

# Densities, Excess and Partial Molar Volumes of (DFM + *n*-pentane or *n*-hexane or *n*-heptane or *n*-octane) Binary Mixtures at (T = 293.15, 298.15 and 303.15) K and Atmospheric Pressure

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**Abstract** Densities ( $\rho$ ) of pure difuryl methane (DFM), *n*-pentane or *n*-hexane or *n*-heptane or *n*-octane and those of (DFM + *n*-pentane or *n*-hexane or *n*-heptane or *n*-octane) binary mixtures over the entire composition range, have been measured at (T = 293.15, 298.15 and 303.15) K and atmospheric pressure. Excess molar volumes ( $V_m^E$ ), of each binary system were determined and correlated by the Redlich-Kister equation. The  $V_m^E$  vs  $x_2$  isotherms for the (DFM + *n*-pentane or *n*-hexane or *n*-heptane) binary mixtures exhibit a sigmoidal behavior while that for the (DFM + *n*-octane) binary system positive deviation for  $V_m^E$  function was observed. The  $V_m^E$  values decreased with temperature increase for each binary systems which suggested a possible structural effects. The  $V_m^E$  data have been used to derive excess partial molar volumes ( $\bar{V}_i^E$ ). Results are discussed in terms of possible geometrical and dispersive intermolecular interactions.

**Keywords** Difurylmethane, *n*-alkane, Excess molar volume, Excess partial molar volume, Binary mixtures, Intermolecular interactions

## 1. Introduction

Research activities in our laboratory consist of systematic measurements of physicochemical properties of non-aqueous binary mixtures in which difuryl methane (DFM) is one of the two components [1-4]. Studies of thermodynamic properties such as excess molar volumes contribute to understanding the nature of molecular interactions in liquid mixtures. It has been reported that DFM comprise of polar molecules and its liquid structure is determined by the dipole-dipole interactions [4].

On the other hand for pure *n*-alkanes, the intermolecular interactions in part comprise of van der Waals forces. In addition, thermodynamic evidence obtained from Depolarized Raleigh Scattering studies on pure *n*-alkanes, indicates that there is short range orientational order between chains of molecules in the pure state which increases with the carbon chain length [5, 6].

The objective of the present study is to obtain information on intermolecular interactions in the binary mixtures of DFM

with *n*-pentane or *n*-hexane or *n*-heptane or *n*-octane. We herewith report densities,  $\rho$ , excess molar volumes,  $V_m^E$ , and excess partial molar volumes,  $\bar{V}_i^E$ , for (DFM + *n*-pentane or *n*-hexane or *n*-heptane or *n*-octane) binary mixtures at (T = 293.15, 298.15 and 303.15) K and atmospheric pressure. The  $V_m^E$  data of the binary mixtures have been fitted to the Redlich – Kister equation [7] to allow determination of the fitting parameters. The results obtained have been used to interpret intermolecular interactions that exist in these binary mixtures. A survey of the literature has indicated that there has been no reported study on volumetric properties for (DFM + *n*-pentane or *n*-hexane or *n*-heptane or *n*-octane) binary mixtures at (T = 293.15, 298.15 and 303.15) K.

## 2. Experimental

### 2.1. Materials and Purification of Solvents

The following chemicals were used: *n*-pentane (Fluka, analytical reagent  $\geq 99.8\%$ ), *n*-hexane (Merck Co.,  $\geq 98.0\%$ ), *n*-heptane (Merck Co.,  $\geq 99.0\%$ ), *n*-octane (Saarchem chemicals, 99.0%), furfuryl alcohol (Merck Co., 98.0%), borontrifluoride-dietherate,  $\text{BF}_3(\text{OEt}_2)_2$ , (Sigma-Aldrich Chemicals Co., 99.0%). Each of ( $C_5$  -  $C_8$ ) *n*-alkanes was purified by distillation using 1m fractionation column fitted with glass beads. DFM was prepared as described elsewhere [8], and its purity was confirmed by  $^1\text{H-NMR}$  and density

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measurements. The elemental analysis of DFM was found to be as follows: Calcd for  $C_9H_8O_2$ : C, 72.96; H, 5.44; O, 21.60. Found: C, 73.02; H, 5.46; O, 21.52%. The percentage carbon and hydrogen content of DFM were each slightly higher, while that for oxygen was lower than the expected values. This difference was attributed to a low contamination level of *n*-hexane solvent used in the DFM purification process.

All purified organic liquids were stored in brown glass bottles and fractionally distilled just before use. The purity of each ( $C_5 - C_8$ ) *n*-alkanes and DFM was tested by density measurement which was compared to literature values. Measured densities for pure components at various temperatures together with corresponding literature data are listed in Table 1. Ultrapure water required for the calibration of the densimeter was obtained as follows. Distilled water was first refluxed over  $KMnO_4$  and finally doubly distilled under nitrogen flow using a two-stage Heraeus-Destamat quartz still instrument. The conductivity of water was always less than  $1.0 \times 10^{-6} S \cdot cm^{-1}$ .

**Table 1.** Densities,  $\rho$  ( $kg \cdot m^{-3}$ ) of pure components at ( $T = 293.15, 298.15$  and  $303.15$ ) K

Compound	T /K	$\rho$ ( $kg/m^3$ )	
		Exp	Lit
<i>n</i> -Pentane	293.15	626.34	626.24 <sup>a</sup>
			626.14 <sup>b</sup>
	298.15	621.37	621.39 <sup>a</sup>
<i>n</i> - Hexane	293.15	659.98	621.26 <sup>c</sup>
			659.85 <sup>d</sup>
	298.15	655.42	659.57 <sup>b</sup>
	303.15	650.86	655.21 <sup>d, e</sup>
<i>n</i> - Heptane	293.15	684.19	650.51 <sup>b</sup>
			684.16 <sup>d</sup>
	298.15	679.96	683.92 <sup>b</sup>
			679.91 <sup>d</sup>
			679.69 <sup>b</sup>
<i>n</i> - Octane	293.15	702.76	679.67 <sup>c</sup>
			702.67 <sup>a, b</sup>
	298.15	698.74	675.19 <sup>a</sup>
	303.15	694.70	675.47 <sup>b</sup>
Difurylmethane	293.15	1095.68	1095.94 <sup>f</sup>
	298.15	1090.63	1090.88 <sup>f</sup>
	303.15	1085.57	1085.82 <sup>f</sup>

<sup>a</sup> Ref [9], <sup>b</sup> Ref [10], <sup>c</sup> Ref [11], <sup>d</sup> Ref [12], <sup>e</sup> Ref [22], <sup>f</sup> Ref [1,2,3]

## 2.2. Apparatus and Procedure

Each one of the (DFM + *n*-pentane or *n*-hexane or *n*-heptane or *n*-octane) binary mixtures was prepared by weighing appropriate amounts of DFM and the corresponding *n*-alkane co-solvent on an analytical balance ( $\Delta m = \pm 0.0001$  g), by syringing each component into a stoppered flask. Pure components were first separately

degassed in an ultrasonic bath shortly before sample preparations. All binary mixtures were completely miscible over the entire composition range. Solution density measurements were performed at atmospheric pressure with an Anton Paar DMA 4500 vibrating-tube densimeter at the experimental temperature. The densimeter was first calibrated with pure water and benzene as reference liquids. A sample volume of not more than  $1.0 \text{ cm}^3$  was needed to fill the densimeter cell and thermal equilibrium was attained quickly. The temperature of the sample was controlled electronically 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 density measurements to offset possible instrument drift. A linear relation between the density of the fluid and the square of the vibrating period  $\tau$ , ( $\rho = A + B\tau^2$ ), was assumed. Buoyancy corrections were made by taking into account of the air density at each of the three temperatures, the barometric pressure, and the relative humidity. Under such conditions triplet density measurements of each sample were reproducible to within  $\pm 0.01 \text{ kg} \cdot m^{-3}$ . The reliability of density measurements was ascertained by comparing the experimental density of pure liquids with the corresponding literature values (Table 1) at the studied temperatures.

## 3. Results and Discussion

Excess molar volumes  $V_m^E$ , were calculated from density measurements for each of [DFM + *n*-pentane or *n*-hexane or *n*-heptane or *n*-octane) binary systems using equation (1) [13-15];

$$V_m^E = V_m - V_m^{id} = M/\rho - \sum x_i M_i/\rho_i \quad (1)$$

where  $M$  is the molar mass of the mixture, which is the mole fraction weighted adduct of the molar masses of the two pure components in each binary mixture, *i.e.* ( $M = M_1 x_1 + M_2 x_2$ ).  $V_m^{id}$  is the ideal molar volume,  $\rho$  is the density of the mixture, and  $x_i$ ,  $M_i$  and  $\rho_i$  are respectively the mole fraction, the molar mass and the density of the pure liquid component *i*. The Redlich-Kister polynomial equation (2) [7] in which all points are weighted equally was least-square fitted to the  $V_m^E$  data (Table 2) for each binary system:

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

where  $n$  is the order of the polynomial,  $x_1$  is the mole fractions of the *n*-alkane co-solvent and  $x_2$  is the mole fraction of DFM. For each binary system at a specific temperature, the degree of the polynomial and the number of regression coefficients  $A_k$ , in equation (2) were fixed by testing the statistical significance of including each further term using an F-test at a 99.5% confidence level [16]. The optimized number of regression coefficients for each of the four binary systems are listed in Table 3 along with the corresponding standard deviation  $\sigma(V_m^E)$ , calculated from equation (3):

$$\sigma(V_m^E) = [\sum (V_{m,exp}^E - V_{m,calc}^E)^2 / (N - n)]^{1/2} \quad (3)$$

where  $N$  is the number of data points and  $n$  represents number of regression coefficients.

**Table 2.** Experimental densities  $\rho$  ( $kg\ m^{-3}$ ), excess molar volume,  $V_m^E$  and excess partial molar volumes  $\bar{V}_i^E$  ( $cm^3\ mol^{-1}$ ) for (DFM +  $n$ -Pentane or  $n$ -Hexane or  $n$ -Heptane or  $n$ -Octane) binary mixtures at ( $T = 293.15, 298.15$  and  $303.15$ ) K

$x_2$	$\rho$	$V_m^E$	$\bar{V}_1^E$	$\bar{V}_2^E$
		(DFM + $n$ -Pentane)		
		$T = 293.15\ K$		
0.00000	626.34	0.00000	0.00000	3.35934
0.00237	627.58	0.01180	0.00526	2.76560
0.00591	629.45	0.02610	0.01463	1.95600
0.00935	631.28	0.03755	0.02607	1.25324
0.01155	632.45	0.04340	0.03402	0.84665
0.01975	636.93	0.04622	0.05598	-0.43781
0.02739	641.27	0.01572	0.05419	-1.35044
0.03124	643.49	0.00537	0.04992	-1.71959
0.04018	648.40	0.01379	0.08298	-2.32540
0.05043	654.18	0.05257	0.09123	-2.76008
0.06282	661.00	0.07467	0.11888	-2.96228
0.08197	671.68	0.14131	0.10615	-2.91267
0.10130	682.22	0.17790	0.09551	-2.60358
0.15077	708.95	0.27795	-0.00581	-1.81083
0.20126	735.78	0.37367	-0.08061	-1.53673
0.25220	762.47	0.47563	-0.09813	-1.59493
0.35191	812.97	0.59058	-0.11916	-1.45878
0.40132	837.41	0.64557	-0.24367	-1.24511
0.50397	886.84	0.73608	-0.59906	-0.87094
0.65159	953.91	0.68707	-1.11771	-0.45680
0.75103	996.88	0.59535	-1.66097	-0.24208
0.84966	1037.62	0.43573	-2.00318	-0.15837
0.89796	1056.81	0.32180	-2.33810	-0.09268
0.95704	1079.79	0.17383	-3.44541	-0.02696
1.00000	1095.68	0.00000	-4.31860	0.00000
		$T = 298.15\ K$		
0.00000	621.37	0.00000	0.00000	3.79052
0.00237	622.60	0.01300	0.00561	3.12817
0.00591	624.45	0.02999	0.01694	2.22664
0.00935	626.29	0.03854	0.02532	1.43932
0.01155	627.45	0.04558	0.03458	0.98694
0.01975	631.92	0.04747	0.05737	-0.44406
0.02739	636.25	0.01576	0.05722	-1.45654
0.03124	638.47	-0.00692	0.05303	-1.86588
0.04018	643.36	-0.01469	0.09089	-2.53676
0.05043	649.12	-0.05364	0.10364	-3.01485
0.06282	655.92	-0.07617	0.13576	-3.23794
0.08197	666.56	-0.14213	0.12917	-3.18044
0.10130	677.16	-0.19476	0.10590	-2.86216
0.15077	703.92	-0.31207	-0.00400	-2.04760

0.20126	730.79	-0.42408	-0.07396	-1.81358
0.25220	757.41	-0.52240	-0.06109	-1.89020
0.35191	808.01	-0.66129	-0.11542	-1.66660
0.40132	832.78	-0.76691	-0.33463	-1.41179
0.50397	881.91	-0.81240	-0.72109	-0.90226
0.65159	949.15	-0.77636	-1.22267	-0.53771
0.75103	992.07	-0.66643	-1.91497	-0.25252
0.84966	1032.58	-0.46305	-2.41215	-0.11816
0.89796	1051.81	-0.34649	-2.64457	-0.08535
0.95704	1074.68	-0.17458	-3.49876	-0.02536
1.00000	1090.63	0.00000	-4.64234	0.00000
		(DFM + $n$ -Hexane)		
		$T = 293.15\ K$		
0.00000	659.98	0.00000	0.00000	0.42763
0.00102	660.44	0.00058	0.00015	0.42613
0.00202	660.89	0.00080	-5.4E-05	0.42437
0.00410	661.82	0.00154	-0.00019	0.42110
0.00603	662.69	0.00253	3.55E-06	0.41855
0.00801	663.58	0.00311	-0.00022	0.41566
0.01005	664.49	0.00428	0.00013	0.41343
0.01589	667.11	0.00671	0.00025	0.40699
0.02751	672.33	0.00951	-0.00141	0.39548
0.04246	679.03	0.01564	-0.00088	0.38817
0.05570	684.94	0.02316	0.00171	0.38681
0.07395	693.10	0.03003	0.00180	0.38351
0.08716	699.00	0.03516	0.00210	0.38130
0.12031	713.78	0.04685	0.00283	0.36871
0.15151	727.65	0.05909	0.00809	0.34469
0.23626	765.26	0.07491	0.03968	0.18880
0.30591	796.04	0.08021	0.10843	0.01619
0.34734	814.30	0.07957	0.16300	-0.07719
0.37207	825.22	0.07191	0.19112	-0.12927
0.40008	837.61	0.05660	0.21598	-0.18239
0.46056	864.25	0.02894	0.26019	-0.24192
0.48698	875.91	0.00851	0.25925	-0.25563
0.57618	914.88	-0.02151	0.21633	-0.19646
0.60756	928.57	-0.03693	0.16585	-0.16791
0.67985	959.86	-0.05205	0.02346	-0.08761
0.73457	983.44	-0.06270	-0.10385	-0.04784
0.79902	1010.88	-0.04593	-0.21177	-0.00422
0.84676	1031.11	-0.03185	-0.26210	0.009825
0.89350	1050.90	-0.02436	-0.28109	0.006244
1.00000	1095.68	0.00000	-0.03874	0.00000
		$T = 298.15\ K$		
0.00000	655.42	0.00000	0.00000	0.15243
0.00102	655.88	0.00047	0.00032	0.15550
0.00202	656.32	0.00079	0.00047	0.15839
0.00410	657.26	0.00129	0.00062	0.16440
0.00603	658.12	0.00190	0.00088	0.17025
0.00801	659.01	0.00229	0.00089	0.17613

0.01005	659.92	0.00325	0.00143	0.18284
0.01589	662.54	0.00396	0.00079	0.20040
0.02751	667.74	0.00733	0.00081	0.23758
0.04246	674.44	0.00927	-0.00274	0.27986
0.05570	680.35	0.01326	-0.00444	0.31331
0.07395	688.49	0.01926	-0.00688	0.34656
0.08716	694.38	0.02301	-0.00907	0.35893
0.12031	709.12	0.03442	-0.00872	0.34982
0.15151	722.96	0.04542	0.00119	0.29314
0.23626	760.50	0.05778	0.07307	0.00832
0.30591	791.27	0.05432	0.16522	-0.19730
0.34734	809.70	0.02062	0.18530	-0.28880
0.37207	820.65	0.00567	0.19519	-0.31420
0.40008	833.02	-0.00887	0.19935	-0.32110
0.46056	859.59	-0.02986	0.17870	-0.27410
0.48698	871.18	-0.04118	0.15083	-0.24350
0.57618	910.06	-0.06166	0.02667	-0.12660
0.60756	923.71	-0.07218	-0.02609	-0.10200
0.67985	954.93	-0.07841	-0.11927	-0.05920
0.73457	978.35	-0.06700	-0.16814	-0.03050
0.79902	1005.81	-0.05213	-0.24792	-0.00290
0.84676	1026.04	-0.03674	-0.33107	0.01653
0.89350	1045.81	-0.02495	-0.40401	0.02024
1.00000	1090.63	0.00000	0.44266	0.00000
		$T = 303.15\text{ K}$		
0.00000	650.86	0.00000	0.00000	-0.05379
0.00102	651.31	0.00036	0.00040	-0.04382
0.00202	651.76	0.00057	0.00064	-0.03439
0.00410	652.69	0.00083	0.00089	-0.01551
0.00603	653.55	0.00165	0.00165	0.00193
0.00801	654.44	0.00163	0.00149	0.01828
0.01005	655.35	0.00217	0.00184	0.03496
0.01589	657.96	0.00310	0.00189	0.07833
0.02751	663.15	0.00501	0.00093	0.14904
0.04246	669.83	0.00656	-0.00255	0.21205
0.05570	675.74	0.00686	-0.00719	0.24497
0.07395	683.87	0.00993	-0.01047	0.26550
0.08716	689.75	0.01222	-0.01184	0.26423
0.12031	704.45	0.02323	-0.00416	0.22348
0.15151	718.28	0.02916	0.00820	0.14657
0.23626	755.77	0.03433	0.07573	-0.09948
0.30591	786.59	0.01179	0.12952	-0.25534
0.34734	804.92	-0.01061	0.14845	-0.30947
0.37207	815.84	-0.02357	0.15515	-0.32517
0.40008	828.19	-0.03789	0.15673	-0.32972
0.46056	854.74	-0.06111	0.13914	-0.29564
0.48698	866.32	-0.07282	0.11613	-0.27186
0.57618	905.17	-0.09335	-0.00336	-0.15954
0.60756	918.79	-0.10052	-0.06412	-0.12403
0.67985	949.98	-0.10365	-0.21101	-0.05309

0.73457	973.35	-0.08510	-0.30196	-0.00674
0.79902	1000.75	-0.06103	-0.37859	0.01884
0.84676	1020.96	-0.04165	-0.39384	0.02209
0.89350	1040.71	-0.02550	-0.36085	0.01447
1.00000	1085.57	0.00000	-0.00824	0.00000
		(DFM + <i>n</i> -Heptane)		
		$T = 293.15\text{ K}$		
0.00000	684.19	0.00000	0.00000	2.15190
0.00105	684.57	0.00362	0.00140	2.12966
0.00203	684.93	0.00671	0.00243	2.10865
0.00404	685.67	0.01145	0.00313	2.06520
0.00605	686.41	0.01658	0.00438	2.02316
0.00805	687.16	0.02013	0.00422	1.98074
0.01065	688.12	0.02543	0.00495	1.92807
0.02047	691.78	0.04205	0.00654	1.74138
0.04190	699.84	0.06655	0.00829	1.39886
0.06413	708.22	0.09376	0.02231	1.13646
0.08505	716.10	0.12500	0.04739	0.95992
0.09963	721.64	0.13953	0.06004	0.85787
0.15055	741.20	0.16721	0.09160	0.59385
0.20019	760.46	0.18454	0.12749	0.41245
0.25405	781.58	0.19282	0.17800	0.23635
0.30182	800.49	0.19451	0.23903	0.09150
0.35906	823.42	0.18197	0.31880	-0.06230
0.45157	861.16	0.12305	0.41236	-0.22830
0.50205	881.94	0.10125	0.44666	-0.24130
0.55484	904.01	0.05447	0.42122	-0.23980
0.61140	927.71	0.02986	0.37046	-0.18660
0.65009	944.11	0.00411	0.29872	-0.15450
0.70711	968.37	-0.01757	0.17697	-0.09820
0.79823	1007.44	-0.02769	-0.01670	-0.03050
0.84778	1028.88	-0.02554	-0.08730	-0.01440
0.90629	1054.41	-0.02218	-0.13170	-0.01090
0.94036	1069.35	-0.01523	-0.16370	-0.00580
1.00000	1095.68	0.00000	-0.46490	0.00000
		$T = 298.15\text{ K}$		
0.00000	679.96	0.00000	0.00000	1.91888
0.00105	680.34	0.00336	0.00136	1.91049
0.00203	680.70	0.00598	0.00212	1.90183
0.00404	681.44	0.01041	0.00282	1.88270
0.00605	682.19	0.01286	0.00162	1.86083
0.00805	682.93	0.01695	0.00215	1.84000
0.01065	683.89	0.02265	0.00338	1.81254
0.02047	687.54	0.03881	0.00416	1.69707
0.04190	695.56	0.06609	0.00666	1.42522
0.06413	703.91	0.09384	0.02065	1.16190
0.08505	711.77	0.12405	0.04653	0.95797
0.09963	717.31	0.13498	0.05783	0.83223
0.15055	736.81	0.16254	0.09662	0.53451
0.20019	756.02	0.17848	0.12922	0.37530

0.25405	777.09	0.18497	0.16832	0.23383
0.30182	795.94	0.18837	0.22665	0.09980
0.35906	818.82	0.17432	0.31337	-0.07388
0.45157	856.49	0.11220	0.42770	-0.27099
0.50205	877.23	0.08983	0.45686	-0.27420
0.55484	899.25	0.04402	0.40809	-0.24807
0.61140	922.95	0.01305	0.31971	-0.18185
0.65009	939.27	-0.00467	0.24777	-0.14054
0.70711	963.47	-0.02281	0.15537	-0.09661
0.79823	1002.51	-0.03533	0.03513	-0.05314
0.84778	1024.00	-0.04260	-0.09000	-0.03408
0.90629	1049.41	-0.02583	-0.30360	0.00290
0.94036	1064.33	-0.01748	-0.39760	0.00663
1.00000	1090.63	0.00000	0.08783	0.00000
		$T = 303.15\text{ K}$		
0.00000	675.71	0.00000	0.00000	2.03536
0.00105	676.09	0.00309	0.00099	2.01462
0.00203	676.46	0.00348	-0.00057	1.99282
0.00404	677.19	0.00934	0.00146	1.95437
0.00605	677.94	0.01123	-0.00034	1.91295
0.00805	678.68	0.01500	-9.1E-05	1.87458
0.01065	679.63	0.02197	0.00252	1.82848
0.02047	683.28	0.03548	0.00161	1.65643
0.04190	691.26	0.06561	0.00935	1.35219
0.06413	699.59	0.09180	0.02192	1.11162
0.08505	707.42	0.12305	0.04651	0.94636
0.09963	712.94	0.13444	0.05593	0.84394
0.15055	732.38	0.16175	0.08974	0.56801
0.20019	751.54	0.17617	0.12950	0.36265
0.25405	772.57	0.17883	0.18259	0.16779
0.30182	791.37	0.18214	0.24963	0.02603
0.35906	814.21	0.16483	0.32387	-0.11907
0.45157	851.80	0.10130	0.39973	-0.26115
0.50205	872.50	0.07843	0.42294	-0.26327
0.55484	894.47	0.03368	0.38977	-0.25201
0.61140	918.11	0.00554	0.32910	-0.20011
0.65009	934.44	-0.01765	0.25993	-0.16705
0.70711	958.58	-0.03194	0.15370	-0.10883
0.79823	997.57	-0.04374	-0.02480	-0.04852
0.84778	1019.01	-0.04690	-0.11797	-0.03413
0.90629	1044.50	-0.04301	-0.23978	-0.02266
0.94036	1059.31	-0.02125	-0.32484	-0.00200
1.00000	1085.57	0.00000	-0.63551	0.00000
		(DFM + n-Octane)		
		$T = 293.15\text{ K}$		
0.00000	702.76	0.00000	0.00000	1.36022
0.00208	703.42	0.00461	0.00154	1.47812
0.00410	704.06	0.00917	0.00269	1.58407
0.00601	704.67	0.01289	0.00284	1.67658
0.00809	705.34	0.01585	0.00155	1.76851

0.01048	706.11	0.01837	-0.00120	1.86328
0.02170	709.72	0.03603	-0.01190	2.19563
0.04573	717.39	0.09784	-0.01460	2.44488
0.06068	722.20	0.13344	-0.01230	2.39026
0.07982	728.44	0.16845	-0.00730	2.19450
0.10932	738.00	0.25150	0.05684	1.83752
0.15059	751.86	0.29523	0.11061	1.33663
0.20332	769.90	0.34108	0.18649	0.94683
0.25390	787.50	0.38606	0.25522	0.77053
0.30544	805.88	0.40663	0.30315	0.64192
0.34968	821.96	0.41691	0.35335	0.53511
0.40906	844.05	0.41128	0.43768	0.37313
0.45307	860.73	0.40725	0.52807	0.26139
0.50500	880.78	0.39897	0.65862	0.14446
0.55731	901.55	0.36091	0.78711	0.02237
0.60238	919.86	0.31557	0.90099	-0.07085
0.65073	939.90	0.26029	1.01550	-0.14507
0.69975	960.59	0.20762	1.09724	-0.17410
0.75628	984.98	0.14279	1.06919	-0.15575
0.79952	1004.10	0.08089	0.90653	-0.12614
0.85572	1029.20	0.03569	0.57033	-0.05446
0.90193	1050.10	0.02125	0.28189	-0.00709
0.95170	1073.03	0.00724	0.13140	0.00093
1.00000	1095.68	0.00000	0.25608	0.00000
		$T = 298.15\text{ K}$		
0.00000	698.74	0.00000	0.00000	1.27712
0.00208	699.40	0.00407	0.00117	1.39397
0.00410	700.04	0.00811	0.00198	1.49968
0.00601	700.65	0.01133	0.00177	1.59260
0.00809	701.32	0.01373	9E-05	1.68559
0.01048	702.08	0.01794	-0.00080	1.78457
0.02170	705.68	0.03496	-0.01160	2.13511
0.04573	713.33	0.09541	-0.01660	2.43311
0.06068	718.12	0.13188	-0.01480	2.40256
0.07982	724.34	0.16663	-0.01160	2.22124
0.10932	733.87	0.24949	0.05193	1.85913
0.15059	747.68	0.29399	0.11033	1.32995
0.20332	765.66	0.34001	0.19143	0.92219
0.25390	783.21	0.38381	0.25691	0.75671
0.30544	801.53	0.40493	0.29930	0.64512
0.34968	817.59	0.40977	0.34147	0.53680
0.40906	839.58	0.41062	0.43490	0.37555
0.45307	856.21	0.40699	0.52766	0.26132
0.50500	876.21	0.39776	0.65484	0.14577
0.55731	896.93	0.35866	0.77917	0.02464
0.60238	915.20	0.31201	0.89889	-0.07537
0.65073	935.18	0.25819	1.03911	-0.16095
0.69975	955.82	0.20551	1.15038	-0.19992
0.75628	980.20	0.13394	1.10966	-0.18050
0.79952	999.32	0.06620	0.88145	-0.13822

0.85572	1024.30	0.03088	0.45560	-0.04074
0.90193	1045.13	0.02069	0.20143	0.00104
0.95170	1068.03	0.00544	0.22468	-0.00569
1.00000	1090.63	0.00000	-0.18320	0.00000
		$T = 303.15\text{ K}$		1.27712
0.00000	694.70	0.00000	0.00000	1.10966
0.00208	695.36	0.00351	0.00093	1.24227
0.00410	696.00	0.00703	0.00145	1.36209
0.00601	696.61	0.00974	0.00092	1.46736
0.00809	697.28	0.01157	-0.00120	1.57273
0.01048	698.03	0.01750	-0.00020	1.68698
0.02170	701.62	0.03386	-0.01160	2.08535
0.04573	709.25	0.09293	-0.01910	2.42977
0.06068	714.03	0.12800	-0.01920	2.40735
0.07982	720.22	0.16478	-0.01450	2.23123
0.10932	729.72	0.24746	0.04854	1.86809
0.15059	743.48	0.29276	0.10754	1.33751
0.20332	761.40	0.33899	0.18996	0.92293
0.25390	778.90	0.38163	0.25766	0.74592
0.30540	797.16	0.40334	0.30351	0.63035
0.34968	813.18	0.40649	0.34262	0.52526
0.40906	835.10	0.40836	0.42924	0.37821
0.45307	851.69	0.40345	0.51503	0.26876
0.50500	871.62	0.39690	0.64559	0.15313
0.55731	892.29	0.35680	0.78029	0.02040
0.60238	910.51	0.31051	0.91336	-0.08742
0.65073	930.44	0.25663	1.05964	-0.17438
0.69975	951.07	0.19791	1.15401	-0.21234
0.75628	975.36	0.13155	1.09057	-0.17751
0.79952	994.45	0.06207	0.84725	-0.13482
0.85572	1019.36	0.02967	0.44461	-0.04029
0.90193	1040.16	0.01849	0.22546	-0.00401
0.95170	1063.03	0.00217	0.22635	-0.00921
1.00000	1085.57	0.00000	-0.35310	0.00000

**Table 3.** Least square fitted ( $A_i$ ) coefficients of Equation (34) and corresponding standard deviation of fit  $\sigma(V_m^E)$  for the [DFM + (*n*-Pentane or *n*-Hexane or *n*-Heptane or *n*-Octane)]

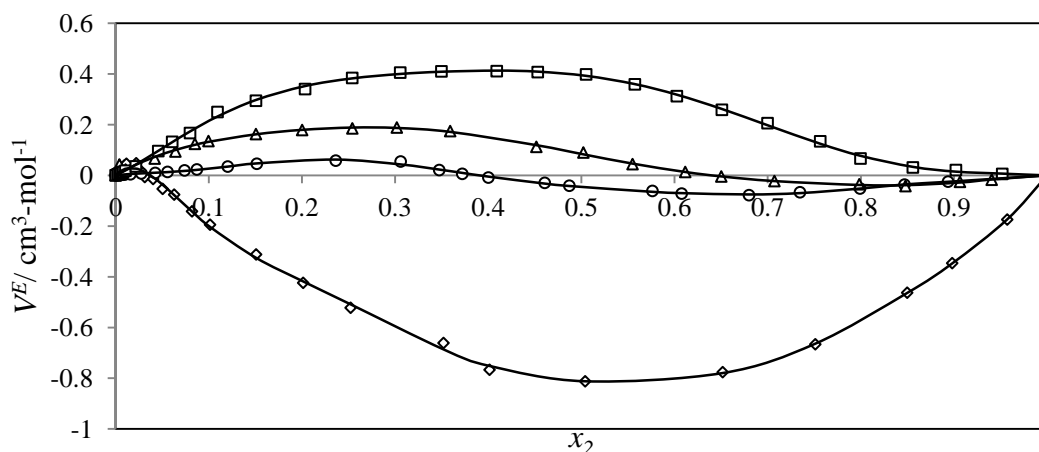
	<i>n</i> -Pentane	<i>n</i> -Hexane	<i>n</i> -Heptane	<i>n</i> -Octane
<i>Coefficients</i>		$T = 293.15\text{ K}$		
$A_0$	-2.880	0.039	0.387	1.574
$A_1$	0.592	1.027	1.375	0.980
$A_2$	0.154	0.185	0.251	-0.826
$A_3$	2.386	-1.409	-1.001	1.048
$A_4$	3.859	-0.306	-0.061	-0.315
$A_5$	-9.117	0.858	0.703	0.907
$A_6$	-14.482	0.277	0.641	3.629
$A_7$	9.979	-0.243	0.231	-2.384
$A_8$	12.868		-0.375	-3.253
$\sigma(V_m^E)$	0.015	0.003	0.004	0.006
		$T = 298.15\text{ K}$		

$A_0$	-3.244	-0.194	0.337	1.566
$A_1$	0.412	0.723	1.464	0.972
$A_2$	-0.051	1.108	0.518	-0.755
$A_3$	4.552	-0.148	-2.004	0.928
$A_4$	5.355	-2.030	-1.270	-1.773
$A_5$	-14.489	-0.720	3.871	3.245
$A_6$	-15.955	1.413	1.927	7.399
$A_7$	13.740		-2.415	-8.033
$A_8$	13.469		-0.509	-5.891
$A_9$				3.619
$\sigma(V_m^E)$	0.014	0.004	0.004	0.006
		$T = 303.15\text{ K}$		
$A_0$		-0.312	0.298	1.560
$A_1$		0.721	1.373	0.936
$A_2$		0.798	0.359	-0.878
$A_3$		-0.564	-0.836	1.532
$A_4$		-0.517	-0.187	-1.337
$A_5$		-0.179	0.798	1.024
$A_6$			0.231	7.015
$A_7$				-5.066
$A_8$				-5.982
$A_9$				2.305
$\sigma(V_m^E)$		0.003	0.004	0.006

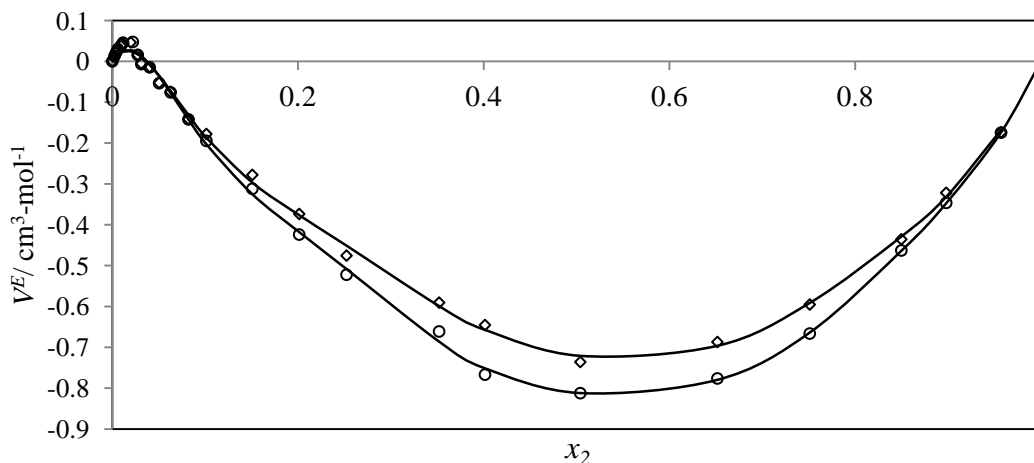
Figure 1 presents  $V_m^E$  vs  $x_2$  data for each of the (DFM + *n*-pentane or *n*-hexane or *n*-heptane or *n*-octane) binary mixtures at 298.15 K. For each binary mixture, the fitted curve was calculated by using the corresponding Redlich-Kister polynomial regression coefficients (Table 3). Figure 1 shows that the  $V_m^E$  vs  $x_2$  isotherms for (DFM + *n*-pentane or *n*-hexane or *n*-heptane) binary mixtures exhibited sigmoidal-shaped behavior, with positive deviations limited to  $0.00 \leq x_2 \leq 0.039$ ,  $0.00 \leq x_2 \leq 0.39$  and  $0.00 \leq x_2 \leq 0.64$  respectively, and negative deviations over the remaining  $x_2$  - ranges. It has been suggested that the sigmoidal-shaped behavior for the  $V_m^E$  vs  $x_2$  isotherm arises from opposing effects which result from differences in energies of interaction between molecules in solution and packing effects [17, 18]. When DFM is added to the *n*-alkane, the mixing process may lead to a net destruction of the weak intermolecular interactions in the *n*-alkane and partial disruption of the dipole-dipole interactions in DFM liquid structure. In the low- $x_2$  compositions, positive  $V_m^E$  values indicate dominance of the entropy increasing dispersive intermolecular interactions due to possible loosening of the *n*-alkane molecular parking and the partial disruption of the dipole-dipole liquid structure in DFM which results in the observed volume expansion for each of the three binary systems. The sequence for the positive  $V_m^E$  ( $_{max}$ ) values is in the order: *n*-heptane > *n*-hexane > *n*-pentane and were:  $+0.188\text{ cm}^3\text{ mol}^{-1}$  (at  $x_2 = 0.254$ ),  $+0.062\text{ cm}^3\text{ mol}^{-1}$  (at  $x_2 = 0.236$ ) and  $+0.0474\text{ cm}^3\text{ mol}^{-1}$  (at  $x_2 = 0.022$ ), respectively. The inflection points for *n*-pentane, *n*-hexane and *n*-heptane occur at  $x_2 = 0.039$ ,  $x_2 = 0.39$  and  $x_2 = 0.64$  respectively. Thus, the DFM mole fraction at which the transition from a

positive to negative  $V_m^E$  values occurs increases with the increase in the  $n$ -alkane chain length. Since weak van der Waals intermolecular interactions exist between  $n$ -alkane and DFM molecules, the negative  $V_m^E$  values observed for (DFM +  $n$ -pentane or  $n$ -hexane or  $n$ -heptane) binary mixtures may be arising from geometrical interstitial accommodation effects which result from the free volume differences between the unlike components in each the three binary mixtures [19]. The magnitude of  $V_m^E$  values is in the order:  $n$ -pentane >  $n$ -hexane >  $n$ -heptane and were  $-0.812 \text{ cm}^3 \text{ mol}^{-1}$  (at  $x_2 = 0.504$ ),  $-0.075 \text{ cm}^3 \text{ mol}^{-1}$  (at  $x_2 = 0.680$ ) and  $-0.039 \text{ cm}^3 \text{ mol}^{-1}$  (at  $x_2 = 0.848$ ) respectively. It is possible that DFM component in each binary mixture, forms a relatively open liquid structure with sufficiently large cavities for the  $n$ -alkane molecular interstitial accommodation resulting in closer molecular packing which is reflected in negative  $V_m^E$  values for  $n$ -pentane or  $n$ -hexane or  $n$ -heptane in the  $x_2$  - range:  $0.039 \leq x_2 \leq 1.00$ ,  $0.39 \leq x_2 \leq 1.00$  and  $0.64 \leq x_2 \leq 1.00$  respectively. The trend in the

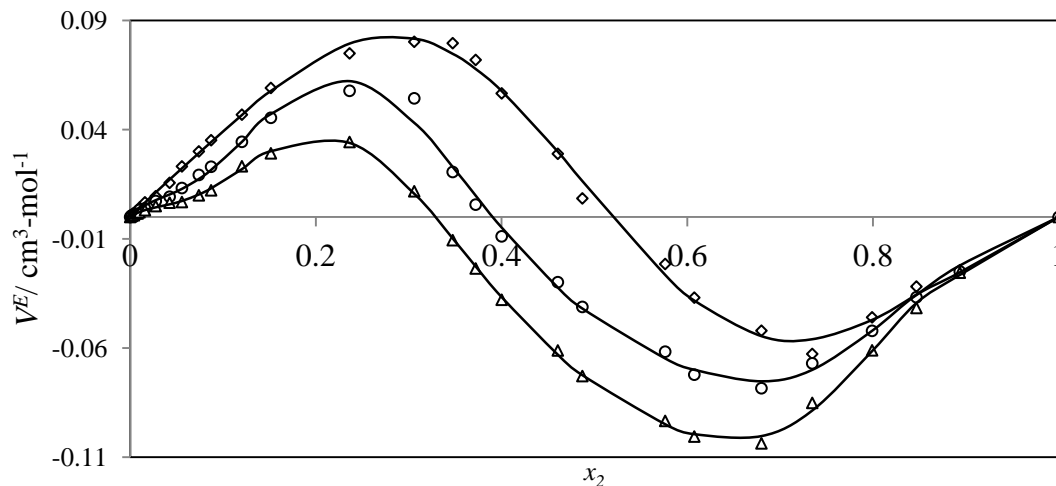
$V_m^E$  values suggest that the geometrical interstitial accommodation of the  $n$ -alkane molecules into the DFM liquid structure becomes less efficient as the  $n$ -alkane chain length increases. It can also be noticed that the (DFM +  $n$ -pentane) binary system exhibits a comparatively large  $V_m^E$  values in comparison to the (DFM +  $n$ -hexane or  $n$ -heptane) binary systems. The contributing factors to this behavior is the difference in molecular shape and size between DFM and  $n$ -pentane or  $n$ -hexane or  $n$ -heptane. DFM being a polar molecule, would tend to remain self-associated in the binary solution. It is possible that the smaller  $n$ -pentane molecules are more efficiently accommodated into voids of DFM liquid structure in comparison with either  $n$ -hexane or  $n$ -heptane molecules causing more negative  $V_m^E$  values for (DFM +  $n$ -pentane) binary system at each temperature investigated. For the (DFM +  $n$ -octane) binary system, positive  $V_m^E$  values were observed over the entire  $x_2$  range suggesting the dominance of the dispersive intermolecular interactions over the geometrical effects.



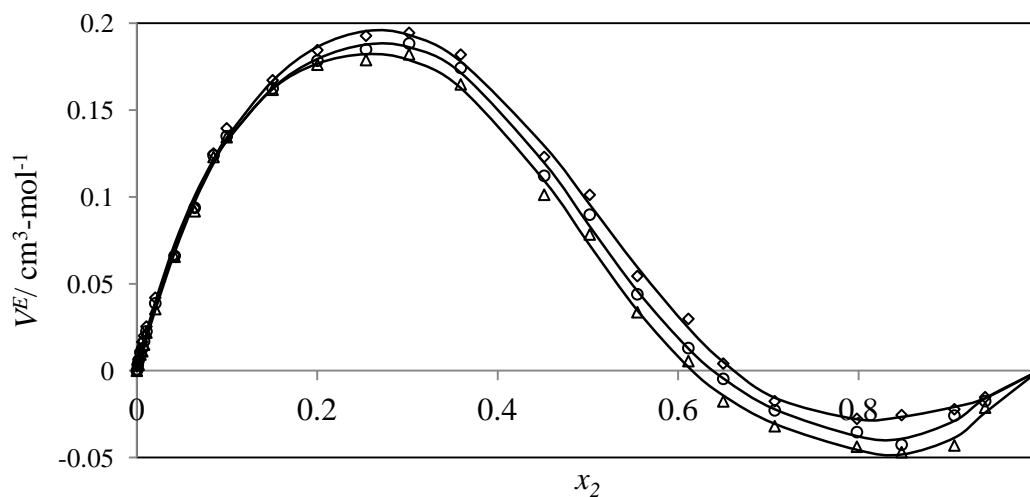
**Figure 1.** Excess molar volume,  $V_m^E$  vs  $x_2$  for the [DFM (2) +  $n$ -alkane (1)] binary mixtures: ( $\diamond$ )  $n$ -pentane; ( $\circ$ )  $n$ -hexane; ( $\Delta$ )  $n$ -heptane and ( $\square$ )  $n$ -octane at 298.15 K. The solid lines are from the appropriate Redlich-Kister fitting equations



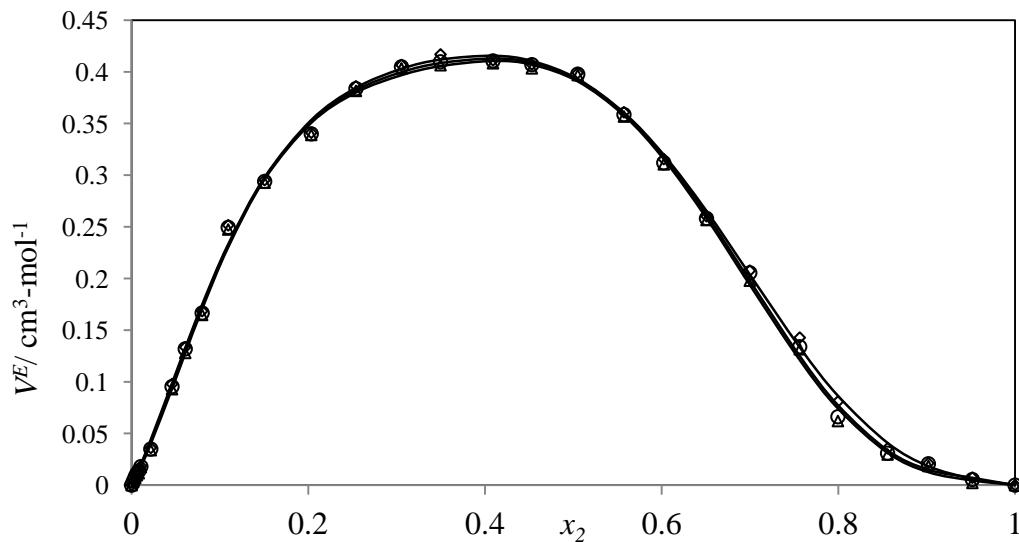
**Figure 2.** Excess molar volume,  $V_m^E$  vs  $x_2$  for the [DFM (2) +  $n$ -pentane (1)] binary mixtures at ( $\diamond$ ) 293.15 K; ( $\circ$ ) 298.15 K. The solid lines are from the appropriate Redlich-Kister fitting equations



**Figure 3.** Excess molar volume,  $V_m^E$  vs  $x_2$  for the [DFM (2) + *n*-hexane (1)] binary mixtures at (◇) 293.15 K; (○) 298.15 K, and (Δ) 303.15 K. The solid lines are from the appropriate Redlich-Kister fitting equations

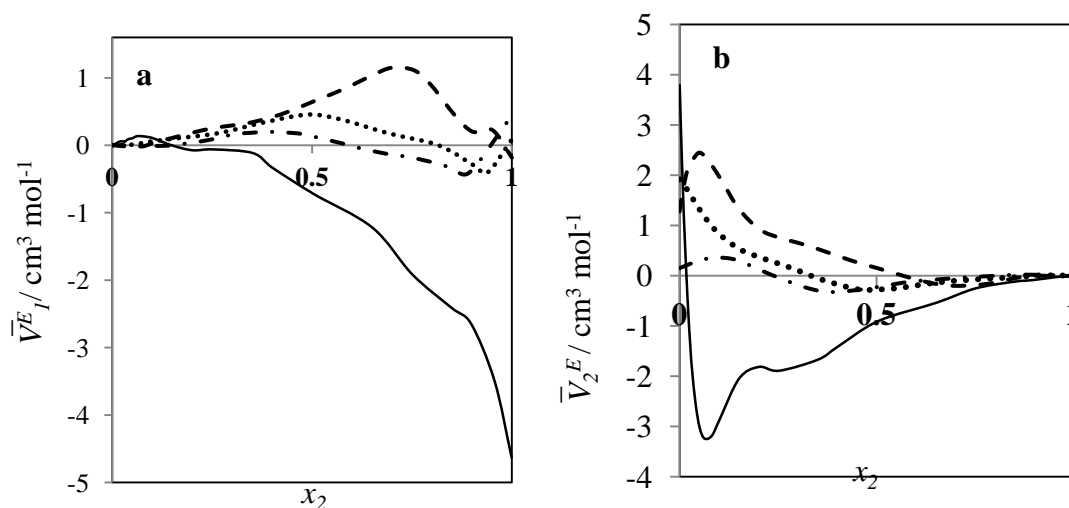


**Figure 4.** Excess molar volume,  $V_m^E$  vs  $x_2$  for the [DFM (2) + *n*-heptane (1)] binary mixtures at (◇) 293.15 K; (○) 298.15 K, and (Δ) 303.15 K. The solid lines are from the appropriate Redlich-Kister fitting equations

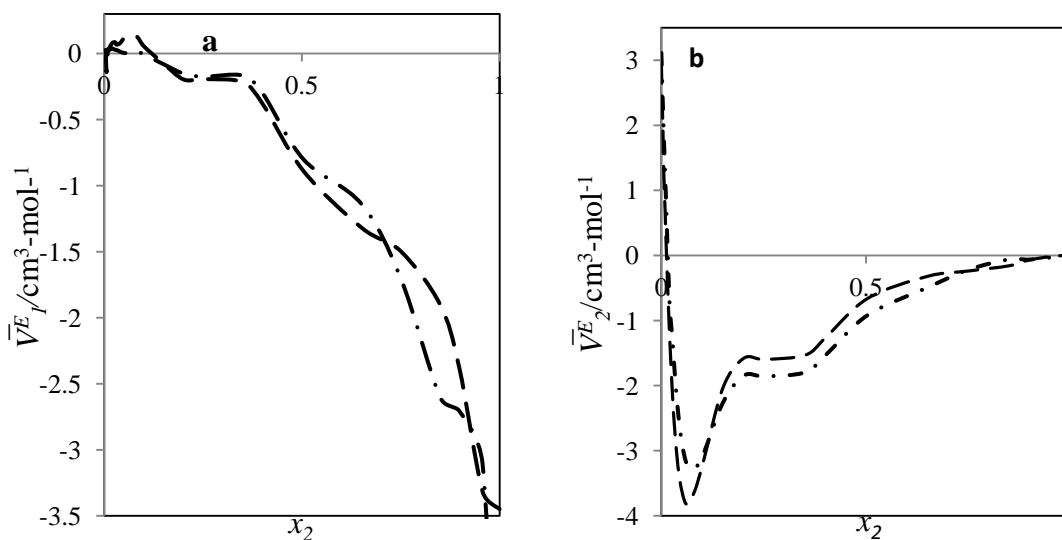


**Figure 5.** Excess molar volume,  $V_m^E$  vs  $x_2$  for the [DFM (2) + *n*-octane (1)] binary mixtures at (◇) 293.15 K; (○) 298.15 K, and (Δ) 303.15 K. The solid lines are from the appropriate Redlich-Kister fitting equations

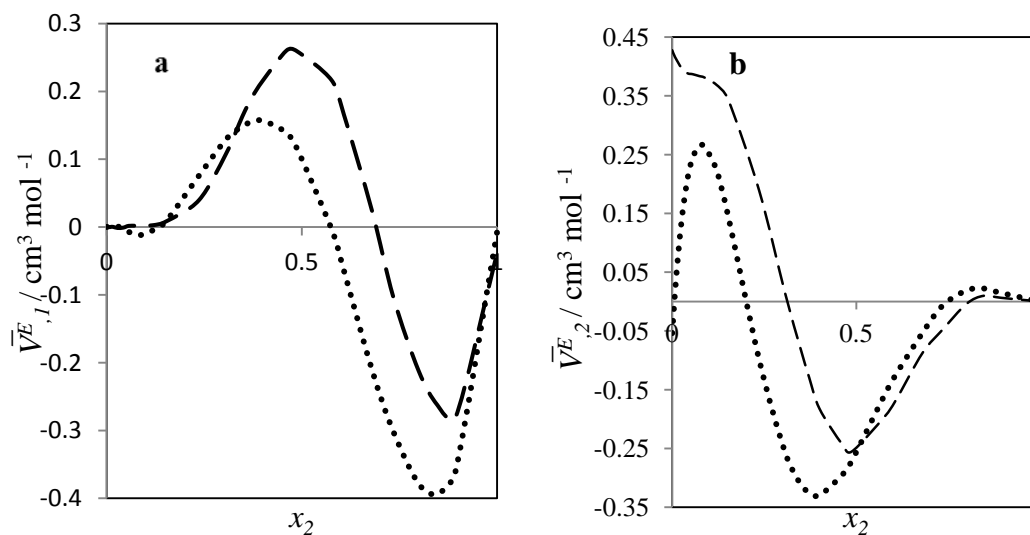




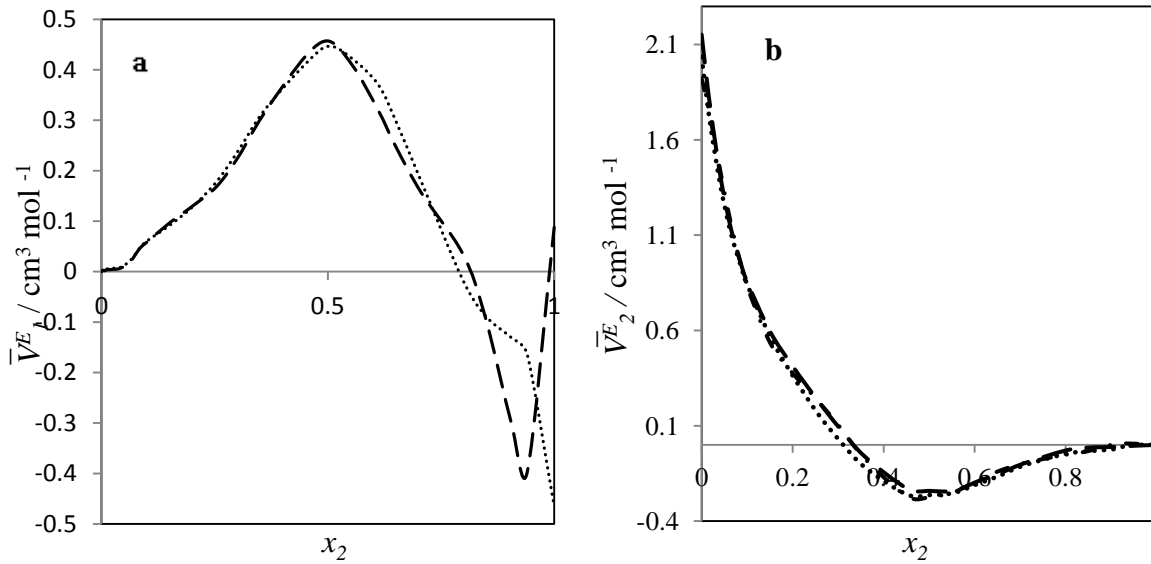
**Figure 6.** Excess partial molar volumes,  $V_i^E$  vs  $x_2$  for the [DFM (2) + *n*-alkane (1)] binary mixtures: (—) *n*-pentane; (---) *n*-hexane; (·····) *n*-heptane; (- · - ·) *n*-octane; at 298.15 K



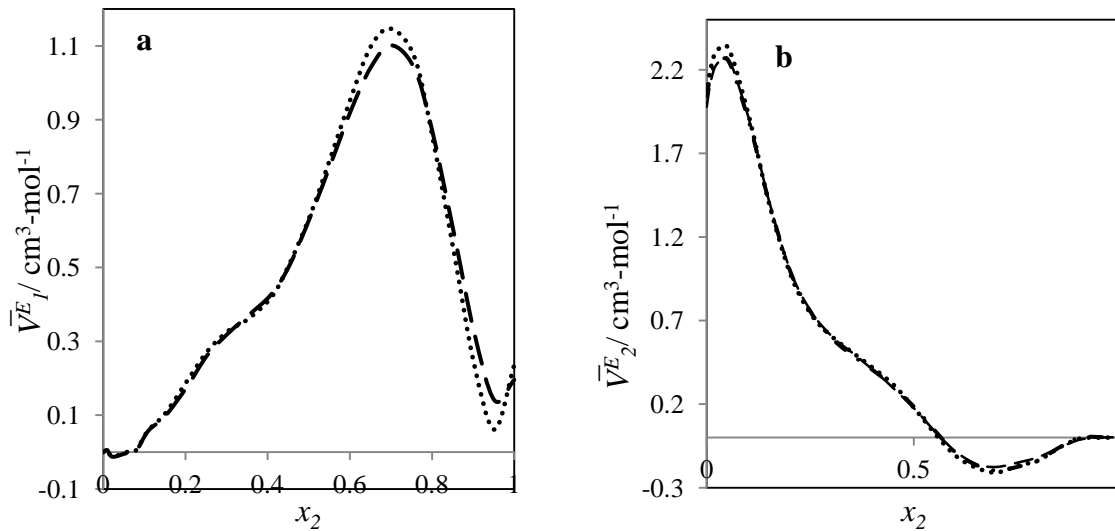
**Figure 7.** Excess partial molar volume,  $V_i^E$  vs  $x_2$  for the [DFM (2) + *n*-pentane (1)] binary mixtures at temperatures: (—) 293.15; (- · - ·) 298.15 K



**Figure 8.** Excess partial molar volume,  $V_i^E$  vs  $x_2$  for the [DFM (2) + *n*-hexane (1)] binary mixtures at temperatures: (—) 293.15 and (·····) 303.15 K



**Figure 9.** Excess partial molar volume,  $V_i^E$  vs  $x_2$  for the [DFM (2) + *n*-heptane (1)] binary mixtures at temperatures: (—) 293.15 and (.....) 303.15K



**Figure 10.** Excess partial molar volume,  $V_i^E$  vs  $x_2$  for the [DFM (2) + *n*-octane (1)] binary mixtures at temperatures: (—) 293.15 and (.....) 303.15K

The temperature dependent measurements of  $V_m^E$  in general are of interest for better understanding of the structural behavior between molecules of components in a binary mixture. Figures 2, 3, 4 and 5 represent the temperature effect on  $V_m^E$  vs  $x_2$  isotherms for each of (DFM + *n*-pentane or *n*-hexane or *n*-heptane or *n*-octane) binary systems. It was observed that for each of the four binary systems, the algebraic magnitude of the  $V_m^E$  function over the entire composition range decreases with temperature rise. It was also observed that as temperature is raised, the  $V_m^E$  vs  $x_2$  isotherm for each of (DFM + *n*-pentane or *n*-hexane or *n*-heptane) systems maintains the sigmoidal behavior, but exhibited a diminished region for positive  $V_m^E$  values and an enhanced region for negative  $V_m^E$  values. In general the increase in temperature would promote increased molecular motion which would result in a decrease in close molecular packing leading to a positive increase in  $V_m^E$  values. The experimentally observed volume contraction in each case

may suggest that the volume expansion caused by temperature increase, results in a more favourable geometrical interstitial accommodation of *n*-alkane molecules into the expanded cavities in the DFM liquid structures. Similar temperature effect on binary systems containing *n*-alkanes has been reported elsewhere [12].

Excess partial molar volumes,  $V_i^E$ , are more sensitive to changes in the aggregation schemes arising from the mixing process. The  $V_i^E$  values of component *i* in a mixture describe the rate of change of the excess molar volume with composition, and represent the individual component response to the overall intermolecular interactions. Excess partial molar volumes for components in each binary system have been calculated in accordance with Equations (4) and (5) [14, 20];

$$\bar{V}_1^E = V_m^E - x_2 (\partial V_m^E / \partial x_2)_{P,T} \quad (4)$$

$$\bar{V}_2^E = V_m^E + (1 - x_2) (\partial V_m^E / \partial x_2)_{P,T} \quad (5)$$

The Redlich-Kister polynomial equation (2) of an appropriate degree for each (DFM + *n*-alkane) binary system was used to obtain values of the derivative ( $\partial V_m^E / \partial x_2$ )<sub>P, T</sub> over the entire concentration range. Table 2 shows the calculated excess partial molar volumes,  $\bar{V}_i^E$ , for components in each of the four binary systems at (T = 293.15, 298.15 and 303.15) K. Figures 6 (a) and 6 (b) depict the excess partial molar volumes of the components in each of (DFM + *n*-pentane or *n*-hexane or *n*-heptane or *n*-octane) binary systems at 298.15K. The  $V_2^E$  vs  $x_2$  isotherm for (DFM + *n*-pentane) binary system in the *n*-pentane rich region ( $0.00 < x_2 < 0.017$ ) (Figure 6 b) is characterized by a steep positive variation in  $V_2^E$  values, which may have resulted from the predominance of dispersive intermolecular interactions over the geometrical effects in this region. Thereafter the  $V_2^E$  values are negative in the mole fraction range; ( $0.017 < x_2 < 1.00$ ), with a sharp minimum centred at  $x_2 \approx 0.06$  ( $V_2^E(\min) \approx -3.24 \text{ cm}^3$ ) and broadened minimum at  $x_2 \approx 0.25$  ( $V_2^E(\min) \approx -1.89 \text{ cm}^3$ ). It is also observed that the variation with composition of  $V_1^E$  values for *n*-pentane (Figure 6 a) in this system revealed a small positive in the mole fraction range:  $0.00 < x_2 < 0.02$  which may be due to dispersive interactions. Negative  $V_1^E$  values for composition in the mole fraction range: ( $0.02 < x_2 < 1.00$ ) were observed for this system. Negative values for  $V_1^E$  and  $V_2^E$  may be a result of geometrical effects in which the small *n*-pentane molecules are interstitially accommodated into the DFM liquid structure. The sharp negative variation of  $\bar{V}_1^E$  values in the DFM-rich region (low *n*-pentane concentrations) suggested enhanced structural effects when the *n*-pentane molecules are completely dispersed into the DFM liquid structure. The  $V_2^E$  isotherms for (DFM + *n*-hexane or *n*-heptane or *n*-octane) systems exhibit sigmoidal behaviour (Figure 6 b), in which the positive magnitude of  $\bar{V}_2^E(\max.)$  values increase with the *n*-alkane chain length in the order: *n*-octane > *n*-heptane > *n*-hexane. The  $V_1^E$  values for *n*-alkane components in each of (DFM + *n*-hexane or *n*-heptane or *n*-octane) systems exhibited a similar trend to  $V_m^E$  or  $V_2^E(\max.)$  at a specified temperature. Thus at each temperature investigated, the magnitude of  $V_1^E(\max.)$  values was in the order: *n*-hexane < *n*-heptane < *n*-octane respectively. The increase in the positive magnitude for  $V_i^E$  is further evidence of the increase in dominance of dispersive intermolecular interactions with increase of *n*-alkane chain-length. Figures 7 – 10 represent the effect of temperature on  $\bar{V}_i^E$  data for the two components in each of (DFM + *n*-pentane or *n*-hexane or *n*-heptane or *n*-octane) binary systems, at 293.15 and 303.15K. The positive magnitude of  $V_1^E$  and  $V_2^E$  data in each binary system decreased with temperature rise. It was observed that the magnitude of the contraction in  $\bar{V}_i^E$  decreased with the *n*-alkane chain-length for the same temperature increase. The decrease in magnitude of  $V_i^E$  values with temperature rise corroborated the corresponding  $V_m^E$  vs  $x_2$  isotherms (Figures 2-5) and suggested an increase in effectiveness of the geometrical interstitial accommodation effects with temperature rise.

Information about the solute-solvent intermolecular

interactions can be obtained from the limiting excess partial molar volumes data ( $\bar{V}_i^{E,\infty}$ ) for components in the mixture [21, 22]. The optimized Redlich - Kister least squares fitting correlation coefficients for each (FM + *n*-pentane or *n*-hexane or *n*-heptane or *n*-octane) binary systems at the three temperatures investigated have been used to calculate values of the limiting excess partial molar volumes for *n*-alkanes ( $\bar{V}_1^{E,\infty}$ ) and DFM ( $V_2^{E,\infty}$ ) using equations (6) and (7) [21-23] respectively,

$$\begin{aligned} \bar{V}_1^{E,\infty} &= [A_0 - A_1 + A_2 - A_3 + A_4 - A_5, \dots] \\ &= \sum_{n=\text{even}} A_k - \sum_{n=\text{odd}} A_k \quad (x_1 \rightarrow 0) \end{aligned} \quad (6)$$

$$V_2^{E,\infty} = \sum_k A_k \quad (x_2 \rightarrow 0) \quad (7)$$

**Table 4.** Limiting excess molar volumes ( $V_i^{E,\infty}$ ) for the components in [DFM + (C<sub>5</sub>-C<sub>8</sub>) *n*-alkane] binary systems at experimental temperatures

T/K	293.15K	298.15	303.15
<b>(DFM + <i>n</i>-Pentane)</b>			
$\bar{V}_1^{E,\infty}$	-4.319	-4.642	
$\bar{V}_2^{E,\infty}$	3.359	3.790	
<b>(DFM + <i>n</i>-Hexane )</b>			
$\bar{V}_1^{E,\infty}$	-0.039	-0.044	-0.008
$\bar{V}_2^{E,\infty}$	0.428	0.152	-0.054
<b>(DFM + <i>n</i>- Heptane )</b>			
$\bar{V}_1^{E,\infty}$	-0.465	-0.088	-0.635
$\bar{V}_2^{E,\infty}$	2.152	1.919	2.035
<b>(DFM + <i>n</i>-Octane )</b>			
$\bar{V}_1^{E,\infty}$	-0.025	-0.183	-0.353
$\bar{V}_2^{E,\infty}$	1.360	1.277	1.110

The calculated  $\bar{V}_i^{E,\infty}$  values are listed in Table 4. For all (DFM + *n*-pentane or *n*-hexane or *n*-heptane or *n*-octane) binary systems,  $\bar{V}_2^{E,\infty}$  values were positive at the three temperatures investigated (293.15, 298.15 and 303.15) K, due to an expansion in volume. This suggests that in the low  $x_2$  region, the molar volume of DFM in the mixture is greater than its molar volume in the pure state. The observed positive  $\bar{V}_2^{E,\infty}$  values for DFM in each binary system at the three temperatures investigated may be evidence for possible presence of DFM-DFM associate species in the infinite dilute solutions (low  $x_2$  region). The  $\bar{V}_1^{E,\infty}$  values for (C<sub>5</sub>-C<sub>8</sub>) *n*-alkane components in the binary mixtures were negative at the three temperatures investigated. Negative  $\bar{V}_1^{E,\infty}$  values in the high  $x_2$  range (low  $x_1$ ) suggest possible enhancement of the DFM-*n*-alkane molecular packing arising from the geometrical interstitial accommodation of *n*-alkane molecules into the bulk DFM-DFM, dipole-dipole liquid structure. The more negative  $\bar{V}_1^{E,\infty}$  values observed for (DFM *n*-pentane) binary system at the two temperatures investigated suggested a efficient structural accommodation of *n*-pentane molecules into the DFM liquid structure.

## 4. Conclusions

In this study, measured densities on pure DFM, *n*-pentane, *n*-hexane, *n*-heptane and *n*-octane) as well as their binary mixtures, (DFM + *n*-pentane or *n*-hexane or *n*-heptane or *n*-octane), are reported at (T = 293.15, 298.15 and 303.15) K. For each binary mixture, the density data were used to derive the excess molar volumes,  $V_m^E$  and excess partial molar volumes  $V_i^E$ . The  $V_m^E$  vs  $x_2$  isotherms for the (DFM + *n*-pentane or *n*-hexane or *n*-heptane) binary mixtures exhibit a sigmoidal behavior while for the (DFM + *n*-octane) binary system, positive deviation of the  $V_m^E$  function was observed over the entire composition range. For each binary mixture, the magnitude of excess molar volume,  $V_m^E$  for mixture and  $V_1^{E,\infty}$  exhibited a decrease with rise in temperature. The decrease in the positive magnitude of  $V_m^E$  or  $V_1^{E,\infty}$  with increase in temperature was attributed to the enhancement of geometrical interstitial accommodation of *n*-alkane molecules into the expanded DFM liquid structure. The estimated excess partial molar volumes  $V_i^E$  and limiting excess partial molar volumes  $V_i^{E,\infty}$  complimented the  $V_m^E$  data for each of (DFM + *n*-pentane or *n*-hexane or *n*-heptane or *n*-octane) binary mixtures at each temperature investigated.

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