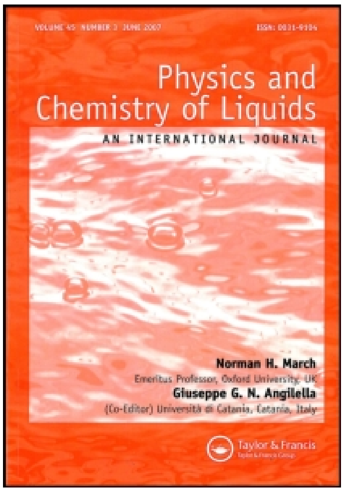

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Study of densities, viscosity deviations, and isentropic compressibilities of ternary liquid mixtures of water and ethane-1,2-diol with some monoalcohols at various temperatures

Bhoj Bahadur Gurung[a]; Mahendra Nath Roy[a]
[a] Department of Chemistry, North Bengal University, Darjeeling-734 013, India

To cite this Article Gurung, Bhoj Bahadur and Roy, Mahendra Nath(2007) 'Study of densities, viscosity deviations, and isentropic compressibilities of ternary liquid mixtures of water and ethane-1,2-diol with some monoalcohols at various temperatures', Physics and Chemistry of Liquids, 45: 3, 331 — 343

To link to this Article: DOI: 10.1080/00319100600574143

URL: http://dx.doi.org/10.1080/00319100600574143

Physics and Chemistry of Liquids
Vol. 45, No. 3, June 2007, 331–343

Study of densities, viscosity deviations, and isentropic compressibilities of ternary liquid mixtures of water and ethane-1,2-diol with some monoalcohols at various temperatures

BHOJ BAHADUR GURUNG and MAHENDRA NATH ROY*

Department of Chemistry, North Bengal University, Darjeeling-734 013, India

(*Received 9 January 2006; accepted 13 January 2006*)

Excess molar volume (V^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 ternary liquid mixture of water + ethane-1,2-diol + methanol, water + ethane 1,2-diol + ethanol, and water + ethane-1,2-diol + 1-propanol over the entire range of composition at 298.15, 308.15 and 318.15 K. The speeds of sound are also observed for these mixtures and thus, the isentropic compressibility (K_S) and excess isentropic compressibility (K_S^E) calculated at 298.15 K. The results are discussed in terms of specific interactions and nature of liquid mixtures. The system studied here exhibits a very strong cross association through hydrogen bonding.

Keywords: Densities; Viscosities; Excess molar volume; Viscosity deviation; Excess Gibbs energy of activation of viscous flow; Ethane-1,2-diol; Monoalcohol; Sound speed; Isentropic compressibility; Excess isentropic compressibility; Specific interactions

1. Introduction

A knowledge of the thermodynamic behavior of liquid mixtures has been the main aim during recent years. The investigated mixtures were chosen in order to obtain information about the molecular interactions between their components [1–4]. This is the case for the systems studied in this research, which contain water, ethane-1,2-diol, and some monoalcohols.

Rheology is a branch of science [5] that studies material deformation and flow, and is increasingly applied to analyze the viscous behavior of many pharmaceutical products [6] and to establish their stability and even their bio-availability, since it has been firmly established that viscosity influences the drug absorption rate in the body.

The liquids were selected on the basis of their industrial use [7]. Ethane-1,2-diol and monoalcohols are important liquids which find a variety of applications in pharmaceuticals, cosmetics etc. In our systematic investigation of the thermodynamics, acoustic, and transport properties of ternary mixtures, we have reported viscosities (η),

---

*Corresponding author. Tel.: +91-0353-2581140. Fax: +91-0353-258154. Email: mahendraroy2002@yahoo.co.in

Physics and Chemistry of Liquids
ISSN 0031-9104 print/ISSN 1029-0451 online
DOI: 10.1080/00319100600574143

densities (ρ), speeds of sound (u), isentropic compressibilities and excess molar volumes for the ternary liquid mixtures of water + ethane-1,2 diol + methanol, water + ethane-1,2-diol + ethanol, and water + ethane-1,2-diol + 1-propanol. Viscosity and density of these ternary liquid mixtures are useful in understanding molecular interactions between the components of the mixture which may be used to develop new theoretical models and also for engineering applications [8]. In our previous investigation of the properties, we have reported viscosities, densities and speeds of sound of various polar mixtures [3,9,10].

The present work contributes to the study of various thermodynamics and transport properties viz. excess molar volumes (V^E), viscosity deviations ($\Delta\eta$), excess Gibbs energy of activation (ΔG^{*E}) of viscous flow, Grunberg and Nissan parameters (d) and isentropic compressibility (K_S) of various ternary mixtures.

To the best of our knowledge, the properties of mixtures of this liquid have not been reported earlier.

2. Experimental

2.1. *Source and purity of samples*

Ethane-1,2-diol ($C_2H_6O_2$), methanol (CH_3OH), ethanol (C_2H_5OH), and 1-propanol (C_3H_7OH) were obtained from Merck and A.R. These were further purified by standard methods [14]. Triply distilled water was used. The purity of the liquids was checked by measuring their densities, viscosities, and sound velocities at 298.15 K which were in good agreement with the literature values. The purity of the solvents were $>99.5\%$.

2.2. *Method*

The speeds of sound (u) in pure liquids and in ternary mixtures were measured with multi-frequency ultrasonic interferometer supplied by Mittal Enterprise, New Delhi. In the present work, a steel cell fitted with a quartz crystal of 2 MHz [11] frequency was employed. Densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 298.15, 308.15, 318.15 K with triply distilled water and benzene. The pycnometer with the test solution was equilibrated in a thermostatic water bath maintained at ± 0.01 K of the desired temperature by means of a mercury in glass thermoregulator and the temperature was determined with a calibrated thermometer and a Muller bridge [12]. The viscosities were measured by means of a suspended Ubbelohde type viscometer [13] which was calibrated at the desired temperatures with water and methanol. The solutions were prepared by mixing known volumes of pure liquids in air-tight, narrow-mouth ground stoppered bottles taking due precautions to minimize the evaporation losses. The masses were determined by using a Mettler electronic analytical balance (AG285, Switzerland) accurate to 0.0002 g. The uncertainties in the liquid composition, density, viscosity, and speeds of sound measurements were estimated to be 1×10^{-4}, $2 \times 10^{-4}\,g\,cm^{-3}$, $3 \times 10^{-4}\,m\,Pa\,s$, and $0.2\,m\,s^{-1}$ respectively.

Table 1. Comparison of experimental densities (ρ), viscosities (η), and ultrasonic speeds (u) of pure liquids with literature values.

		$\rho \times 10^{-3}$ (kg m^{-3})		$\eta \times 10^{3}$ (kg m^{-1}s^{-1})		u (m s^{-1})	
Liquids	T(K)	Expt	Lit.	Expt	Lit.	Expt	Lit.
Water	298.15	0.99707	0.9971 [15]	0.8904	0.890 [15]	1498.2	1497.4 [21]
	308.15	0.99406	0.9940 [15]	0.7194	0.719 [15]		
	318.15	0.99025	0.9902 [15]	0.596	0.597 [15]		
Ethane-1,2-diol	298.15	1.10998	1.1100 [16,21]	16.47362	16.472 [16,21]	1660.7	1662.0 [21]
	308.15	1.10299	1.1029 [16,21]	10.47212	10.470 [16,21]		
	318.15	1.09764	1.0956 [16,21]	7.69443	7.694 [16,21]		
Methanol	298.15	0.78664	0.78656 [17,20]	0.54230	0.5422 [17,20]	1105.1	1103.0 [21]
	308.15	0.77728	0.7772 [17,20]	0.47424	0.4742 [17,20]		
	318.15	0.76775	0.7677 [17,20]	0.41739	0.4174 [17,20]		
Ethanol	298.15	0.78514	0.7851 [18,20]	1.08805	1.088 [18,20]	1144.9	–
	308.15	0.77658	0.7765 [18,20]	0.90421	0.904 [18,20]		
	318.15	0.76781	0.7677 [18,20]	0.76304	0.763 [18,20]		
Propanol	298.15	0.79958	0.79954 [19,20]	1.93968	1.9324 [19,20]	1207.2	1206.5 [19,20]
	308.15	0.79166	0.79162 [19,20]	1.56776	1.560 [19,20]		
	318.15	0.78456	–	1.14998	–		

3. Results and discussion

The comparison of the experimentally determined densities, viscosities at 298.15, 308.15, and 318.15 K, and sound velocities at 298.15 K of the pure components with the literature values [15–21] have been presented in table 1.

The experimentally determined density, viscosity, and calculated excess thermodynamic properties for ternary liquid mixtures are listed in table 2. Representatives plots of η, $\Delta\eta$, V^E, ΔG^{*E}, and K_S^E against mole fraction of water (x_1) at 298.15 K are shown in figures 1–5, since for other temperature the curves are similar.

3.1. *Viscosity deviations*

In table 2, the measured η and calculated $\Delta\eta$ of the ternary mixtures are shown along with the mole fraction of water (x_1) and ethane-1,2-diol (x_2) at the three temperatures.

The viscosity deviations from linear dependence on mole fraction were calculated [22] by,

$$\Delta\eta = \eta - \sum_{i=1}^{n} x_i \eta_i \tag{1}$$

where, η is the viscosity of the mixture and x_i, η_i is the mole fraction and viscosity of pure component, i respectively.

It is observed that $\Delta\eta$ values increases to attain a maximum and then decreases over the entire range of composition for each temperature (figure 2). This trend is observed for all the ternary mixtures examined here. The values become more and more positive as the temperature rises from 298.15 to 318.18 K. The positive value of $\Delta\eta$ support the existence of the specific interactions [23,18,24] between the unlike molecules.

For (1) + (2) + methanol, the maxima of $\Delta\eta$ is observed at $x_1 = 0.89$, for (1) + (2) + ethanol at $x_1 = 0.92$, and for (1) + (2) + 1-propanol at $x_1 = 0.93$ for all

Table 2. Densities (ρ), viscosities (η), excess molar volumes (V^E), Gibbs energy of activation (ΔG^{*E}) of viscous flow, interactions parameters (d), and viscosity deviation ($\Delta\eta$) for water (1) + ethane-1,2-diol (2) + methanol, ethanol, and 1-propanol at 298.15, 308.15 and 318.15 K.

Mole fraction of water (x_1)	Mole fraction of ethane-1,2-diol (x_2)	$\rho \times 10^{-3}$ (kgm^{-3})	$\eta \times 10^3$ (kgm^{-1}s^{-1})	$V^E \times 10^3$ (m^{3}mol^{-1})	ΔG^{*E} (J mol^{-1})	d	$\Delta\eta \times 10^3$ (kgm^{-1}s^{-1})
Water (1) + ethane-1,2-diol (2) + methanol							
298.15 K							
0	0.29693	0.91470	1.99757	−0.46412	720.91933	–	−3.27522
0.20125	0.23344	0.92896	2.12681	−0.71701	1279.13480	17.69101	−2.20455
0.36081	0.18311	0.94147	2.31497	−0.83732	1776.10648	21.48512	−1.27011
0.49042	0.14222	0.95227	2.34765	−0.86844	2018.48838	28.75390	−0.63112
0.59779	0.10835	0.96148	2.18441	−0.84101	1991.38454	38.20262	−0.29214
0.68819	0.07983	0.96959	2.02624	−0.78402	1915.170859	55.28743	−0.02740
0.76536	0.05549	0.97666	1.78830	−0.70712	1684.88063	82.03357	0.09554
0.81399	0.03447	0.98221	1.58294	−0.60502	1440.21583	141.25689	0.20187
0.89010	0.01613	0.98664	1.34916	−0.49132	1084.85606	307.40161	0.24005
0.94125	0	0.98699	1.10039	−0.31205	614.79326	–	0.23044
1.00000	0	0.99707	0.89040	0	0	–	0
308.15 K							
0	0.29693	0.90956	1.63445	−0.66112	805.38420	–	−1.80846
0.20125	0.23344	0.92350	1.70923	−0.85766	1329.56768	19.91352	−1.14827
0.36081	0.18311	0.93652	1.84429	−0.96310	1813.45279	21.27794	−0.54912
0.49042	0.14222	0.94782	1.87559	−0.98087	2064.8945	28.51184	−0.14078
0.59779	0.10835	0.95720	1.74204	−0.93115	2027.76717	37.66037	0.03798
0.68819	0.07983	0.96560	1.62360	−0.85810	1957.06212	54.69905	0.18251
0.76536	0.05549	0.97289	1.43721	−0.76545	1723.15866	81.22125	0.22055
0.81399	0.03447	0.97915	1.27898	−0.66005	1479.61422	140.66394	0.25614
0.89010	0.01613	0.98286	1.11393	−0.52812	1167.45246	320.81800	0.26021
0.94125	0	0.98455	0.93606	−0.34503	752.71494		0.23106
1.00000	0	0.99406	0.71940	0	0	–	0
318.15 K							
0	0.29693	0.90411	1.35988	−0.83101	813.73667	–	−1.21828
0.20125	0.23344	0.91846	1.45387	−1.00971	1417.12126	18.67391	−0.69822
0.36081	0.18311	0.93217	1.53852	−1.11006	1867.14629	21.32097	−0.27581
0.49042	0.14222	0.94476	1.57187	−1.14125	2138.52520	28.76058	0.03195
0.59779	0.10835	0.95575	1.44264	−1.11025	2066.86750	37.38858	0.13001
0.68819	0.07983	0.96437	1.34133	−1.01401	1989.14140	54.12886	0.22010
0.76536	0.05549	0.97049	1.20811	−0.86732	1798.47426	82.58307	0.25021

0.81399	0.03447	0.97689	1.08745	−0.74521	1578.72382	146.41136	0.27061
0.89010	0.01613	0.97978	0.96463	−0.56405	1308.5924	351.88657	0.27088
0.94125	0	0.98109	0.81807	−0.37325	906.93254	–	0.23256
1.00000	0	0.99026	0.59600	0	0	–	0
Water (1) + ethane 1,2-diol (2) + ethanol							
298.15 K							
0	0.37783	0.91083	3.56697	−0.41845	380.77010	–	−3.33421
0.24310	0.28199	0.92474	3.12739	−0.70440	1048.99560	10.38940	−2.25118
0.41901	0.21264	0.93725	3.00454	−0.83334	1632.95151	15.90263	−1.27228
0.55220	0.16013	0.94806	2.80252	−0.85564	1888.59731	24.43785	−0.64008
0.65654	0.11900	0.95738	2.41869	−0.81704	1844.05730	34.61152	−0.37048
0.74051	0.08590	0.96553	2.10754	−0.74732	1732.96578	52.18853	−0.15577
0.80953	0.05869	0.97251	1.79958	−0.65658	1508.47676	80.82641	−0.03146
0.86726	0.03593	0.97881	1.60019	−0.56232	1338.15418	152.96767	0.13075
0.91627	0.01661	0.98401	1.38094	−0.45611	1060.62018	369.5337	0.21843
0.95839	0	0.98560	1.10848	−0.29501	585.19882	–	0.20986
1.00000	0	0.99707	0.89040	0	0	–	0
308.15 K							
0	0.37783	0.90524	2.68819	−0.60101	394.65607	–	−1.83106
0.24310	0.28199	0.91908	2.40732	−0.83314	1094.98909	10.56769	−1.15001
0.41901	0.21264	0.93176	2.31123	−0.93250	1637.93848	15.64411	−0.55006
0.55220	0.16013	0.94334	2.18552	−0.95389	1936.65108	24.15345	−0.14875
0.65654	0.11900	0.95296	1.88388	−0.89701	1867.49864	33.78925	−0.03758
0.74051	0.08590	0.96138	1.66572	−0.81121	1773.99394	51.61752	0.07648
0.80953	0.05869	0.96891	1.43802	−0.71412	1555.92148	80.71840	0.12187
0.86726	0.03593	0.97543	1.28085	−0.60612	1373.02040	151.82249	0.19314
0.91627	0.01661	0.98029	1.11946	−0.47732	1110.40185	374.85924	0.22565
0.95839	0	0.98260	0.93895	−0.31504	722.16454	–	0.21186
1.00000	0	0.99406	0.71940	0	0	–	0
318.15 K							
0	0.37783	0.89962	2.12960	−0.77730	371.63570	–	−1.25233
0.24310	0.28199	0.91399	1.97635	−0.99220	1167.22148	11.05933	−0.70066
0.41901	0.21264	0.92775	1.89041	−1.10098	1700.11398	15.82461	−0.27653
0.55220	0.16013	0.94058	1.77488	−1.13257	1975.02648	24.00011	−0.00584
0.65654	0.11900	0.95086	1.53876	−1.06302	1908.31704	33.55912	0.06055

(*continued*)

Table 2. Continued.

Mole fraction of water (x_1)	Mole fraction of ethane-1,2-diol (x_2)	$\rho \times 10^{-3}$ (kgm^{-3})	$\eta \times 10^{3}$ (kgm^{-1}s^{-1})	$V^E \times 10^3$ (m^{3}mol^{-1})	ΔG^{*E} (J mol^{-1})	d	$\Delta\eta \times 10^3$ (kgm^{-1}s^{-1})
0.74051	0.08590	0.95945	1.35820	−0.95124	1799.70709	50.81977	0.12345
0.89010	0.01613	0.97978	0.96463	−0.56405	1308.5924	351.88657	0.27088
0.94125	0	0.98109	0.81807	−0.37325	906.93254	–	0.23256
1.00000	0	0.99026	0.59600	0	0	–	0
Water (1) + ethane-1,2-diol (2) + 1-propanol							
298.15 K							
0	0.44203	0.91960	4.97192	−0.35625	2.32850	–	−3.39220
0.27341	0.31716	0.93291	3.96902	−0.69250	941.93126	7.05350	−2.29336
0.45843	0.23265	0.94443	3.48948	−0.81935	1552.54048	13.55001	−1.35050
0.59195	0.17166	0.95460	3.07220	−0.84733	1847.28747	23.04513	−0.74125
0.69285	0.12558	0.96333	2.54730	−0.81229	1799.3841	34.38759	−0.49056
0.77179	0.08953	0.97073	2.11686	−0.74135	1632.04139	51.85844	−0.31424
0.83522	0.06055	0.97709	1.81609	−0.65433	1459.10388	86.32559	−0.12724
0.88731	0.03676	0.98262	1.60514	−0.56084	1300.44857	170.52862	0.06223
0.93085	0.01687	0.96878	1.39411	−0.45225	1057.36129	436.56056	0.18598
0.96780	0	0.98762	1.10989	−0.29355	573.64575	–	0.18570
1.00000	0	0.99707	0.89040	0	0		0
308.15 K							
0	0.44203	0.91402	3.67039	−0.52805	40.17761		−1.83336

0.27341	0.31716	0.92731	2.99794	−0.80909	993.19384	7.29452	−1.16198
0.45843	0.23265	0.93940	2.66833	−0.92484	1604.68756	13.56883	−0.58212
0.59195	0.17166	0.95027	2.37968	−0.94851	1904.69620	22.99942	−0.21442
0.69285	0.12558	0.95916	1.98952	−0.89065	1848.98043	34.14452	−0.10866
0.77179	0.08953	0.96701	1.67581	−0.80955	1688.28789	51.96625	−0.03442
0.83522	0.06055	0.97373	1.46391	−0.71122	1537.92542	88.63395	0.06556
0.88731	0.03676	0.97929	1.29579	−0.60058	1363.71786	173.73409	0.15346
0.93085	0.01687	0.98337	1.12109	−0.47466	1091.16953	435.73864	0.19283
0.96780	0	0.98469	0.94006	−0.31244	713.02579	–	0.19334
1.00000	0	0.99406	0.71940	0	0	–	0
318.15 K							
0	0.44203	0.90955	2.75457	−0.70445	90.0749	–	−1.28825
0.27341	0.31716	0.92308	2.31963	−0.95303	1072.66058	7.84557	−0.75452
0.45843	0.23265	0.93593	2.07145	−1.07006	1652.91411	13.58418	−0.34714
0.59195	0.17166	0.94812	1.85600	−1.11458	1929.55597	22.54220	−0.08947
0.69285	0.12558	0.95793	1.57359	−1.05621	1875.13960	33.56327	−0.01442
0.77179	0.08953	0.96592	1.35940	−0.95068	1751.11126	52.65067	0.05104
0.83522	0.06055	0.97122	1.21703	−0.81212	1642.74673	93.08035	0.13348
0.88731	0.03676	0.97722	1.10035	−0.67539	1503.70099	189.19690	0.20135
0.93085	0.01687	0.98076	0.96084	−0.52344	1234.59604	487.27481	0.21614
0.96780	0	0.98193	0.81900	−0.34666	876.46701	–	0.20516
1.00000	0	0.99025	0.59600	0	0	–	0

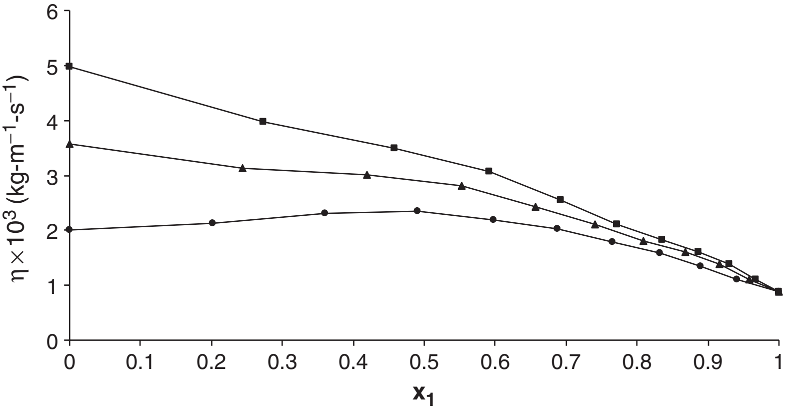

Figure 1. Viscosity, η, for water + ethane-1,2-diol + alkanol at 298.15 k. Experimental points: Alkanol : CH_3OH (●), C_2H_5OH (▲), and C_3H_7OH (■).

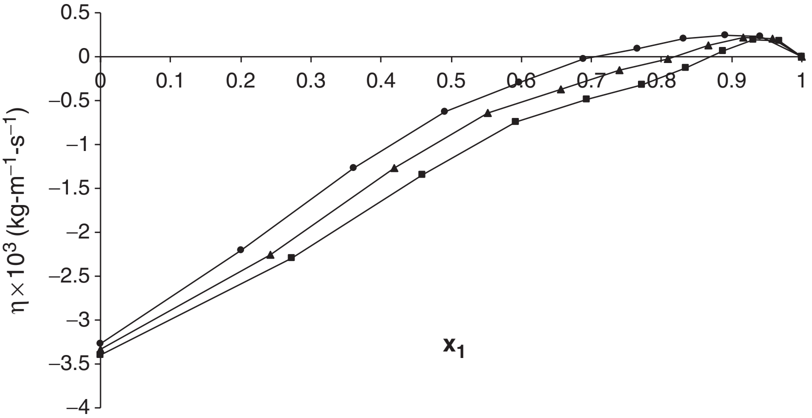

Figure 2. Viscosity deviation, $\Delta\eta$, in water + ethane-1,2-diol + alkanol at 298.15. Experimental points: Alkanol : CH_3OH (●), C_2H_5OH (▲), and C_3H_7OH (■).

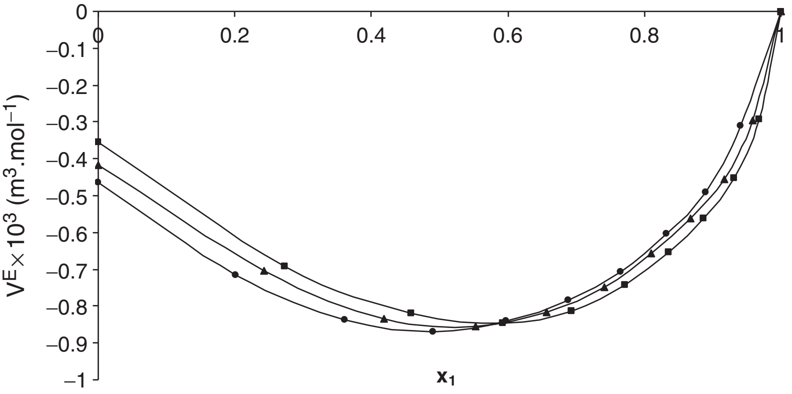

Figure 3. Excess molar volume, V^E, of water + ethane-1,2-diol + alkanol at 298.15 K. Experimental points: Alkanol : CH_3OH (●), C_2H_5OH (▲), and C_3H_7OH (■).

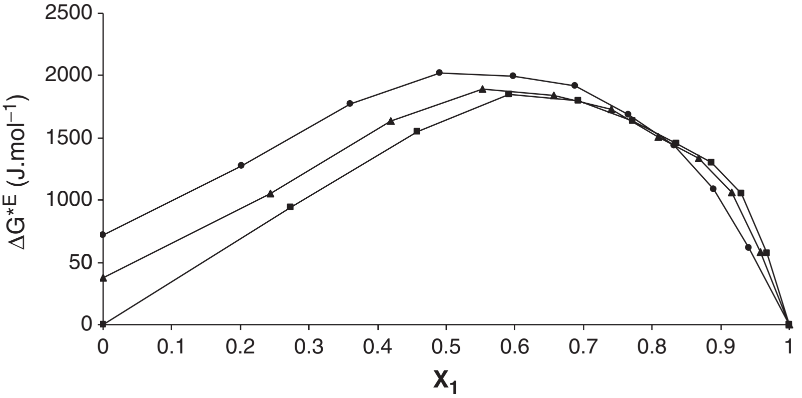

Figure 4. Excess Gibbs energy, ΔG^{*E}, of activation of viscous flow for water + ethane-1,2-diol + alkanol at 298.15 K. Experimental points: Alkanol : CH_3OH (●), C_2H_5OH (▲), and C_3H_7OH (■).

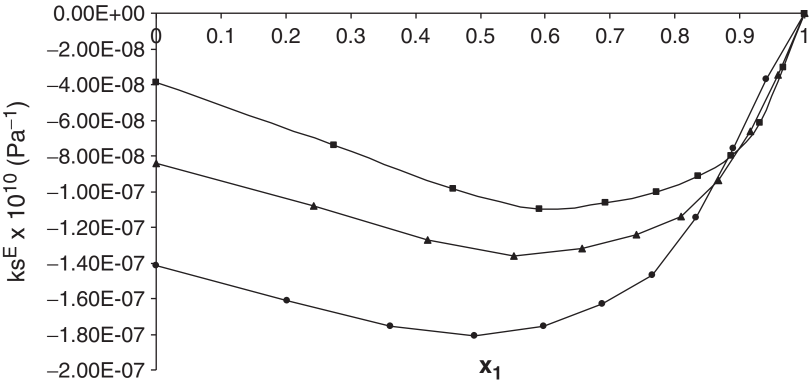

Figure 5. Excess isentropic compressibility, K_s^E for water + ethane-1,2-diol + alkanol at 298.15 K. Experimental points: Alkanol : CH_3OH (●), C_2H_5OH (▲), and C_3H_7OH (■).

the temperatures. From the value of $\Delta\eta$ as shown in table 2, the positive values of $\Delta\eta$ follows the trend:

$$(1) + (2) + \text{methanol} > \text{ethanol} > \text{1-propanol}.$$

Here, dispersion and dipolar interactions are operating between water, ethane-1,2-diol, and $CH_3OH/C_2H_5OH/C_3H_7OH$ molecules resulting in negative $\Delta\eta$ but with the increase in temperature and mole fraction of water, the hydrogen bonding interactions come into play leading to the formation of complex species between unlike molecules thereby resulting in positive $\Delta\eta$ [25–27].

3.2. *Excess molar volume*

The excess molar volumes, V^E, are calculated from density data according to the following equation [28]:

$$V^E = \sum_{i=1}^{n} x_i M_i (1/\rho - 1/\rho_i) \tag{2}$$

where, M_i, ρ_i and ρ are the molar mass, density of the ith component and density of the mixture respectively.

It can be seen from table 2 and figure 3 that V^E is negative for all the water (1) + ethane-1,2-diol (2) + monoalcohol mixtures at all temperatures and over the entire range of composition. The negative values of V^E increases with rising temperature from 298.15 to 318.15 K. The magnitude of the negative values of V^E decreases with increasing chain length of the monoalcohol in water (1) + ethane-1,2-diol (2) + monoalcohol mixture series. The values of V^E at first decreases to minima and then increases over the entire range of compositions for all ternary mixtures.

For (1) + (2) + methanol mixture, the minima is observed at $x_1 = 0.49$, for (1) + (2) + ethanol, the minima is found at $x_1 = 0.55$, and for (1) + (2) + 1-propanol, the minima observed at $x_1 = 0.59$.

From the values of V^E as shown in table 2, the observed trend is as follows:

$$(1) + (2) + \text{methanol} < \text{ethanol} < \text{1-propanol}.$$

The negative V^E indicates the presence of strong molecular interactions between the components of the mixture. Volume changes for a mixed system result from changes in the free volume of the liquids, since the bond lengths and bond distances in the molecules themselves do not change. The optimum packing condition is directly related to differences in molecular sizes and intermolecular attractions, in particular when hydrogen bonding occurs between unlike molecules creating association complexes, as well as being effected by the breaking of interactions between like molecules [24].

To account for temperature effect on V^E, the following considerations are important. It is known that pure monoalcohol can form either ring or chain-like complexes, and while the fraction of ring complexes increases with the number of CH_2 groups in the monoalcohol, the degree of association decreases [23,30]. The associated rings break down to chains with increasing temperature, which is then followed by a total break down of the associated species. The degree of association of water and ethane-1,2-diol also decreases with increasing temperature. The formation of mixed complexes is an exothermic process and hence, the equilibrium constant decreases with increasing temperature. Thus, the number of the mixed associated species is influenced by two opposing effects with rise of temperature: (i) The number of species which are able to form mixed complexes increases with temperature, while the self -associated monoalcohol rings, water and also ethane-1,2-diol break down. (ii) The equilibrium constant of the association resulting mixed complexes decreases with increasing temperature. The first effect seems to be dominant in presently investigated mixtures, i.e., the number of hydrogen bonds increases with temperature so the contraction of mixture increases.

3.3. *Excess Gibbs energy of activation of viscous flow*

On the basis of the theory of absolute reaction rates [22], the excess Gibbs energy, ΔG^{*E}, of viscous flow was calculated from

$$\Delta G^{*E} = \mathrm{RT}\ln(\eta M/\rho) - \mathrm{RT}\sum_{i=1}^{n} x_i \ln(\eta_i M_i/\rho_i), \tag{3}$$

where n stands for the number of components of the mixture and M_i are the molar mass of the mixture and of the pure components i.

The values of ΔG^{*E} are positive for all the ternary mixtures and decreases from methanol to propanol (figure 4 and table 2), and attain a maximum value and then decreases over the entire range of composition. With the increase in temperature, the values of ΔG^{*E} show an increasing trend. The values of ΔG^{*E} decreases with the chain length of the monoalcohol.

The positive values of ΔG^{*E} over the entire range of mole fraction indicate the presence of strong interactions [23,] between the mixing components accompanied by the complex formation.

3.4. *Grunberg and Nissan interactions parameter*

Grunberg and Nissan [31] suggested a logarithmic relation between the viscosity of liquid mixture and that of its pure components,

$$\ln \eta = \sum_{i=1}^{n} x_i \ln \eta_i + \mathrm{d} \prod_{i=1}^{n} x_i \tag{4}$$

where *d* is a constant, regarded as a measure of the strength of molecular interactions between the mixing components.

The positive value of Grunberg and Nissan parameter (*d*) gives an indication of specific hydrogen bonding interaction between unlike molecules [32,33]. This parameter (*d*) has been calculated (vide eq. 4) for the ternary liquid mixtures under discussion as a function of the composition of the mixtures. It is seen from table 2 that the values of d are positive over the entire range of composition for all the ternary liquid mixtures at all temperatures. The observed value of *d* indicates the presence of strong molecular interactions between the mixing components [32, 33].

3.5. *Isentropic compressibility*

Table 3 contains the sound velocity (*u*), isentropic compressibility (K_S) and excess isentropic compressibility (K_S^E) data for the mixtures at 298.15 K.

Isentropic compressibility (K_S) and excess isentropic compressibility (K_S^E) are obtained using the following equation [29]:

$$K_\mathrm{S} = 1/u^2 \cdot \rho \tag{5}$$

$$K_\mathrm{S}^\mathrm{E} = K_\mathrm{S} - \sum_{i=1}^{n} x_i K_{\mathrm{S},i} \tag{6}$$

where, $K_{\mathrm{S},i}$ gives the isentropic compressibility for the *i*th component of the mixture.

As can be seen from table 3 and figure 5 that K_S^E is negative and such magnitude of negative values decreases with increasing number of carbon atoms of monoalcohol over the whole composition range for all the mixtures. However, the values of K_S^E decreases to reach a minima at $x_1 = 0.49$, 0.55 and 0.59 for (1) + (2) + methanol, + ethanol, and + 1-propanol, respectively and thereafter increases for every mixture. The trend follows the sequence:

$$(1) + (2) + \text{methanol} < \text{ethanol} < \text{1-propanol}.$$

Table 3. Speeds of sound (u), isentropic compressibility (K_S), and excess isentropic compressibility (K_S^E) of ternary liquid mixtures of various compositions (mole fraction) at 298.15 K.

x_1	u (ms^{-1})	$K_S \times 10^{10}$ (Pa^{-1})	$K_S^E \times 10^{10}$ (Pa^{-1})	x_1	u ($m\,s^{-1}$)	$K_S \times 10^{10}$ (Pa^{-1})	$K_S^E \times 10^{10}$ (Pa^{-1})
Water (1) + ethane-1,2-diol (2) + methanol				Water (1) + ethane-1,2-diol(2) + ethanol			
0	1261.26	46.87243	−1.42	0	1305.72	6.43967	−0.84
0.20125	1347.07	5.93228	−1.61	0.24310	1396.89	5.54184	−1.08
0.36081	1428.55	4.20481	−1.75	0.41901	1479.25	4.87599	−1.27
0.49042	1499.42	4.67085	−1.81	0.55220	1544.33	4.42264	−1.36
0.59779	1550.40	4.32688	−1.76	0.65654	1580.53	4.1813	−1.32
0.68819	1581.90	4.12151	−1.63	0.74051	1602.50	4.03309	−1.24
0.76536	1600.12	3.9990	−1.47	0.80953	1613.36	3.95044	−1.14
0.81399	1580.98	4.07328	−1.15	0.86726	1598.63	3.99765	−0.94
0.89010	1544.20	4.25043	−0.755	0.91627	1566.91	4.13914	−0.66
0.94125	1509.34	4.44746	−0.37	0.95839	1528.71	4.34161	−0.35
1.00000	1498.20	4.46822	0	1.00000	1498.20	4.46822	0
Water (1) + ethane-1,2-diol (2) + 1-propanol							
0	1363.82	5.84636	−0.39				
0.27341	1435.34	5.20294	−0.74				
0.45843	1538.32	4.47445	−0.99				
0.59195	1591.98	4.13337	−1.10				
0.69285	1610.91	4.00023	−1.06				
0.77179	1618.78	3.93120	−1.00				
0.83522	1617.83	3.91023	−0.91				
0.88731	1608.20	3.93490	−0.80				
0.93085	1582.44	4.04692	−0.62				
0.96780	1535.64	4.29368	−0.31				
1.00000	1498.20	4.46822	0				

These results can be explained in terms of molecular interactions [20, 29] between unlike molecules. It appears from the sign and magnitude of K_S^E that specific interactions exist between mixing components [34]. The exaltation of polarization supported the specific interactions between components in the mixtures [34, 35]. This graded behavior is consistent with the present viscosity results.

4. Conclusions

The investigated mixtures were chosen in order to obtain information about the molecular interactions between their components. In this work, the mixed systems have been studied in terms of excess molar volumes, viscosity deviations, excess Gibbs energy of activation of viscous flow, Grunberg and Nissan parameter, and excess isentropic compressibility. The measured data and calculated values of all systems are in good accordance, and are theoretically and statistically satisfying.

Acknowledgments

The authors are thankful to the Departmental Special Assistance scheme under the University Grants commission, New Delhi (540/6/DRS/2002) for the financial support and also to the Head of Chemistry Department, University of North Bengal, Darjeeling for providing various facilities.

References

[1] C. Reichardt, *Solvents and Solvent effects in Organic Chemistry*, VCH: Weinheim, Germany (1998), Chaps. 5&7.

[2] R.W. Gurney. *Ionic process in solutions*, McGraw Hill, New York (1954).

[3] B.B. Gurung, M.N. Roy. *J.T.R. Chem.*, **11**(2), 7–17 (2005).

[4] C.R. Reid, B.E. Poling. *The properties of gases and liquids*, McGraw Hill, New York (1998), Chap. 1.

[5] J.V. Herraez, R. Belda. *J. Soln. Chem.*, **33**, 117–119 (2004).

[6] J. Swarbrik, J.C. Boyland. *Encyclopedia of Pharmaceutical Technology*, Marcel Dekker Inc., New York (1993).

[7] R. Jasinki. *High Energy Battery*, Plenum, New York (1967).

[8] C.G. Janz, R.P.T. Tomkins, Non-Aqueous Electrolytes Handbook, Vol. 2, Academic, New York (1973).

[9] M.N. Roy, A. Jha, A. Choudhury. *Chem. Eng. Data.*, **49**, 291–296 (2004).

[10] M.N. Roy, A. Sinha, B. Sinha. *J. of Solution Chemistry*, **34**, 1311–1325 (2005).

[11] M.N. Roy, R. Dey, A. Jha. *J. Chem. Eng. Data*, **46**, 1327–1329 (2001).

[12] M.N. Roy, D.K. Hazra. *Ind. J. Chem. Technol.*, **1**, 93–97 (1994).

[13] R.H. Stokes, R. Mills. *Viscosity of Electrolytes and Related Properties*, New York, Pergamon (1965).

[14] D.D. Perrin, W.L.F. Armarego. *Purification of Laboratory Chemicals*, 3rd edn, Great Britain (1988).

[15] J.A Riddick, W.B. Bunger, T.K. Sakano. *Organic Solvents: Physical Properties and Methods of Purification*, Wiley, New York (1986).

[16] U.R. Kapadi, D.G. Hundiwale, N.B. Patil, P.R. Patil, M.K. Lande. *J. Ind. Chem. Soc.*, **77**, 319–321 (2000).

[17] H. Doe, T. Kitagawa, K. Sasabe. *J. Phys. Chem.*, **88**, 3341–3345 (1984).

[18] K. Hsu-Chen, T. Chein-Hsiun. *J. Chem. Eng. Data.*, **50**, 608–615 (2005).

[19] A. Ali, A.K. Nain, D. Chand, R. Ahmad. *Physics and Chemistry of Liquids*, **43**, 205–224 (2005).

[20] M.J.W. Povey, S.A. Hindle, J.D. Kennedy, Z. Stec, R.G. Taylor. *Phys. Chem. Chem. Phys.*, **5**, 73–78 (2003).

[21] David R. Lide, CSIR Handbook of Chemistry and Physics, 7th edn, 1990–1991.

[22] S. Glasstone, K.J. Laidner, H. Eyring. *The Theory of Rate Processes*, McGraw-Hill, New York (1941).

[23] S.L. Oswal, H.S. Desai. *Fluid Phase Equilibria.*, **161**, 191–204 (1999).

[24] P.S. Nikam, S.J. Kharat. *J. Chem. Eng. Data.*, **50**, 455–459 (2005).

[25] D. Papaioannou, M. Bridakis, C.G. Panayiotou. *J. Chem. Eng. Data*, **38**, 370–378 (1993).

[26] D. Papaioannou, C. Panayiotou. *J. Chem. Eng. Data*, **40**, 202–209 (1995).

[27] Y. Jing-Da, T. Chein-Hsiun. *J. Chem. Eng. Data*, **50**, 1060–1067 (2005).

[28] Z. Atik. *J. Sol. Chem.*, **33**, 1447–1446 (2004).

[29] C. Lafuente, B. Giner, A. Villares, I. Gascon, P. Cea. *International J. Thermo physics.*, **25**, 735–1746 (2004).

[30] S.L. Oswal, H.S. Desai. *Fluid Phase Equilibria*, **186**, 81–102 (2001).

[31] L. Grunberg, A.H. Nissan. *Nature*, **164**, 799 (1949).

[32] G. Maheshwari, M. Singh. *J. Indian. Chem. Soc.*, **79**, 659–664 (2002).

[33] B.B. Gurung, M.N. Roy. *J. Indian Chem. Soc.*, **81**, 1–6 (2004).

[34] T.M. Aminbhavi, H.T.S. Phyade, M.I. Aralaguppi, R.S. Khinnavar. *J. Chem. Eng. Data.*, **38**, 540–541 (1993).

[35] S.L. Oswal, D.B. Gheewala, K.D. Prajapati, R.L. Gardas, N.Y. Ghael, S.P. Ijardar. *Thermochimica Acta*, **426**, 141–149 (2005).