Volumetric Properties of (Difurylmethane + Alkan-1-ol) Binary Mixtures at 298.15 K

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Abstract Densities (ρ) of the binary systems of {difurylmethane + (ethanol or propan-1-ol or butan-1-ol or pentan-1-ol or hexan-1-ol)} have been measured with an Anton Paar DMA 4500 vibrating-tube densimeter over the entire composition range at 298.15 K and atmospheric pressure. Excess molar volumes (V_m^E) of each binary system were determined and correlated by the Redlich-Kister equation. Limiting ($V_i^{E,\infty}$) and excess partial molar volumes (V_i^E) of components of each binary system have been calculated to provide insight into the intermolecular interactions present and the packing efficiencies. The results have been discussed in terms of specific intermolecular interactions, dispersive forces and structural effects.

1. Introduction

In a previous paper [1], we have reported studies of the volumetric properties of the [difurylmethane (DFM)+methanol] binary system in the temperature range between 288.15 and 308.15 K, which revealed significant deviations from ideal solution behavior. Such studies contribute to the understanding of the intermolecular interactions existing between the various species in a solution and provide information about changes with respect to composition, and in the packing efficiencies that take place in solution during the mixing process [2–5]. DFM is an aprotic liquid and is a typical example of a dipolar fluid whose liquid structure is determined by the dipole-dipole interactions between molecules. On the other hand, alkanols are strongly self-associated by hydrogen bonding, the degrees of which depend on temperature, the alkyl chain-length and the position of the hydroxyl group [6]. Thus pure methanol exists mainly as a cyclic dimer, ethanol as a trimer, propan-1-ol as a 1:1 cyclic dimer/trimer

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mixture, butan-1-ol as a dimer, pentan-1-ol as a 1:1 monomer/cyclic dimer mixture and hexan-1-ol as a 1:1 monomer/open dimer equilibrium mixture [7–9]. As an extension of the studies on volumetric properties, we report in this paper precise density measurements for the (DFM + n-alkanol) binary systems, over the entire composition range at 298.15 K and atmospheric pressure. The n-alkanols studied are ethanol, propan-1-ol, butan-1-ol, pentan-1-ol and hexan-1-ol. For each (DFM + alkanol) system, the excess molar volumes, V_m^E, have been determined and correlated with the Redlich-Kister polynomial [10] of an appropriate degree. Excess partial molar volumes, V_i^E, were determined over the entire composition range and, hence, limiting excess partial molar volumes, $V_i^{E,\infty}$, of both components in each binary system were calculated. The (DFM + methanol) [1] data at 298.15 K is reproduced in this paper for comparison purposes.

2. Experimental

2.1. Materials

All alcohols used in this study: ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, and hexan-1-ol were purchased from Aldrich. The claimed purity for the chemicals was more than 99 mass%. Each alcohol was fractionally distilled after a 6 h reflux over baked calcium oxide and further refluxed over activated magnesium granules as described elsewhere [1]. Thereafter, ethanol and propan-1-ol were fractionally distilled using a 1 m long fractionation column with the distillate collected under dry nitrogen at atmospheric pressure. Butan-1-ol, pentan-1-ol and hexan-1-ol were fractionally distilled in a short column under partial vacuum with a nitrogen leak. The purity of alcohols was tested by density measurements and as can be observed from the reported data in Table 1, the value for the densities: ethanol (0.78498 g·cm^{-3}), propan-1-ol (0.79954 g·cm^{-3}), butan-1-ol (0.80569 g·cm^{-3}), pentan-1-ol (0.81084 g·cm^{-3}), and hexan-1-ol (0.81516 g·cm^{-3}) are in good agreement with the literature values [11–13]: 0.78493, 0.79960, 0.80575, 0.81080, 0.81515 g·cm^{-3} at 298.15 K, respectively. Benzene (Aldrich Chemicals, $p.a.$) was purified as reported elsewhere [11]. Water was first deionized by means of ion-exchange resins and then doubly distilled over KMnO$_4$ under nitrogen. Its conductivity was always less than 1.0×10^{-6} S·cm^{-1}. DFM was prepared as described elsewhere [14] and its purity was confirmed by ^{1}H-NMR, density measurements and elemental analyses. All purified organic liquids were stored in brown glass bottles and fractionally distilled immediately before use.

2.2. Apparatus and procedure

Solution density measurements were performed at atmospheric pressure with an Anton Paar DMA 4500 vibrating-tube precision densimeter thermostatted at 298.15 K. The densimeter was first calibrated with ultra pure water and benzene as reference liquids [15]. The (DFM + alkanol) binary mixtures were prepared by weighing appropriate amounts of the purified DFM and alkan-1ol on a Sartorius Supermicro balance (Fabr.-Nr., $\Delta m = \pm 1 \times 10^{-6}$ g), by syringing each component into Teflon stoppered flasks in order to minimize preferential evaporation. Pure components were separately degassed by ultrasound shortly before sample preparations. This procedure eliminated possible changes in mixture composition that could occur during the degassing of already prepared binary mixtures. All (DFM + alkanol) mixtures were completely miscible over the entire composition range. The uncertainty in solution composition expressed in mole fraction was found to be less than 8×10^{-5}. A

Table 1 Experimental densities, ρ (kg·m^{-3}), for the [alkan-1-ol (1) + DFM (2)] binary mixtures at 298.15 K

x_2	ρ	x_2	ρ	x_2	ρ	x_2	ρ
				Ethanol + DFM			
0.000000	784.98	0.028739	805.96	0.139731	872.27	0.427435	982.07
0.000589	785.46	0.034673	809.92	0.149249	877.12	0.460882	991.36
0.000848	785.63	0.041646	814.84	0.149795	877.35	0.498263	1001.00
0.001828	786.44	0.044415	816.69	0.150301	877.65	0.523194	1007.26
0.002401	786.91	0.048762	819.47	0.161357	883.04	0.530891	1009.06
0.003720	787.88	0.052732	822.01	0.165640	885.12	0.604173	1025.60
0.005006	788.80	0.055407	823.72	0.173930	889.07	0.650788	1035.16
0.006944	790.26	0.058690	825.89	0.182059	892.95	0.704098	1045.40
0.008116	791.07	0.069678	832.79	0.185648	894.61	0.740232	1051.89
0.008612	791.60	0.075529	836.41	0.209000	905.16	0.805699	1062.92
0.009210	791.99	0.081392	839.92	0.217687	908.94	0.863646	1071.84
0.011068	793.42	0.090477	845.25	0.229371	913.87	0.864183	1071.90
0.012198	794.21	0.096773	848.90	0.248824	921.84	0.892449	1076.05
0.016004	797.07	0.105279	853.74	0.269552	929.97	0.937191	1082.36
0.020294	799.98	0.112632	857.78	0.308053	944.25	0.975022	1087.50
0.020704	800.30	0.120899	862.31	0.326072	950.46	0.975835	1087.62
0.022492	801.65	0.128526	866.48	0.345170	956.90	1.000000	1090.88
0.026464	804.47	0.137112	870.93	0.374131	966.23		
				Propan-1-ol + DFM			
0.000000	799.54	0.024037	812.20	0.096697	847.80	0.323583	936.34
0.001819	800.57	0.024396	812.43	0.107844	852.88	0.356598	946.93
0.004985	802.29	0.025903	813.13	0.112023	854.75	0.396271	959.16
0.006050	802.83	0.026059	813.35	0.118537	857.69	0.418142	965.53
0.007597	803.66	0.027885	814.22	0.119489	858.14	0.449197	974.45
0.008401	804.07	0.030815	815.71	0.124264	860.21	0.486316	984.64
0.008816	804.30	0.031215	815.88	0.130522	862.97	0.493452	986.54
0.010725	805.32	0.034357	817.51	0.134654	864.76	0.544566	999.66
0.012132	806.06	0.034816	817.73	0.145235	869.25	0.592750	1011.33
0.012721	806.38	0.036673	818.72	0.156865	874.16	0.610941	1015.48
0.013233	806.64	0.037982	819.42	0.162549	876.49	0.650360	1024.52
0.014416	807.27	0.041557	821.17	0.163555	876.90	0.671062	1029.09
0.015818	808.01	0.042905	821.85	0.168918	879.13	0.738515	1043.33
0.016226	808.23	0.043787	822.28	0.183168	884.92	0.771486	1049.94
0.017614	808.98	0.054527	827.64	0.199297	891.33	0.823061	1059.90
0.018399	809.34	0.058504	829.68	0.205022	893.58	0.859378	1066.61
0.018771	809.49	0.068927	834.79	0.228022	902.52	0.894602	1072.94
0.020666	810.55	0.079089	839.61	0.240554	907.17	0.930332	1079.13
0.021843	811.13	0.084689	842.29	0.270868	918.25	0.972948	1086.33
0.023588	811.98	0.089908	844.66	0.310091	931.85	1.000000	1090.88
0.023959	812.19						
				Butan-1-ol + DFM			
0.000000	805.69	0.039609	822.25	0.108484	849.38	0.328076	925.16
0.000327	805.87	0.042830	823.56	0.115898	852.17	0.346745	930.96
0.000754	806.07	0.046808	825.18	0.116372	852.36	0.396666	946.07
0.002129	806.69	0.055455	828.67	0.116876	852.54	0.437252	957.91
0.002946	807.04	0.056118	828.91	0.125448	855.76	0.471550	967.60
0.004448	807.66	0.060915	830.83	0.130738	857.74	0.504940	976.84

Table 1 Continued

x_2	ρ	x_2	ρ	x_2	ρ	x_2	ρ
0.004676	807.78	0.062540	831.47	0.136962	860.05	0.531794	984.02
0.006211	808.40	0.066656	833.11	0.145663	863.26	0.576002	995.67
0.007476	808.92	0.069426	834.21	0.149227	864.56	0.604401	1002.93
0.008718	809.43	0.070234	834.55	0.161666	869.11	0.669288	1018.92
0.009211	809.66	0.074064	836.05	0.170083	872.14	0.706945	1027.89
0.010205	810.05	0.076168	836.86	0.175802	874.20	0.730036	1033.26
0.014664	811.90	0.079669	838.25	0.183134	876.81	0.766193	1041.57
0.020951	814.56	0.083609	839.77	0.197571	881.88	0.835038	1056.78
0.023926	815.80	0.084349	840.08	0.218272	889.11	0.875807	1065.52
0.027738	817.39	0.088006	841.49	0.231038	893.47	0.900562	1070.71
0.029561	818.13	0.091585	842.88	0.256699	902.10	0.929399	1076.66
0.033846	819.90	0.102888	847.24	0.274405	907.95	0.956849	1082.24
0.037684	821.47	0.106934	848.75	0.309950	919.46	1.000000	1090.88

Pentan-1-ol + DFM

x_2	ρ	x_2	ρ	x_2	ρ	x_2	ρ
0.000000	810.84	0.011523	814.91	0.123142	852.34	0.446487	950.29
0.000267	810.94	0.013954	815.75	0.134335	855.94	0.475545	958.45
0.000858	811.16	0.014933	816.08	0.143854	859.03	0.510391	968.08
0.001188	811.28	0.017946	817.12	0.164948	865.80	0.540662	976.36
0.001901	811.53	0.019542	817.65	0.179663	870.48	0.568080	983.74
0.002866	811.89	0.020360	817.94	0.190109	873.81	0.610513	995.01
0.003224	811.99	0.020712	818.06	0.208932	879.74	0.639666	1002.65
0.003626	812.16	0.030288	821.34	0.216739	882.17	0.699023	1017.96
0.004372	812.40	0.041128	825.03	0.226670	885.27	0.732964	1026.55
0.005288	812.73	0.045662	826.55	0.240282	889.49	0.763809	1034.31
0.006528	813.17	0.048613	827.55	0.253678	893.56	0.821331	1048.44
0.007195	813.37	0.052986	829.04	0.289439	904.48	0.849922	1055.38
0.008073	813.69	0.057663	830.62	0.315628	912.31	0.886220	1064.06
0.008925	814.00	0.074928	836.42	0.344218	920.81	0.915061	1070.91
0.009155	814.08	0.092504	842.28	0.363414	926.41	0.930343	1074.52
0.010178	814.44	0.095652	843.33	0.376255	930.17	0.966294	1083.00
0.010707	814.63	0.105360	846.50	0.410710	940.13	1.000000	1090.88
0.011282	814.82						

Hexan-1-ol + DFM

x_2	ρ	x_2	ρ	x_2	ρ	x_2	ρ
0.000000	815.16	0.026325	822.84	0.153174	859.48	0.594539	982.81
0.001195	815.51	0.040232	826.90	0.172644	865.01	0.602602	984.99
0.001472	815.60	0.044206	828.03	0.187602	869.32	0.652006	998.33
0.002591	815.92	0.050758	829.97	0.212320	876.28	0.694740	1009.85
0.006241	816.99	0.054812	831.14	0.250094	887.03	0.729487	1019.16
0.007084	817.23	0.063014	833.48	0.256898	888.99	0.788432	1034.85
0.011320	818.44	0.067019	834.66	0.266827	891.79	0.819846	1043.16
0.013014	818.98	0.072477	836.26	0.284901	896.85	0.841299	1048.95
0.017417	820.22	0.082634	839.16	0.292869	899.10	0.868450	1056.07
0.019200	820.76	0.088807	840.92	0.322380	907.42	0.899246	1064.20
0.019743	820.90	0.097762	843.51	0.349828	915.15	0.922569	1070.36
0.021032	821.32	0.099817	844.08	0.406600	931.00	0.941605	1075.33
0.022246	821.66	0.110923	847.31	0.447131	942.29	0.958695	1079.90
0.024621	822.36	0.121898	850.45	0.506327	958.65	0.975432	1084.34
0.024894	822.46	0.140084	855.70	0.548582	970.22	1.000000	1090.88

sample volume of not more than $1.0\,cm^3$ was needed to fill the densimeter cell and thermal equilibrium was attained quickly. The temperature of the sample was controlled electrically by means of a built-in thermostat (a semiconductor Peltier element and a resistance thermometer temperature control system) and was measured with an accuracy of $\pm 0.01\,K$. The densimeter was calibrated after each set of four sample measurements to offset any problem of instrument drift. There was, however, no noticeable drift in the density of the reference fluid and a linear relation between the density of the fluid and the square of the vibrating period τ ($\rho = A + B\tau^2$) was assumed. Buoyancy corrections were made by taking into account the air density at 298.15 K, the barometric pressure and the relative humidity. Under such conditions quadruplet density measurements of each sample were reproducible to within $\pm 1 \times 10^{-2}\,kg\cdot m^{-3}$.

3. Results and discussion

Experimental densities as a function of composition for {DFM+(ethanol or propan-1-ol or butan-1-ol or pentan-1-ol or hexan-1-ol)} binary systems at 298.15 K are reported in Table 1. These densities cover the entire composition range, but with a bias towards the alkanol-rich region in all cases. To the best of our knowledge no data have been reported previously for the density of any of the binary mixture systems under investigation. Excess molar volumes, V_m^E, were calculated for each composition from density measurements using Eq. (1) [3–5]:

$$V_m^E = V_m - V_m^{id} = \frac{M}{\rho} - \frac{\sum x_i M_i}{\rho_i^*} \tag{1}$$

where M is the molar mass of the mixture, which is the mole fraction weighted average of the molar masses of the two pure components in each binary mixture, V_m^{id} is the ideal molar volume, ρ is the density of the mixture, and x_i, M_i and ρ_i^* are, respectively, the mole fraction, the molar mass and the density of the pure liquid component i. The V_m^E values of each of the (DFM + alkanol) systems were least-squares fitted by the Redlich-Kister [10] polynomial Eq. (2):

$$V_m^E = x_1 x_2 \sum_{k=0}^{n} A_k (1 - 2x_2)^k \tag{2}$$

where x_1 and x_2 are, respectively, the mole fractions of the alkanol and DFM. In each case the degree of the polynomial was optimized by applying the F-test and the A_k fitting coefficients and k, the number of fitting coefficients, were evaluated by least squares [16]. The optimized number of the regression coefficients for the (DFM + alkanol) systems are listed in Table 2 along with the corresponding standard deviations $\sigma(V_m^E)$. Since for each binary system the values of $\sigma(V_m^E)$ are less than the experimental uncertainty, the regression coefficients, A_k, in the appropriate form of Eq. (2) adequately represent the experimental V_m^E values and indicate the good quality of fits for all isotherms. Figure 1 displays the experimental V_m^E *versus* x_2 data and the fitted curves calculated from smoothing Eq. (2) of an appropriate degree for each of the (DFM + alkanol) binary systems at 298.15 K. For comparison, the V_m^E curve for (DFM + methanol) mixtures at 298.15 K [1] is included.

   As a result of mutual intermolecular interactions, many properties of liquid mixtures are not additive with respect to the pure components and excess thermodynamic functions such

Table 2 Least-squares fitted A_k (cm$^3 \cdot$mol^{-1}) coefficients of Eq. (2), corresponding standard deviations of the fits, σ (V_m^E), and limiting excess partial molar volumes, $V_i^{E,\infty}$ (cm$^3 \cdot$mol^{-1}), for the [alkan-1-ol (1) + DFM (2)] binary mixtures at 298.15 K

	Ethanol	Propan-1-ol	Butan-1-ol	Pentan-1-ol	Hexan-1-ol
A_o	−1.123	−0.490	0.112	0.591	0.897
A_1	−1.049	−1.019	−0.278	−0.125	0.208
A_2	−0.826	0.226	0.0172	0.00640	0.526
A_3	0.0790	1.900	−0.873	−0.796	−1.025
A_4	0.776	−0.735	0.0441	0.206	−0.983
A_5	−1.293	−3.668	2.146	2.024	1.934
A_6	−0.893	0.715	−0.273	−0.208	1.170
A_7	—	1.878	−1.928	−2.037	−1.907
A_8	—	—	—	—	0.0408
A_9	—	—	—	—	0.368
A_{10}	—	—	—	—	−0.375
$\sigma(V_m^E)$	0.006	0.003	0.006	0.007	0.0003
$V_1^{E,\infty}$	0.197	0.624	0.834	1.531	1.697
$V_2^{E,\infty}$	−4.240	−1.192	−1.032	−0.339	1.230

as the V_m^E values measure the extent of deviations from ideal behavior. These deviations arise from chemical, physical, structural and dipole-dipole interaction effects. The chemical effects involve the (entropy increasing) break up of liquid order due to dipole-dipole association and the rupture of the hydrogen-bond structure, both of which contribute positively to V_m^E. Physical contributions comprise non-specific unfavorable interactions between unlike

Fig. 1 Excess molar volume, V_m^E, *versus* x_2 for the [alkan-1-ol (1) + DFM (2)] binary mixtures: ($\triangle$) methanol; ($\circ$) ethanol; ($\square$) propan-1-ol; (X) butan-1-ol; ($\diamond$) pentan-1-ol and (+) hexan-1-ol at 298.15 K
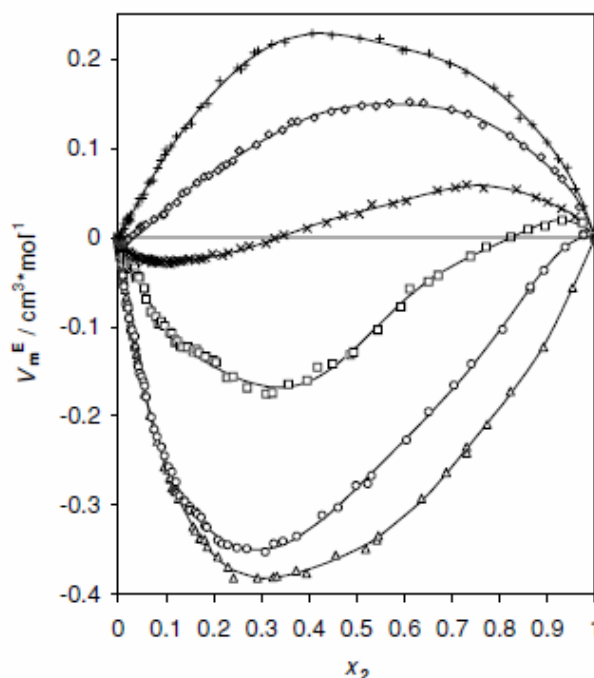
molecules, which also contribute positively to V_m^E. Structural effects arise from the restriction of the rotational degrees of freedom due to the geometrical interstitial accommodation of liquid components into each other's cavities (clathrate formation), due to differences in the molar masses, shape and free volumes of pure components, and they contribute negatively to V_m^E. The presence of specific dipole-dipole interactions between unlike component molecules also contributes negatively to the V_m^E values.

The V_m^E curve for DFM-ethanol mixtures displays a negative deviation with a slight tendency to positive values at $x_2 \approx 0.98$ and it is qualitatively similar to the variation reported previously for the (DFM + methanol) binary system [1]. The decrease in V_m^E may suggest that the contribution from the dipole-dipole interactions between the −OH groups in ethanol and the polarized π-electron of the DFM furan ring systems, and the geometrical interstitial fitting of DFM and ethanol into cavities of each other's liquid structure, more than offset the positive contributions from the physical and chemical effects. It is noticeable that the V_m^E versus x_2 plots for (DFM + methanol) and (DFM + ethanol) binary mixtures in the concentration range, $0.00 \leq x_2 \leq 0.15$ show an identical steep variation. Assuming that the DFM-alkan-1-ol, dipole-dipole intermolecular interactions and the geometrical interstitial accommodation are the dominant effects. A possible explanation for this behavior is as follows: the trimeric [6, 7] species present in the ethanol liquid structure may form a relatively more open liquid structure with accessible cavities for DFM interstitial accommodation leading to a close molecular packing in the very-low x_2 range of the (DFM + ethanol) mixtures. It is possible that the geometric relaxation processes of the trimeric species present in ethanol partly contribute to an enhanced open liquid structure. Moreover, the slightly lower density for ethanol (0.78498 g·cm^{-3}) in comparison to methanol (0.78644 g·cm^{-3}) [1] would suggest a more open ethanol liquid structure. This structural effect may partially compensate for the stronger DFM—methanol dipole-dipole interaction that arises from the higher polarity of the −OH group in methanol [17] relative to ethanol. The V_m^E values for {DFM + (propan-1-ol or butan-1-ol or pentan-1-ol)} binary mixtures present a sigmoidal shaped behavior, with negative deviations limited, respectively, to $0.00 \leq x_2 \leq 0.82$, $0.00 \leq x_2 \leq 0.31$ and $0.00 \leq x_2 \leq 0.02$, and positive deviations over the remaining composition ranges. It is also observed that the V_m^E versus x_2 curves are shifted at zero values of V_m^E towards lower x_2 as the alkan-1-ol molar mass increases. The sigmoidal behavior in the V_m^E data is the result of several opposing effects as was suggested by Treszczanowicz et al. [18]. At lower DFM concentrations, negative V_m^E values can be attributed to the predominance of DFM-alkanol, dipole-dipole intermolecular interactions and the geometrical interstitial accommodation of DFM molecules within the branched structure of the alkan-1-ol multimers. The minimum value, V_m^E (min.), of the excess molar volume decreases in magnitude in the sequence: methanol > ethanol > propan-1-ol > butan-1-ol > pentan-1-ol and are -0.38 cm^3·mol^{-1} (at $x_2 = 0.32$) [1], -0.35 cm^3·mol^{-1} (at $x_2 = 0.30$), -0.17 cm^3·mol^{-1} (at $x_2 = 0.31$), -0.026 cm^3·mol^{-1} (at $x_2 = 0.091$) and -0.006 cm^3·mol^{-1} (at $x_2 = 0.013$), respectively. The most negative V_m^E value is observed for the (DFM + methanol) system and suggests the strongest association, as would be expected since the −OH group in methanol constitutes the greatest surface area and volume fraction of the molecule relative to the −OH groups in the higher alkanol molecules [17]. The greater polarity of the −OH groups in methanol ($\mu = 2.87$ D, $\varepsilon = 32.6$) in comparison to higher alkan-1-ols ($\mu \leq 1.7$ D and $\varepsilon \leq 10$ at 298.15 K) [19] would result in stronger dipole-dipole association in DFM-methanol mixtures, leading to more negative V_m^E values than in binary systems containing higher alkan-1-ols at the same temperature and composition. Thus, the expected decrease in the −OH group proton donor capacity with the increase in the alkan-1-ol chain length results

in weaker DFM-alkan-1-ol, dipole-dipole intermolecular interactions and smaller values of V_m^E (min.). At higher DFM concentrations, positive V_m^E values indicate that there are no strong specific interactions between component molecules but rather indicate an increase in dispersive intermolecular forces, which contribute to the disruption of the alkan-1-ol hydrogen bond structure leading to the observed volume expansion. The sequence for positive V_m^E values are in the order: hexan-1-ol > pentan-1-ol > butan-1-ol > propan-1-ol and were $+0.26 \, \text{cm}^3 \cdot \text{mol}^{-1}$ (at $x_2 = 0.41$), $+0.15 \, \text{cm}^3 \cdot \text{mol}^{-1}$ (at $x_2 = 0.57$), $+0.058 \, \text{cm}^3 \cdot \text{mol}^{-1}$ (at $x_2 = 0.77$) and $+0.019 \, \text{cm}^3 \cdot \text{mol}^{-1}$ (at $x_2 = 0.93$), respectively. The inflection points for propan-1-ol, butan-1-ol and pentan-1-ol occur at $x_2 = 0.82$, $x_2 = 0.31$ and $x_2 = 0.021$, respectively. Thus, the DFM concentration at which the transition from a negative to a positive V_m^E occurs, decreases with increasing chain length in the alkanol and points to steric effects which, in each binary system, arise from a change in the proportion of different structural forms of the alkanol molecules with the increase in x_2. When the molecular size ratio DFM/alkan-1-ol is sufficiently decreased, then the negative contribution from the DFM-alkan-1-ol, dipole-dipole intermolecular interactions and geometrical effects become minimal, and the V_m^E versus x_2 curve completely reverts to positive deviations over the entire composition range, as in the case of the (DFM + hexan-1-ol) binary mixtures that exhibited the highest V_m^E (max.).

Differential properties such as the excess partial molar volumes (V_i^E) are more sensitive to the effects on volume, of changes in the aggregation schemes arising from the mixing process, and have the merit of leading to plots with enhanced visual impact [4, 20, 21]. The V_i^E values of a component in the mixtures describe the rate of change with composition of the excess molar volumes and provide information on individual component response to the intermolecular interactions. The excess partial molar volumes of alkan-1-ol (V_1^E) and DFM (V_2^E) for each binary system have been obtained in accordance with Eqs. (3) and (4) [4, 20], respectively,

$$V_1^E = V_m^E - x_2 \left(\frac{\partial V_m^E}{\partial x_2} \right)_{p,T} \tag{3}$$

$$V_2^E = V_m^E + (1 - x_2) \left(\frac{\partial V_m^E}{\partial x_2} \right)_{p,T}. \tag{4}$$

The Redlich-Kister equation, Eq. (2), of an appropriate degree for each (DFM+alkan-1-ol) binary system has been used to obtain values of the derivative $(\partial V_m^E / \partial x_2)_{p,T}$ for the entire concentration range. Figure 2 displays the excess partial molar volumes, V_i^E, versus x_2 curves of DFM and alkanols. The data for the DFM-methanol system at 298.15 K [1] has been included for comparison purposes. The trend in the negative excess partial molar volume function, V_2^E, for the {DFM+(ethanol or propan-1-ol)} mixtures in the excess alkan-1-ol region support the V_m^E data (Fig. 2) and may be attributed to the strong DFM-alkanol, dipole-dipole interaction and structural effects arising from the geometrical interstitial accommodation of DFM into the hydrogen bonded alkanol liquid structure. The sharply negative V_2^E values for the (DFM + ethanol) binary mixtures in the excess alkan-1-ol region $(0.00 \leq x_2 \leq 0.12)$ are significantly more apparent and support the possibility of an enhanced structural effect in the low x_2 regime. The V_2^E plots of the {DFM + (butan-1-ol or pentan-1-ol or hexan-1-ol)} systems in the same x_2 range present maxima in the following order: butan-1-ol < pentan-1-ol < hexan-1-ol. This trend in the volume expansion supports the V_m^E variation (Fig. 1) for the same mixtures and it is attributed to the positive effect from the disruption of the alkanol hydrogen-bonded structure. On the other hand, the increase in
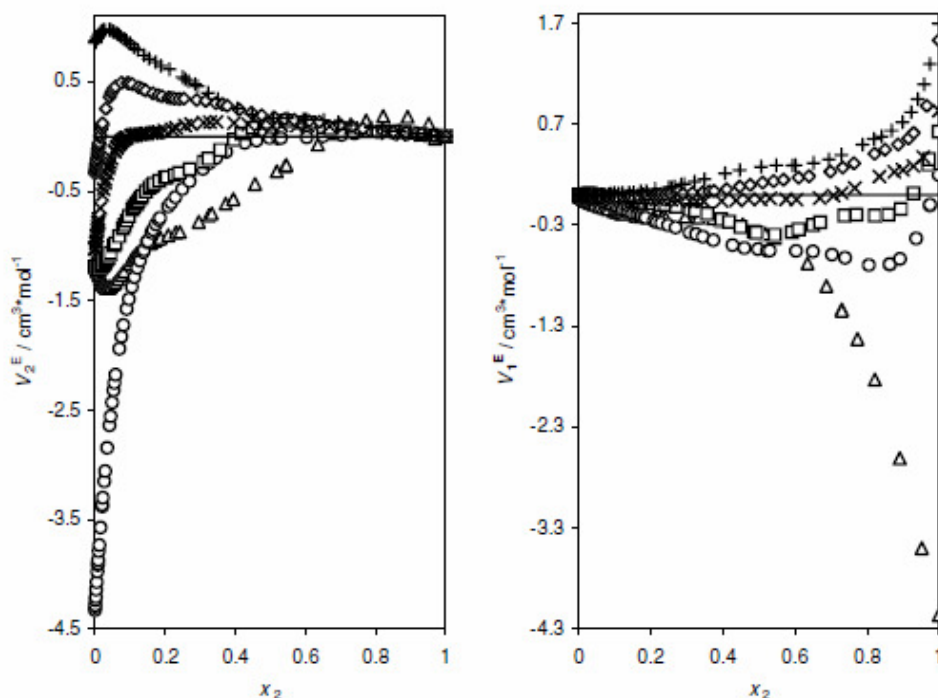
Fig. 2 Excess partial molar volumes, V_i^E, *versus* x_2 for the [alkan-1-ol (1) + DFM (2)] binary mixtures: (△) methanol; (○) ethanol; (□) propan-1-ol; (X) butan-1-ol; (◇) pentan-1-ol and (+) hexan-1-ol at 298.15 K. The curves are from the appropriate Redich-Kister fitting equations

the positive trend for the V_1^E plots in the DFM-rich region suggests a volume expansion whose magnitude increases with the alkanol chain-length. Thus, the disruption of the alkan-1-ol hydrogen-bond structure and dispersal of non-hydrogen bonded alcohol molecules in excess liquid DFM may contribute to the observed volume expansion effect for the binary mixtures. An exception to this trend was the (DFM+methanol) system, in which the geometrical interstitial accommodation of the non-hydrogen bonded small methanol molecules into the DFM liquid structure was suggested to account for the sharp decrease in V_1^E values in the DFM-rich region [1].

Further information about the solute-solvent intermolecular interactions can be obtained from the limiting excess partial molar volumes ($V_i^{E,\infty}$) of components in mixtures [22]. Using the optimized Redlich-Kister least-squares fitting correlation coefficients for each of the (DFM + alkanol) binary systems, values of the limiting excess partial molar volumes for the alkan-1-ols ($V_1^{E,\infty}$) and DFM ($V_2^{E,\infty}$) are determined from Eqs. (5) and (6) [22], respectively,

$$V_1^{E,\infty} = \sum_{k=even} A_k - \sum_{k=odd} A_k \tag{5}$$

$$V_2^{E,\infty} = \sum A_k \tag{6}$$

In Table 2, the values of limiting excess partial molar volumes $V_i^{E,\infty}$ at 298.15 K for each component in the {DFM + (ethanol or propan-1-ol or butan-1-ol or pentan-1-ol or hexan-1-ol)} binary systems are presented. The $V_i^{E,\infty}$ values can be interpreted in terms of packing

efficiencies and geometric fits arising from cooperative effects. As can be seen in this table, $V_2^{E,\infty}$ displays very negative values for the (DFM + ethanol) binary mixtures, indicating a better packing efficiency for DFM in the infinite dilute solution than in the pure state. As the chain length of the alkanol increases, the molecular packing becomes less efficient as can be judged from the increase in $V_2^{E,\infty}$ values. On the other hand, the positive $V_1^{E,\infty}$ values suggest that the disruption of the hydrogen-bonded polymeric aggregates in alkan-1-ols and dispersive intermolecular interactions that are predominant in the DFM-rich region result in poorer molecular packing in all (DFM + alkanol) mixtures than in the corresponding pure components. Thus, it can be concluded from the trend in the $V_i^{E,\infty}$ values that DFM modifies the structure of alkan-1-ols in the order: hexan-1-ol > pentan-1-ol > butan-1-ol > propan-1-ol > ethanol > methanol.

Results of the study presented in this paper are part of a continuing effort towards the understanding of the mixing behavior of the (DFM + alkanol) binary liquid mixtures.

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