswal[c], N.Y. Ghael[a], S.P. Ijardar[a]

[a]*Department of Chemistry, South Gujarat University Surat 395 007, India*
[b]*Department of Chemistry, V.S. Patel College of Arts and Science, Bilimora 396 321, India*
[c]*Department of Chemistry, Govt. Meera Girls College, Udaipur 313 001, India*

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Abstract

The viscosities of 18 binary mixtures of ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol, 1-dodecanol, 2-propanol, 2-butanol, 2-pentanol and 2-octanol with cyclohexane and of 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol with methylcyclohexane have been measured at 303.15 K over the entire range of composition. The viscosity deviations $\Delta\eta$ and excess Gibbs energy of activation ΔG^{*E} of viscous flow have been analyzed in terms of change in the structure of pure component molecules and molecular interactions. The results obtained for dynamic viscosity of binary mixtures were used to test the semi-empirical relations of Grunberg–Nissan, Katti–Chaudhri, McAllister and Auslaender.

Keywords: Alkanol; Cycloalkane; Gibbs energy of activation; Liquid mixtures; Molecular interactions; Viscosity

1. Introduction

We have been engaged in systematic study of the thermodynamic, acoustic and transport properties of binary liquid mixtures of alkanol with cycloalkane. In previous papers from our laboratory, the speeds of sound, isentropic compressibilities and excess molar volumes for 1-alkanol+cyclohexane [1], 2-alkanol+cyclohexane, 1-alkanol+-methylcyclohexane [2] and cyclohexanol+cyclohexane [3] were reported. The excess thermodynamic properties were dependent on the number of carbon atoms and the position of the –OH group in the alkyl chain in the alkanol as well as on the methyl group substitution into the cyclohexane molecule. In this paper, we extend our studies to viscosity behaviour of binary mixtures to seek more in-depth understanding of molecular interactions. The results obtained for dynamic viscosities of binary mixtures were used to test the semi-empirical relations of Grunberg–Nissan [4], Katti–Chaudhri [5], McAllister [6] and Auslaender [7].

2. Experimental

2.1. Method

The viscosities η were measured with a modified suspended-level Ubbelohde viscometer [8]. The viscometer was designed so as to reduce surface tension effects to negligible values [9]. The apparatus was submerged in a thermostatic bath at 303.15 K with a resolution of ±0.05 K and allowed to attain thermal equilibrium. 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, toluene and cyclohexane [10–12]. The flow time of a definite volume of liquid through the capillary was

* Corresponding author. Tel.: +91 261 225 8384; fax +91 261 222 7312.
E-mail address: oswalsl@satyam.net.in (S.L. Oswal).

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measured with an accurate stopwatch with a precision of ±0.1 s. Four to five sets of readings for the flow times were taken for each pure liquid or liquid mixture and the arithmetic mean was taken for the calculations. The densities ρ required to convert kinematic viscosities into dynamic viscosities η were taken from our earlier work [1,2]. The mixtures were prepared by mixing known masses of pure liquids in airtight narrow mouth stoppered bottles. The possible error in the mole fractions is estimated to be $<10^{-4}$. The error in the viscosity η is estimated to less than 0.002 mPa s.

2.2. Materials

Cyclohexane (Ranbaxy, AR) and methylcyclohexane (S.D. Fine Chemical, AR) were dried over a molecular sieve 4 Å (Fluka) and fractionally distilled over Na. Ethanol (Alembic, LR) dried over a molecular sieve 4 Å (Fluka) was fractionally distilled twice just before use. 1-Propanol and 2-propanol (E. Merck, AR) were refluxed over lime for 5 h and then distilled through a 1-m column [12]. 1-Butanol and 2-butanol (BDH, AR) were washed with sulphuric acid and with sodium bisulphate solution to remove bases, alkanols and alkanones. Alkanoates were removed by boiling for 1.5 h with 20% NaOH. They were dried with anhydrous K_2CO_3, followed by calcium oxide and finally fractionally distilled through an efficient column [12]. 1-Pentanol (Merck-Schuchardt, AG), 2-pentanol (E. Merck, AG), 1-hexanol (Merck-Schuchardt, AG), 1-heptanol (Merck-Schuchardt, AG), 1-octanol (Fluka, AG) and 2-octanol (Sisco, AR), 1-nonanol (Fluka, AG), 1-decanol (Merck-Schuchardt, AG) and 1-dodacanol (Koch-Light, AG) were used as received without any purification except drying over a molecule sieve 4 Å.

The purities of all the liquid samples were checked by measuring boiling points and by gas liquid chromatography analysis at Gujarat Insecticide, Ankleswar. The estimated purities of all the samples were better then 99.5 mol% for alkanols and 99.9 mol% for cyclohexane and methylcyclohexane. The experimental densities and viscosities are compared with the literature values [12–22] in Table 1. The agreement between the two sets of data is good, except η for 1-hexanol, 1-heptanol and 1-decanol. Present values of η at 303.15 K for 1-hexanol and 1-heptanol lie in between the reported literature values

Table 1
Pure component properties at 303.15 K

Liquids	ρ (kg m^{-3})		η (mPa s)	
	Exp.	Lit.	Exp.	Lit.
Cyclohexane	769.12	769.04[a], 769.15[b]	0.8210	0.820[c], 0.8226[d]
Methylcyclohexane	760.60	760.31[c], 760.69[e]	0.6390	0.639[c]
Ethanol	780.69	780.64[f], 780.69[c]	0.9931	0.9892[d], 0.999[g]
1-Propanol	795.62	795.61[f], 795.88[h]	1.7263	1.725[c]
1-Butanol	801.90	801.91[f], 801.93[h]	2.2568	2.2266[i], 2.271[c]
1-Pentanol	807.11	807.12[f], 807.2[i]	2.8390	2.833[g], 2.844[c]
1-Hexanol	811.95	811.95[h], 812.01[c]	3.7510	3.670[g], 3.759[j]
1-Heptanol	815.32	815.50[c], 815.85[h]	4.7830	4.771[g], 4.995[k]
1-Octanol	818.34	818.30[c], 819.06[h]	6.2071	6.215[c]
1-Nonanol	822.40	821.03[h]	7.3761	7.375[l]
1-Decanol	822.92	822.85[f], 822.90[h]	8.8427	9.652[k]
1-Dodecanol	826.77	826.20[f], 826.58[h]	16.116*	16.134*[,m]
2-Propanol	776.90	776.75[f], 776.90[g]	1.7770	1.778[n]
2-Butanol	798.51	798.25[f], 798.60[c]	2.7413	2.743[l]
2-Pentanol	801.99	801.70[g], 802.01[o]	2.8870	2.884[c]
2-Octanol	813.00	813.10[c]	4.8040	4.803[l]

[a] Ref. [13].
[b] Ref. [14].
[c] Ref. [12].
[d] Ref. [15].
[e] Ref. [16].
[f] Ref. [17].
[g] Ref. [18].
[h] Ref. [19].
[i] Ref. [20].
[j] Ref. [21].
[k] Ref. [22].
[l] Ref. [23].
[m] Ref. [24].
[n] Ref. [25].
[o] Ref. [26].
* At 298.15 K.