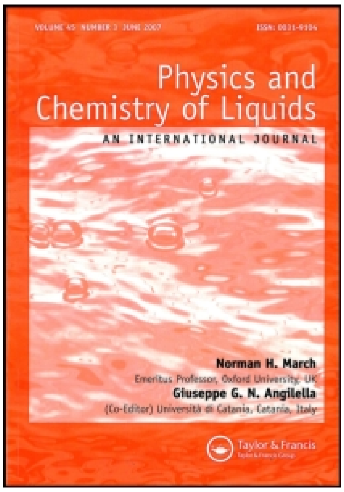

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Excess molar volumes and viscosities of some alkanols with cumene

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Excess molar volumes and viscosities of some alkanols with cumene

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Densities, ρ, viscosities, η, of the systems, cumene + 1-propanol, +2-propanol, +1-butanol and +*t*-butanol, have been determined from 303.15 to 323.15 K, with an interval of 5 K. Excess molar volumes, V_m^E, and excess viscosities, η^E, have been calculated from density and viscosity data. ρ, V_m^E, η and η^E of the systems have been plotted against the mole fraction of alcohols. Some of these properties and their excess values have been represented satisfactorily by appropriate polynomials. For the systems, cumene + 1-propanol and cumene + 1-butanol, V_m^E are both positive and negative, but for the systems, cumene + 2-propanol and cumene + *t*-butanol, positive V_m^E have been observed for the whole range of composition. The observed volumetric and viscometric properties have been explained by the concepts: (a) dissociation of alkanols in cumene-rich region, (b) partial accommodation of cumene into interstitial positions of 1-alkanols in alkanol-rich region, (c) donor–acceptor interaction between alkanols and cumene and (d) steric hindrance of branched alkanols.

Keywords: Excess molar volume; Viscosity; Cumene; 1-Propanol; 2-Propanol; 1-Butanol; *t*-Butanol

1. Introduction

This is a part of our ongoing research on volumetric and viscometric properties of binary liquid mixtures with the objective of understanding homo- and heteromolecular interaction in liquid systems. In recent years, a number of studies have been made on volumetric and viscometric properties of the mixtures of alkanols + a variety of aromatic hydrocarbons, such as, benzene, toluene, xylenes, trimethylbenzenes, etc. [1–11], but hardly any systematic study on the mixtures of cumene and alkanols is available. This prompted us to undertake a study on the volumetric, viscometric and thermodynamic properties of viscous flow of cumene + alkanols. We wish to report here the above properties of cumene + isomers of alkanols containing 3 and 4 carbon atoms, with the intention to see the effect of branching as well as chain length of alkanols.

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Very recently, we have studied the volumetric and viscometric properties of the same alkanols + *m*-xylene [12,13].

2. Experimental

Chemicals used for this investigation have been procured from Aldrich with quoted purities: 1-propanol, 99.5%; 2-propanol, 99.5%; 1-butanol, 99.8%; *t*-butanol, 99.5% and cumene (isopropyl benzene), 99%. These have been used without any further treatment, except that alkanols were kept over molecular sieves (4A) for at least three weeks prior to their use. As measures of purity check, densities of pure liquids were compared with the available literature values, which show satisfactory agreement.

An analytical balance of accuracy ± 0.0001 g was used in density measurement. The solutions were prepared by weighing the masses of the components by the same balance. The mole fraction was accurate up to fourth place of decimal. The density was measured by a 25 mL specific gravity bottle previously calibrated with doubly distilled water. An Ostwald U-tube viscometer with sufficiently long efflux time was used in viscosity measurement, so that no kinetic energy correction was necessary. The time of flow was recorded by a timer accurate up to ±0.1 s. For every measurement, a thermostatic water bath controlled to ±0.05 K was used. The average uncertainty in the measured density and viscosity was not more than 0.14 $\mathrm{kg\,m^{-3}}$ and $5.5 \times 10^{-7}\,\mathrm{kg\,m^{-1}\,s^{-1}}$, respectively.

3. Results and discussion

Densities and viscosities of the pure compounds, cumene, 1-propanol, 2-propanol, 1-butanol and *t*-butanol at 303.15, 308.15, 313.15, 318.15 and 323.15 K are shown in table 1. The literature values for alkanols are cited which compare well with our experimental values. The literature values of density and viscosity of cumene have been found only at 298.15 K, which are 857.1 $\mathrm{kg\,m^{-3}}$ and $7.390 \times 10^{-4}\,\mathrm{kg\,m^{-1}\,s^{-1}}$ respectively [29]. Our interpolated values for cumene at this temperature are 857.3 $\mathrm{kg\,m^{-3}}$ and $7.217 \times 10^{-4}\,\mathrm{kg\,m^{-1}\,s^{-1}}$, correspoding well with the literature values. Densities of the systems are represented in table 2 at temperatures ranging from 303.15 to 323.15 K. Figure 1 shows the variation of densities of all the systems at 303.15 K as a function of mole fraction of alkanols. The fact that the density of *t*-butanol (0.7752 $\mathrm{g\,cm^{-3}}$) < 1-butanol (0.8019 $\mathrm{g\,cm^{-3}}$) and 2-propanol (0.7768 $\mathrm{g\,cm^{-3}}$) < 1-propanol (0.7953 $\mathrm{g\,cm^{-3}}$) at 303.15 K and the boiling point of *t*-butanol (82°C) < 1-butanol (117.7°C) and 2-propanol (82°C) < 1-propanol (97°C) is an obvious consequence of impaired self-association of branched chain alkanols caused by steric hindrance.

Densities, $\rho/\mathrm{kg\,m^{-3}}$, and viscosities, $\eta/\mathrm{kg\ m^{-1}s^{-1}}$, have been fitted to the following polynomial equation of the form,

$$Y = \sum_{i=0}^{n} A_i x_2^i \tag{1}$$

Table 1. Densities, $\rho \times 10^{-3}$ (kg m^{-3}) and viscosities, $\eta \times 10^{4}$ (kg m^{-1}s^{-1}), of pure compounds at different temperatures.

		Temperature (K)				
Compound	Property	303.15	308.15	313.15	318.15	323.15
Cumene	ρ	0.8530	0.8488	0.8445	0.8402	0.8360
	η	6.881	6.488	6.116	5.767	5.447
1-Propanol	ρ	0.7953 (0.7956)^{a,b} (0.7954)^{c} (0.7955)^{d}	0.7912 (0.7912)^{a} (0.7913)^{c}	0.7871 (0.7874)^{b} (0.7871)^{c}	0.7830	0.7789 (0.7789)^{e}
	η	17.309 (17.21)^{a} (17.25)^{f}	15.440 (15.26)^{a,c,g} (15.46)^{h}	13.80 (13.72)^{c} (13.66)^{g} (13.85)^{h}	12.253 (12.45)^{g}	11.02 (11.21)^{g}
2-Propanol	ρ	0.7768 (0.7769)^{i}	0.7724 (0.7725)^{a} (0.7726)^{i}	0.7679 (0.7683)^{i}	0.7634 (0.7636)^{i}	0.7588 (0.7589)^{i}
	η	17.868 (17.81)^{a}	15.504 (15.51)^{a}	13.474	11.784	10.307
1-Butanol	ρ	0.8019 (0.8018)^{a,d} (0.80194)^{j}	0.7980 (0.7981)^{a,h}	0.7941 (0.7943)^{h} (0.79405)^{j}	0.7902	0.7863 (0.7862)^{e} (0.7865)^{g}
	η	22.924 (22.68)^{a} (22.46)^{c}	20.254 (19.82)^{a,c} (20.17)^{h}	17.949 (17.64)^{c,g} (17.93)^{h}	15.937 (15.75)^{g}	14.237 (14.06)^{g}
t-Butanol	ρ	0.7754 (0.77541)^{f}	0.7704 (0.7643)^{a}	0.7650	0.7599	0.7546
	η	33.401 (33.59)^{c} (33.16)^{f} (33.653)^{k}	26.122 (26.23)^{c}	20.964 (20.807)^{k}	17.003	14.144

References ^{a}[25]; ^{b}[20]; ^{c}[2]; ^{d}[22]; ^{e}[23]; ^{f}[24]; ^{g}[27]; ^{h}[26]; ^{i}[19]; ^{j}[21]; ^{k}[28].

where, Y stands for each of the above properties. The coefficients, A_i, and the squares of the regression coefficients, r^2, are shown in tables 4 and 5 respectively for ρ and η. In all cases, very large values of r^2 have been found, indicating highly satisfactory fitting of the curve.

Excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}}$, have been calculated by the following equation,

$$V_{\mathrm{m}}^{\mathrm{E}} = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left\{ \frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right\} \tag{2}$$

where x_1, M_1, ρ_1 represent respectively mole fraction, molar mass and density of cumene, and x_2, M_2 and ρ_2 are the corresponding quantities of alkanols. The excess molar volumes of the systems at 303.15, 308.15, 313.15, 318.15 and 323.15 K are listed in table 2.

The excess properties have been fitted to a Redlich–Kister polynomial equation of the form,

$$Y^{\mathrm{E}} = x_1 x_2 \sum_{i=0}^{n} A_i (1 - 2x_1)^i \tag{3}$$

Table 2. Densities, $\rho \times 10^{-3}$ (kg m^{-3}), excess molar volumes, $V_m^E \times 10^6$ (m^3 mol^{-1}), of the systems, cumene + 1-propanol, +2-propanol, +1-butanol and +*t*-butanol, at different temperatures.

	T (K)									
	303.15		308.15		313.15		318.15		323.15	
x_2	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E
	Cumene (x_1) + 1-propanol (x_2)									
0.0000	0.8530	0.0000	0.8488	0.0000	0.8445	0.0000	0.8402	0.0000	0.8360	0.0000
0.0996	0.8493	0.0742	0.8450	0.0917	0.8406	0.1105	0.8362	0.1451	0.8318	0.1649
0.1997	0.8454	0.1195	0.8411	0.1375	0.8367	0.1580	0.8323	0.1924	0.8279	0.2138
0.2988	0.8415	0.1106	0.8372	0.1288	0.8328	0.1501	0.8284	0.1839	0.8240	0.2063
0.4008	0.8371	0.0913	0.8328	0.1095	0.8284	0.1317	0.8240	0.1648	0.8196	0.1882
0.5012	0.8323	0.0514	0.8279	0.0824	0.8235	0.1056	0.8191	0.1377	0.8146	0.1620
0.6002	0.8271	0.0203	0.8228	0.0381	0.8184	0.0621	0.8140	0.0933	0.8096	0.1183
0.7002	0.8210	−0.0120	0.8167	0.0040	0.8124	0.0220	0.8080	0.0460	0.8037	0.0640
0.8000	0.8140	−0.0386	0.8098	−0.0318	0.8055	−0.0171	0.8012	0.0013	0.7969	0.0166
0.8991	0.8058	−0.0525	0.8015	−0.0345	0.7973	−0.0281	0.7930	−0.0093	0.7887	0.0081
1.0000	0.7953	0.0000	0.7912	0.0000	0.7871	0.0000	0.7830	0.0000	0.7789	0.0000
	Cumene (x_1) + 2-propanol (x_2)									
0.0000	0.8530	0.0000	0.8488	0.0000	0.8445	0.0000	0.8402	0.0000	0.836	0.0000
0.1013	0.8475	0.1822	0.8432	0.1977	0.8388	0.2437	0.8346	0.2427	0.8301	0.2747
0.2013	0.8419	0.2915	0.8376	0.3052	0.8331	0.3616	0.8286	0.4055	0.8241	0.4346
0.2991	0.8365	0.3065	0.8320	0.3470	0.8275	0.3971	0.8229	0.4513	0.8184	0.4763
0.4002	0.8302	0.3375	0.8258	0.3601	0.8211	0.4318	0.8167	0.4115	0.8120	0.5009
0.4993	0.8239	0.2898	0.8193	0.3353	0.8147	0.3850	0.8101	0.4272	0.8054	0.4704
0.6002	0.8167	0.2398	0.8122	0.2673	0.8076	0.3088	0.8028	0.3704	0.7980	0.4203
0.7002	0.8085	0.2041	0.8040	0.2273	0.7993	0.2733	0.7946	0.3151	0.7899	0.3455
0.8006	0.7993	0.1458	0.7949	0.1531	0.7905	0.1557	0.7860	0.1667	0.7807	0.1424
0.9002	0.7890	0.0645	0.7845	0.0787	0.7799	0.0966	0.7753	0.1131	0.7700	0.1301
1.0000	0.7768	0.0000	0.7724	0.0000	0.7679	0.0000	0.7634	0.0000	0.7588	0.0000
	Cumene (x_1) + 1-butanol (x_2)									
0.0000	0.8530	0.0000	0.8488	0.0000	0.8445	0.0000	0.8402	0.0000	0.8360	0.0000
0.1001	0.8488	0.1014	0.8445	0.1369	0.8402	0.1129	0.8358	0.1655	0.8315	0.1873
0.1998	0.8449	0.1340	0.8406	0.1710	0.8363	0.1818	0.8319	0.2088	0.8276	0.2340
0.3007	0.8409	0.1174	0.8366	0.1555	0.8323	0.1708	0.8279	0.2020	0.8236	0.2301
0.3997	0.8366	0.1160	0.8323	0.1553	0.8281	0.1604	0.8237	0.1955	0.8194	0.2266
0.4999	0.8320	0.0988	0.8278	0.1251	0.8235	0.1494	0.8192	0.1741	0.8149	0.2080
0.6000	0.8275	0.0687	0.8229	0.0965	0.8187	0.1114	0.8144	0.1405	0.8101	0.1771
0.6992	0.8217	0.0529	0.8176	0.0686	0.8134	0.0885	0.8093	0.0952	0.8051	0.1209
0.7999	0.8163	−0.0398	0.8123	−0.0347	0.8082	−0.0233	0.8041	0.0128	0.8000	0.0035
0.9006	0.8094	−0.0185	0.8054	−0.0101	0.8014	−0.0049	0.7973	−0.0119	0.7933	−0.0202
1.0000	0.8019	0.0000	0.7980	0. 0000	0.7941	0.0000	0.7902	0.0000	0.7863	0.0000
	Cumene (x_1) + *t*-butanol (x_2)									
0.0000	0.8530	0.0000	0.8488	0.0000	0.8445	0.0000	0.8402	0.0000	0.8360	0.0000
0.0995	0.8459	0.2700	0.8416	0.2786	0.8372	0.3001	0.8327	0.3068	0.8284	0.3120
0.2007	0.8391	0.4045	0.8347	0.4196	0.8302	0.4434	0.8256	0.4540	0.8211	0.4784
0.3001	0.8323	0.4843	0.8278	0.5048	0.8233	0.5143	0.8186	0.5277	0.8141	0.5370
0.3998	0.8251	0.5481	0.8206	0.5578	0.8160	0.5678	0.8112	0.5830	0.8066	0.5929
0.5009	0.8168	0.6777	0.8122	0.6922	0.8075	0.7028	0.8026	0.7200	0.7979	0.7305
0.6007	0.8096	0.5758	0.8050	0.5776	0.8002	0.5853	0.7953	0.5861	0.7905	0.5936
0.7002	0.8014	0.5314	0.7967	0.5350	0.7918	0.5400	0.7869	0.5258	0.7823	0.4872
0.8005	0.7928	0.4355	0.7879	0.4531	0.7830	0.4405	0.7779	0.4379	0.7731	0.4105
0.9002	0.7849	0.1565	0.7801	0.1452	0.7750	0.1387	0.7699	0.1170	0.7649	0.0962
1.0000	0.7754	0.0000	0.7704	0.0000	0.7650	0.0000	0.7599	0.0000	0.7546	0.0000

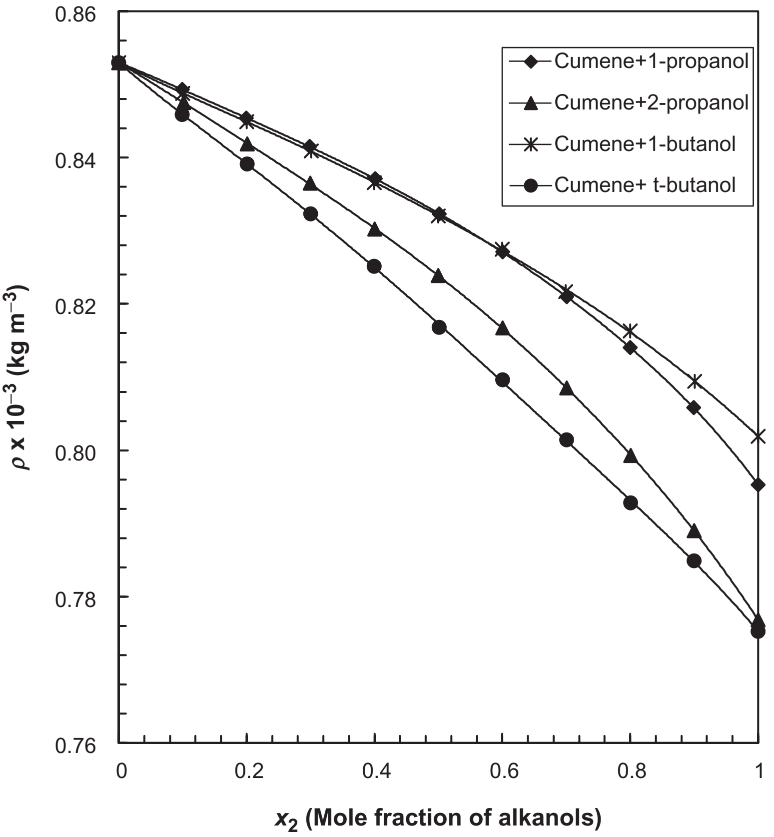

Figure 1. Variation of densities of cumene+1-propanol, +2-propanol +1-butanol, and +*t*-butanol at 303.15 K as a function of mole fraction of alkanols.

where, Y^E stands for V_m^E and η^E. The coefficients of the equation, A_i, and the standard deviations, σ, are listed in tables 6 and 7 respectively for V_m^E and η^E.

V_m^E for the systems, cumene + 1-propanol, cumene + 2-propanol, cumene + 1-butanol and cumene + *t*-butanol at temperature 303.15 K have been represented in figure 2. Examination of the figure reveals the following characteristics:

(a) V_m^E are positive in cumene-rich region, but negative in alkanol-rich region for the systems, cumene + 1-propanol and cumene + 1-butanol, although the negative values are very small,

(b) V_m^E are positive for the whole range of composition for the systems, cumene + 2-propanol and cumene + *t*-butanol and

(c) V_m^E of the system, cumene + 1-butanol are only slightly greater than those for the system cumene + 1-propanol throughout the whole range of composition. But for the system, cumene + *t*-butanol, V_m^E are substantially larger than those for the system, cumene + 2-propanol.

The sign of V_m^E depends upon the resultant of the factors contributing to expansion of volume and those contributing to contraction of volume. In the present system,

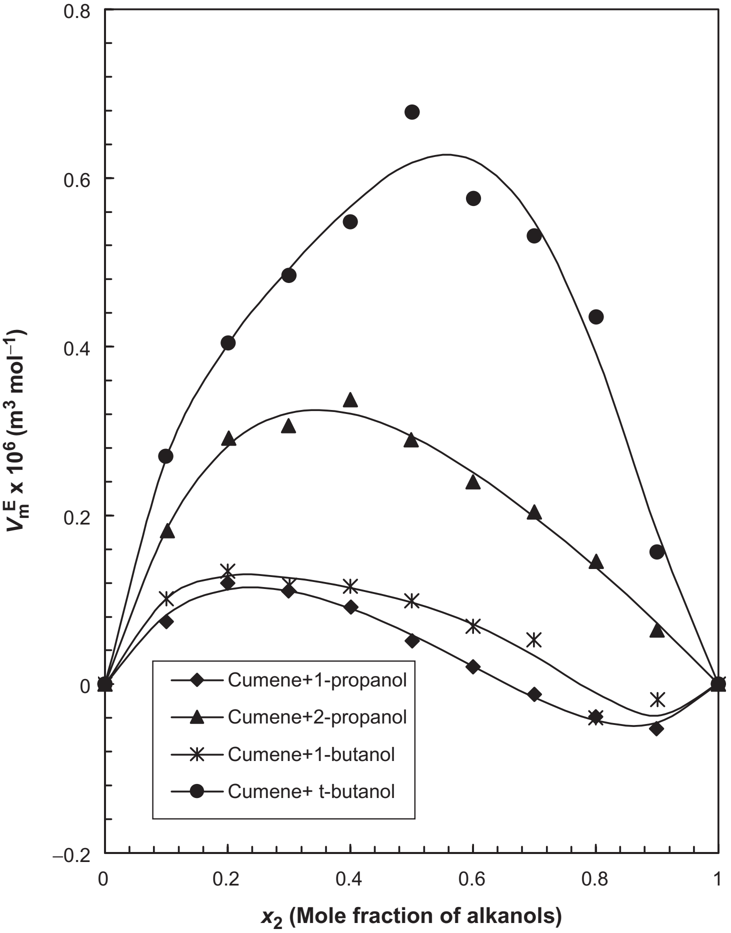

Figure 2. Comparison of excess molar volumes for the systems, cumene (x_1) + alkanols (x_2), against mole fraction of alkanols (x_2) at 303.15 K.

we envisage that the main factors contributing to expansion of volume are:

(a) dissociation of associated alkanols in solution systems, particularly in cumene-rich region and
(b) steric hindrance due to branching in cumene and in alkanols (2-propanol and *t*-butanol).

On the other hand, the following factors are considered responsible for volume contraction:

(a) donor–acceptor interaction between π-electrons of aromatic ring and hydroxyl hydrogen of alkanols and
(b) possible inclusion of isopropyl group of cumene, at least partially, into the structural network of alkanols.

Alkanols are thought to form multimers through self-association in the liquid phase via hydrogen bonding [14–18]. In presence of cumene, a non-polar aromatic

Table 3. Viscosities, $\eta \times 10^4$ (kg m^{-1}s^{-1}), excess viscosities, $\eta^E \times 10^4$ (kg m^{-1}s^{-1}), of the systems, cumene + 1-propanol, +2-propanol, +1-butanol and +*t*-butanol at different temperatures.

	T (K)									
	303.15		308.15		313.15		318.15		323.15	
x_2	η	η^E	η	η^E	η	η^E	η	η^E	η	η^E
Cumene (x_1) + 1-propanol (x_2)										
0.0000	6.881	0.000	6.488	0.000	6.116	0.000	5.767	0.000	5.447	0.000
0.0996	6.838	−0.723	6.412	−0.648	6.020	−0.612	5.678	−0.540	5.436	−0.507
0.1997	6.995	−1.296	6.529	−1.172	6.120	−1.075	5.746	−0.959	5.400	−0.870
0.2988	7.297	−1.784	6.794	−1.600	6.333	−1.466	5.920	−1.304	5.542	−1.181
0.4008	7.751	−2.224	7.176	−1.996	6.661	−1.814	6.202	−1.600	5.777	−1.447
0.5012	8.411	−2.529	7.731	−2.278	7.142	−2.054	6.612	−1.802	6.129	−1.625
0.6002	9.284	−2.698	8.470	−2.438	7.762	−2.205	7.145	−1.921	6.596	−1.718
0.7002	10.457	−2.6800	9.475	−2.424	8.652	−2.160	7.897	−1.879	7.201	−1.720
0.8000	12.052	−2.349	10.856	−2.121	9.820	−1.907	8.912	−1.628	8.100	−1.471
0.8991	14.257	−1.518	12.749	−1.395	11.461	−1.251	10.330	−1.027	9.322	−0.941
1.0000	17.309	0.000	15.440	0.000	13.800	0.000	12.253	0.000	11.020	0.000
Cumene (x_1) + 2-propanol (x_2)										
0.0000	6.881	0.000	6.488	0.000	6.116	0.000	5.767	0.000	5.447	0.000
0.1013	6.764	−0.816	6.347	−0.741	5.971	−0.649	5.620	−0.580	5.287	−0.517
0.2013	6.831	−1.507	6.402	−1.330	5.990	−1.175	5.619	−1.039	5.275	−0.912
0.2991	7.003	−2.151	6.534	−1.886	6.093	−1.648	5.682	−1.459	5.322	−1.264
0.4002	7.299	−2.782	6.776	−2.418	6.291	−2.094	5.853	−1.823	5.444	−1.581
0.4993	7.766	−3.314	7.151	−2.873	6.596	−2.472	6.110	−2.129	5.654	−1.830
0.6002	8.482	−3.719	7.732	−3.214	7.081	−2.741	6.508	−2.348	5.976	−2.007
0.7002	9.452	−3.970	8.534	−3.407	7.742	−2.899	7.041	−2.471	6.419	−2.091
0.8006	11.04	−3.732	9.869	−3.163	8.854	−2.655	7.975	−2.243	7.195	−1.879
0.9002	13.396	−2.849	11.827	−2.387	10.456	−1.995	9.303	−1.670	8.272	−1.397
1.0000	17.868	0.000	15.504	0.000	13.474	0.000	11.784	0.000	10.307	0.000
Cumene (x_1) + 1-butanol (x_2)										
0.0000	6.881	0.000	6.488	0.000	6.116	0.000	5.767	0.000	5.447	0.000
0.1001	6.982	−0.813	6.545	−0.748	6.143	−0.678	5.795	−0.607	5.481	−0.541
0.1998	7.295	−1.479	6.815	−1.342	6.366	−1.219	5.969	−1.107	5.613	−1.004
0.3007	7.788	−2.127	7.225	−1.933	6.725	−1.738	6.285	−1.560	5.885	−1.410
0.3997	8.423	−2.740	7.784	−2.463	7.209	−2.204	6.696	−1.977	6.249	−1.770
0.4999	9.355	−3.233	8.588	−3.893	7.901	−2.583	7.288	−2.313	6.767	−2.059
0.6000	10.68	−3.513	9.725	−3.138	8.867	−2.808	8.131	−2.495	7.485	−2.227
0.6992	12.516	−3.468	11.287	−3.108	10.216	−2.773	9.275	−2.474	8.480	−2.199
0.7999	14.745	−3.290	13.233	−2.906	11.871	−2.604	10.676	−2.335	9.682	−2.076
0.9006	18.366	−1.983	16.286	−1.807	14.522	−1.608	12.976	−1.434	11.677	−1.269
1.0000	22.924	0.000	20.254	0.000	17.949	0.000	15.937	0.000	14.237	0.000
Cumene (x_1) + *t*-butanol (x_2)										
0.0000	6.881	0.000	6.488	0.000	6.116	0.000	5.767	0.000	5.447	0.000
0.0995	6.893	−1.198	6.458	−1.017	6.059	−0.866	5.703	−0.730	5.370	−0.637
0.2007	7.128	−2.369	6.665	−1.940	6.215	−1.627	5.814	−1.360	5.452	−1.159
0.3001	7.481	−3.633	6.941	−2.941	6.451	−2.410	6.002	−1.984	5.604	−1.660
0.3998	7.954	−5.059	7.344	−4.009	6.782	−3.233	6.279	−2.612	5.835	−2.149
0.5009	8.754	−6.517	8.007	−5.060	7.352	−3.989	6.742	−3.172	6.218	−2.569
0.6007	9.692	−8.192	8.782	−6.233	7.980	−4.840	7.269	−3.771	6.649	−3.009
0.7002	11.295	−9.638	10.071	−7.173	9.019	−5.469	8.117	−4.172	7.349	−3.264
0.8005	14.154	−10.379	12.321	−7.507	10.802	−5.582	9.531	−4.160	8.485	−3.186
0.9002	18.74	−9.985	15.780	−7.000	13.433	−5.091	11.533	−3.711	10.010	−2.816
1.0000	33.639	0.000	26.173	0.000	20.941	0.000	16.975	0.000	14.099	0.000

Table 4. Coefficients, A_i, of equation (1), expressing density, $\rho \times 10^{-3}$ (kg m^{-3}) and the squares of the regression coefficients, r^2, for the systems, cumene + 1-propanol, +2-propanol, +1-butanol and +*t*-butanol.

System	Temperature (K)	A_0	A_1	A_2	A_3	A_4	A_5	r^2
Cumene + 1-propanol	303.15	−0.036	−0.0186	0.0801	−0.212	0.2105	−0.0817	>0.9999
	308.15	−0.0397	0.0191	−0.078	0.0943	−0.0643	0.011	>0.9999
	313.15	−0.0418	0.0349	−0.1325	0.1873	−0.1397	0.0345	>0.9999
	318.15	−0.0442	0.0538	−0.2002	0.3064	−0.2405	0.0675	>0.9999
	323.15	−0.0496	0.1031	−0.395	0.6726	−0.5633	0.1751	>0.9999
Cumene + 2-propanol	303.15	−0.0526	−0.024	0.1044	−0.2506	0.2231	−0.0765	>0.9999
	308.15	−0.0549	−0.0035	0.0076	−0.0489	0.0357	−0.0124	>0.9999
	313.15	−0.0571	0.0142	−0.0725	0.1156	−0.1153	0.0385	>0.9999
	318.15	−0.0544	−0.0247	0.0869	−0.1865	0.1541	−0.0523	>0.9999
	323.15	−0.0617	0.043	−0.2006	0.3987	−0.4092	0.1526	>0.9999
Cumene + 1-butanol	303.15	−0.0454	0.0499	−0.1701	0.2500	−0.1874	0.0519	0.9999
	308.15	−0.0499	0.0944	−0.3416	0.5493	−0.4261	0.1230	>0.9999
	313.15	−0.0500	0.0949	−0.3363	0.5287	−0.3998	0.1121	>0.9999
	318.15	−0.0528	0.1204	−0.4439	0.7484	−0.6071	0.1850	>0.9999
	323.15	−0.0551	0.1380	−0.5040	0.8465	−0.6811	0.2059	>0.9999
Cumene + *t*-butanol	303.15	−0.0757	0.0644	−0.1971	0.2049	−0.0624	−0.0117	0.9999
	308.15	−0.0749	0.0390	−0.0781	−0.0327	0.1520	−0.0837	0.9999
	313.15	−0.0770	0.0509	−0.1148	0.0149	0.1282	−0.0816	0.9999
	318.15	−0.0800	0.0670	−0.1793	0.1453	0.0045	−0.0378	0.9999
	323.15	−0.0829	0.0885	−0.2756	0.3424	−0.1762	0.0224	0.9999

Table 5. Coefficients, A_i, of equation (1), expressing viscosity, $\eta \times 10^4$ (kg m^{-1}s^{-1}) and the squares of the regression coefficients, r^2, for the systems, cumene + 1-propanol, +2-propanol, +1-butanol and +*t*-butanol.

System	Temperature (K)	A_0	A_1	A_2	A_3	A_4	A_5	r^2
Cumene + 1-propanol	303.15	−1.413	11.395	−9.8736	10.743	−3.2627	2.8416	>0.9999
	308.15	−2.0959	15.904	−29.397	45.068	−32.959	12.432	>0.9999
	313.15	−2.3221	17.078	−37.528	61.413	−48.582	17.627	>0.9999
	318.15	−1.6709	8.6705	−3.9512	−6.0177	14.513	−5.056	>0.9999
	323.15	0.6571	−15.47	82.713	−154.42	133.93	−41.835	>0.9999
Cumene + 2-propanol	303.15	−3.6746	34.445	−131.97	284.15	−286.09	114.12	>0.9999
	308.15	−3.7995	32.93	−120.82	247.97	−241.3	94.029	0.9999
	313.15	−3.5066	27.741	−99.46	203.14	−197.47	76.908	0.9999
	318.15	−2.9186	19.297	−63.427	129.63	−128.24	51.673	0.9999
	323.15	−3.194	21.562	−73.207	144.42	−137.36	52.636	0.9999
Cumene + 1-butanol	303.15	0.6432	4.3424	19.431	−39.675	42.746	−11.427	0.9999
	308.15	−0.1876	10.013	−8.2885	15.093	−9.3148	6.4633	0.9999
	313.15	−0.4218	8.6339	−2.1483	−1.6098	7.2878	0.1023	0.9999
	318.15	−0.0246	2.932	16.763	−35.271	34.242	−8.461	0.9999
	323.15	0.4051	−2.821	36.702	−71.529	64.523	−18.481	0.9999
Cumene + *t*-butanol	303.15	−2.8434	26.763	−107.77	217.63	−206.12	75.303	0.9995
	308.15	−10.209	143.03	−669.34	1478.5	−1510	587.66	0.9995
	313.15	−7.766	102.84	−468.66	1026.5	−1043.2	405.09	0.9995
	318.15	−5.9453	75.093	−335.67	730.84	−738.72	285.59	0.9996
	323.15	−5.1343	61.232	−267.8	576.01	−576.23	220.56	0.9995

hydrocarbon, disintegration of such multimers of alkanols into smaller units or monomers through disruption of H-bonding in alkanols takes place. This causes the volume to expand. Another important factor that contributes significantly towards volume expansion is the steric hindrance of the branched chain alkanols (2-propanol

Table 6. Coefficients, A_i, of Redlich–Kister equation expressing $V_m^E \times 10^6\,(\mathrm{m^3\,mol^{-1}})$, and standard deviation, σ, for the systems.

System	Temperature (K)	A_0	A_1	A_2	A_3	σ
Cumene + 1-propanol	303.15	0.2333	−0.7048	−0.0490	−0.2875	0.00690
	308.15	0.3162	−0.7332	0.0163	−0.2806	0.00452
	313.15	0.4069	−0.7179	0.0757	−0.4317	0.00398
	318.15	0.5262	−0.7506	0.2668	−0.5615	0.00651
	323.15	0.6160	−0.7667	0.3820	−0.5799	0.00995
Cumene + 2-propanol	303.15	1.1750	−0.7192	0.3910	−0.0838	0.01333
	308.15	1.3124	−0.7841	0.3278	−0.0089	0.00798
	313.15	1.5263	−0.9190	0.4047	−0.1695	0.01818
	318.15	1.7164	−0.9185	0.3418	−0.2275	0.02069
	323.15	1.8937	−0.9347	0.1815	−0.5411	0.03674
Cumene + 1-butanol	303.15	0.3887	−0.4111	0.0514	−0.8635	0.01839
	308.15	0.5065	−0.5273	0.0652	−0.9835	0.02124
	313.15	0.5743	−0.4694	0.0701	−1.1039	0.02173
	318.15	0.6791	−0.6099	0.1623	−0.9467	0.02338
	323.15	0.8138	−0.5794	0.1673	−1.1611	0.02496
Cumene + *t*-butanol	303.15	2.4722	0.6484	0.0310	−1.9443	0.04189
	308.15	2.5166	0.6007	0.0653	−1.9903	0.04946
	313.15	2.5511	0.5899	0.0992	−2.3393	0.04754
	318.15	2.5973	0.4708	−0.0580	−2.3807	0.05396
	323.15	2.6212	0.2414	−0.2502	−2.3852	0.05586

Table 7. Coefficients, A_i, of Redlich–Kister equation expressing $\eta^E \times 10^4\,(\mathrm{kg\,m^{-1}s^{-1}})$, and standard deviation, σ, for the systems.

System	Temperature (K)	A_0	A_1	A_2	A_3	σ
Cumene + 1-propanol	303.15	−10.0960	−5.1905	−3.5817	−0.5302	0.01121
	308.15	−9.0849	−4.7242	−3.3883	−0.6042	0.00770
	313.15	−8.2017	−4.0737	−3.1601	−0.5262	0.01285
	318.15	−7.2242	−3.4395	−2.3241	0.0897	0.00748
	323.15	−6.5036	−3.1359	−2.3491	0.1688	0.01243
Cumene + 2-propanol	303.15	−13.0934	−9.4287	−10.0626	−7.0953	0.06886
	308.15	−11.3649	−8.0204	−8.2934	−5.1379	0.05801
	313.15	−9.7850	−6.5507	−6.7865	−4.1457	0.04869
	318.15	−8.4562	−5.3087	−5.6304	−3.3809	0.03834
	323.15	−7.2695	−4.3308	−4.6086	−2.6288	0.03608
Cumene + 1-butanol	303.15	−12.8150	−8.3452	−4.8121	−0.7268	0.08399
	308.15	−11.4714	−7.1804	−4.4901	−1.0406	0.05636
	313.15	−10.2562	−6.3769	−4.1228	−0.8259	0.05348
	318.15	−9.1635	−5.5687	−3.7751	−0.9260	0.05209
	323.15	−8.1886	−4.8211	−3.3494	−0.9189	0.04674
Cumene + *t*-butanol	303.15	−24.9668	−27.0782	−48.6852	−49.0066	0.54937
	308.15	−19.5577	−19.5701	−32.7489	−31.7002	0.36585
	313.15	−15.6122	−14.5149	−22.8705	−21.1065	0.26599
	318.15	−12.4029	−10.3294	−16.0754	−14.7955	0.18381
	323.15	−10.0729	−7.5817	−11.8101	−10.6609	0.14495

and *t*-butanol) and cumene itself. Branching in the alkyl group of the alkanol affects both hydrogen bonding as well as electron donor–acceptor interactions [9]. The steric effect thus causes much larger positive V_m^E for branched chain alkanols than for straight chain alkanols, as can be seen in figure 2.

In highly rich region of alkanols, where smaller units of alkanols are believed to be reformed into larger units, negative V_m^E are observed for straight chain alkanols at lower temperatures. At higher temperatures, however, these values turn to very small positive (table 2). In this region the combined effect for volume contraction, i.e., donor–acceptor interaction (formation of H bonding between π-electrons of the aromatic ring of cumene and the hydroxyl hydrogen of 1-alkanols) and probable inclusion of isopropyl group of cumene into the structural network of 1-alkanols generally exceed the effects responsible for volume expansion.

Viscosities of the systems at different temperatures are listed in table 3 and plotted in figure 3 as a function of mole fraction of alkanols at 303.15 K. Since the basic nature of the viscosity curves of the systems virtually does not change with temperature, the curves for other temperatures are not shown. Examination of the curves shows that addition of alkanols to cumene increases viscosity slowly up to a substantial concentration of alkanols, following which the viscosity increases rapidly with increasing concentration of alkanols. The slow rise of viscosity (figure 3) can be accounted for

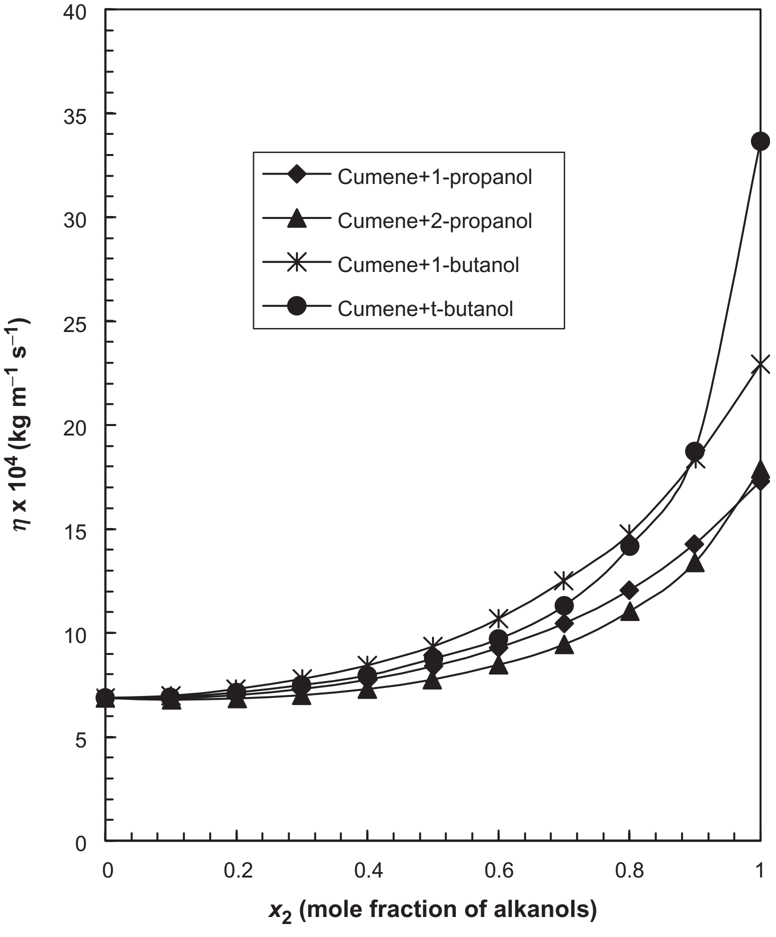

Figure 3. Comparison of viscosities of the systems, cumene (x_1) + alkanols (x_2), as a function of mole fraction of alkanols, x_2, at 303.15 K.

primarily due to dissociation of the multimers of alkanols into their smaller units. In alkanol-rich region the rapid rise of viscosity is thought to be due to continuous increase of self-association of alkanols.

Excess viscosity, η^E, has been calculated by using the following equation,

$$\eta^E = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2) \tag{4}$$

where η_1 and η_2 are the viscosities of the components, cumene and alkanols respectively. η is the viscosity of the solution. x_1 and x_2 are the mole fractions of cumene and alkanols. Figure 4 shows the comparison of the variation of excess

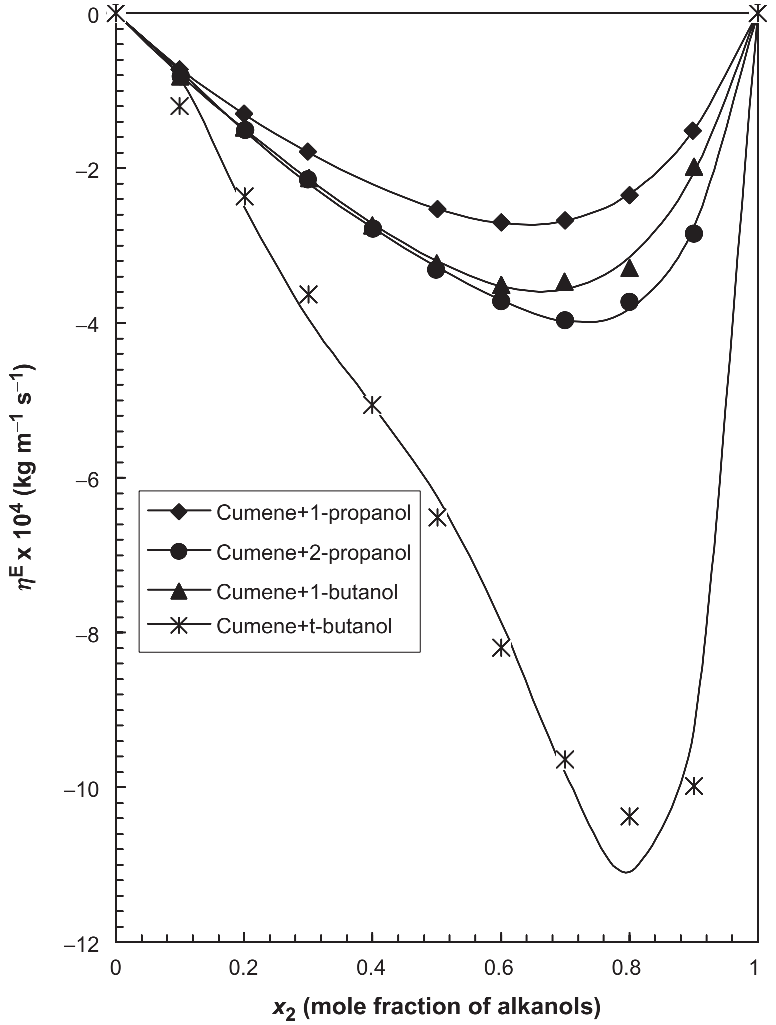

Figure 4. Comparison of excess viscosities of the systems, cumene (x_1) + alkanols (x_2), against mole fraction of alkanols (x_2) at 303.15 K.

viscosities of different systems as a function of mole fraction of alkanols at 303.15 K. An examination of the curves shows that:

(a) η^E are negative for the whole range of composition and
(b) the minima occur between 0.6 and 0.8 mol fraction of alkanols.

The negative excess viscosities throughout the whole range of composition indicate the formation of smaller units of alkanols in different proportions depending upon the concentration of alkanols in solution systems. The figure also reveals that the systems having branched chain alkanols, 2-propanol and *t*-butanol, show larger negative η^E than their straight chain isomers, 1-propanol and 1-butanol, respectively. This leads us to conclude that branched chain alkanols reduce the viscosity more than their straight chain isomers do. Ali *et al.* [6], Akhtar *et al.* [1] and Saleh *et al.* [13] observed similar effects for the systems containing branched chain alkanols + aromatic hydrocarbons and their straight chain isomers + aromatic hydrocarbons. Branched chain alkanols are less strongly associated than *n*-alkanols through H-bonding, because of steric hindrance, and hence more easily dissociable into smaller units. Moreover, the interaction between π-electrons of aromatic ring and branched chain alkanols is weaker than that between aromatic ring and *n*-alkanols, again due to steric effect, which was discussed elaborately in the previous section. Thus, the branched chain alkanols cause greater reduction of viscosity from ideal values, i.e., larger negative η^E, than their straight chain isomers do. In our recent studies [12,13], we used the same argument to explain the volumetric and viscometric properties of the systems containing same alkanols + *m*-xylene. In a study of the viscometric properties of different alkanols in toluene, Nikam *et al.* [2] showed the effects of branching and chain length of alkanols, which are consistent with our observation.

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