Studies of viscosity and excess molar volume of binary mixtures 3. 1-Alkanol + di-*n*-propylamine, and + di-*n*-butylamine mixtures at 303.15 and 313.15 K

S.L. Oswal*, H.S. Desai

Department of Chemistry, South Gujarat University, University Campus, Udhna-Magdalla Road, Surat 395 007, India

Abstract

The excess molar volume V^E, the viscosity deviation $\Delta \eta$ and the excess Gibbs energy of activation ΔG^{*E} of viscous flow have been investigated from density and viscosity measurements of 15 mixtures of ethanol, propanol, butanol, pentanol, heptanol, octanol and decanol with di-*n*-propylamine, and di-*n*-butylamine, and of hexanol with di-*n*-butylamine over the entire range of mole fractions at 303.15 and 313.15 K. The V^E of all the systems are very large negative. Except for the ethanol with di-*n*-propylamine and di-*n*-butylamine mixtures, the magnitude of negative deviations in viscosity increases with chain length of alkanol. The results have been explained considering mixed association of alkanol with diamine through O–H···N bond. The viscosity data have been correlated with the equations of Grunberg and Nissan, Tamura and Kurata, Hind, McLaughlin and Ubbelohde, Katti and Chaudhri, McAllister, Heric, and of Auslaender. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Alkanols; Correlating equations; Di-*n*-alkylamine; Hydrogen bonding; Gibbs energy of activation; Liquid mixtures; Molecular interactions; Viscosity

1. Introduction

In previous papers [1,2], we have reported the viscosity η and the excess molar volume V^E of binary mixtures of primary alkylamines (propylamine and butylamine) with a series of 1-alkanols at 303.15 and 313.15 K. The alkanol (A) and the primary amine (B) have both, a proton donor and a proton acceptor group. Besides AB, and $A_i B$ mixed associates species of type $A_i B_j$ also exists [3]. The latter species that contain many monomers can be formed with or without breaking of the H-bonds present in the pure liquids.

In this paper, we extend our studies to the binary mixtures of secondary amines (di-*n*-propylamine and di-*n*-butylamine) with series of 1-alkanols at 303.15 and 313.15 K. This study will shed some more

---

* Corresponding author. Tel.: +91-261-227-141; fax: +91-261- 227312.
E-mail address: oswalsl@satyam.net.in (S.L. Oswal).

light on the formation of mixed species and their influence on the excess properties of the mixtures. In addition, this work will also provide a test of various empirical equations to correlate viscosity data of binary mixtures containing both polar components.

2. Experiments

2.1. Method

Densities ρ at 303.15 and 313.15 K were measured with an Anton Paar vibrating-tube digital densi-meter (model DMA 60/602) with a thermostated bath controlled to ± 0.01 K. Viscosities η at the same temperatures were measured with a modified calibrated suspended level Ubbelohde viscometer. In the experiments, the viscometer was suspended for a sufficient time in a constant-temperature bath maintained within 0.02 K. The details of the methods and techniques used to determine ρ and η have been described previously [1,4].

The mixtures were prepared by mixing known masses of pure liquids in air tight, narrow-mouth ground stoppered bottles taking due precautions to minimize 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 $<1 \times 10^{-4}$. The error in viscosity η and the density ρ was $<2 \times 10^{-3}$ mPa s and 2×10^{-5} g cm^{-3}, respectively.

2.2. Source and purity of samples

The source and purification process of pure liquids: ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol and decanol have been described in our earlier paper [1,2]. Di-*n*-propylamine and di-*n*-butylamine (Fluka, AG) were stored over sodium hydroxide pellets for several days and fractionally distilled twice [5]. The purity of the liquid samples was checked by gas–liquid chromatography and boiling point measurements. The estimated purity of all the samples was >99.5 mol% for alkanols and amines. The measured values of the densities ρ, refractive indexes n_D and the viscosities η were in agreement with the literature values [5–12] within experimental uncertainties.

3. Results

The measured η and ρ for pure liquids and binary mixtures at number of mole fractions at 303.15 and 313.15 K are given in Tables 1 and 2. The excess molar volumes V^E were calculated from the molar masses M_i and the densities of pure liquids and the mixtures as

$$V^E = x_A M_A \left(\frac{1}{\rho} - \frac{1}{\rho_A} \right) + x_B M_B \left(\frac{1}{\rho} - \frac{1}{\rho_B} \right) \tag{1}$$

In accordance with Quin et al. [13], the relative change of volume in mixing ΔV, have also been computed from Eq. (2)

$$\Delta V = \frac{V^E}{x_A V_A + x_A V_B} \tag{2}$$

Table 1
Densities, viscosities, excess molar volumes and Gibbs energy of activation of viscous flow for alkanol (A) + dipropylamine (B) at 303.15 and 313.15 K

x_B	ρ (g cm^{-3})	η (mPa s)	V^E (cm^3 mol^{-1})	ΔG^{*E} (J mol^{-1})	ρ (g cm^{-3})	η (mPa s)	V^E (cm^3 mol^{-1})	ΔG^{*E} (J mol^{-1})
	303.15 K				313.15 K			
Ethanol + dipropylamine								
0.0000	0.78069	0.9930			0.77183	0.8291		
0.0942	0.78137	1.0495	−0.826	362	0.77151	0.8212	−0.795	210
0.1946	0.77811	1.0476	−1.347	579	0.76776	0.7926	−1.309	350
0.3116	0.77210	0.9952	−1.642	686	0.76149	0.7448	−1.607	435
0.4115	0.76662	0.9229	−1.742	678	0.75582	0.6985	−1.705	458
0.5186	0.76091	0.8291	−1.746	584	0.74997	0.6485	−1.708	450
0.6176	0.75579	0.7485	−1.659	475	0.74473	0.5986	−1.614	397
0.7061	0.75134	0.6803	−1.510	357	0.74019	0.5562	−1.457	334
0.8005	0.74630	0.6208	−1.209	249	0.73526	0.5100	−1.175	237
0.9058	0.74034	0.5600	−0.690	117	0.72942	0.4624	−0.675	116
1.0000	0.73445	0.5119			0.72365	0.4233		
Propanol + dipropylamine								
0.0000	0.79584	1.7843			0.78747	1.3970		
0.1059	0.79285	1.6014	−0.818	85	0.78360	1.2611	−0.796	90
0.2109	0.78746	1.4250	−1.318	143	0.77765	1.1265	−1.287	146
0.3116	0.78122	1.2680	−1.592	181	0.77103	1.0089	−1.557	187
0.4010	0.77535	1.1383	−1.712	197	0.76487	0.8968	−1.671	167
0.5130	0.76777	0.9940	−1.713	210	0.75717	0.7829	−1.689	163
0.5913	0.76259	0.8936	−1.650	185	0.75179	0.7121	−1.615	156
0.7036	0.75499	0.7675	−1.413	144	0.74414	0.6195	−1.392	130
0.8073	0.74795	0.6649	−1.061	93	0.73705	0.5442	−1.046	98
0.8850	0.74260	0.5972	−0.699	52	0.73166	0.4899	−0.685	51
1.0000	0.73455	0.5119			0.72365	0.4233		
Butanol + dipropylamine								
0.0000	0.80194	2.2853			0.79405	1.8170		
0.0954	0.79840	2.0384	−0.682	73	0.78974	1.6209	−0.656	67
0.1904	0.79354	1.7970	−1.161	116	0.78432	1.4259	−1.122	97
0.2859	0.78778	1.5671	−1.480	134	0.77817	1.2517	−1.441	124
0.4163	0.77892	1.2992	−1.680	157	0.76887	1.0307	−1.639	117
0.5205	0.77147	1.1065	−1.691	147	0.76119	0.8851	−1.657	117
0.6150	0.76451	0.9506	−1.589	120	0.75397	0.7697	−1.548	111
0.7107	0.75733	0.8177	−1.383	100	0.74663	0.6675	−1.344	101
0.8108	0.74959	0.6968	−1.035	71	0.73885	0.5735	−1.013	82
0.8924	0.74319	0.6105	−0.660	43	0.73242	0.5037	−0.649	50
1.0000	0.73445	0.5119			0.72365	0.4233		
Penanol + dipropylamine								
0.0000	0.80736	2.8315			0.79987	2.3443		
0.0952	0.80310	2.5102	−0.597	99	0.79506	2.0514	−0.592	69
0.1918	0.79799	2.1848	−1.068	160	0.78944	1.7672	−1.058	107
0.2881	0.79215	1.8747	−1.399	187	0.78318	1.5096	−1.390	122
0.3825	0.78581	1.5928	−1.596	181	0.77629	1.2810	−1.560	115

Table 1 (*Continued*)

x_B	ρ (g cm^{-3})	η (mPa s)	V^E (cm^3 mol^{-1})	ΔG^{*E} (J mol^{-1})	ρ (g cm^{-3})	η (mPa s)	V^E (cm^3 mol^{-1})	ΔG^{*E} (J mol^{-1})
	303.15 K				313.15 K			
0.5157	0.77590	1.2438	−1.652	133	0.76595	1.0204	−1.619	117
0.6160	0.76797	1.0337	−1.554	100	0.75770	0.8452	−1.516	75
0.7094	0.76027	0.8687	−1.354	67	0.74983	0.7187	−1.326	71
0.8061	0.75209	0.7254	−1.049	33	0.74148	0.6045	−1.028	54
0.9023	0.74360	0.6098	−0.615	14	0.73288	0.5061	−0.605	24
1.0000	0.73445	0.5118			0.72365	0.4233		
Heptanol + dipropylamine								
0.0000	0.81530	4.7853			0.80897	3.5786		
0.0952	0.81107	4.1447	−0.567	164	0.80423	3.0626	−0.568	113
0.1932	0.80584	3.4850	−1.008	271	0.79846	2.5555	−1.006	178
0.2891	0.79999	2.8665	−1.324	313	0.79204	2.1114	−1.308	209
0.3853	0.79333	2.3105	−1.514	308	0.78490	1.7241	−1.497	212
0.5194	0.78290	1.6725	−1.594	248	0.77377	1.2830	−1.564	187
0.6089	0.77524	1.3330	−1.534	181	0.76569	1.0445	−1.499	150
0.7170	0.76509	1.0204	−1.309	121	0.75522	0.8136	−1.298	104
0.8156	0.75515	0.8090	−0.987	97	0.74485	0.6509	−0.966	77
0.9054	0.74542	0.6553	−0.572	79	0.73483	0.5273	−0.555	35
1.0000	0.73445	0.5118			0.72365	0.4233		
Octanol + dipropylamine								
0.0000	0.81831	6.1023			0.81188	4.4132		
0.0971	0.81392	5.1651	−0.531	179	0.80699	3.7735	−0.523	177
0.1988	0.80858	4.2097	−0.977	294	0.80110	3.1073	−0.958	287
0.2871	0.80326	3.4624	−1.263	349	0.79530	2.5709	−1.233	329
0.3825	0.79677	2.7520	−1.465	363	0.78834	2.0532	−1.431	323
0.4806	0.78924	2.1349	−1.552	335	0.78033	1.6001	−1.513	271
0.5852	0.78023	1.6097	−1.509	276	0.77085	1.2232	−1.469	211
0.6925	0.76990	1.2024	−1.316	214	0.76011	0.9264	−1.285	144
0.7882	0.75981	0.9319	−1.029	173	0.74967	0.7294	−1.006	109
0.8977	0.74724	0.6909	−0.569	109	0.73672	0.5547	−0.553	71
1.0000	0.73445	0.5119			0.72365	0.4233		
Decanol + dipropylamine								
0.0000	0.82288	8.8347			0.81606	6.9555		
0.1006	0.81852	7.5302	−0.502	324	0.81136	5.8167	−0.510	272
0.1963	0.81369	6.2622	−0.888	550	0.80613	4.7753	−0.888	459
0.2905	0.80826	5.0748	−1.186	698	0.80031	3.8277	−1.183	572
0.3847	0.80206	3.9899	−1.396	770	0.79363	2.9927	−1.370	619
0.5117	0.79230	2.7478	−1.522	741	0.78327	2.0705	−1.481	585
0.6180	0.78257	1.9428	−1.451	630	0.77311	1.4858	−1.412	495
0.7197	0.77180	1.3641	−1.230	467	0.76194	1.0755	−1.196	394
0.8159	0.76019	0.9795	−0.886	321	0.74999	0.7925	−0.861	298
0.8950	0.74966	0.7427	−0.529	189	0.73920	0.6095	−0.515	188
1.0000	0.73445	0.5118			0.72365	0.4233		

Table 2
Densities, viscosities, excess molar volumes and Gibbs energy of activation of viscous flow for alkanol (A) + dibutylamine (B) at 303.15 and 313.15 K

x_B	ρ (g cm^{-3})	η (mPa s)	V^E (cm^3 mol^{-1})	ΔG^{*E} (J mol^{-1})	ρ (g cm^{-3})	η (mPa s)	V^E (cm^3 mol^{-1})	ΔG^{*E} (J mol^{-1})
	303.15 K				313.15 K			
Ethanol + dibutylamine								
0.0000	0.78069	0.9930			0.77183	0.8291		
0.1169	0.78146	1.1067	−0.749	518	0.77158	0.9037	−0.741	465
0.2094	0.77965	1.1263	−1.107	708	0.76924	0.9066	−1.092	613
0.3171	0.77651	1.0991	−1.341	773	0.76571	0.8803	−1.322	654
0.3921	0.77403	1.0651	−1.409	760	0.76302	0.8493	−1.385	619
0.4922	0.77077	1.0080	−1.423	684	0.75958	0.8109	−1.399	551
0.6159	0.76673	0.9427	−1.307	562	0.75540	0.7660	−1.283	434
0.7120	0.76362	0.8965	−1.119	452	0.75223	0.7426	−1.098	358
0.7802	0.76136	0.8625	−0.921	357	0.74995	0.7261	−0.904	293
0.8995	0.75747	0.8089	−0.475	184	0.74605	0.6965	−0.466	157
1.0000	0.75424	0.7584			0.74284	0.6649		
Propanol + dibutylamine								
0.0000	0.79584	1.7843			0.78747	1.3970		
0.0988	0.79307	1.6808	−0.591	138	0.78386	1.3090	−0.583	101
0.1893	0.78966	1.5640	−0.976	201	0.77985	1.2279	−0.959	162
0.3012	0.78490	1.4044	−1.281	208	0.77458	1.1230	−1.260	185
0.4041	0.78025	1.2756	−1.409	203	0.76958	1.0305	−1.386	175
0.4964	0.77596	1.1756	−1.407	196	0.76506	0.9494	−1.383	140
0.5900	0.77169	1.0838	−1.317	180	0.76066	0.8887	−1.302	136
0.6930	0.76712	0.9942	−1.126	159	0.75590	0.8255	−1.105	116
0.7809	0.76328	0.9209	−0.879	125	0.75200	0.7761	−0.866	92
0.8947	0.75852	0.8320	−0.474	63	0.74716	0.7157	−0.467	48
1.0000	0.75424	0.7584			0.74284	0.6649		
Butanol + dibutylamine								
0.0000	0.80194	2.2853			0.79405	1.8170		
0.0951	0.79859	2.1223	−0.554	112	0.78991	1.6796	−0.543	81
0.1888	0.79460	1.9227	−0.951	150	0.78529	1.5316	−0.931	114
0.2886	0.78989	1.7123	−1.229	153	0.78005	1.3797	−1.203	123
0.3967	0.78450	1.5067	−1.382	142	0.77420	1.2252	−1.352	108
0.4924	0.77956	1.3403	−1.394	115	0.76896	1.1060	−1.364	94
0.5903	0.77454	1.2005	−1.312	105	0.76369	0.9976	−1.284	76
0.6884	0.76959	1.0782	−1.142	95	0.75851	0.9063	−1.112	70
0.7951	0.76424	0.9600	−0.849	79	0.75302	0.8105	−0.828	37
0.8941	0.75935	0.8638	−0.482	64	0.74803	0.7369	−0.471	23
1.0000	0.75424	0.7584			0.74284	0.6649		
Pentanol + dibutylamine								
0.0000	0.80736	2.8315			0.79987	2.3443		
0.0971	0.80344	2.4933	−0.538	15	0.79520	2.0778	−0.528	19
0.2014	0.79857	2.1777	−0.956	31	0.78968	1.8141	−0.943	20
0.3007	0.79358	1.9132	−1.229	42	0.78413	1.6009	−1.208	29
0.4003	0.78823	1.6759	−1.369	44	0.77830	1.4095	−1.342	29
0.5004	0.78263	1.4730	−1.387	52	0.77232	1.2408	−1.359	27

Table 2 (*Continued*)

x_B	ρ (g cm^{-3})	η (mPa s)	V^E (cm^3 mol^{-1})	ΔG^{*E} (J mol^{-1})	ρ (g cm^{-3})	η (mPa s)	V^E (cm^3 mol^{-1})	ΔG^{*E} (J mol^{-1})
	303.15 K				313.15 K			
0.5841	0.77783	1.3190	−1.312	51	0.76727	1.1157	−1.288	24
0.6901	0.77171	1.1416	−1.114	34	0.76085	0.9767	−1.091	20
0.7836	0.76632	1.0064	−0.851	20	0.75527	0.8701	−0.836	18
0.8845	0.76057	0.8804	−0.486	8	0.74933	0.7633	−0.474	−2
1.0000	0.75424	0.7584			0.74284	0.6649		
Hexanol + dibutylamine								
0.0000	0.81195	3.7635			0.80414	3.1101		
0.1034	0.80751	3.3039	−0.548	90	0.79903	2.7230	−0.537	71
0.1705	0.80431	2.9917	−0.827	112	0.79546	2.4727	−0.812	91
0.2901	0.79820	2.4949	−1.199	139	0.78876	2.0691	−1.180	109
0.3817	0.79313	2.1563	−1.361	142	0.78330	1.7919	−1.340	104
0.5001	0.78623	1.7760	−1.429	131	0.77594	1.4746	−1.403	73
0.5958	0.78043	1.5204	−1.372	126	0.76979	1.2655	−1.337	59
0.6955	0.77413	1.2773	−1.190	89	0.76326	1.0879	−1.165	65
0.7942	0.76778	1.0883	−0.910	83	0.75667	0.9214	−0.885	28
0.9007	0.76079	0.9036	−0.489	43	0.74949	0.7818	−0.470	26
1.0000	0.75424	0.7584			0.74284	0.6649		
Heptanol + dibutylamine								
0.0000	0.81530	4.7853			0.80897	3.5786		
0.0975	0.81125	4.2264	−0.532	134	0.80409	3.1508	−0.505	91
0.1970	0.80651	3.6294	−0.940	208	0.79867	2.7161	−0.908	137
0.2901	0.80166	3.0986	−1.219	240	0.79327	2.3366	−1.191	151
0.3789	0.79667	2.6303	−1.388	238	0.78775	2.0134	−1.355	151
0.4808	0.79051	2.1502	−1.460	203	0.78104	1.6851	−1.424	134
0.5861	0.78380	1.7407	−1.417	160	0.77378	1.3934	−1.374	101
0.6850	0.77713	1.4323	−1.252	129	0.76674	1.1689	−1.223	79
0.7862	0.77005	1.1708	−0.975	93	0.75926	0.9814	−0.948	69
0.8807	0.76317	0.9696	−0.604	60	0.75210	0.8316	−0.591	55
1.0000	0.75424	0.7584			0.74284	.6649		
Octanol + dibutylamine								
0.0000	0.81831	6.1023			0.81188	4.4132		
0.0912	0.81486	5.3698	−0.550	148	0.80775	3.8651	−0.530	96
0.1863	0.81043	4.5878	−0.954	246	0.80270	3.3360	−0.925	176
0.2846	0.80528	3.8294	−1.249	303	0.79696	2.8121	−1.214	211
0.3857	0.79942	3.1050	−1.425	303	0.79048	2.3356	−1.377	224
0.4878	0.79307	2.4806	−1.498	273	0.78364	1.9212	−1.458	217
0.5882	0.78638	1.9789	−1.459	232	0.77645	1.5688	−1.416	185
0.6862	0.77943	1.5807	−1.309	183	0.76908	1.2771	−1.272	135
0.7892	0.77162	1.2515	−1.016	140	0.76084	1.0260	−0.980	77
0.8929	0.76333	0.9852	−0.594	88	0.75221	0.8270	−0.572	32
1.0000	0.75424	0.7584			0.74284	0.6649		
Decanol + dibutylamine								
0.0000	0.82288	8.8347			0.81606	6.9555		
0.0981	0.81944	7.7705	−0.609	276	0.81206	5.9586	−0.593	190

Table 2 (*Continued*)

x_B	ρ (g cm^{-3})	η (mPa s)	V^E (cm^3 mol^{-1})	ΔG^{*E} (J mol^{-1})	ρ (g cm^{-3})	η (mPa s)	V^E (cm^3 mol^{-1})	ΔG^{*E} (J mol^{-1})
	303.15 K				313.15 K			
0.1964	0.81512	6.6146	−1.042	474	0.80724	4.9846	−1.023	321
0.2860	0.81054	5.5455	−1.313	581	0.80220	4.1504	−1.289	389
0.3857	0.80483	4.4229	−1.504	626	0.79579	3.3053	−1.460	414
0.4851	0.79854	3.4386	−1.593	605	0.78920	2.6114	−1.559	396
0.5846	0.79152	2.6069	−1.552	523	0.78173	2.0214	−1.522	337
0.6877	0.78350	1.9436	−1.381	423	0.77320	1.5446	−1.340	269
0.7856	0.77513	1.4452	−1.087	285	0.76445	1.1988	−1.056	211
0.8866	0.76572	1.0733	−0.649	165	0.75460	0.9135	−0.613	126
1.0000	0.75424	0.7584			0.74284	0.6649		

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

$$\Delta \eta = \eta - (x_A \eta_A + x_B \eta_B) \tag{3}$$

On the basis of the theory of absolute reaction rates [14], the excess Gibbs energy of activation ΔG^{*E} of viscous flow was calculated from

$$\frac{\Delta G^{*E}}{RT} = \ln\left(\frac{\eta V}{\eta_A V_A}\right) - x_B \ln\left(\frac{\eta_B V_B}{\eta_A V_A}\right) \tag{4}$$

where V is the molar volume of the mixture and V_A and V_B the molar volume of the pure components A and B. V^E and ΔG^{*E} data are included in Tables 1 and 2. The estimated accuracy of V^E and ΔG^{*E} is about 0.005 cm^3 mol^{-1} and 15 J mol^{-1}, respectively.

The values of V^E, $\Delta \eta$, and ΔG^{*E} for each mixture have been fitted to the Redlich–Kister polynomial equation

$$Y^E = x_B(1 - x_B) - \sum_{i=0}^{m} A_i (1 - 2x_B)^i \tag{5}$$

The coefficients A_i of Eq. (5), obtained by the method of least-squares are given in Table 3 together with their standard deviations σ. The V^E for ethanol + dipropylamine and ethanol + dibutylamine at 298.15 and 323.15 K have been reported by Domonkos and Ratkovics [15]. The interpolated equimolar negative V^E for dipropylamine and dibutylamine mixtures reported by Domonkos and Ratkovics are 11.0 and 7.2% smaller than the present values at 303.15 and 313.15 K. The present equimolar negative value of V^E of butanol, pentanol, hexanol, and heptanol mixtures with dibutylamine at 303.15 is higher by 6.1–14.3% from those reported by Sastry et al. [16].

4. Correlating equations

Several semi-empirical relations have been proposed to correlate the dynamic viscosity η of liquid-mixtures in terms of pure-component data [17,18]. We have examined equations proposed by, Grunberg

Table 3
Coefficients A_i and standard deviations σ of Eq. (5)

Property	Temperature (K)	A_0	A_1	A_2	A_3	σ
Ethanol + dipropylamine						
V^E (cm^3 mol^{-1})	303.15	−7.0181	−0.5248	−2.8460	−0.7053	0.0049
	313.15	−6.8518	−0.6616	−2.6834	−0.3124	0.0026
$\Delta\eta$ (mPa s)	303.15	0.3770	0.7191	0.3585		0.0021
	313.15	0.1207	0.1994	0.0926		0.0020
ΔG^{*E} (J mol^{-1})	303.15	2415.8	1789.3	581.2		7.7
	313.15	1809.1	637.8	150.8		6.6
Propanol + dipropylamine						
V^E (cm^3 mol^{-1})	303.15	−6.9040	−0.7733	−1.3754	−0.5576	0.0039
	313.15	−6.7772	−0.6891	−1.2975	−0.5887	0.0025
$\Delta\eta$ (mPa s)	303.15	−0.5672	0.0471	0.0132		0.0024
	313.15	−0.4486	0.0514	0.0967		0.0033
ΔG^{*E} (J mol^{-1})	303.15	808.8	227.5	−170.8		5.6
	313.15	694.4	263.5	104.0		10.2
Butanol + dipropylamine						
V^E (cm^3 mol^{-1})	303.15	−6.8041	−0.6089	−0.9034	−0.0341	0.0035
	313.15	−6.6383	−0.6220	−0.8308	0.1838	0.0042
$\Delta\eta$ (mPa s)	303.15	−1.0366	0.0147	0.1587		0.0034
	313.15	−0.8310	−0.0337	0.1595		0.0031
ΔG^{*E} (J mol^{-1})	303.15	578.5	240.0	93.3		5.1
	313.15	481.4	123.0	272.8		4.8
Pentanol + dipropylamine						
V^E (cm^3 mol^{-1})	303.15	−6.6211	−0.4107	−0.5039	0.6814	0.0033
	313.15	−6.4873	−0.5073	−0.5889	0.7718	0.0041
$\Delta\eta$ (mPa s)	303.15	−1.5454	0.1717	0.3618		0.0023
	313.15	−1.3592	−0.0802	0.1933		0.0040
ΔG^{*E} (J mol^{-1})	303.15	583.9	651.3	117.0		5.3
	313.15	481.4	123.0	272.8		4.8
Heptanol + dipropylamine						
V^E (cm^3 mol^{-1})	303.15	−6.3875	0.0419	−0.3537	0.0318	0.0040
	313.15	−6.2901	0.0285	−0.3852	−0.1447	0.0048
$\Delta\eta$ (mPa s)	303.15	−3.5814	0.1936	1.0771		0.0027
	313.15	−2.6556	−0.3165	0.4025	0.2584	0.0023
ΔG^{*E} (J mol^{-1})	303.15	987.2	1281.4	616.5	−1030.7	8.4
	313.15	753.7	545.4	178.2		4.6
Octanol + dipropylamine						
V^E (cm^3 mol^{-1})	303.15	−6.2090	−0.0205	0.1392	0.1560	0.0025
	313.15	−6.0557	−0.0099	0.0949	0.0606	0.0018
$\Delta\eta$ (mPa s)	303.15	−5.1221	−0.4108	1.1313	0.3944	0.0036
	313.15	−3.5676	−0.1006	0.9676	0.2643	0.0024
ΔG^{*E} (J mol^{-1})	303.15	1279.6	924.1	509.8	−620.3	5.8
	313.15	1045.7	1226.0	554.9	−712.3	3.2

Table 3 (*Continued*)

Property	Temperature (K)	A_0	A_1	A_2	A_3	σ
Decanol + dipropylamine						
V^E (cm^3 mol^{-1})	303.15	−6.0669	0.5652	0.7676	−0.8298	0.0020
	313.15	−5.9242	0.4058	0.5877	−0.8096	0.0036
$\Delta\eta$ (mPa s)	303.15	−7.2871	1.0106	2.0303		0.0029
	313.15	−6.1640	−0.1529	1.3595	0.2090	0.0034
ΔG^{*E} (J mol^{-1})	303.15	2960.2	1291.7	−292.9	−494.2	8.4
	313.15	2345.2	1076.2	257.4	−736.0	5.4
Ethanol + dibutylamine						
V^E (cm^3 mol^{-1})	303.15	−5.6865	−0.8904	−0.9984	−0.6883	0.0035
	313.15	−5.5882	−0.8919	−1.0068	−0.7062	0.0039
$\Delta\eta$ (mPa s)	303.15	0.5214	0.6876	0.5301		0.0024
	313.15	0.2427	0.4714	0.4966		0.0023
ΔG^{*E} (J mol^{-1})	303.15	2345.2	1076.2	257.4	−736.0	5.4
	313.15	2167.2	1766.4	1610.1		5.6
Propanol + dibutylamine						
V^E (cm^3 mol^{-1})	303.15	5.6273	−1.0295	−0.3082	0.0380	0.0031
	313.15	−5.5366	−0.9960	−0.3082	0.0047	0.0036
$\Delta\eta$ (mPa s)	303.15	−0.4011	0.1627	0.3328		0.0076
	303.15	−0.3102	0.0635	0.1456		0.0033
ΔG^{*E} (J mol^{-1})	303.15	785.4	261.4	531.2	475.2	3.9
	313.15	630.5	405.9	347.8		9.0
Butanol + dibutylamine						
V^E (cm^3 mol^{-1})	303.15	−5.5808	−0.8182	−0.2854	−0.0250	0.0037
	313.15	−5.4549	−0.8301	−0.2896	0.0065	0.0021
$\Delta\eta$ (mPa s)	303.15	−0.7744	0.0377	0.5555	0.2989	0.0030
	313.15	−0.5758	0.0184	0.2242	0.1664	0.0016
ΔG^{*E} (J mol^{-1})	303.15	462.0	372.3	808.7		4.2
	303.15	374.0	407.7	343.6		5.8
Pentanol + dibutylamine						
V^E (cm^3 mol^{-1})	303.15	−5.5454	−0.7676	0.2010	−0.1770	0.0028
	313.15	−5.4429	−0.7754	0.2021	−0.1658	0.0024
$\Delta\eta$ (mPa s)	303.15	−1.2892	−0.2532	−0.0997		0.0018
	301.15	−1.0542	−0.1826	−0.0028		0.0029
ΔG^{*E} (J mol^{-1})	303.15	204.0	60.0	−129.7		3.5
	313.15	113.7	95.8	−15.4		5.7
Hexanol + dibutylamine						
V^E (cm^3 mol^{-1})	303.15	−5.7246	−0.1962	0.0578	−0.1305	0.0028
	313.15	−5.6228	−0.2519	0.1480	−0.1113	0.0030
$\Delta\eta$ (mPa s)	303.15	−1.9497	−0.1921	0.4270	0.3865	0.0060
	313.15	−1.6341	−0.0498	0.3115		0.0051
ΔG^{*E} (J mol^{-1})	303.15	525.0	272.0	308.5		7.2
	313.15	321.9	321.1	310.7		9.1

Table 3 (*Continued*)

Property	Temperature (K)	A_0	A_1	A_2	A_3	σ
Heptanol + dibutylamine						
V^E (cm^3 mol^{-1})	303.15	5.8522	−0.1004	−0.0607	−0.1255	0.0029
	313.15	−5.7113	−0.1658	0.0409	0.1518	0.0039
$\Delta\eta$ (mPa s)	303.15	−2.7971	0.2090	0.9036	0.2849	0.0033
	313.15	−1.9895	0.0077	0.4969		0.0035
ΔG^{*E} (J mol^{-1})	303.15	797.2	622.4	393.4		7.0
	313.15	493.6	350.8	435.9		7.8
Octanol + dibutylamine						
V^E (cm^3 mol^{-1})	303.15	−5.9890	0.0432	−0.6385	−0.4474	0.0037
	313.15	−5.8197	0.0336	−0.5361	−0.4296	0.0063
$\Delta\eta$ (mPa s)	303.15	−4.0495	0.1856	1.1726	0.2787	0.0043
	313.15	−2.6593	0.0101	0.2701		0.0043
ΔG^{*E} (J mol^{-1})	303.15	1079.9	805.5	426.8	−430.5	2.4
	313.15	852.5	538.2	−172.5		4.0
Decanol + dibutylamine						
V^E (cm^3 mol^{-1})	303.15	−6.3576	0.1203	−0.4747	−0.6104	0.0032
	313.15	−6.2265	0.1186	−0.2759	−0.8096	0.0098
$\Delta\eta$ (mPa s)	303.15	−5.9559	1.6788	2.2808	0.1667	0.0070
	313.15	−5.1814	0.1403	1.1756		0.0043
ΔG^{*E} (J mol^{-1})	303.15	1079.9	805.5	426.8	−430.5	2.4
	313.15	1539.1	851.5	260.3	−482.6	4.3

and Nissan [19], Tamura and Kurata [20], Hind et al. [21], Katti and Chaudhri [22], McAllister [23], Heric [24], and Auslaender [25].

The single parameter Grunberg–Nissan equation [19] reads

$$\eta = \exp(x_A \ln \eta_A + x_B \ln \eta_B + x_A x_B G) \tag{6}$$

where G is a parameter proportional to the interchange energy. The semi-empirical equation due to Tamura and Kurata [20] is

$$\eta = x_A \phi_A \eta_A + x_B \phi_B \eta_B + 2(x_A x_B \phi_A \phi_B)^{1/2} C \tag{7}$$

where ϕ_A and ϕ_B are the volume fractions of components A and B, and C an adjustable parameter.

Hind et al. [21], proposed the following equation:

$$\eta = x_A^2 \eta_A + x_B^2 \eta_B + 2 x_A x_B \eta_{AB} \tag{8}$$

where η_{AB} is attributed to unlike pair interactions. It is approximately equal to 0.5 $(\eta_A + \eta_B)$, but this relation is not sufficiently accurate for the prediction purposes.

Katti and Chaudhri [22] derived following equation:

$$\ln \eta V = x_A \ln V_A \eta_A + x_B \ln V_B \eta_B + x_A x_B \frac{W_{vis}}{RT} \tag{9}$$

where W_{vis} is an interaction term.

Table 4
Values of the parameters in Eqs. (6)–(9) and standard percentage deviations in correlating viscosities of alkanol + dialkylamine

Temperature (K)	Eq. (6)		Eq. (7)		Eq. (8)		Eq. (9)	
	G_{12}	σ (%)	C (mPa s)	σ (%)	η_{12} (mPa s)	σ (%)	W_{vis}/RT	σ (%)
Ethanol + dipropylamine								
303.15	0.74	5.23	1.14	5.17	0.98	7.37	1.01	5.56
313.15	0.43	1.36	0.84	1.58	0.70	2.38	0.71	1.73
Propanol + dipropylamine								
303.15	0.19	0.69	1.10	1.73	0.87	0.42	0.30	0.71
313.15	0.16	0.82	0.88	1.75	0.70	0.74	0.27	0.84
Butanol + dipropylamine								
303.15	0.22	0.83	1.10	1.58	0.90	0.57	0.24	0.78
313.15	0.19	0.67	0.88	1.20	0.73	0.95	0.21	0.64
Pentanol + dipropylamine								
303.15	0.27	2.17	1.09	2.58	0.95	1.68	0.24	2.14
313.15	0.21	1.06	0.85	0.94	0.73	1.32	0.18	1.00
Heptanol + dipropylamine								
303.15	0.50	3.12	0.97	3.10	1.01	3.10	0.46	3.13
313.15	0.35	1.69	0.71	2.78	0.73	2.53	0.31	1.68
Octanol + dipropylamine								
303.15	0.60	2.40	0.69	5.46	0.89	3.61	0.57	2.44
313.15	0.50	3.12	0.62	4.13	0.76	3.09	0.46	3.16
Decanol + dipropylamine								
303.15	1.12	3.62	0.66	5.26	1.31	5.24	1.14	3.68
313.15	0.91	2.60	0.27	9.99	0.80	3.95	0.92	2.64
Ethanol + dibutylamine								
303.15	0.71	5.01	1.39	3.07	1.20	5.75	1.21	6.16
313.15	0.48	4.57	1.08	3.15	0.93	5.00	0.99	5.72
Propanol + dibutylamine								
303.15	0.08	1.27	1.42	1.85	1.12	1.42	0.37	1.64
313.15	−0.01	1.01	1.12	1.52	0.90	0.92	0.28	1.41
Butanol + dibutylamine								
303.15	0.13	1.68	1.50	2.41	1.21	1.86	0.27	1.78
313.15	0.03	1.16	1.21	1.79	0.98	1.00	0.18	1.30
Pentanol + dibutylamine								
303.15	0.01	0.29	1.41	0.31	1.14	1.51	0.07	0.30
313.15	−0.02	0.25	1.20	0.32	0.98	1.39	0.04	0.27
Hexanol + dibutylamine								
303.15	0.23	1.00	1.60	1.45	1.35	1.02	0.24	0.99
313.15	0.15	1.19	1.32	1.35	1.11	1.09	0.16	1.18
Heptanol + dibutylamine								
303.15	0.38	2.21	1.69	2.90	1.50	2.19	0.36	2.19
313.15	0.25	1.41	1.34	1.48	1.19	1.27	0.24	1.39

Table 4 (*Continued*)

Temperature (K)	Eq. (6)		Eq. (7)		Eq. (8)		Eq. (9)	
	G_{12}	σ (%)	C (mPa s)	σ (%)	η_{12} (mPa s)	σ (%)	W_{vis}/RT	σ (%)
Octanol + dibutylamine								
303.15	0.98	3.34	1.92	5.77	2.14	6.62	0.95	3.36
313.15	0.35	1.63	1.33	0.83	1.25	0.68	0.31	1.62
Decanol + dibutylamine								
303.15	1.02	4.42	2.07	8.58	2.28	9.26	0.99	4.46
313.15	0.65	2.16	1.21	2.69	1.37	2.23	0.62	2.19
Average $\langle \sigma$ (%)$\rangle$		1.99		2.69		2.44		2.13

The two-parameter McAllister equation [23] based on the Eyring's theory of absolute reaction rates [14] and a three-body interaction model is

$$\ln v = x_A^3 \ln v_A + 3x_A^2 x_B \ln Z_{AB} + 3x_A x_B^2 \ln Z_{BA} + x_B^3 \ln v_B - \ln\left(x_A + x_B \frac{M_B}{M_A}\right)$$

$$+3x_A^2 x_B \ln\left(\frac{2}{3} + \frac{M_B}{3M_A}\right) + 3x_A x_B^2 \ln\left(\frac{1}{3} + \frac{2M_B}{3M_A}\right) + x_B^3 \ln\left(\frac{M_B}{M_A}\right) \tag{10}$$

where Z_{AB} and Z_{BA} are interaction parameters and M_i and v_i the molecular mass and kinematic viscosity of pure component i. The two-parameter Heric equation [24] is of the form

$$\ln v = x_A \ln v_A + x_B \ln v_B + x_A \ln M_A + x_B \ln M_B + \ln(x_A M_A + x_B M_B)$$

$$+x_A x_B [\alpha_{AB} + \alpha_{BA}(x_A - x_B)] \tag{11}$$

where α_{AB} and α_{BA} are adjustable parameters.

The three-parameter Auslaender equation [25] has the form

$$x_A(x_A + B_{AB}x_B)(\eta - \eta_A) + A_{BA}x_B(B_{BA}x_A + x_B)(\eta - \eta_B) = 0 \tag{12}$$

where B_{AB}, A_{BA} and B_{BA} are the parameters representing binary AB interactions. The correlating ability of each of the Eqs. (6)–(12), was tested by calculating the standard percentage deviations σ (%) between the experimental and the calculated viscosity as

$$\sigma(\%) = \left[\frac{1}{n-k} \sum \left\{\frac{100(\eta_{exp} - \eta_{cal})}{\eta_{exp}}\right\}^2\right]^{1/2} \tag{13}$$

where n represents the number of data points and k the number of numerical coefficients in the respective equations. The results of correlating equations (Eqs. (6)–(12)) are compiled in Tables 4 and 5. Table 4 lists the results of Eqs. (6)–(9) containing single-adjustable parameter. The results of two-parameter McAllister Eq. (10) and Heric Eq. (11) and of three-parameter Auslaender Eq. (12) are summarized in Table 5. The values of the different parameters and the percentage standard deviations listed in Tables 4 and 5 were obtained from the experimental viscosity data with the method of least squares, with equal weights assigned to each point.

Table 5
Values of the parameters in Eqs. (10)–(12) and standard percentage deviations in correlating viscosities of dialkylamine+alkanol

Temprature (K)	Eq. (10)			Eq. (11)			Eq. (12)			
	Z_{AB}	Z_{BA}	σ (%)	α_{AB}	α_{BA}	σ (%)	B_{AB}	A_{BA}	B_{BA}	σ (%)
Ethanol + dipropylamine										
303.15	0.89	1.72	1.12	1.02	−0.70	1.12	−0.46	0.25	3.89	0.39
313.15	0.79	1.12	0.42	0.71	−0.24	0.42	−0.03	0.26	3.93	0.23
Propanol + dipropylamine										
303.15	1.08	1.68	0.38	0.30	−0.09	0.38	0.79	0.58	0.96	0.37
313.15	0.87	1.34	0.46	0.27	−0.10	0.46	0.39	0.30	1.87	0.39
Butanol + dipropylamine										
303.15	1.16	1.97	0.26	0.24	−0.10	0.26	0.45	0.31	1.55	0.25
313.15	0.96	1.57	0.59	0.21	−0.05	0.59	0.23	0.17	3.04	0.19
Pentanol + dipropylamine										
303.15	1.19	2.41	0.32	0.24	−0.26	0.32	0.62	0.43	0.88	0.29
313.15	1.02	1.89	0.45	0.18	−0.12	0.45	0.49	0.31	1.33	0.31
Heptanol + dipropylamine										
303.15	1.49	3.72	1.34	0.46	−0.31	1.34	0.50	0.33	0.89	1.10
313.15	1.18	2.67	0.34	0.31	−0.21	0.34	0.56	0.32	0.96	0.18
Octanol + dipropylamine										
303.15	1.69	4.41	0.98	0.56	−0.26	0.98	0.52	0.31	0.85	0.69
313.15	1.26	3.35	1.06	0.46	−0.35	1.06	0.50	0.31	0.85	0.79
Decanol + dipropylamine										
303.15	2.15	7.13	0.80	1.14	−0.43	0.80	0.71	0.47	0.42	0.81
313.15	1.73	5.12	0.72	0.92	−0.29	0.72	0.68	0.40	0.54	0.98
Ethanol + dibutylamine										
303.15	1.15	1.99	2.34	1.22	−0.74	2.34	−1.09	0.13	14.99	0.63
313.15	0.96	1.55	2.66	0.99	−0.66	2.66	−0.80	0.07	19.94	0.77
Propanol + dibutylamine										
303.15	1.31	1.93	1.10	0.37	−0.20	1.10	0.02	0.06	10.74	0.41
313.15	1.10	1.52	0.75	0.28	−0.16	0.75	0.14	0.14	4.57	0.51
Butanol + dibutylamine										
303.15	1.43	2.24	1.41	0.27	−0.16	1.41	0.02	0.05	11.34	0.66
313.15	1.19	1.81	0.63	0.18	−0.16	0.63	0.17	0.16	3.48	0.19
Pentanol + dibutylamine										
303.15	1.53	2.35	0.27	0.07	−0.02	0.27	2.06	1.15	0.40	0.14
313.15	1.31	1.99	0.21	0.04	−0.04	0.21	0.37	0.22	2.21	0.29
Hexanol + dibutylamine										
303.15	1.74	3.12	0.58	0.24	−0.11	0.58	0.23	0.17	2.78	0.33
313.15	1.46	2.59	0.63	0.16	−0.13	0.63	0.35	0.23	1.88	0.37
Heptanol + dibutylamine										
303.15	1.87	4.00	0.74	0.36	−0.25	0.74	0.40	0.30	1.28	0.35
313.15	1.57	2.94	0.75	0.23	−0.14	0.75	0.37	0.25	1.68	0.39

Table 5 (*Continued*)

Temprature (K)	Eq. (10)			Eq. (11)			Eq. (12)			
	Z_{AB}	Z_{BA}	σ (%)	α_{AB}	α_{BA}	σ (%)	B_{AB}	A_{BA}	B_{BA}	σ (%)
Octanol + dibutylamine										
303.15	2.63	7.61	0.37	0.94	−0.41	0.37	0.56	0.45	0.61	0.49
313.15	1.69	3.54	0.30	0.31	−0.21	0.30	0.99	0.60	0.57	0.21
Decanol + dibutylamine										
303.15	2.60	7.94	1.25	0.98	−0.49	1.25	0.36	0.35	0.79	1.03
313.15	2.14	5.34	0.59	0.62	−0.25	0.59	0.64	0.40	0.72	0.58
Average $\langle \sigma$ (%)$\rangle$			0.78			0.78				0.46

5. Discussion

The values of σ are in the range from 0.25 to 9.26% for the single-parameter Eqs. (6)–(9); and from 0.21 to 2.66% for the two-parameter Eqs. (10) and (11); and from 0.14 to 1.03% for the three-parameter Eq. (12). The average values of percentage standard deviations $\langle \sigma$ (%)$\rangle$ for Eqs. (6)–(9) with a single-parameter are 1.99, 2.69, 2.44 and 2.13, respectively; and for Eqs. (10) and (11) with two parameters $\langle \sigma$ (%)$\rangle$ is 0.78 while for the three-parameter Eq. (12) the $\langle \sigma$ (%)$\rangle$ is 0.46. During the analysis of the results it was observed that the use of two-parameter Eqs. (10) and (11) reduces the σ (%) values significantly below that of single parameter equation. In most systems, the three-parameter Eq. (12) proposed by Auslaender [25] gives a very good correlation.

We have calculated the $\Delta\eta$, V^E, $\Delta V/\phi_A\phi_B$ and ΔG^{*E} at two temperatures 303.15 and 313.15 K, but graphically the results are shown only at 303.15 K, since for the other temperature the curves are similar. The viscosity η decreases with increasing mole fraction x_B of dipropylamine or dibuty-lamine for all the mixtures except for two mixtures involving ethanol. The ethanol + dipropylamine and ethanol + dibutylamine mixtures show a maximum in viscosity which occurs around 0.2 mol fraction of amine. All the other mixtures show negative deviations from mole fraction linearity (Figs. 1 and 2). The magnitude of negative deviations increases with the chain length of the alkanol but decreases on going from dipropylamine to dibutylamine. With rising temperature from 303.15 to 313.15 K, the magnitude of deviations diminishes.

As can be seen from Figs. 3 and 4, V^E is large and negative for all the alkanol + dialkylamine mixtures at both temperatures and over the entire range of compositions. Negative values of V^E decrease with rising temperature from 303.15 to 313.15 K (Fig. 5). The magnitude of negative values of V^E decreases with increasing chain length of the alkanol in alkanol + dipropylamine mixture series (Fig. 5). On the other hand, as can be seen in Fig. 5 in the case of alkanol + dibutylamine mixtures, V^E does not change significantly and regularly with the chain length of alkanol. The negative V^E tends to slightly decrease from ethanol to pentanol and then increases up to decanol.

The plots in Figs. 6 and 7 show $\Delta V/\phi_A\phi_B$ versus x_B. When a given dialkylamine is mixed with a series of alkanols, the values of $\Delta V/\phi_A\phi_B$ increase regularly with the increasing number of carbon atoms in alkanol. The values of $\sum_{i=1}^n A_i$ and $\sum_{i=1}^n A_i(-1)^i$ of Eq. (5) represent the limiting values of excess partial molar volumes $V_i^{E,\infty}$ of both alkanol and amine equivalent to $V_A^{E,\infty}(= \bar{V}_A - V_A^0)$ and $V_B^{E,\infty}(= \bar{V}_B - V_B^0)$, the difference between the partial molar volume of component A or B at infinite dilution and the molar
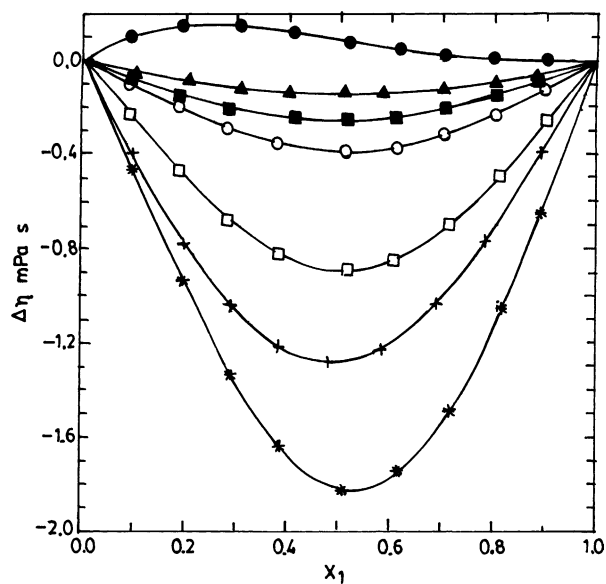
Fig. 1. Viscosity deviations $\Delta\eta$ for alkanol + dipropylamine at 303.15 K. Experimental points: alkanol: C_2H_5OH (●); C_3H_7OH (▲); C_4H_9OH (■); $C_5H_{11}OH$ (○); $C_7H_{15}OH$ (□); $C_8H_{17}OH$ (+); $C_{10}H_{21}OH$ (∗).
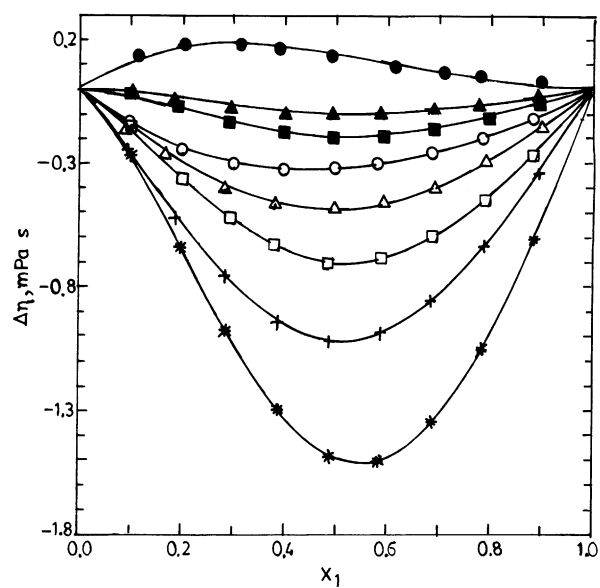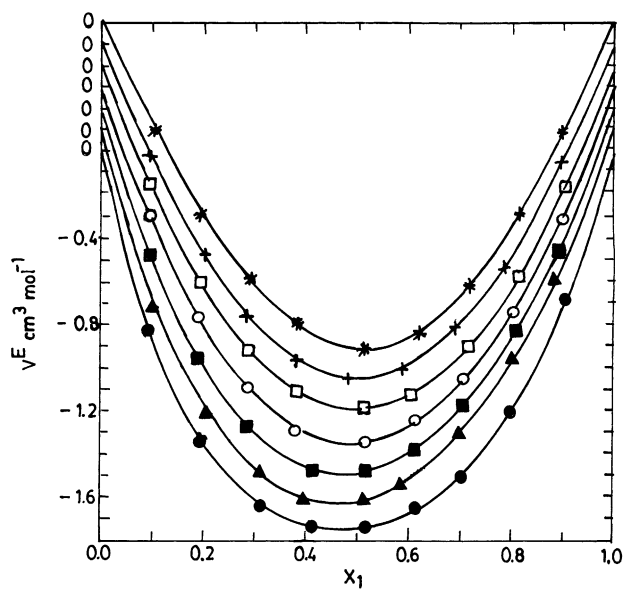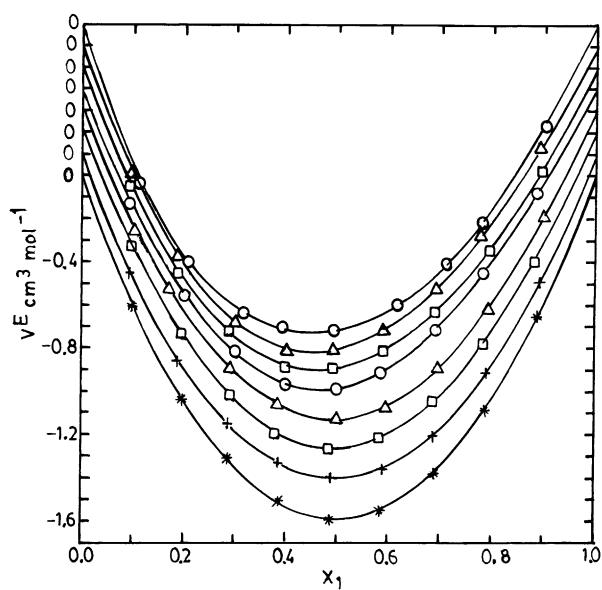

Fig. 2. Viscosity deviations $\Delta\eta$ for alkanol + dibutylamine at 303.15 K. Experimental points: alkanol: C_2H_5OH (●); C_3H_7OH (▲); C_4H_9OH (■); $C_5H_{11}OH$ (○); $C_6H_{13}OH$ (△); $C_7H_{15}OH$ (□); $C_8H_{17}OH$ (+); $C_{10}H_{21}OH$ (∗).

Fig. 3. Excess molar volumes V^E of alkanol + dipropylamine at 303.15 K. Experimental points: alkanol: C_2H_5OH (●); C_3H_7OH (▲); C_4H_9OH (■); $C_5H_{11}OH$ (○); $C_7H_{15}OH$ (□); $C_8H_{17}OH$ (+) and $C_{10}H_{21}OH$ (∗).

Fig. 4. Excess molar volumes V^E of alkanol + dibutylamine at 303.15 K. Experimental points: alkanol: C_2H_5OH (●); C_3H_7OH (▲); C_4H_9OH (■); $C_5H_{11}OH$ (○); $C_6H_{13}OH$ (△); $C_7H_{15}OH$ (□); $C_8H_{17}OH$ (+) and $C_{10}H_{21}OH$ (∗).
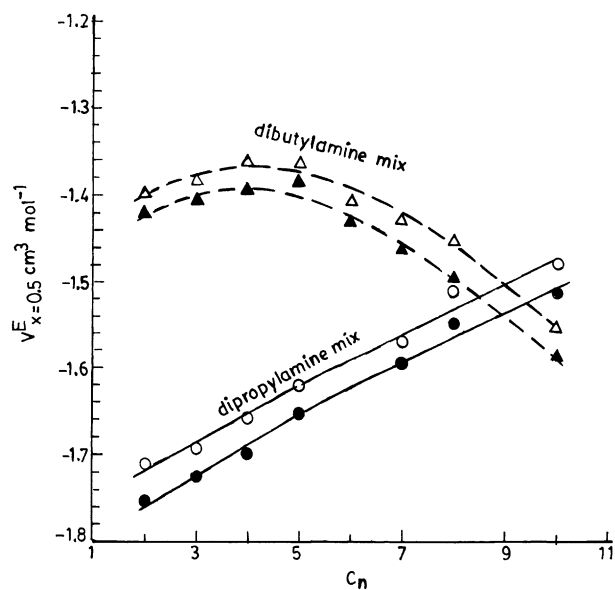
Fig. 5. Equimolar excess molar volumes for dipropyl and dibutylamine as a function of number of carbon atoms (C_n) in alkanols, 303.15 K (●), (▲); and 313.15 K (○), (△).
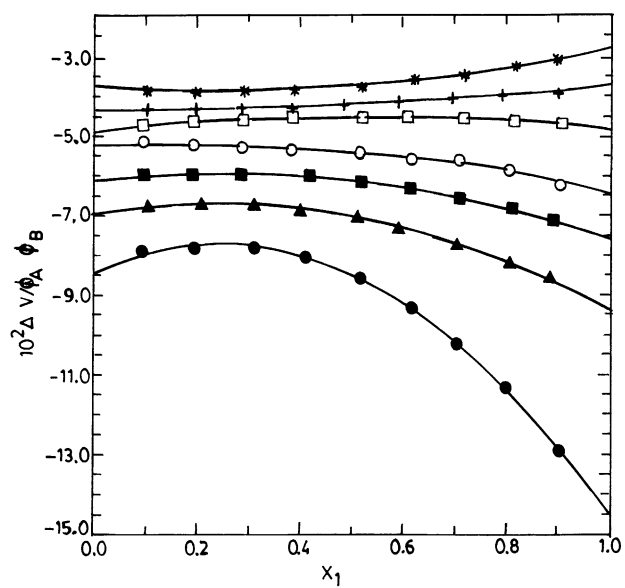
Fig. 6. The plots of $\Delta V/\phi_A \phi_B$ as a function of composition of dipropylamine for alkanol + dipropylamine at 303.15 K. Symbols same as in Fig. 1.
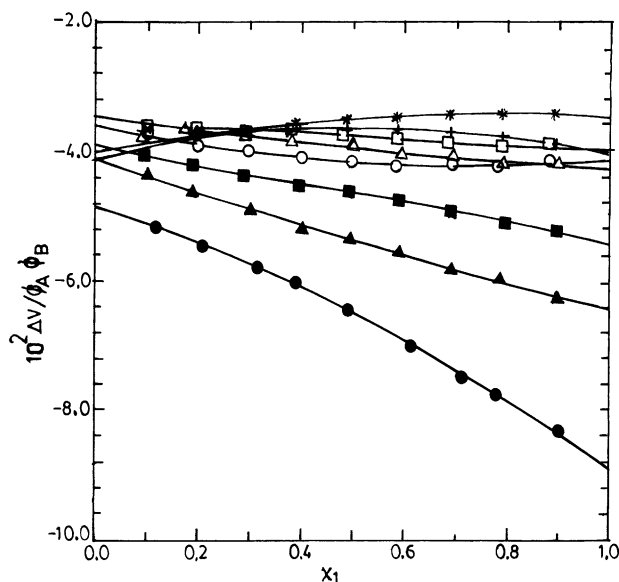
Fig. 7. The plots of $\Delta V/\phi_A\phi_B$ as a function of composition of dibutylamine for alkanol + dibutylamine at 303.15 K. Symbols same as in Fig. 1.

volume of the same pure liquid [26]. The limiting values of $V_i^{E,\infty}$ of dipropylamine $V_B^{E,\infty}$ vary from -11.09 to $-5.56\,\text{cm}^3\,\text{mol}^{-1}$ in ethanol to decanol and for alkanols these values are in the range from -5.04 to $-8.64\,\text{cm}^3\,\text{mol}^{-1}$ in dipropylamine. Similarly, the limiting $V_i^{E,\infty}$ values of dibutylamine $V_B^{E,\infty}$ vary from -8.22 to $-7.19\,\text{cm}^3\,\text{mol}^{-1}$ in ethanol to decanol and of alkanol $V_A^{E,\infty}$ from -5.11 to $-5.81\,\text{cm}^3\,\text{mol}^{-1}$ in dibutylamine. The variation of $V_i^{E,\infty}$ of a given diamine in a series of alkanols is large compared to the $V_i^{E,\infty}$ of various alkanol in the same diamine. The large negative contribution to $V_i^{E,\infty}$ for both amine and alkanol in the present mixtures clearly suggests the dominance of strong specific interactions between components and the free volume effect when mixture is formed. Similar were the conclusions from the study of partial molar volumes of secondary amines in methanol [27].

The values of ΔG^{*E} (Figs. 8 and 9) are positive for all the mixtures and decrease from ethanol to pentanol mixtures, attain a minimum value and than increase regularly from pentanol to decanol mixtures in both the series. With the increase in temperature the values of ΔG^{*E} show a diminishing trend. Like primary amines [1,2], the present large negative V^E results can be interpreted qualitatively by taking into account the fact that several expansion and contraction processes proceed simultaneously when alkanol-amine mixtures are formed. The following effects were considered: (i) expansion due to depolymerization of alcohol and disruption of dipolar order of diamine by one another, (ii) contraction due to free volume difference of unlike molecules and (iii) contraction due to mutual association through hydrogen bond $-\text{OH}\cdots\text{NH}$ formation between diamine and alcohol. The large positive V^E observed in the case of $\text{ROH} + \text{C}_6\text{H}_{12}$ [28,29], and $\text{R}_2\text{NH} + \text{C}_6\text{H}_{12}$ [30,31] mixtures, as a result of disruption of the self association of alkanol and amine by the addition of inert globular hydrocarbon molecules, suggests a positive contribution to V^E due to effect (i). The estimated free volume contribution (ii) to V^E as per the Prigogine–Flory–Patterson theory [32] ranges from $-0.001\,\text{cm}^3\,\text{mol}^{-1}$ for ethanol + dibutylamine to $-0.338\,\text{cm}^3\,\text{mol}^{-1}$ for decanol + dipropylamine. Thus, the observed very large negative values of V^E can
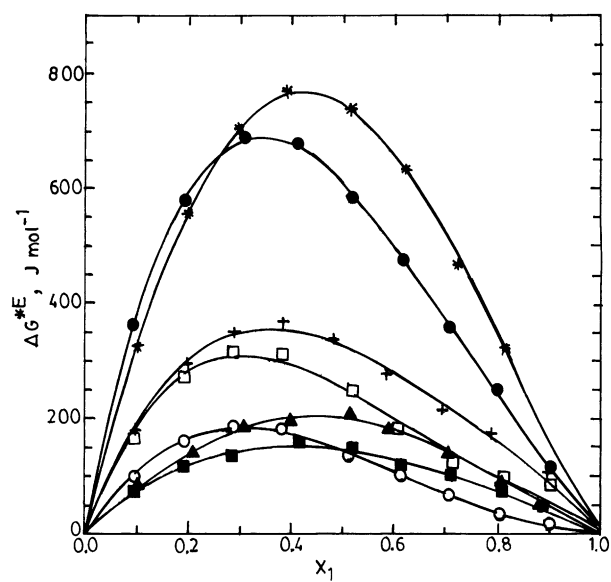
Fig. 8. Excess Gibbs Energy of activation ΔG^{*E} of viscous flow for alkanol + dipropylamine at 303.15 K. Symbols same as in Fig. 1.
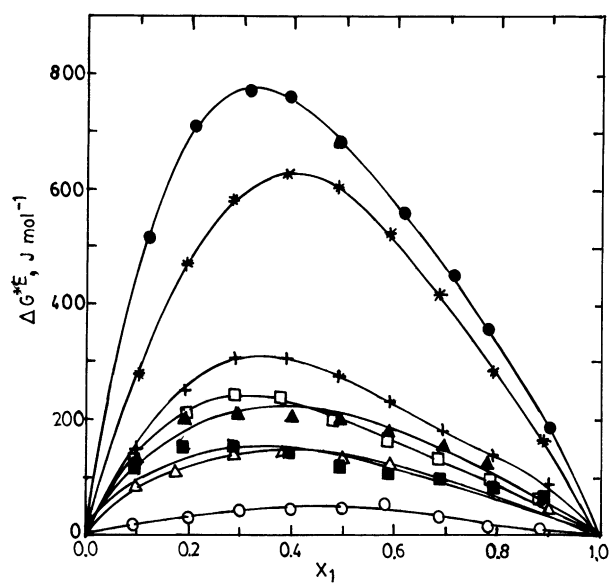

Fig. 9. Excess Gibbs Energy of activation ΔG^{*E} of viscous flow for alkanol + dibutylamine at 303.15 K. Symbols same as in Fig. 1.

be accounted only by considering predominance of the formation of OH$\cdots$NH, bonds over the rupture of the OH$\cdots$OH and >NH$\cdots$NH bonds present in pure alkanol and diamine. The free electron pair in the N atom has a higher polarizability and therefore acts as a more efficient proton acceptor for the O–H group than the O–H itself.

Furthermore, excess enthalpies H^E are $-2432, -2438, -2346, -2298$, and -2213 J mol^{-1} for dipropyl-amine + butanol, +pentanol, +hexanol, +heptanol and +octanol, respectively [33]; and $-2232, -2268, -2320, -2280$, and -2228 J mol^{-1} for dibutylamine + propanol, +butanol, +pentanol, +hexanol, and +heptanol, respectively [34] at 298.15 K. These values are some of the largest negative values found for organic mixtures in the literature [35,36]. The very large negative H^E supports the existence of strong molecular interactions between the >NH group of amine molecules and the –OH group of the alkanol molecules. The negative values of V^E and H^E can best be explained by considering the formation of a block copolymer of type A_iB_j with two blocks of length i and j present in a cross-associated multimer of chain length $i + j$ [3,37]. The complexes A_iB_j can form ring as well as chain like associates. The ring associates involve one extra hydrogen bridge than the hydrogen bridges in chain associations. Furthermore, in A_iB_j type complexes fewer self-associated bonds are broken than in AB type 1:1 complexes. The enthalpy of complex formation between butanol and DBA is –23.1 kJ mol^{-1} [38]. The existence of strong O–H$\cdots$N bond has also been confirmed through NMR, IR and UV studies [39–41].

The positive deviations in viscosity (Figs. 1 and 2) over the entire range of composition which are observed for ethanol + dipropylamine and ethanol + dibutylamine mixtures support the existence of the specific interactions [42]. But for the rest of the mixtures, negative deviations are observed which regularly increase as the size or viscosity of the alkanol is increased. It is known that the strength of the intermolecular hydrogen bonding is not the only factor influencing the viscosity deviations in liquid mixtures [1,43,44]. The molecular size and shape of the components and average degree of association of the mixture are equally important factors. The negative values of $\Delta\eta$ assume the formation of cyclic structures of multimer A_iB_j species and/or average degree of cross-association of mixture gradually decreases on proceeding from the alkanol towards the amine concentration [45,46]. The larger the chain length of alkanol, the greater is the decrease in the average degree of association, as result more negative deviations in viscosity versus mole fraction curve are observed.

List of symbols

A	1-alkanols
A_i	coefficients of Eq. (5)
AB, A_iB, A_iB_j	mixed associates
B	di-n-propylamine or di-n-butylamine
B_{AB}, A_{BA}, B_{BA}	binary interaction parameters of Eq. (12)
C	adjustable parameters of Eq. (7)
G	parameter of Eq. (6)
ΔG^{*E}	excess Gibbs energy of activation of viscous flow
H^E	excess enthalpy
M_i	molar mass of component i
V^E	excess molar volumes
V_i	molar volumes of pure component i
ΔV	relative change of volume in mixing
W_{vis}	interaction term in Eq. (9)

x_A	mole fraction of alkanol
x_B	mole fraction of di-*n*-alkylamine
Z_{AB}, Z_{BA}	binary parameters of McAllister Eq. (10)

Greek letters

α_{AB}, α_{BA}	adjustable parameters of Eq. (11).
ϕ_A	volume fraction of alkanol
ϕ_B	volume fraction of di-*n*-alkylamine
η	viscosity of mixtures
η_A, η_B	viscosity of components A and B
η_{AB}	parameters of Eq. (8)
$\Delta\eta$	viscosity deviation
ν	kinematic viscosity
ρ	density of mixture
ρ_A, ρ_B	density of component A and B
σ	standard deviations
$\sigma\,(\%)$	percentage standard deviations

References

[1] S.L. Oswal, H.S. Desai, Fluid Phase Equil. 149 (1998) 359–376.
[2] S.L. Oswal, H.S. Desai, Fluid Phase Equil. 161 (1999) 191–204.
[3] F. Ratkovics, M. Laszlo, Acta Chim. Acad. Sci. Hung. 79 (4) (1973) 395–400.
[4] S.G. Patel, S.L. Oswal, J. Chem. Soc., Faraday Trans. 88 (1992) 2497–2502.
[5] T.M. Letcher, J.W. Bayles, J. Chem. Eng. Data 16 (1971) 266–271.
[6] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents: Physical Properties and Methods of Purification, 4th Edition, Wiley/Interscience, New York, 1986.
[7] J. Timmermans, Physico Chemical Constants of Pure Organic Compounds, Elsevier, Amsterdam, Vol. 1, 1950, Vol. 2, 1965.
[8] M. Diaz-Pena, G. Tardajos, J. Chem. Thermodyn. 11 (1979) 441.
[9] J. Ortega, J. Chem. Eng. Data 27 (1982) 312–317.
[10] J.L. Hales, J.H. Ellender, J. Chem. Thermodyn. 8 (1976) 1177–1184.
[11] S.K. Garg, T.S. Banipal, J.C. Ahluwalia, J. Chem. Eng. Data 38 (1993) 227–230.
[12] S.L. Oswal, R.G. Sindhe, A.T. Patel, J.P. Dave, S.G. Patel, B.M. Patel, Int. J. Thermophys. 13 (1992) 617–627.
[13] A.W. Quin, D.F. Hoffman, P. Munk, J. Chem. Eng. Data 37 (1992) 55–61.
[14] S. Glasstone, K.J. Laidler, H. Eyring, The Theory of Rate Process, McGraw-Hill, New York, 1941, pp. 514–516.
[15] L. Domonkos, F. Ratkovics, Montshefte Fur Chem. 113 (1982) 1119–1126.
[16] G.S. Sastry, M. Ramamurthy, P.R. Naidu, Acta Chim. Hung. 114 (2) (1983) 113–116.
[17] J. B. Irving, Viscosity of Liquid Mixtures, NEL Report No 630 and 631, National Engineering Laboratory, East Kilbride, Glasgow, 1977.
[18] W. Cao, A. Fredenslund, P. Rasmussen, Ind. Eng. Chem. Res. 31 (1992) 2603–2619.
[19] L. Grunberg, A.H. Nissan, Nature 164 (1949) 799–800.
[20] M. Tamura, M. Kurata, Bull. Chem. Soc. Jpn. 25 (1952) 32–37.
[21] R.K. Hind, E. McLaughlin, A.R. Ubbelohde, Trans. Faraday Soc. 56 (1960) 328–334.
[22] P.K. Katti, M.M. Chaudhri, J. Chem. Eng. Data 9 (1964) 442–443.
[23] R.A. McAllister, AIChE J. 6 (1960) 427–431.
[24] E.L. Heric, J. Chem. Eng. Data 11 (1966) 66–68.
[25] G. Auslaender, Brit. Chem. Eng. 10 (1965) 196.
[26] K. Nakanishi, H. Shairai, Bull Chem. Soc. Jpn. 43 (1970) 1634–1642.

[27] I.M.S. Lampreia, E.F.G. Barbosa, Fluid Phase Equil. 71 (1992) 125–142.

[28] S.L. Oswal, K.D. Prajapati, J. Chem. Eng. Data 43 (1998) 367–372.

[29] J.M. Jansens, M. Rule, Can. J. Chem. Eng. 50 (1972) 591–594.

[30] T.M. Letcher, J. Chem. Thermodyn. 4 (1972) 159–173.

[31] S.L. Oswal, A.T. Patel, J. Chem. Eng. Data 40 (1995) 607–610.

[32] D. Patterson, G. Delmas, Disc. Faraday Soc. 49 (1970) 98–105.

[33] F. Sarmiento, M.I. Paz Andrade, J. Fernandez, R. Bravo, M Pintos, J. Chem. Eng. Data 30 (1985) 321–323.

[34] J. Fernandez, M.I. Paz Andrade, M. Pintos, F. Sarmiento, R. Bravo, J. Chem. Thermodyn. 15 (1983) 581–584.

[35] J.J. Christiansen, R.W. Hanks, R.M. Izatt, Handbook of Heats of Mixing, Wiley/Interscience, New York, 1982.

[36] J.J. Christiansen, R.L. Rowley, R.M. Izatt, Handbook of Heats of Mixing, Supplementary Volume, Wiley/Interscience, New York, 1988.

[37] H. Funke, M. Wetzal, A. Heintz, Pure Appl. Chem. 61 (1989) 1429–1439.

[38] J.N. Spencer, W.S. Wolbach, J.W. Hovick, L. Ansel, K.J. Modarress, J. Sol. Chem. 14 (1985) 805–814.

[39] P. Huyskens, T.Z. Huyskens, Bull. Soc. Chim. Belge. 69 (1960) 267–281.

[40] K. Nakanishi, S. Ichinose, H. Shirai, Ind. Eng. Chem. Fundam. 7 (1968) 381.

[41] S. Sawamura, Y. Taniguchi, K. Suzuki, Ber. Bunsenges Phys. Chem. 92 (1988) 880.

[42] R.J. Fort, W.R. Moore, Trans. Faraday Soc. 62 (1966) 1112–1119.

[43] D. Papaioannou, M. Bridakis, C. Panayiotou, J. Chem. Eng. Data 38 (1993) 616–626.

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

[45] F. Ratkovics, T. Salamon, L. Domonkos, Acta. Chim. Acad. Sci. Hung. 83 (1) (1974) 53–61.

[46] F. Ratkovics, T. Salamon, L. Domonkos, Acta. Chim. Acad. Sci. Hung. 83 (1) (1974) 71–77.