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Volumetric Properties of (Difurylmethane + an Amide) Binary Mixtures at 293.15K, 298.15K and 303.15 K

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Abstract: Densities *(ρ)* of pure difuryl methane (DFM), N-methylformamide (NMF), N-ethylformamide (NEF), N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMA) and those of [DFM + (NMF or NEF or DMF or DMA] 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 calculated and correlated by the Redlich-Kister equation. V_m^E values for each binary system were negative at each of the three temperatures investigated (T = 293.15, 298.15 and 303.15) K. The V_m^E values decreased with temperature increase for each of the binary systems investigated. Sign and magnitude of V_m^E are discussed in-terms of type and nature of intermolecular interactions that occur in a binary mixture. The V_m^E data have been used to derive excess partial molar volumes (V_i^E), limiting excess partial molar volumes ($V_i^{E,\infty}$) and limiting partial molar volumes at infinite dilute region (V_i^∞) of each component of the binary mixture. Results are discussed in terms of possible intermolecular interactions and structural effects that occur in the binary mixtures.

Keywords: Difurylmethane, an Amide, Excess Molar Volume, Excess Partial Molar Volume, Binary Mixtures, Dipole-Dipole Interactions, Hydrogen Bond

1. Introduction

In previous papers we have reported studies on volumetric [1, 2, 3] and acoustic properties [4] of binary mixtures containing difuryl methane (DFM) and (C_1-C_6) *n*-alkanols at various temperatures. These investigations provided a deep insight with respect to understanding of the DFM / (C_1-C_6) *n*-alkanols intermolecular interactions and revealed significant deviation from ideal behavior which was attributed to chemical and structural interaction effects. The present investigations are focused on the study of intermolecular interactions in binary systems containing DFM with N-methylformamide (NMF), N-ethylformamide (NEF), N,N-dimethylformamide (DMF) and N,N -dimethylacetamide (DMA) over the entire composition range at (T =293.15, 298.15 and 303.15) K and atmospheric pressure. DFM is an aprotic dipolar substance whose liquid structure is determined by the dipole-dipole interactions [1-3] and has the potential for use in solvent extraction processes for separating polar organic substances from aqueous media. On the other hand secondary amides (NMF and NEF) are strongly self-associated through hydrogen bonding and dipole-dipole interactions (NMF, μ = *3.86*D; NEF, μ = *3.80D* at 298.15K) [5-9]. This association is reported to decrease with the size of alkyl group in the amide molecule [6,10]. DMF and DMA lack any significant liquid structural effects due to the absence of hydrogen bonding. However, DMF and DMA possess strong electron pair donating and accepting abilities due to the presence of large dipoles in their structure (DMF, μ = 3.86; DMA, μ = 3.72D at 298.15K) [6]. Thus significant intermolecular interactions between unlike components in binary mixtures of DFM with NMF or NEF or DMF or DMA would be expected to occur. A survey of the literature has revealed no study on the volumetric behavior of these binary systems. Therefore the present investigation was expected to reveal data on the intermolecular interactions in (DFM + an amide) binary systems.

In the present study we report densities ρ, of (DFM + NMF or NEF or DMF or DMA) binary mixtures at (T = 293.15, 298.15 and 303.15)K and atmospheric pressure over the entire composition range. From the experimental density

measurements, the excess molar volumes V_m^E were calculated at each temperature and composition. For each of the binary mixture investigated, the Redlich-Kister polynomial equation of an appropriate degree was fitted to the V_m^E data. From the V_m^E data, derived properties which included excess partial molar volume, $\overline{V}_i^E$, limiting partial molar volume, V_i^∞ and limiting excess partial molar volume $\overline{V}_i^{E,\infty}$ were calculated. The magnitude and sign of V_m^E as well as derived properties (V_m^E, $\overline{V}_i^E$, $\overline{V}_i^{E,\infty}$) provided a better understanding of the intermolecular interactions existing between the various species in each of (DFM + NMF or NEF or DMF or DMA) binary mixtures.

2. Experimental

2.1. Materials

The following chemicals were used: *n*-hexane (Merck Co., ≥ 98.0%), NMF, (Sigma-Aldrich chemicals, 99.0%), NEF (Fluka, analytical reagent 99.0%), DMA, (Sigma-Aldrich chemicals, 99.0%), DMF, (BDH chemicals, analytical reagent, 99.5%). All amides used in the present study (NMF, NEF, DMA and DMF) were analytical reagents of good quality as reflected by the measured density in comparison to the corresponding ρ -literature data (Table 1). Before use, each of the amides was stored over 0.40 *nm* molecular sieves for 74 *h* to remove water content, as much as possible. DFM was prepared as described elsewhere [20] and its purity was confirmed by ^{1}H-NMR, density measurements and elemental analysis. All purified organic liquids were stored in brown glass bottles. The conductivity of ultrapure water used to calibrate the densimeter was always less than $1.0\text{x}10^{-6}$ *S-cm*$^{-1}$.

2.2. Apparatus and Procedure

Each one of the (DFM + NMF or NEF or DMF or DMA) binary mixtures was prepared by weighing appropriate amounts of purified DFM and the corresponding co-solvent (amide) on an analytical balance ($\Delta m = \pm 0.0001$ *g*), by syringing each component into a teflon stoppered flask. Pure components were first separately degassed in an ultrasonic bath shortly before sample preparations. All (DFM + NMF or NEF or DMF or DMA) binary mixtures were completely miscible over the entire composition range. The average uncertainty in solution composition expressed in mole fraction was found to be less than $8.5\text{x}10^{-4}$. 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 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 ± 0.01 K. The densimeter was calibrated after each set of four sample measurements to offset possible instrument drift. 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 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 ± 0.01 *kg-m*$^{-3}$. The reliability of experimental measurements of density was ascertained by comparing the experimental data of pure liquids with the corresponding literature values at the studied temperatures.

3. Results and Discussion

3.1. Excess Molar Volumes

Excess molar volumes, V_m^E, were calculated for each of (DFM + NMF or NEF or DMF or DMA) binary systems from density measurements using equation (1):

$$V_m^E = \text{V}_\text{m} - V_m^{id} = \text{M}/\rho - \sum \text{x}_\text{i}\,\text{M}_\text{i}/\,\rho_\text{i} \qquad (1)$$

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, 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 experimental V_m^E values of each of the (DFM + NMF or NEF or DMF or DMA) binary systems (Table 2) were least-squares fitted to the Redlich-Kister polynomial equation [21]:

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

where n is the order of the polynomial, x_1 is the mole fraction of the amide and x_2 is the mole fraction of DFM. For each binary system at a specified temperature, the degree of the polynomial and the number of A_k coefficients 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. The optimized number of regression coefficients A_k for each of the four binary systems are listed in Table 4 along with the corresponding standard deviation $\sigma(V_m^E)$, defined by Equation (3):

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

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

Excess thermodynamic functions such as the excess molar volume V_m^E, measure the extent of deviation from the ideal solution behavior. In addition, the temperature dependent measurements of V_m^E in general, are of interest for a better understanding of the structural effects between unlike molecules in a binary mixture. Figure 1 represent the experimental V_m^E *vs* x_2 isotherms for (DFM + NMF or NEF or DMF or DMA) binary systems at 298.15K. Negative V_m^E values were observed over the entire composition range at the three temperatures examined for each binary system. The V_m^E *vs* x_2 isotherms for all [DFM + (NMF or NEF or DMF or DMA)] binary systems show $V_{m\,(min)}^E$ values at $x_2 \approx 0.5$, which

in each case corresponds to formation of a 1:1, DFM: amide associates. The sequence in the negative magnitude of $V_{m\ (min)}^{E}$ values at 298.15K is: DMA > DMF > NEF > NMF and were -0.739 $cm^3\ mol^{-1}$ (at x_2 = 0.501), -0.697 $cm^3\ mol^{-1}$ (at x_2 = 0.501), -0.336 $cm^3\ mol^{-1}$ (at x_2 = 0.519), -0.249 $cm^3\ mol^{-1}$ (at x_2 = 0.449), respectively. Negative values for V_m^E *vs* x_2 isotherms suggest the presence of specific intermolecular interactions between DFM and amide molecules in each binary system.

Assuming the DFM-amide, dipole-dipole intermolecular interactions as the dominant effects, a possible qualitative explanation for the observed volumetric behavior is as follows starting with (DFM + NMF or NEF) binary systems. The liquid structure of the pure DFM is determined by the dipole-dipole interactions [2]. On the other hand, molecules of secondary amides are self-associated through hydrogen bonding due to the presence of a strong proton-acceptor group (C = O) and a proton-donor group (-NH) in their molecules and the dipole-dipole intermolecular interactions [6, 8, 9]. Thus the mixing of DFM with the secondary amides to form [DFM + (NMF or NEF)] binary systems would result in mutual disruption of the dipole-dipole associates in the DFM liquid structure and the hydrogen-bonded aggregates as well as the dipole-dipole interactions in pure NMF or NEF, which would contribute positively to V_m^E values. On the other hand, the intermolecular associative dipole-dipole interactions between the amide molecules (NMF or NEF) and the polarized π-electron system of the furan rings in DFM would lead to closer molecular packing which would contribute to a decrease in V_m^E values. From the negative V_m^E experimental values observed, formation of DFM-NMF or DFM-NEF associates supersedes the positive contribution to V_m^E, arising from the rupture of the liquid structures in the pure unlike components of (DFM + NMF or NEF) binary systems. The negative V_m^E values thus indicate that DFM and NMF/NEF molecules are more efficiently packed in the binary mixtures than in their pure states. Spectroscopic and dielectric studies confirm the strong self-association of secondary amides through N-H····O = C hydrogen bonds which has been reported to persist even in the infinite dilute amide solutions [8, 9]. It is possible that addition of DFM to NMF or NEF may only partially disrupt the hydrogen-bonded aggregates in each of the secondary amides. The hydrogen bond density in secondary amides would be expected to decrease with increase in the alkyl chain length and the degree of hydrogen bonding in pure NMF would be greater than in NEF. As a consequence of this dilution effect on the hydrogen bond density arising from a bigger -CH_2CH_3 group in NEF, the disruption of the hydrogen-bonds in NEF when (DFM + NEF) binary mixture is formed, a bigger proportion of NEF molecules would be released for formation of DFM: NEF, 1:1 associates. This would result in a more efficient intermolecular interaction as reflected in the more negative V_m^E values for (DFM + NEF) compared to (DFM + NMF) binary system.

In pure DMF or DMA, molecules are weakly associated via non-specific van der Waal interactions and dipole-dipole interactions [6]. When each of the (DFM + DMF or DMA) binary mixture is formed, negative V_m^E *vs* x_2 isotherms observed are attributed to strong DFM: DMF and DFM: DMA, dipole-dipole intermolecular interactions. It is also observed that the V_m^E values are more negative for (DFM + DMA) than in (DFM + DMF) binary system over the entire x_2 - range. The lone-pair on the nitrogen atom in both DMF and DMA is protected by the two –CH_3 groups rendering it less accessible. However the presence of the –CH_3 group at the carbon atom of the C=O group has the effect of increasing the electron density at the oxygen atom in DMA [11] compared to the hydrogen at the same position in DMF. This effect is reflected in the greater proton affinity at the oxygen site of DMA *(*904.04 kJ mol^{-1}) compared to that in DMF *(*879.02 $kJ\ mol^{-1}$*)*. [22]. Consequently, this effect may contribute to a more favorable DFM: DMA, dipole - dipole interaction, which results in more negative V_m^E values for (DFM + DMA) compared to (DFM + DMF) binary system.

Another possible contribution to negative V_m^E values may arise from structural effects due to the geometrical interstitial accommodation of the smaller amide component molecules (NMF = 59.09, NEF =77.12, DMF = 77.41 and DMA = 92.98 $cm^3\ mol^{-1}$) into cavities created by molecules of the larger DFM component (DFM = 135.85 $cm^3\ mol^{-1}$ at 298.15 K) when (DFM + NMF or NEF or DMF or DMA) binary systems are formed. This effect to a more closely packed liquid structure in the corresponding binary mixture. Geometrical effects also may result from differences in shape and molar free volumes of unlike pure components [6].

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

Compound	T /K	ρ (kg/m^3)	
		Exp	Lit
N-methylformamide	293.15	1003.84	1003.18[a]
	298.15	999.5	999.29 [b]
			999.20 [c]
	303.15	995.15	994.80 [d]
			994.65 [e]
N-Ethylformamide	293.15	951.87	951.59 [f]
	298.15	947.78	947.48 [f]
	303.15	943.68	943.29 [f]
*N,N*Dimethylformamide	293.15	949.04	948.51 [c]
			948.73[g]
	298.15	944.3	944.09 [h]
			944.40 [b]
			944.60 [i,e]
			943.85 [j]
	303.15	939.53	938.88 [k]
			939.83[l]
N,N-Dimethylacetamide	293.15	941.53	941.02 [a]
			941.50 [g]
	298.15	936.94	936.41 [a]
			936.50 [i,l]
			936.34 [g]
	303.15	932.33	931.79 [b]
			931.69 [g]
Difurylmethane	293.15	1095.68	1095.94 [m]
	298.15	1090.63	1090.88 [m]
	303.15	1085.57	1085.82 [m]

[a] Ref.[5], [b]Ref.[7], [c] Ref. [15], [d] Ref. [12], [e] Ref. [16], [f] Ref.[8], [g] Ref. [14], [h] Ref. [17], [i] Ref. [11], [j]Ref.[19], [k]Ref.[13], [l]Ref. [18], [m] Ref. [1].

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

x_2	ρ	V_m^E	V_1^E	V_2^E
		(DFM + NMF)		
		T = 293.15 K		
0.00000	1003.84	0.00000	0.00000	-1.25358
0.00101	1004.11	-0.00336	-0.00211	-1.24577
0.00201	1004.35	-0.00512	-0.00264	-1.23643
0.00265	1004.52	-0.00724	-0.00399	-1.23146
0.00384	1004.81	-0.00963	-0.00496	-1.22063
0.00455	1004.98	-0.01093	-0.00544	-1.21407
0.00985	1006.22	-0.01938	-0.00799	-1.16383
0.01562	1007.55	-0.02856	-0.01141	-1.10977
0.02716	1009.87	-0.02979	-0.00304	-0.98791
0.04010	1012.59	-0.04312	-0.00852	-0.87133
0.05974	1016.56	-0.06355	-0.02206	-0.71652
0.08048	1020.52	-0.08283	-0.03902	-0.58333
0.10837	1025.50	-0.10535	-0.06299	-0.45390
0.15016	1032.41	-0.13950	-0.10115	-0.35659
0.20594	1040.55	-0.17299	-0.13310	-0.32679
0.25133	1046.45	-0.19496	-0.14878	-0.33251
0.29949	1052.00	-0.20552	-0.15530	-0.32297
0.34944	1057.32	-0.22196	-0.17850	-0.30288
0.40170	1062.40	-0.23898	-0.21846	-0.26955
0.44950	1066.56	-0.24538	-0.25825	-0.22962
0.51032	1071.20	-0.23488	-0.30148	-0.17097
0.55198	1074.12	-0.22670	-0.33644	-0.13763
0.60061	1077.30	-0.21687	-0.38890	-0.10247
0.64969	1080.25	-0.20315	-0.46335	-0.06286
0.70096	1083.10	-0.18675	-0.58251	-0.01791
0.74545	1085.44	-0.17504	-0.73097	0.01479
0.80117	1088.05	-0.14581	-0.93997	0.05129
0.84704	1089.90	-0.10329	-1.07598	0.07237
0.89937	1091.95	-0.06239	-1.11542	0.05544
0.94877	1093.83	-0.03102	-0.91257	0.01658
1.00000	1095.68	0.00000	-0.34466	0.00000
		T=298.15 K		
0.00000	999.50	0.00000	0.00000	-1.36646
0.00101	999.80	-0.00526	-0.00389	-1.36159
0.00201	1000.03	-0.00654	-0.00383	-1.35293
0.00265	1000.19	-0.00814	-0.00458	-1.34823
0.00384	1000.50	-0.01185	-0.00673	-1.34028
0.00455	1000.68	-0.01383	-0.00779	-1.33540
0.00985	1001.95	-0.02464	-0.01199	-1.29633
0.01562	1003.20	-0.02966	-0.01029	-1.24996
0.02716	1005.50	-0.03074	0.00069	-1.15655
0.04010	1008.20	-0.04412	-0.00101	-1.07596
0.05974	1012.14	-0.06458	-0.00674	-0.97496
0.08048	1016.10	-0.08582	-0.01535	-0.89088
0.10837	1021.00	-0.10565	-0.02151	-0.79796
0.15016	1027.98	-0.14826	-0.04829	-0.71407
0.20594	1036.00	-0.17807	-0.06397	-0.61800
0.25133	1041.84	-0.19916	-0.08100	-0.55115
0.29949	1047.37	-0.21169	-0.09937	-0.47439
0.34943	1052.68	-0.23094	-0.13797	-0.40405
0.40170	1057.68	-0.24492	-0.18669	-0.33165
0.44950	1061.86	-0.25615	-0.24015	-0.27575
0.51032	1066.51	-0.25038	-0.29616	-0.20646
0.55198	1069.38	-0.24010	-0.32979	-0.16729
0.60061	1072.52	-0.22924	-0.37076	-0.13513
0.64969	1075.46	-0.21726	-0.41545	-0.11039
0.70096	1078.29	-0.20157	-0.47412	-0.08529
0.74545	1080.56	-0.18473	-0.54612	-0.06133
0.80116	1083.15	-0.15588	-0.67212	-0.02776
0.84704	1084.99	-0.11413	-0.78570	0.00715
0.89937	1086.99	-0.06955	-0.88745	0.02197
0.94877	1088.81	-0.03290	-0.80527	0.00881
1.00000	1090.63	0.00000	-0.20043	0.00000
		T=303.15K		
0.00000	995.15	0.00000	0.00000	-1.40895
0.00101	995.46	-0.00600	-0.00459	-1.40501
0.00201	995.70	-0.00798	-0.00518	-1.39720

x_2	ρ	V_m^E	V_1^E	V_2^E
0.00265	995.88	-0.01085	-0.00718	-1.39384
0.00384	996.15	-0.01231	-0.00703	-1.38374
0.00455	996.34	-0.01497	-0.00874	-1.37957
0.00985	997.60	-0.02578	-0.01270	-1.34017
0.01562	998.83	-0.03016	-0.01015	-1.29187
0.02716	1001.11	-0.03109	0.00136	-1.19366
0.04010	1003.80	-0.04514	-0.00078	-1.10679
0.05974	1007.74	-0.06754	-0.00849	-0.99690
0.08048	1011.65	-0.08757	-0.01620	-0.90294
0.10837	1016.53	-0.10863	-0.02378	-0.80675
0.15016	1023.43	-0.14956	-0.04723	-0.72874
0.20594	1031.50	-0.18760	-0.06440	-0.66265
0.25133	1037.20	-0.20193	-0.06764	-0.60193
0.29949	1042.79	-0.22270	-0.08926	-0.53483
0.34943	1048.08	-0.24419	-0.13052	-0.45583
0.40170	1053.11	-0.26465	-0.19250	-0.37212
0.44950	1057.19	-0.27067	-0.24989	-0.29611
0.51032	1061.82	-0.26710	-0.31774	-0.21850
0.55198	1064.68	-0.25851	-0.35553	-0.17976
0.60061	1067.77	-0.24578	-0.39280	-0.14801
0.64969	1070.66	-0.23162	-0.43087	-0.12418
0.70096	1073.48	-0.21771	-0.48871	-0.10210
0.74545	1075.74	-0.20219	-0.56470	-0.07841
0.80116	1078.28	-0.17063	-0.69827	-0.03968
0.84704	1080.10	-0.12863	-0.82328	-0.00319
0.89937	1082.07	-0.08279	-0.94293	0.01346
0.94877	1083.84	-0.04214	-0.91135	0.00479
1.00000	1085.57	0.00000	-0.50597	0.00000
		DFM + NEF		
		T =293.15K		
0.00000	951.87	0.00000	0.00000	-1.65625
0.00111	952.20	-0.00396	-0.00213	-1.64364
0.00204	952.48	-0.00755	-0.00422	-1.63349
0.00308	952.75	-0.00828	-0.00331	-1.61916
0.00410	953.03	-0.01011	-0.00353	-1.60626
0.00450	953.14	-0.01087	-0.00368	-1.60132
0.01361	955.58	-0.02432	-0.00408	-1.49180
0.01594	956.20	-0.02774	-0.00445	-1.46576
0.02020	957.35	-0.03594	-0.00735	-1.42224
0.04015	962.49	-0.06189	-0.01269	-1.23795
0.06177	967.75	-0.07807	-0.01236	-1.07613
0.07842	971.70	-0.09127	-0.01563	-0.98032
0.10212	977.26	-0.11796	-0.03076	-0.88466
0.14911	987.60	-0.15733	-0.05135	-0.76212
0.20091	998.21	-0.19588	-0.07012	-0.69606
0.25106	1007.71	-0.22317	-0.07783	-0.65676
0.30142	1016.65	-0.24966	-0.08713	-0.62634
0.35325	1025.23	-0.27129	-0.10044	-0.58410
0.40012	1032.61	-0.29713	-0.13500	-0.54019
0.44808	1039.63	-0.31096	-0.18246	-0.46924
0.50137	1047.00	-0.32677	-0.27375	-0.37950
0.51906	1049.29	-0.32574	-0.30757	-0.34257
0.59582	1058.70	-0.31762	-0.50318	-0.19174
0.65102	1064.87	-0.29669	-0.66179	-0.10097
0.69331	1069.14	-0.25593	-0.75436	-0.03545
0.75499	1075.21	-0.21461	-0.85747	-0.00599
0.79986	1079.30	-0.17306	-0.85888	-0.00146
0.83529	1082.48	-0.14869	-0.83021	-0.01431
0.89267	1087.41	-0.10925	-0.76760	-0.03010
0.93921	1091.08	-0.06015	-0.82625	-0.01057
1.00000	1095.68	0.00000	-1.56197	0.00000
		T= 298.15K		
0.00000	947.78	0.00000	0.00000	-1.94746
0.00111	948.11	-0.00414	-0.00200	-1.92954
0.00204	948.40	-0.00869	-0.00479	-1.91585
0.00308	948.67	-0.00957	-0.00375	-1.89679
0.00410	948.94	-0.01073	-0.00304	-1.87854
0.00450	949.05	-0.01155	-0.00314	-1.87185
0.01361	951.48	-0.02549	-0.00203	-1.72641
0.01594	952.09	-0.02843	-0.00148	-1.69190
0.02020	953.23	-0.03642	-0.00346	-1.63488
0.04015	958.34	-0.06268	-0.00644	-1.40702
0.06177	963.75	-0.09428	-0.01908	-1.23642

x_2	ρ	V_m^E	V_1^E	V_2^E
0.07708	967.47	-0.11556	-0.02942	-1.14691
0.10212	973.21	-0.13554	-0.03454	-1.02349
0.14911	983.59	-0.18471	-0.06465	-0.86984
0.20091	994.03	-0.21502	-0.08815	-0.71962
0.25106	1003.50	-0.24578	-0.12306	-0.61187
0.30142	1012.32	-0.26716	-0.14855	-0.54204
0.35325	1020.81	-0.28610	-0.16178	-0.51371
0.40012	1028.06	-0.30442	-0.16846	-0.50825
0.44808	1035.03	-0.31815	-0.18020	-0.48807
0.50097	1042.27	-0.33134	-0.23281	-0.42950
0.51906	1044.66	-0.33679	-0.26716	-0.40130
0.59582	1054.00	-0.32836	-0.47886	-0.22627
0.65102	1060.18	-0.31328	-0.68267	-0.11527
0.69331	1064.47	-0.27817	-0.79986	-0.04739
0.75499	1070.47	-0.23410	-0.88328	-0.02343
0.79986	1074.47	-0.18569	-0.85511	-0.01819
0.83529	1077.66	-0.16518	-0.84772	-0.03060
0.89267	1082.46	-0.11456	-0.94106	-0.01519
0.93921	1086.10	-0.06490	-1.13614	0.00443
1.00000	1090.63	0.00000	-0.71023	0.00000
		T= 303.15 K		
0.00000	943.68	0.00000	0.00000	-2.17412
0.00111	944.01	-0.00432	-0.00195	-2.13922
0.00204	944.30	-0.00904	-0.00474	-2.11187
0.00308	944.58	-0.01089	-0.00450	-2.07905
0.00410	944.84	-0.01137	-0.00299	-2.04618
0.00450	944.95	-0.01225	-0.00311	-2.03427
0.01361	947.36	-0.02588	-0.00153	-1.79066
0.01594	947.97	-0.02915	-0.00147	-1.73760
0.02020	949.11	-0.03777	-0.00448	-1.65233
0.04015	954.18	-0.06353	-0.00924	-1.36119
0.06177	959.56	-0.09565	-0.02289	-1.20096
0.07708	963.25	-0.11651	-0.03131	-1.13658
0.10212	968.95	-0.13634	-0.03178	-1.05571
0.14911	979.28	-0.18727	-0.05638	-0.93421
0.20083	989.66	-0.21986	-0.08495	-0.75673
0.25106	999.11	-0.25345	-0.13140	-0.61754
0.30142	1007.86	-0.27404	-0.15961	-0.53926
0.35325	1016.30	-0.29390	-0.16736	-0.52557
0.40012	1023.50	-0.31235	-0.16489	-0.53343
0.44808	1030.43	-0.32704	-0.17365	-0.51597
0.50137	1037.66	-0.33916	-0.23458	-0.44316
0.51906	1040.00	-0.34662	-0.27616	-0.41191
0.59582	1049.27	-0.33791	-0.51495	-0.21780
0.65102	1055.40	-0.32223	-0.72364	-0.10705
0.69331	1059.61	-0.28161	-0.82685	-0.04042
0.75499	1065.54	-0.23433	-0.88640	-0.02272
0.79986	1069.54	-0.18908	-0.85315	-0.02292
0.83529	1072.71	-0.16886	-0.84649	-0.03525
0.89267	1077.49	-0.11988	-0.94311	-0.02091
0.93921	1081.08	-0.06723	-1.13626	0.00196
1.00000	1085.56	0.00000	-0.92458	0.00000
		(DFM + DMF)		
		T = 293.15 K		
0.00000	949.04	0.00000	0.00000	-2.32012
0.00107	949.35	-0.00291	-0.00040	-2.34974
0.00203	949.65	-0.00706	-0.00222	-2.37676
0.00305	949.92	-0.00777	-0.00045	-2.40039
0.00407	950.20	-0.00946	0.00040	-2.42364
0.00504	950.52	-0.01517	-0.00283	-2.44905
0.01178	952.36	-0.02568	0.00462	-2.56810
0.01574	953.50	-0.03712	0.00426	-2.62374
0.02021	954.76	-0.04866	0.00543	-2.67015
0.04020	960.39	-0.10787	0.00251	-2.74344
0.06107	966.05	-0.16529	-0.00220	-2.67307
0.08010	971.00	-0.21149	-0.00749	-2.55422
0.10229	976.63	-0.26716	-0.02322	-2.40808
0.14985	987.92	-0.36667	-0.05841	-2.11554
0.19979	999.04	-0.47111	-0.12600	-1.85332
0.25060	1009.32	-0.54761	-0.20714	-1.56577
0.30247	1018.90	-0.60135	-0.30870	-1.27623
0.35085	1027.25	-0.64614	-0.42024	-1.06412
0.40052	1035.09	-0.66808	-0.51465	-0.89773

x_2	ρ	V_m^E	V_1^E	V_2^E
0.44895	1042.24	-0.68241	-0.60267	-0.78029
0.50148	1049.51	-0.69247	-0.71869	-0.66641
0.54987	1055.56	-0.67241	-0.84628	-0.53007
0.59758	1061.25	-0.65546	-1.02630	-0.40573
0.65041	1067.05	-0.61797	-1.22956	-0.28924
0.70114	1072.06	-0.55241	-1.35795	-0.20905
0.75060	1076.91	-0.51172	-1.45524	-0.19822
0.80186	1081.31	-0.42572	-1.56939	-0.14313
0.85015	1085.35	-0.35531	-1.95969	-0.07252
0.89870	1088.90	-0.24544	-2.67869	0.02883
0.95012	1092.15	-0.08810	-2.97312	0.06335
1.00000	1095.68	0.00000	0.63665	0.00000
		T = 298.15 K		
0.00000	944.30	0.00000	0.00000	-2.51916
0.00107	944.62	-0.00373	-0.00103	-2.53234
0.00203	944.91	-0.00724	-0.00206	-2.54396
0.00305	945.18	-0.00801	-0.00022	-2.55287
0.00407	945.47	-0.01059	-0.00017	-2.56312
0.00504	945.78	-0.01558	-0.00261	-2.57512
0.01178	947.61	-0.02573	0.00523	-2.62372
0.01574	948.75	-0.03749	0.00431	-2.65069
0.02021	950.01	-0.04937	0.00477	-2.67375
0.04020	955.62	-0.10852	0.00083	-2.71936
0.06107	961.28	-0.16753	-0.00383	-2.68451
0.08010	966.23	-0.21509	-0.00715	-2.60299
0.10229	971.84	-0.27063	-0.01896	-2.47933
0.14985	983.11	-0.37146	-0.05555	-2.16374
0.19979	994.20	-0.47630	-0.13235	-1.85389
0.25060	1004.48	-0.55549	-0.21713	-1.56732
0.30247	1014.05	-0.61071	-0.30704	-1.31101
0.35085	1022.40	-0.65762	-0.40937	-1.11695
0.40052	1030.22	-0.67950	-0.51083	-0.93196
0.44895	1037.33	-0.69154	-0.62416	-0.77425
0.50148	1044.59	-0.70222	-0.77268	-0.63218
0.54987	1050.64	-0.68332	-0.90460	-0.50219
0.59758	1056.22	-0.65589	-1.04146	-0.39625
0.65041	1062.04	-0.62137	-1.19562	-0.31272
0.70114	1067.10	-0.56184	-1.31899	-0.23911
0.75060	1071.87	-0.51295	-1.46600	-0.19628
0.80186	1076.34	-0.43522	-1.65994	-0.13259
0.85015	1080.37	-0.36407	-1.97172	-0.08071
0.89870	1083.85	-0.24588	-2.36918	-0.00654
0.95012	1087.40	-0.12467	-2.67276	0.00910
1.00000	1090.63	0.00000	-1.87364	0.00000
		T=303.15 K		
0.00000	939.53	0.00000	0.00000	-2.83829
0.00107	939.85	-0.00383	-0.00080	-2.82663
0.00203	940.15	-0.00824	-0.00251	-2.81762
0.00305	940.42	-0.00908	-0.00052	-2.80485
0.00407	940.70	-0.01090	0.00046	-2.79369
0.00504	941.01	-0.01600	-0.00195	-2.78676
0.01178	942.87	-0.02908	0.00309	-2.72860
0.01574	944.00	-0.04033	0.00231	-2.70590
0.02021	945.24	-0.05089	0.00343	-2.68382
0.04020	950.84	-0.11078	-0.00483	-2.64043
0.06107	956.49	-0.17051	-0.01185	-2.61014
0.08010	961.43	-0.21857	-0.01510	-2.55518
0.10229	967.03	-0.27479	-0.02665	-2.45249
0.14985	978.29	-0.37775	-0.07227	-2.11090
0.19979	989.35	-0.48292	-0.16960	-1.73784
0.25060	999.61	-0.56292	-0.26905	-1.44171
0.30247	1009.11	-0.61388	-0.34617	-1.23124
0.35085	1017.50	-0.66655	-0.43304	-1.09859
0.40052	1025.31	-0.68918	-0.52041	-0.94179
0.44895	1032.40	-0.70075	-0.63765	-0.77821
0.50148	1039.64	-0.71093	-0.80149	-0.62091
0.54987	1045.69	-0.69310	-0.93252	-0.49711
0.59758	1051.26	-0.66554	-1.03022	-0.41996
0.65041	1057.05	-0.62869	-1.10314	-0.37367
0.70114	1062.12	-0.57083	-1.16562	-0.31731
0.75060	1066.86	-0.51915	-1.31806	-0.25370
0.80186	1071.55	-0.46727	-1.61895	-0.18270
0.85015	1075.36	-0.37088	-1.94587	-0.09327

x_2	ρ	V_m^E	V_1^E	V_2^E
0.89870	1078.87	-0.25615	-2.21982	-0.03480
0.95012	1082.52	-0.14719	-2.47449	-0.02502
1.00000	1085.57	0.00000	-3.47870	0.00000
		(DFM + DMA)		
		T = 293.15 K		
0.00000	941.53	0.00000	0.00000	-4.10693
0.00102	941.85	-0.00886	-0.00474	-4.05106
0.00203	942.12	-0.01304	-0.00494	-3.99316
0.00319	942.44	-0.01891	-0.00640	-3.93037
0.00416	942.73	-0.02608	-0.00998	-3.88215
0.00512	942.97	-0.02836	-0.00877	-3.83075
0.01014	944.20	-0.03911	-0.00276	-3.58909
0.01488	945.43	-0.05627	-0.00573	-3.40313
0.02106	946.91	-0.06725	0.00001	-3.19390
0.03965	951.64	-0.13262	-0.02165	-2.82072
0.06127	956.87	-0.19069	-0.03222	-2.61877
0.08031	961.24	-0.22603	-0.02556	-2.52165
0.10829	967.90	-0.31471	-0.05494	-2.45366
0.15051	977.27	-0.40857	-0.07858	-2.27096
0.20771	989.17	-0.50644	-0.13769	-1.91300
0.24943	997.55	-0.58228	-0.22458	-1.65868
0.30098	1007.36	-0.65859	-0.35003	-1.37520
0.35107	1016.08	-0.68648	-0.45273	-1.11854
0.40899	1025.70	-0.71431	-0.58436	-0.90208
0.44904	1032.00	-0.72245	-0.66650	-0.79111
0.50099	1039.89	-0.73297	-0.77455	-0.69156
0.55685	1047.80	-0.71792	-0.88726	-0.58317
0.60252	1053.93	-0.69491	-1.01447	-0.48409
0.65092	1060.14	-0.66303	-1.20409	-0.37288
0.70818	1067.07	-0.60921	-1.46879	-0.25500
0.75093	1071.89	-0.54922	-1.63689	-0.18845
0.80734	1077.93	-0.45813	-1.79467	-0.13918
0.85560	1082.91	-0.38002	-1.98442	-0.10925
0.90937	1087.99	-0.25970	-2.50644	-0.03580
0.94691	1091.29	-0.15910	-3.04155	0.00252
1.00000	1095.68	0.00000	-2.25263	0.00000
		T = 298.15 K		
0.00000	936.94	0.00000	0.00000	-4.20745
0.00102	937.27	-0.01002	-0.00579	-4.14934
0.00203	937.54	-0.01431	-0.00602	-4.08834
0.00319	937.85	-0.01933	-0.00652	-4.02118
0.00416	938.15	-0.02763	-0.01117	-3.97131
0.00512	938.41	-0.03198	-0.01196	-3.91931
0.01014	939.60	-0.03924	-0.00214	-3.66209
0.01488	940.84	-0.05790	-0.00639	-3.46863
0.02106	942.31	-0.06843	0.00001	-3.25006
0.03965	947.01	-0.13276	-0.02009	-2.86204
0.06127	952.23	-0.19188	-0.03102	-2.65663
0.08031	956.68	-0.23690	-0.03338	-2.56745
0.10829	963.22	-0.31621	-0.05272	-2.48581
0.15051	972.60	-0.41470	-0.08106	-2.29770
0.20771	984.47	-0.51396	-0.14219	-1.93206
0.24943	992.83	-0.59094	-0.22942	-1.67879
0.30098	1002.61	-0.66777	-0.35283	-1.39922
0.35107	1011.30	-0.69551	-0.45310	-1.14357
0.40899	1020.91	-0.72558	-0.58878	-0.92325
0.44904	1027.21	-0.73585	-0.67984	-0.80458
0.50099	1034.92	-0.74139	-0.80124	-0.68178
0.55685	1042.89	-0.72885	-0.94674	-0.55544
0.60252	1048.79	-0.69422	-1.08615	-0.43567
0.65092	1054.90	-0.66181	-1.28092	-0.32980
0.70818	1061.62	-0.59826	-1.48933	-0.23109
0.75093	1066.56	-0.54281	-1.58996	-0.19548
0.80734	1072.56	-0.45653	-1.67996	-0.16457
0.85560	1077.33	-0.38070	-1.95571	-0.11490
0.90937	1082.62	-0.25763	-2.78471	-0.00579
0.94691	1086.09	-0.14024	-3.35752	0.04015
1.00000	1090.63	0.00000	-0.50403	0.00000
		T = 303.15 K		
0.00000	932.33	0.00000	0.00000	-4.21568
0.00102	932.68	-0.01220	-0.00795	-4.16990
0.00203	932.95	-0.01661	-0.00825	-4.11837
0.00319	933.25	-0.02076	-0.00783	-4.06024

x_2	ρ	V_m^E	V_1^E	V_2^E
0.00416	933.56	-0.03021	-0.01356	-4.01913
0.00512	933.80	-0.03267	-0.01238	-3.97229
0.01014	934.98	-0.03935	-0.00143	-3.74289
0.01488	936.22	-0.05854	-0.00556	-3.56616
0.02106	937.69	-0.06961	0.00111	-3.35731
0.03965	942.36	-0.13285	-0.01662	-2.94849
0.06127	947.60	-0.19606	-0.03272	-2.69886
0.08031	952.10	-0.24788	-0.04368	-2.58630
0.10829	958.54	-0.31965	-0.05648	-2.48665
0.15051	967.90	-0.41974	-0.08237	-2.32380
0.20771	979.75	-0.52139	-0.14135	-1.97098
0.24943	988.09	-0.59946	-0.23359	-1.70041
0.30098	997.85	-0.67783	-0.36440	-1.40577
0.35107	1006.52	-0.70642	-0.46108	-1.15990
0.40899	1016.10	-0.73656	-0.58261	-0.95902
0.44904	1022.38	-0.74677	-0.67066	-0.84014
0.50099	1030.19	-0.75379	-0.80927	-0.69854
0.55685	1038.07	-0.74041	-0.98076	-0.54913
0.60252	1044.11	-0.71096	-1.12506	-0.43778
0.65092	1050.25	-0.67471	-1.27546	-0.35255
0.70818	1057.05	-0.60956	-1.41996	-0.27563
0.75093	1061.88	-0.55303	-1.52995	-0.22899
0.80734	1068.17	-0.49455	-1.78531	-0.18653
0.85560	1072.87	-0.38518	-2.12074	-0.09227
0.90937	1077.94	-0.26543	-2.70102	-0.02270
0.94691	1081.20	-0.16076	-3.04404	0.00090
1.00000	1085.57	0.00000	-2.63786	0.00000

Figures 2, 3, 4 and 5 show that for each of the (DFM + NMF or NEF or DMF or DMA) binary systems, an increase in temperature (293.15 to 303.15)K, resulted in an increase in the negative magnitude of the V_m^E *vs* x_2 isotherms over the entire x_2 - range. This effect may be resulting from a more favorable mutual geometrical fitting of component molecules into the expanded cavities of the unlike component liquid structure in binary mixture. Another plausible explanation for the observed increase in the negative magnitude of V_m^E values is as follows. Increase in temperature leads to increase in kinetic energy which would promote dissociation of self-associated species of pure components (amide-amide or DFM-DFM) as well as the DFM-amide complex associates and would positively contribute to V_m^E values. The observed contraction in $V_m{}^E$ values may suggest that an increase in temperature causes a greater dissociation effect on the amide-amide or DFM-DFM self-associates than on the formation of DFM-amide complexes. As result, the equilibrium would be shifted more favorably towards the DFM-amide complex formation leading to closer molecular packing and more negative $V_m{}^E$ values.

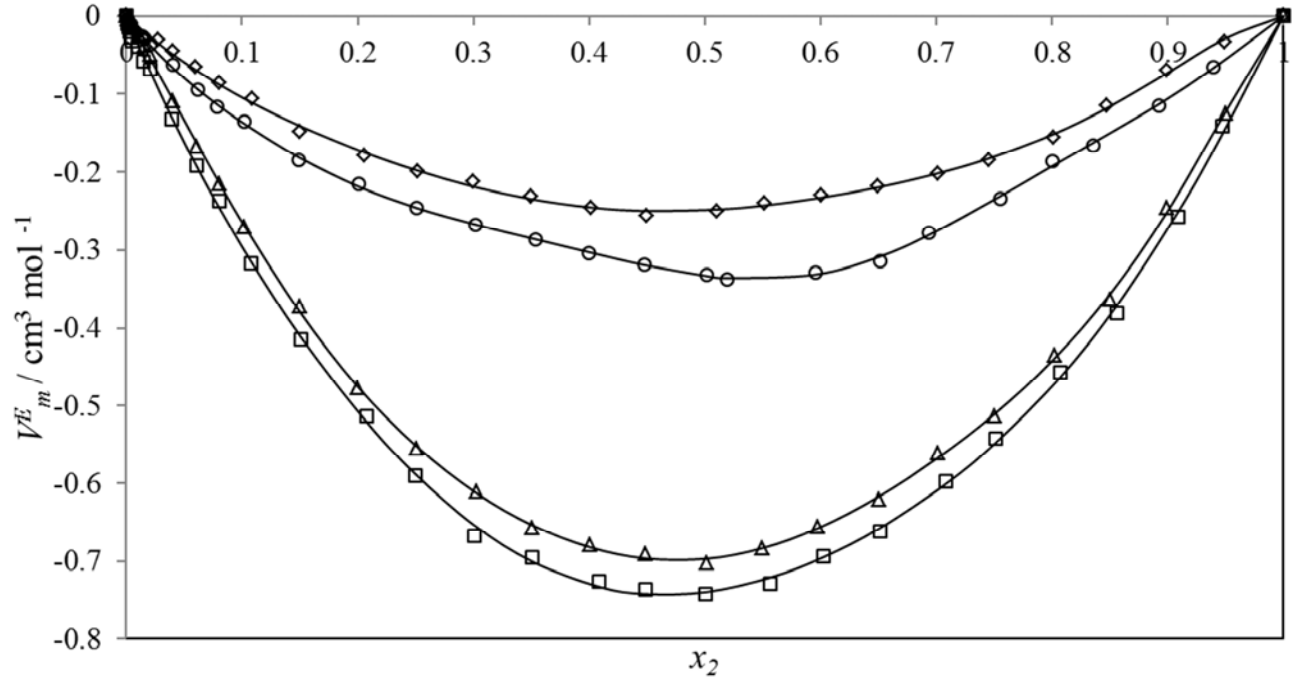

Figure 1. *Excess molar volume, V_m^E vs x_2 for the [DFM (2) + amides (1)] binary mixtures: (◊) NMF; (○) NEF; (Δ) DMF and (□) DMA at 298.15 K. Each solid line has been calculated from the Redlich-Kister fitting correlation coefficients (Table 3).*

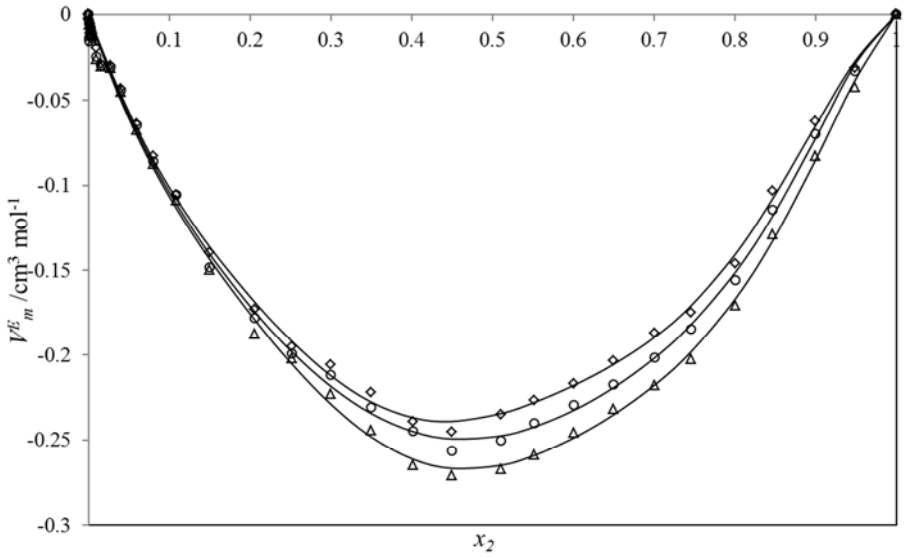

Figure 2. *Excess molar volume, V_m^E vs x_2 for the [DFM (2) + NMF (1)] binary mixtures at (◊) 293.15 K; (○) 298.15 K, and (Δ) 303.15 K.*

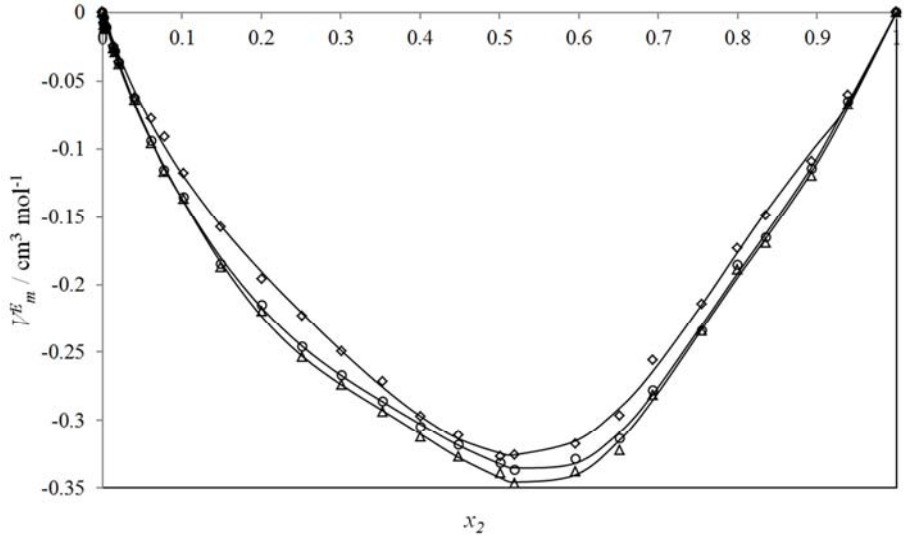

Figure 3. *Excess molar volume, V_m^E vs x_2 for the [DFM (2) + NEF (1)] binary mixtures at (◊) 293.15 K; (○) 298.15 K, and (Δ) 303.15 K.*

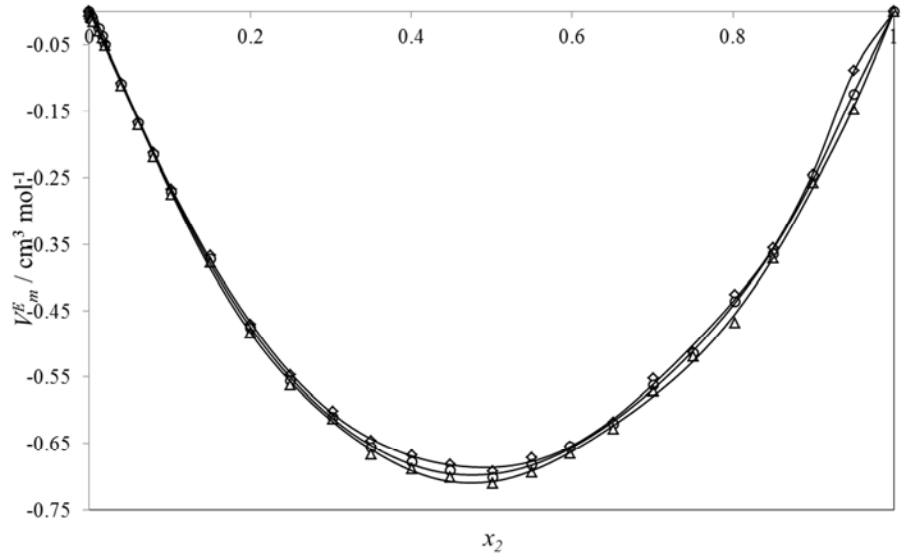

Figure 4. *Excess molar volume, V_m^E vs x_2 for the [DFM (2) + DMF (1)] binary mixtures at (◊) 293.15 K; (○) 298.15 K, and (Δ) 303.15 K.*

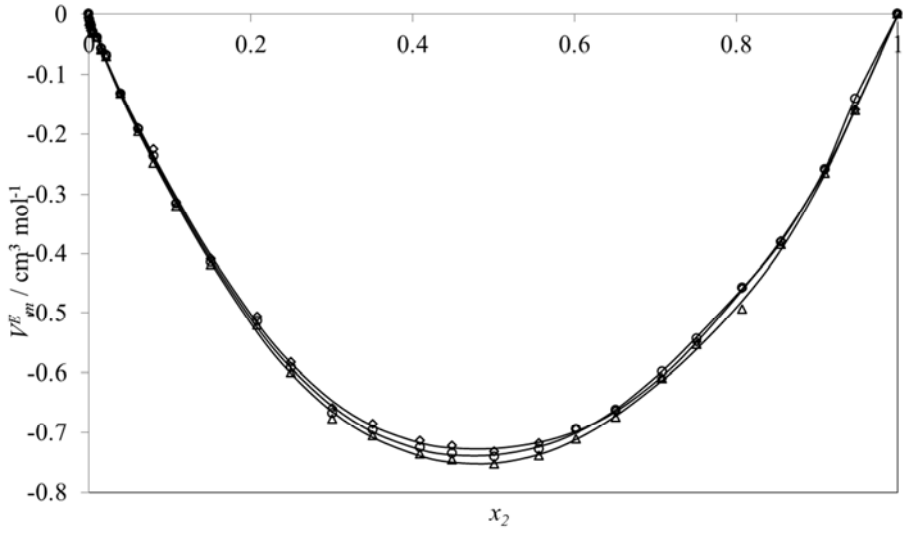

Figure 5. *Excess molar volume, V_m^E vs x_2 for the [DFM (2) + DMA (1)] binary mixtures at (◊) 293.15 K; (○) 298.15 K, and (Δ) 303.15 K.*

3.2. Excess Partial Molar Volumes ($\bar{V}_i^E$)

Differential properties such as excess partial molar volumes (V_i^E) separate the two component contributions in the binary system and 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 provide information on the individual component response to the intermolecular interactions. For each binary system the V_1^E and V_2^E values have been obtained in accordance with equations (4) and (5) respectively [23]:

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

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

The optimized Redlich-Kister polynomial least squares fitting correlation coefficients (Table 3) for a specific binary system at a given temperature have been used to evaluate the $(\partial V_m^E / \partial x_2)_{P,T}$ function over the entire composition range.

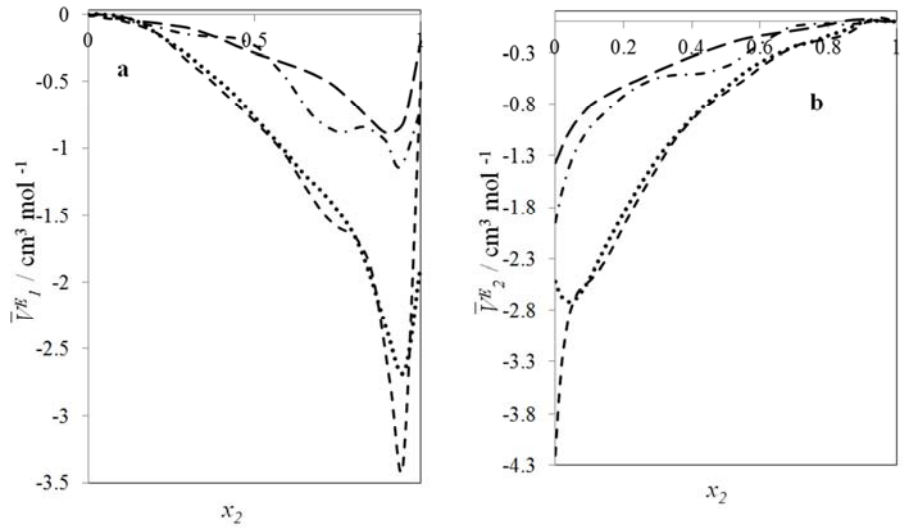

Figure 6. *Excess partial molar volumes, $\bar{V}_i^E$ vs x_2 for the [DFM (2) + amide (1)] binary mixtures: (— — —) NMF; (—·—·—) NEF; (·····) DMF; (– – –) DMA at 298.15 K.*

Table 2 shows the calculated excess partial molar volumes, 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 (b) represent the excess partial molar volumes for amides, (V_1^E) and that for DFM, (V_2^E) respectively in (DFM + NMF or NEF or DMF or DMA) binary systems at 298.15 K. Negative V_i^E values were observed for both components of each of the four binary systems over the entire x_2-range. Negative V_i^E values signify that both components are more closely packed in the binary mixture than in their pure states. The negative magnitude of the $\bar{V}_i^E$ function in the infinite dilute regions of the four binary systems is in the order: DMA > DMF > NEF > NMF. Negative $\bar{V}_i^E$ values corroborate the V_m^E data (Figure 1) and suggest enhancement of the DFM-amide, dipole-dipole interactions and possible mutual structural effects arising from the geometrical interstitial

accommodation of each component into the bulk liquid structure of second component. Therefore for each binary system, the solute-solvent interactions are stronger than the intermolecular interactions in the pure components. Table 3 shows that the negative magnitude of $\bar{V}_i^E$ values for a component in each of (DFM + NMF or NEF or DMF or DMA) binary mixtures increases with the rise in temperature as was observed for the V_m^E data (Figures 2-5).

3.3. Limiting Excess ($\bar{V}_i^{E,\infty}$) and Partial ($\bar{V}_i^{\infty}$) Molar Volumes

Information about the solute-solvent intermolecular interactions and their dependence on temperature can be obtained from the limiting excess partial molar volumes ($\bar{V}_i^{E,\infty}$) of each component in a mixture [24]. The optimized Redlich-Kister polynomial fitting correlation coefficients for each of (DFM + NMF or NEF or DMF or DMA) binary systems at (T =293.15, 298.15 and 303.15) K (Table 3) have been used to obtain values of the limiting excess partial molar volumes for an amide ($\bar{V}_1^{E,\infty}$) and DFM ($\bar{V}_2^{E,\infty}$) using Equations (6) and (7) [24] respectively,

$$\bar{V}_1^{E,\infty} = \sum_{k=even} A_k - \sum_{k=odd} A_k \quad (6)$$

$$\bar{V}_2^{E,\infty} = \sum_k A_k \quad (7)$$

Table 4 lists the calculated $\bar{V}_i^{E,\infty}$ data for components in each binary system. A negative value for the $\bar{V}_i^{E,\infty}$ function was obtained for each component in each binary mixture at the three temperatures, further suggesting the enhancement molecular parking efficiency and supporting the observed negative V_m^E data. Thus in the infinite dilute solutions of DFM or amide in each of the four binary systems, the solute-solvent interactions are stronger than the intermolecular interactions in the pure components which gives rise to greater packing efficiency.

The limiting partial molar volume, $\bar{V}_i^{\infty}$ of component *i* in a mixture can be calculated from the expression: $\bar{V}_i^{\infty} = \bar{V}_i^{E,\infty} + V_{m,i}^{*}$, where $V_{m,i}^{*}$ is the molar volume of the pure component**.** It can be observed that values of both V_1^{∞} and V_2^{∞} (Table 4) show an increase with the rise in temperature.

Table 3. *Least square fitted (A_k) coefficients of Equation (4) and corresponding standard deviation of fit $\sigma(V_m^E)$ for the (DFM + NMF or NEF or DMF or DMA) binary systems at (T = 293.15, 298.15 and 303.15)K.*

	NMF	NEF	DMF	DMA
Coefficients		*T = 293.15 K*		
A_0	-0.943	-1.297	-2.746	-2.909
A_1	-0.227	0.222	-0.090	-0.158
A_2	-0.119	0.623	-0.339	-1.022
A_3	0.892	-1.139	-2.031	0.017
A_4	0.178	-0.350	2.007	3.525
A_5	-2.045	0.870	7.892	-2.082
A_6	0.085	-0.585	-7.257	-6.179
A_7	0.926		-8.181	8.202
A_8			7.493	3.405
A_9			0.932	-6.906
$\sigma(V_m^E)$	0.005	0.004	0.005	0.006
		T =298.15 K		
A_0	-0.994	-1.328	-2.786	-2.953
A_1	-0.140	0.399	-0.265	-0.230
A_2	-0.021	0.201	-0.037	-0.644
A_3	0.383	-2.914	-0.093	0.428
A_4	-2.310	0.533	-0.674	3.019
A_5	-0.735	5.177	1.485	-0.352
A_6	0.462	-2.611	0.106	-8.051
A_7	-0.091	-3.281	-1.450	7.813
A_8		1.876	1.195	6.273
A_9				-8.655
$\sigma(V_m^E)$	0.006	0.003	0.004	0.006
		T = 303.15 K		
A_0	-1.063	-1.369	-2.831	-3.009
A_1	-0.154	0.427	-0.344	-0.210
A_2	0.030	0.462	0.470	-0.210
A_3	0.777	-3.365	1.103	0.867
A_4	-0.282	-0.889	-4.844	-1.069
A_5	-1.426	6.351	-1.926	4.460
A_6	0.358	0.247	9.451	1.856
A_7	0.352	-4.038	1.487	-4.172
A_8			-5.404	-0.994
$\sigma(V_m^E)$	0.006	0.003	0.005	0.008

Table 4. *Limiting excess ($\bar{V}_i^{E,\infty}$) and partial ($\bar{V}_i^{\infty}$) molar volumes for the components in [DFM + (NMF or NEF or DMF or DMA)] binary systems at (T = 293.15, 298.15 and 303.15) K derived from Equations (8) and (9).*

T/K	293.15K	298.15	303.15
	(DFM + NMF)		
$\bar{V}_1^{E,\infty}$	-0.345	-0.200	-0.506
$\bar{V}_2^{E,\infty}$	-1.254	-1.366	-1.409
$\bar{V}_1^{\infty}$	-1.409	58.897	58.850
$\bar{V}_2^{\infty}$	133.966	134.483	135.071
	(DFM + NEF)		
$\bar{V}_1^{E,\infty}$	-1.562	-0.710	-0.925
$\bar{V}_2^{E,\infty}$	-1.656	-1.947	-2.174
$\bar{V}_1^{\infty}$	75.228	76.411	76.531
$\bar{V}_2^{\infty}$	133.564	133.902	134.306
	(DFM + DMF)		
$\bar{V}_1^{E,\infty}$	-0.637	-1.874	-3.479
$\bar{V}_2^{E,\infty}$	-2.320	-2.519	-2.838
$\bar{V}_1^{\infty}$	77.656	75.531	74.319
$\bar{V}_2^{\infty}$	133.172	133.331	133.642
	(DFM + DMA)		
$\bar{V}_1^{E,\infty}$	-2.253	-0.504	-2.638
$\bar{V}_2^{E,\infty}$	-4.107	-4.207	-4.216
$\bar{V}_1^{\infty}$	90.278	92.480	90.806
$\bar{V}_2^{\infty}$	131.113	131.643	132.264

The $\bar{V}_i^{\infty}$ value for a component in a liquid mixture has two contributing terms: one due to the intrinsic molar volume, V_{int}, of the non-solvated solute molecule and the other due to the co-sphere, V_s, which arises from the interaction of the solute with solvent molecules. For a polyatomic solute molecule the change in V_{int} with temperature is negligible. Therefore any observed temperature dependence of $\bar{V}_i^{\infty}$ indicates how the co-sphere V_s depends on temperature [25]. In this study, the observed increase in $\bar{V}_1^{\infty}$ and $\bar{V}_2^{\infty}$ is attributed to the positive contribution from V_s which increases with temperature due to a decrease in the interaction between the unlike molecules as a result of the increase in Brownian motion. Since for each of the [DFM + (*N*MF or *N*EF or DMF or DMA)] binary systems, the negative magnitude of V_m^E values slightly

increases with temperature rise, it is possible that the geometric effects more than offset the entropic expansion effects reflected in the increase of $\bar{V}_i^{\infty}$ values.

4. Conclusions

In this study, measured density values of pure DFM, NMF, NEF, DMF and DMA as well as their (DFM + NMF or NEF or DMF or DMA) binary mixtures over the entire composition range are reported at (T = 293.15, 298.15 and 303.15) K. These data have been used to derive: the excess molar volumes of solution, V_m^E, excess partial molar volumes $\bar{V}_i^E$, limiting excess partial molar volumes $\bar{V}_i^{E,\infty}$, and limiting partial molar volumes (V_i^{∞}) of each component of a binary mixture. The excess molar volumes for each of (DFM + NMF or NEF or DMF or DMA) binary systems were negative over the entire composition range at the three temperatures investigated. The negative excess molar volumes observed for each of the four binary systems have been discussed in terms of specific interactions and structural effects. The magnitude of the negative deviation in V_m^E values follows the order: DMA > DMF > NEF > NMF. The results indicated that the increase in temperature had a greater effect on component self-association than on complex formation between molecules of components in (DFM + NMF or NEF or DMF or DMA) binary mixture. Calculated excess partial molar volumes, $\bar{V}_i^E$, limiting excess partial molar volumes $\bar{V}_i^{E,\infty}$ and limiting partial molar volumes V_i^{∞} of each component in (DFM + NMF or NEF or DMF or DMA) binary mixture complimented the V_m^E data.

Acknowledgement

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