Densities, Viscosities, and Relative Permittivities for Pentane + 1-Alcohols (C_1 to C_{12}) at 298.15 K

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New experimental data on densities, viscosities, and relative permittivities for pentane + methanol, + 1-propanol, + 1-butanol, + 1-pentanol, + 1-hexanol, + 1-heptanol, + 1-octanol, + 1-decanol, and + 1-dodecanol are reported at 298.15 K. The molar and orientation polarizations were obtained by combining relative permittivity and molar volume data. The excess volumes and deviations in relative permittivities and molar and orientation polarizations were also calculated. The viscosities of all the mixtures were also correlated by Grunberg−Nissan, McAllister, and Auslander equations. The correlation factor, g_K, was derived from the relative permittivity data over the whole 1-alcohol mole fraction range for all the mixtures.

Introduction

A literature survey on 1-alcohol + alkane binary systems revealed that the majority of studies report mostly the experimental data of either excess volumes or excess enthalpies. A comprehensive review on excess volumes of 1-alcohol + alkane mixtures with a few recommended data sets has been made (Treszczanowicz et al., 1993). Similarly excellent reviews are also available on the excess enthalpies (Fernandez et al., 1990; Roux et al., 1993). In comparison to the above-mentioned properties, only few measurements on the transport and dielectric properties of 1-alcohol + alkane mixtures have been reported. Thermodynamic data on binary mixtures of 1-alcohols with alkanes, lower than hexane and larger than decane, are also lacking in the literature. We are engaged in the systematic study of volumetric, acoustic, transport, and dielectric properties of 1-alcohols with various industrially important organic solvents such as alkanes and acrylic esters. The densities, speeds of sound, viscosities, relative permittivities and refractive indexes of binary mixtures containing homologous series of 1-alcohols and either hexane or heptane in the temperature range (298.15−313.15) K have been previously reported (Sastry and Raj, 1996a; Sastry and Valand, 1996a,b, 1997).

In an effort to make available data on various physical properties of 1-alcohol + pentane mixtures, this paper reports the densities, viscosities, and relative permittivities for nine binary mixtures of homologous series of 1-alcohols with pentane at 298.15 K. From the experimental data, the excess volumes, V^E, deviation in relative permittivities, $\delta\epsilon$, and molar and orientation polarizations, δP_m and δP_o, have been calculated. The mixture viscosities were correlated by semiempirical equations (Grunberg and Nissan, 1949; McAllister, 1960; Auslaender, 1964). The correlation factor, g_K, was also derived from the relative permittivity and refractive index data over the whole 1-alcohol mole fraction range.

Experimental Section

Materials. Methanol, 1-propanol, and 1-butanol were BDH reagent chemicals and were purified further by standard procedures (Riddick et al.,1970). 1-Pentanol and 1-hexanol were of Riedel make, and 1-heptanol and 1-dodecanol were Merck products. 1-Octanol and 1-decanol were Fluka puriss grade chemicals and used as received from the manufacturer without any purification. Pentane of research grade was purchased from May & Baker, England, and was stored over molecular sieves and distilled freshly. The purity of all the reagents was found to be greater than 99.9% on a mole basis. The purity was assessed with a Waters HPLC equipped with a multisolvent delivery system, 46 k injector, micro-bondapak C_{18} column and 991-photodiode array detector. Tetrahydrofuran of HPLC grade was used a solvent. The measured densities, viscosities, relative permittivities, and refractive indexes of all the pure components were also found to be in close agreement with the literature data, and such a comparison is given in Table 1.

The binary solutions were prepared for each composition afresh in a stoppered glass bottle with due precaution to minimize the evaporation loss. All the mass measurements were made with a Dhona single-pan analytical balance, Dhona 100 DS (India), accurate to ±0.02 mg. The calculated mole fractions were accurate up to ±0.0001.

Methods. The densities were determined with a calibrated double-stem pycnometer having a bulb volume of about 11 cm^3, and the internal diameter of pycnometer capillaries was 1 mm. Viscosities of pure and mixture components were obtained from the measured flow times using two different suspended type Ubbelohde viscometers to cover all the mixtures. The calibration of the pycnometer and viscometers was done with triple-distilled water and double-distilled cyclohexane or toluene. The relative permittivities of the individual pure components and binary mixtures were calculated from the capacitance measurements with a universal dielectrometer type OH-301 of Radelkis, Hungary. The refractive indexes for the sodium D line were measured by an Abbe type research refractometer. The procedure used in the calibration of dielectric cells was the same as described in detail elsewhere (Sastry and Raj, 1996b). The temperature during the measurements of all the above properties was maintained thermostatically accurate to ±0.01 K. The measured densities, viscosities, relative permittivities, and refractive indexes

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Table 1. Physical Properties of Pure Components at 298.15 K

	ρ/g·cm^{-3}		η/mPa·s		ϵ		n_D	
	exptl	lit.	exptl	lit.	exptl	lit.	exptl	lit.
pentane	0.6214	0.62139[a]	0.220	0.225[a]	1.818		1.3546	1.35465[b]
methanol	0.7866	0.78664[c]	0.550	0.553[c]	32.700	32.70[a]	1.3268	1.3268[d]
1-propanol	0.7996	0.79975[c]	1.943	1.943[c]	20.331	20.33[a]	1.3831	1.3832[e]
1-butanol	0.8061	0.8060[c]	2.570	2.571[c]	17.505	17.51[a]	1.3967	1.3967[e]
1-pentanol	0.8107	0.81077[f]	3.510	3.513[c]	15.558	15.13[g]	1.4075	1.4074[e]
1-hexanol	0.8160	0.8162[c]	4.477	4.590[h]	13.250	13.28[g]	1.4160	1.4160[d]
1-heptanol	0.8189	0.8189[h]	5.770	5.774[c]	11.793		1.4225	1.4222[i]
1-octanol	0.8212	0.8216[e]	7.363	7.363[c]	9.858		1.4260	1.4267[e]
1-decanol	0.8265	0.82652[j]	11.790	11.798[k]	7.600		1.4345	1.4345[e]
1-dodecanol	0.8281		16.134		6.274		1.4420	

[a] Riddick and Bunger (1970). [b] Treszczanowicz and Benson (1980). [c] TRC Tables (1994). [d] Aminabhavi et al., (1993). [e] Ortega (1982). [f] Iglesias et al. (1993). [g] D'Aprano et al. (1979). [h] Ortega and Matos (1986). [i] Fernandez et al. (1985). [j] Treszczanowicz et al. (1982). [k] Bravo et al. (1991).

Table 2. Densities (ρ) and Excess Volumes (V^E) for 1-Alcohol + Pentane Mixtures at 298.15 K

x_1	ρ/ g·cm^{-3}	V^E/ cm^3·mol^{-1}	x_1	ρ/ g·cm^{-3}	V^E/ cm^3·mol^{-1}	x_1	ρ/ g·cm^{-3}	V^E/ cm^3·mol^{-1}
methanol (1) + pentane (2)			1-propanol (1) + pentane (2)			1-butanol (1) + pentane (2)		
0.1362	0.6285	0.261	0.0534	0.6271	0.097	0.0571	0.6294	0.089
0.2538	0.6366	0.374	0.1578	0.6396	0.191	0.1573	0.6447	0.081
0.4275	0.6525	0.410	0.2257	0.6485	0.203	0.2579	0.6613	−0.011
0.5597	0.6690	0.369	0.3520	0.6667	0.165	0.3570	0.6784	−0.098
0.6628	0.6856	0.310	0.4541	0.6830	0.108	0.4589	0.6966	−0.147
0.7438	0.7018	0.251	0.5034	0.6914	0.080	0.5013	0.7043	−0.155
0.8153	0.7193	0.191	0.5548	0.7006	0.052	0.5557	0.7144	−0.155
0.8727	0.7361	0.138	0.6570	0.7200	0.010	0.6589	0.7341	−0.139
0.9203	0.7524	0.090	0.7563	0.7405	−0.011	0.7573	0.7538	−0.119
0.9365	0.7586	0.073	0.8553	0.7628	−0.013	0.8595	0.7753	−0.097
0.9554	0.7663	0.052	0.9559	0.7878	−0.004	0.9559	0.7963	−0.048
0.9768	0.7756	0.027						
1-pentanol (1) + pentane (2)			1-hexanol (1) + pentane (2)			1-heptanol (1) + pentane (2)		
0.0535	0.6307	0.049	0.0575	0.6338	−0.071	0.0562	0.6354	−0.114
0.1050	0.6400	0.019	0.1463	0.6530	−0.216	0.1572	0.6597	−0.306
0.2074	0.6595	−0.145	0.2569	0.6765	−0.389	0.2556	0.6824	−0.464
0.3106	0.6795	−0.320	0.3564	0.6971	−0.497	0.3557	0.7043	−0.584
0.4154	0.6996	−0.421	0.4581	0.7175	−0.550	0.4549	0.7248	−0.654
0.5094	0.7175	−0.430	0.5040	0.7265	−0.557	0.4990	0.7336	−0.668
0.6036	0.7352	−0.380	0.5574	0.7368	−0.550	0.5520	0.7439	−0.671
0.7149	0.7561	−0.283	0.6519	0.7547	−0.514	0.6530	0.7627	−0.633
0.8091	0.7740	−0.199	0.7544	0.7737	−0.441	0.7565	0.7808	−0.530
0.8588	0.7836	−0.157	0.8568	0.7919	−0.322	0.8570	0.7973	−0.364
0.9034	0.7921	−0.117	0.9518	0.8082	−0.139	0.9535	0.8121	−0.136
0.9527	0.8017	−0.066						
1-octanol (1) + pentane (2)			1-decanol (1) + pentane (2)			1-dodecanol (1) + pentane (2)		
0.0571	0.6376	−0.170	0.0583	0.6416	−0.223	0.0560	0.6446	−0.354
0.1566	0.6640	−0.399	0.1564	0.6721	−0.514	0.1555	0.6797	−0.768
0.2580	0.6888	−0.566	0.2572	0.6997	−0.723	0.2548	0.7087	−0.994
0.3564	0.7111	−0.680	0.3587	0.7242	−0.858	0.3568	0.7337	−1.099
0.4547	0.7319	−0.752	0.4582	0.7454	−0.922	0.4551	0.7543	−1.120
0.5013	0.7412	−0.772	0.5018	0.7540	−0.930	0.5040	0.7637	−1.106
0.5552	0.7515	−0.782	0.5529	0.7635	−0.922	0.5587	0.7729	−1.072
0.6550	0.7696	−0.757	0.6551	0.7809	−0.851	0.6534	0.7878	−0.968
0.7512	0.7858	−0.669	0.7567	0.7963	−0.703	0.7530	0.8014	−0.789
0.8551	0.8017	−0.479	0.8597	0.8101	−0.468	0.8504	0.8130	−0.538
0.9543	0.8154	−0.183	0.9555	0.8216	−0.167	0.9576	0.8241	−0.170

were accurate to ±0.0001 g·cm^{-3}, ±0.002 mPa·s, ±0.001, and ±0.0002 units, respectively.

Results

The measured densities along with the excess volumes, V^E, for all the binary mixtures are given in Table 2. The experimental relative permittivites and the molar and orientation polarizations are presented in Table 3. The molar polarizations were calculated by combining the relative permittivity and molar volume data using the well-known Clausius−Mossoti equation. The equation used for calculating the orientation polarization was the same as described elsewhere (Sastry and Valand, 1997). The deviations $\delta\epsilon$, δP_m, and δP_o were calculated from the difference between the real mixture values and that of pure state values of respective functions. The values for the pure state were calculated as the mole fraction averages.

The excess volumes and deviations in various dielectric functions were represented mathematically by following equation

$$\delta Y = x_1(1 - x_1) \sum a_i \, (2x_1 - 1)^i \qquad (1)$$

where $Y = V^E$, $\delta\epsilon$, δP_m, or δP_o, x_1 is the mole fraction of 1-alcohol, and a_i are the coefficients. The values of the coefficients a_i were determined by a multiple regression

Table 3. Relative Permittivity (ϵ), Molar Polarization (P_{12}/cm^3·mol^{-1}) and Orientation Polarization ($P°_{12}$/cm^3·mol^{-1}) for 1-Alcohol + Pentane Mixtures at 298.15 K

x_1	ϵ	P_{12}	$P°_{12}$	x_1	ϵ	P_{12}	$P°_{12}$	x_1	ϵ	P_{12}	$P°_{12}$
methanol (1) + pentane (2)				1-propanol (1) + pentane (2)				1-butanol (1) + pentane (2)			
0.1362	2.238	30.9	8.8	0.0534	1.884	25.9	1.2	0.0571	1.872	25.8	0.8
0.2538	2.607	34.0	14.8	0.1578	2.338	33.9	11.0	0.1573	2.285	33.7	9.8
0.4275	5.318	49.7	48.7	0.2257	2.886	41.3	21.1	0.2579	3.079	45.0	24.6
0.5597	9.644	55.1	87.8	0.3520	4.436	54.4	44.9	0.3570	4.224	55.8	43.3
0.6628	14.345	54.3	120.8	0.4541	6.195	61.9	67.7	0.4589	5.801	64.5	65.5
0.7438	18.660	51.5	144.6	0.5034	7.195	64.4	79.5	0.5013	6.547	67.4	75.5
0.8153	22.729	48.2	161.5	0.5548	8.331	66.3	92.2	0.5557	7.576	70.4	88.7
0.8727	26.025	45.1	171.0	0.6570	10.841	68.4	118.0	0.6589	9.720	74.4	114.8
0.9203	28.676	42.3	175.6	0.7563	13.520	68.7	142.8	0.7573	11.933	76.7	140.0
0.9365	29.546	41.3	176.3	0.8553	16.314	67.8	165.7	0.8595	14.312	77.7	165.1
0.9554	30.531	40.1	176.7	0.9559	19.139	66.0	185.6	0.9559	16.529	77.9	187.0
0.9768	31.603	38.7	176.4								
1-pentanol (1) + pentane (2)				1-hexanol (1) + pentane (2)				1-heptanol (1) + pentane (2)			
0.0535	1.879	26.2	0.9	0.0575	1.889	26.7	1.1	0.0562	1.928	27.8	2.0
0.1050	1.974	28.3	3.0	0.1463	2.151	32.5	6.9	0.1572	2.135	32.9	6.4
0.2074	2.421	36.8	12.5	0.2569	2.755	43.6	19.4	0.2556	2.482	40.4	13.9
0.3106	3.332	49.6	29.5	0.3564	3.563	54.8	34.7	0.3557	3.091	51.2	26.6
0.4154	4.707	62.2	52.3	0.4581	4.650	65.7	53.9	0.4549	3.998	63.6	44.5
0.5094	6.217	71.1	75.4	0.5040	5.212	70.2	63.5	0.4990	4.501	69.1	54.1
0.6036	7.857	77.4	99.2	0.5574	5.928	75.0	75.5	0.5520	5.178	75.4	66.9
0.7149	9.810	82.4	126.5	0.6519	7.330	82.5	98.6	0.6530	6.647	86.4	94.3
0.8091	11.429	85.4	148.3	0.7544	9.002	89.1	125.9	0.7565	8.283	95.6	124.8
0.8588	12.294	86.6	159.8	0.8568	10.773	94.6	154.7	0.8570	9.812	102.8	153.0
0.9034	13.101	87.6	170.4	0.9518	12.439	98.7	181.8	0.9535	11.001	108.1	177.7
0.9527	14.072	88.7	183.0								
1-octanol (1) + pentane (2)				1-decanol (1) + pentane (2)				1-dodecanol (1) + pentane (2)			
0.0571	1.944	28.3	2.3	0.0583	1.946	28.8	2.2	0.0560	1.923	28.7	1.5
0.1566	2.147	33.8	6.7	0.1564	2.167	35.7	7.1	0.1555	2.161	36.9	6.8
0.2580	2.493	42.0	14.4	0.2572	2.510	45.1	15.2	0.2548	2.478	47.1	14.7
0.3564	3.082	53.5	27.3	0.3587	3.052	57.8	28.3	0.3568	2.890	59.4	25.8
0.4547	3.972	67.0	46.2	0.4582	3.801	72.3	46.5	0.4551	3.365	72.5	39.3
0.5013	4.493	73.5	57.0	0.5018	4.189	78.8	56.0	0.5040	3.625	79.3	47.0
0.5552	5.167	80.8	70.9	0.5529	4.681	86.4	68.2	0.5587	3.929	86.9	56.2
0.6550	6.545	92.9	99.5	0.6551	5.731	100.8	94.7	0.6534	4.512	100.4	74.5
0.7512	7.904	102.7	128.2	0.7567	6.730	113.2	121.6	0.7530	5.036	113.2	92.6
0.8551	9.154	111.1	156.1	0.8597	7.487	123.4	144.3	0.8504	5.527	125.2	110.9
0.9543	9.823	116.8	173.4	0.9555	7.721	130.0	155.3	0.9576	5.928	136.9	128.4

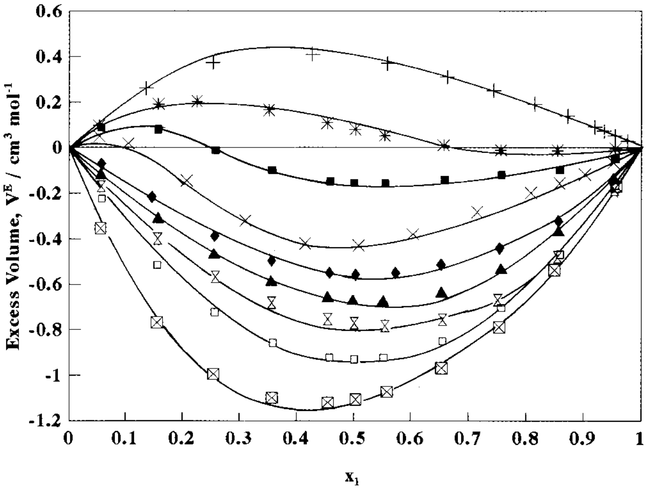

Figure 1. Excess volumes for 1-alcohol + pentane at 298.15 K: (+) methanol, (*) 1-propanol, (■) 1-butanol, (×) 1-pentanol, (◆) 1-hexanol, (▲) 1-heptanol, (⧖) 1-octanol, (□) 1-decanol and (□ with ×) 1-dodecanol.

analysis based on the least-squares method and are summarized along with the standard deviations between the experimental and fitted values of the respective functions in Table 4.

The experimental V^E values are also graphically presented as a function of 1-alcohol mole fraction in Figure 1. The variation of excess volumes with the mole fraction of 1-alcohol and their dependence on the carbon chain length of 1-alcohol species can be described in the following manner; V^E is positive over the whole mole fraction range in methanol + pentane, while the curves are sigmoid in 1-propanol to 1-pentanol + pentane mixtures. The positive portions of the curves were, however, found to diminish with an increase in the carbon chain length from 1-propanol to 1-pentanol. The excess volumes were negative in 1-hexanol to 1-dodecanol + pentane mixtures. As far as we are aware there exist few literature V^E data for 1-alcohol + pentane binary mixtures for a direct comparison. Our observed equimolar excess volumes of (0.394 and −1.107) cm^3 mol^{-1} for methanol and 1-dodecanol + pentane mixtures are in good agreement with the literature reported values of 0.395 (Tenn and Missen, 1963) and −0.9998 (Treszcznawociz et al., 1981) for the same mixtures. We could not find the literature V^E data for other mixtures for comparison. It was also noted that the excess volumes of the present mixtures were considerably smaller in magnitude than our previously reported V^E data for 1-alcohol + heptane mixtures at 298.15 K.

The variations of $\delta\epsilon$, δP_m, or δP_o are shown graphically as a function of 1-alcohol mole fraction in Figure 2. Figure 2a shows that the $\delta\epsilon$ values are negative in all the mixtures except for a few positive points in the alcohol-rich regions for 1-octanol to 1-dodecanol + pentane mixtures. A gradual increase in the negative magnitude of $\delta\epsilon$ values was observed from 1-dodecanol to 1-propanol + pentane mixtures, and strikingly large negative $\delta\epsilon$ deviations were noted in methanol + pentane mixtures. No data on the relative permittivities for 1-alcohol + pentane mixtures was

Table 4. Coefficients, a_i, Eq 3, for the Least-Squares Representation of Excess Volumes, Dielectric Constant Deviation, and Molar and Orientation Polarization Deviations for 1-Alcohol + Pentane Binary Mixtures at 298.15 K

	pentane +								
	methanol	1-propanol	1-butanol	1-pentanol	1-hexanol	1-heptanol	1-octanol	1-decanol	1-dodecanol
V^E/cm^3·mol^{-1}									
a_0	1.5767	0.3257	−0.6179	−1.7305	−2.2229	−2.6741	−3.0855	−3.7173	−4.4294
a_1	−0.6653	−1.1270	−0.1979	0.3964	−0.0676	−0.4064	−0.6378	−0.0729	0.8306
a_2	0.2928	0.7314	1.1525	1.8704	0.9921	0.0895	−0.7268	−0.3507	−1.2876
a_3			−1.7139	−2.1903	−1.1189	−0.1339	0.0950	0.1949	0.7317
σ	0.002	0.001	0.002	0.002	0.001	0.001	0.003	0.002	0.001
$\delta\epsilon$									
a_0	−39.283	−15.805	−12.551	−9.661	−9.530	−8.385	−5.438	−2.145	−1.251
a_1	4.865	5.125	4.895	7.028	2.634	4.967	7.528	6.929	2.439
a_2	19.667	2.667	1.624	−1.791	1.308	5.979	7.552	5.716	1.167
a_3				−6.326					
σ	0.050	0.005	0.005	0.003	0.003	0.001	0.001	0.001	0.010
δP_m/cm^3·mol^{-1}									
a_0	81.563	77.494	64.222	48.569	27.583	4.128	3.315	−0.808	−16.721
a_1	52.840	14.455	22.482	50.339	40.732	76.701	87.940	82.706	45.808
a_2	−41.809	−69.241	−68.706	−64.001	−41.641	−2.900	7.003	17.382	1.544
a_3	−22.132	41.542	39.656		11.273	−39.124	−43.700	−24.467	−6.730
σ	1.50	0.50	0.40	0.90	0.30	0.80	1.50	0.80	0.40
δP_o/cm^3·mol^{-1}									
a_0	−64.936	−69.565	−89.834	−101.473	−139.592	−155.341	−125.771	−87.265	−81.131
a_1	202.512	108.157	94.091	113.074	46.986	86.065	140.316	153.947	59.085
a_2	127.739	−3.026	−9.835	−48.922	2.651	98.302	144.848	140.165	36.577
a_3				−80.409					
σ	1.50	0.50	0.50	0.40	0.50	0.30	0.40	0.40	0.40

Table 5. Parameters of Correlating Equations for the Prediction of Mixture Viscosities of 1-Alcohol + Pentane 298.15 K

	pentane +								
	methanol	1-propanol	1-butanol	1-pentanol	1-hexanol	1-heptanol	1-octanol	1-decanol	1-dodecanol
G_{12}[a]	−0.5444	−0.9838	−0.6970	−0.6709	−0.2108	0.0603	0.4759	1.1990	2.1665
σ	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
M_{12}[b]	0.3573	0.6786	0.9016	1.1174	1.5433	2.1185	2.7055	4.7266	8.0317
M_{21}	0.2536	0.3280	0.3947	0.4438	0.5632	0.6536	0.8544	1.3059	2.0709
σ	0.002	0.005	0.001	0.002	0.001	0.001	0.003	0.001	0.001
A_{21}[c]	1.1102	3.1025	2.8788	3.4511	3.9611	4.2177	3.4920	2.0884	2.5189
B_{21}	3.0955	1.3786	1.4670	1.3497	0.9767	0.8762	1.0624	2.2354	1.3714
B_{12}	0.3912	0.4678	0.4688	0.4788	0.5683	0.5524	0.4229	0.1927	0.2126
σ	0.002	0.001	0.002	0.001	0.002	0.001	0.001	0.001	0.001

[a] Grunberg−Nissan, [b]McAllister, and [c]Auslaender equations.

found in the literature for a direct comparison of our results. However similar negative increments in the relative permittivities were reported for 1-alcohol + hexane (Iglesias et al., 1993a) and 1-alcohol + octane (Iglesias et al., 1993b). The trend in the δP_m vs x_1 curves (Figure 2b) is also found to be typical. The curves are asymmetric with initial negative regions followed by positive lobes in the alcohol-rich regions. The cross over of δP_m values from negative to positive portions of the curve is found to extend systematically to higher mole fractions from methanol to 1-dodecanol. The curves for methanol to 1-hexanol + pentane mixtures have few initial negative points followed by large positive lobes. An almost equal share of negative and positive values was noted in the δP_m curves for 1-heptanol to 1-decanol + pentane mixtures, while a large negative region followed by a small positive region was observed in pentane + 1-dodecanol mixtures. The δP_o vs x_1 curves (Figure 2c) can be described in the following manner. Initial negative regions followed by positive lobes at 1-alcohol-rich regions in methanol +, 1-propanol +, 1-octanol +, and 1-decanol + pentane mixtures were observed. The δP_o values were found to be all negative over the whole mole fraction for the rest of the mixtures. No systematic dependence of δP_o values on the carbon chain length of 1-alcohols was observed. This is in contrast to the typical variations in $\delta\epsilon$ and δP_m curves as described earlier.

The correlation of mixture viscosities with semiempirical equations is of great utility both from academic and industrial point of view. All the three equations, namely, Grunberg−Nissan, McAllister, and Auslaender, were used to correlate the mixture viscosities. The adjustable parameters of these equations were estimated from the fits of experimental viscosity data by a nonlinear regression analysis using Marquardt algorithm. The results of the analysis are summarized in Table 5. It may be seen from the table that the standard deviations between the experimental and correlated mixture viscosities for the Grunberg−Nissan equation were smaller as compared to other two equations. A graphical representation of experimental and Grunberg−Nissan equation correlated viscosities for all the mixtures is given in Figure 3.

Discussion

The trend in the variation of the excess volume curves as a function of 1-alcohol mole fraction as shown in Figure 1 is typical and follows the same pattern both in the magnitude and type as observed previously for the similar mixtures (Treszczanowicz et al., 1993). The detailed qualitative interpretation of excess volume curves of 1-alcohol + alkanes, in terms of chemical, physical, and structural factors, has been discussed in the above reference. The disruption of hydrogen bonds in 1-alcohol associates and dipole−dipole repulsive interactions be-

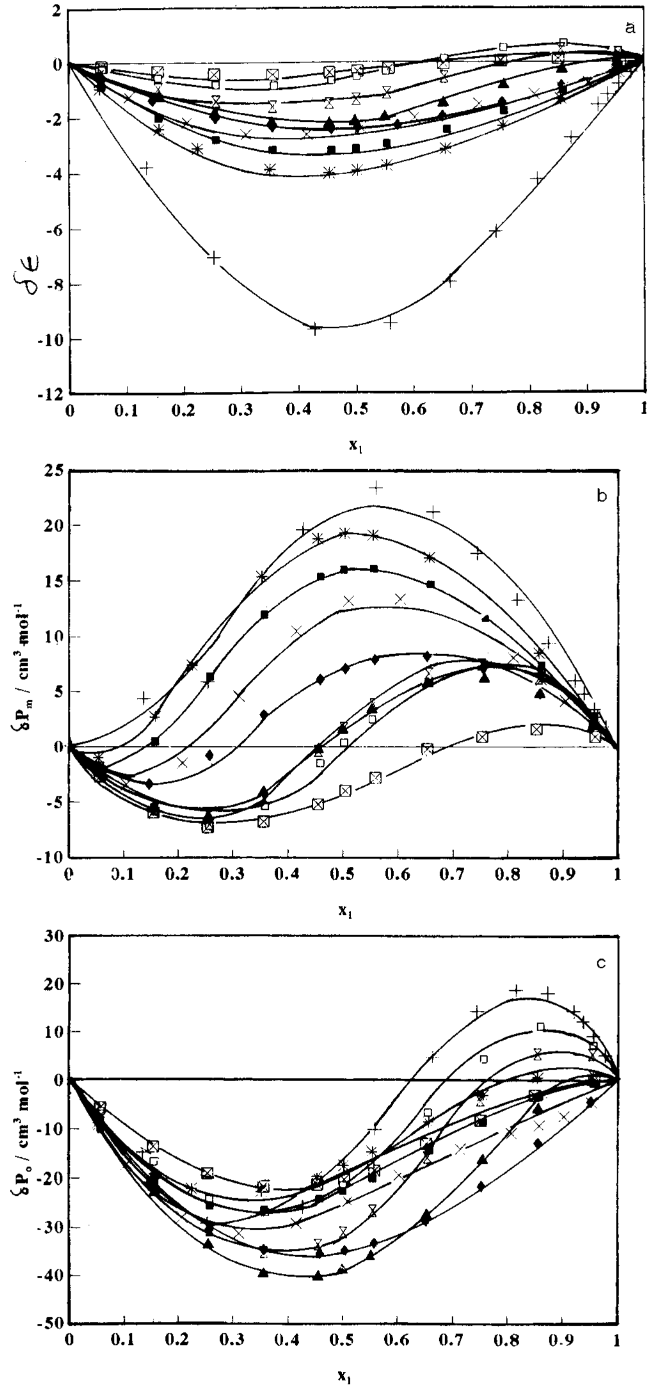

Figure 2. Deviations in dielectric functions for 1-alcohol + pentane at 298.15 K. Legends same as in Figure 1.

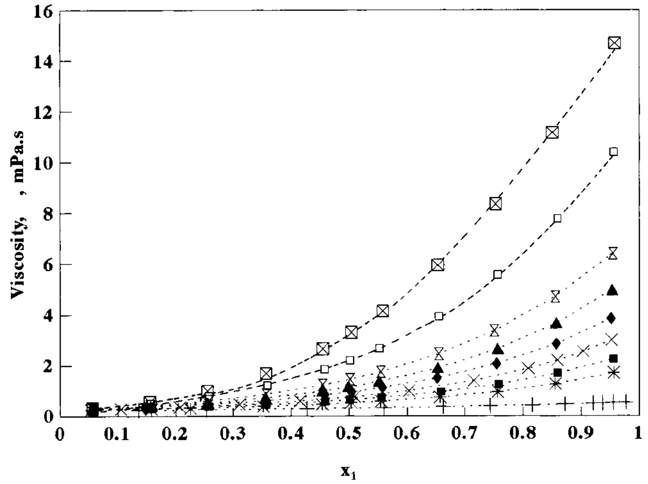

Figure 3. Viscosities for 1-alcohol + pentane at 298.15 K. Legends (experimental) same as in Figure 1; (---) correlated values as per the Grunberg–Nissan equation.

tween multimer and unimer 1-alcohol species are mainly responsible for the observed positive excess volumes. The free volume differences and interstitial accommodation of smaller pentane molecules into 1-alcohol associate structures in turn are the chief factors that contribute to the observed negative excess volumes. A comparison of our previously reported excess volumes of 1-alcohol + heptane mixtures with the present V^E data showed decreased positive and increased negative magnitudes for any given 1-alcohol + pentane mixtures. Thus it can be stated that smaller pentane molecules cause less disruption in 1-alcohol associate structures and penetrate into them more easily.

The observed negative $\delta\epsilon$ values (Figure 2a) in general can be ascribed to the dipole–dipole repulsive interactions between the multimer and unimer 1-alcohol species. The systematic increase in the magnitude of $\delta\epsilon$ values with the rise in the carbon chain length of 1-alcohols from methanol to 1-dodecanol can be attributed to the diminished structure-breaking interactions in higher alcohol + pentane mixtures. Similarly the observed initial negative δP_m and δP_o values (Figure 2b,c) for 1-alcohol + pentane mixtures also further suggest the decreased polarizations in the presence of pentane. The decreased polarizations may be ascribed to the change in the alignment of dipoles from the parallel to antiparallel state because of dominance of dipole–dipole interactions. However, this type of effect seems to be weakened in the alcohol-rich regions, where large positive δP_m and δP_o values were noted.

The change in the local structural order of a polar solute due to the presence of a nonpolar inert solvent has also been examined by evaluating the correlation factor, g_K, from the relative permittivity data using the relation

$$g_K = \frac{9kT(2\epsilon_{12}+\epsilon_\alpha)^2}{4\pi N\mu^2 x_2(\epsilon_\alpha+2)^2\,(2\epsilon_{12}+1)} \times \left[V_{12}\frac{\epsilon_{12}-1}{\epsilon_{12}} - \frac{3x_1V_1(\epsilon_1-1)}{(2\epsilon_{12}+\epsilon_1)} - \frac{3x_2V_2(\epsilon_\alpha-1)}{(2\epsilon_{12}+\epsilon_\alpha)}\right] \qquad (2)$$

where μ is the dipole moment of 1-alcohol, ϵ_α is the relative permittivity characteristic of electronic polarization of the 1-alcohol ($\epsilon_\alpha = n_D^2$, where n_D is the refractive index), ϵ_{12} and V_{12} are the relative permittivity and molar volume of the mixture, and x_1, x_2, V_1, and V_2 are the mole fraction and molar volumes of 1-alcohol and pentane, respectively. k is the Boltzmann constant, N is the Avogadro number, and T is the absolute temperature.

The variation of g_K as a function of 1-alcohol mole fraction for all the 1-alcohol + pentane mixtures at 298.15 K is shown in Figure 4. There is a definite trend in g_K values with an increase in the 1-alcohol mole fraction in all the mixtures. The value of g_K was found to be lower than unity in the alcohol-deficient region (x_1 up to about 0.25) although the g_K values for pure 1-alcohols are always greater than unity. The g_K value was found to increase rapidly up to $x_1 \approx 0.35-0.45$, above which the rise was gradual. A value of g_K greater than unity indicates a favorable alignment of dipoles as can be expected in the linear associates of pure 1-alcohol molecules, while a g_K value less than unity corresponds to the decreased polar-

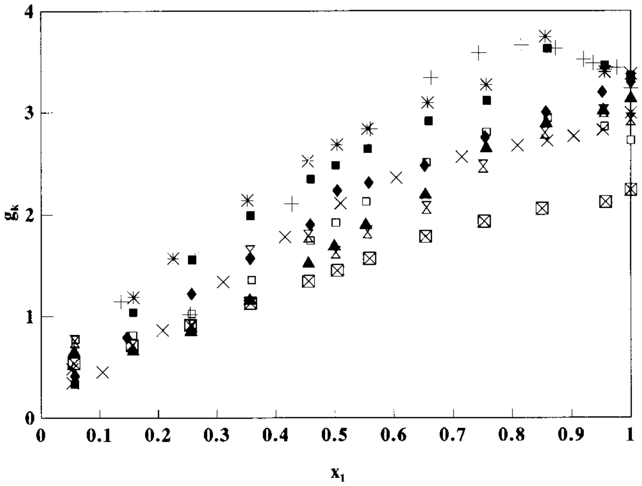

Figure 4. Variation of correlation factor, g_K, as a function of 1-alcohol mole fraction for 1-alcohol + pentane at 298.15 K. Legends same as in Figure 1.

izations due to the antiparallel alignment of dipoles in the dissociated state where various species such as dimers, trimers, tetramers, and even cyclic associates are formed. These results confirm the explanation offered earlier in describing the excess volumes and deviations in the dielectric functions of 1-alcohol + pentane mixtures.

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