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# Excess and Partial Molar Volumes for [Difurylmethane+Acetonitrile] Binary Mixtures in the Temperature Range: 288.15–323.15 K

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Densities of binary systems of difurylmethane in acetonitrile have been measured with an Anton Paar DMA 4500 vibrating-tube densimeter over the entire composition range at intervals of 5 K in the temperature range between 288.15 and 323.15 K and atmospheric pressure. Excess molar volumes ($V_m^E$) of mixtures, limiting ($\overline{V}_i^{E,\infty}$) and excess partial ($\overline{V}_i^E$) molar volumes of components of the binary system have been examined to provide insight into the variation with temperature, of the intermolecular interactions and molecular packing efficiencies. The observed dependence of these functions on both composition and temperature has been discussed in terms of specific intermolecular interactions and structural effects.

**Key Words: Difurylmethane, Acetonitrile, Excess molar volume, Excess partial molar volume, Excess limiting partial molar volume, Binary mixtures, Dipole-dipole interactions.**

## INTRODUCTION

Investigation of binary liquid systems *via* volumetric properties is useful in obtaining detailed information concerning self-organization and associative processes in liquid mixtures. Such systematic investigation of the internal structures of liquid mixtures that result from intermolecular interactions, involve studies of intensive macroscopic properties such as density[1,2]. Precise density measurements are also needed to develop correlations for a specific system. In the previous works[3-5], we have reported studies on volumetric properties of binary mixtures containing difurylmethane and ($C_1$–$C_6$) alkan-1-ol. In continuation of previous work, studies have been performed on volumetric properties for the binary mixture of difurylmethane with acetonitrile, over the entire composition range at various temperatures and atmospheric pressure. Acetonitrile molecules are highly polar ($\mu$ = 3.7 D at 298.15 K)[6-8] with their dipoles oriented anti-parallel to each other[6-8]. Therefore the strongly associated liquid structure in acetonitrile results from the dipole-dipole interactions[9,10]. Difurylmethane is an aprotic liquid which is assumed to be a typical example of a pure dipolar fluid[3,4]. Since hydrogen bonding is absent, the liquid structure of the neat difurylmethane is determined by the dipole-dipole interactions between molecules. Therefore for solutions of difurylmethane in acetonitrile, dipole-dipole association complexes may be expected to be formed. The present volumetric studies on the [difurylmethane + acetonitrile] binary system are aimed to provide the information on the mixtures with a view to understand the nature of possible intermolecular interactions in these solutions.

In this work, precise density measurements for the [difurylmethane + acetonitrile] binary mixtures over the entire composition range at temperatures (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15) K are reported. For each temperature investigated, $V_m^E$ values have been determined and correlated with the Redlich-Kister polynomial[11] of an appropriate degree. Limiting, $\overline{V}_i^{E,\infty}$ and excess partial molar volumes, $\overline{V}_i^E$, of components in the binary system were calculated to probe the variation of the intermolecular interactions and molecular packing efficiencies, with both composition and temperature.

## EXPERIMENTAL

Acetonitrile supplied by Rochelle Chemicals, (quoted purity > 99.9 mass %, *ca.* 0.1 % $H_2O$) was first dried and distilled over anhydrous di-phosphoruspentoxide $P_2O_5$ (Merck, P.A.) as described elsewhere[12]. The purity of acetonitrile was tested by density ($\rho$) measurements and the $\rho$ values were in good agreement with the literature values at various temperatures and atmospheric pressure (Table-1). Due to its hygroscopic nature, acetonitrile was always purified shortly before use. Difurylmethane was prepared and purified by the method described in the literature[13] and its purity was confirmed by $^1H$ NMR, density measurements and elemental analyses. Both purified difurylmethane and acetonitrile were stored over molecular sieves 3 Å (Aldrich, 1/8-inch. 4-8 mesh) in brown glass bottles and fractionally distilled immediately before the preparation of binary mixtures.

The [difurylmethane + acetonitrile] binary mixtures were prepared by weighing appropriate amounts of the purified difurylmethane and acetonitrile on a Sartorius Supermicro balance (Fabr.-Nr., $\Delta m = \pm 0.000001$ 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 [difurylmethane + acetonitrile] mixtures were completely miscible over the entire composition range. The uncertainty in solution composition expressed as mole fraction was found to be less than $8 \times 10^{-5}$. The density measurements of pure liquid and mixtures were performed at atmospheric pressure at various temperatures by means of a vibrating-tube densimeter (Anton Paar, model 4500, resolution $1 \times 10^{-5}$ g $cm^{-3}$). A sample volume of not more than 1.0 $cm^3$ was needed to fill the densimeter cell and thermal equilibrium was attained quickly at each temperature. 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 any problem of 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 to the weight were made by taking into account the air density, the barometric pressure and the relative humidity. Under such conditions quadruplet density measurements of each sample were reproducible to within $\pm 1 \times 10^{-5}$ g cm$^{-3}$.

## RESULTS AND DISCUSSION

Experimental density values for pure acetonitrile and difurylmethane at temperatures (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15) K are listed in Table-1, together with the literature data. The agreement, within the experimental uncertainties for the measured and literature values at various temperatures confirmed the purity of the chemicals used as well as the accuracy of the equipment and the experimental procedure. The experimental densities as a function of composition for [difurylmethane + acetonitrile] binary mixtures at various temperatures are listed in Table-2. These densities cover the entire composition range as expressed by the mole fraction $x_2$ of difurylmethane. For each [difurylmethane + acetonitrile] binary system, the data showed an increase in ρ with the increase in concentration of difurylmethaneat constant temperature and the expected decrease in ρ with increasing temperature at a fixed difurylmethane mole fraction. Fig. 1 displays the experimental ρ *vs.* $x_2$ data for the [difurylmethane + acetonitrile] binary systems at 288.15, 308.15 and 323.15 K as examples.

TABLE-1
REFERENCE DENSITY VALUES, ρ (g cm$^{-3}$) FOR ACETONITRILE AND DIFURYLMETHANE AT EXPERIMENTAL TEMPERATURES

| Compd. | T (K) | ρ (g cm$^{-3}$) | |
|---|---|---|---|
| | | Present work | Literature reference are given in brackets |
| Acetonitrile | 288.15 | 0.78759 | 0.78738 [9] |
| | 293.15 | 0.78222 | 0.78209 [9], 0.7821 [8], 0.7822 [11] |
| | 298.15 | 0.77681 | 0.7768 [8], 0.77675[13], 0.77649 [11] 0.77662 [9] |
| | 303.15 | 0.77139 | 0.7715 [8], 0.7715 [14], 0.77125 [11] |
| | 308.15 | 0.76593 | 0.7663 [8], 0.7662 [14] |
| | 313.15 | 0.76044 | 0.7610 [8], 0.7610 [14] |
| | 318.15 | 0.75492 | 0.7557 [8], 0.7556 [14] |
| | 323.15 | 0.74936 | |
| Difurylmethane | 288.15 | 1.10109 | 1.10099 [3,4] |
| | 293.15 | 1.09609 | 1.09594 [3,4] |
| | 298.15 | 1.09120 | 1.09088 [3,4] |
| | 303.15 | 1.08616 | 1.08582 [3,4] |
| | 308.15 | 1.08125 | 1.08076 [3.4] |
| | 313.15 | 1.07850 | |
| | 318.15 | 1.07341 | |
| | 323.15 | 1.06831 | |

TABLE-2
EXPERIMENTAL DENSITIES ρ (g $cm^{-3}$) AND EXCESS MOLAR VOLUMES $V_m^E$ ($cm^3$ $mol^{-1}$) FOR THE [ACETONITRILE (1) + DIFURYLMETHANE (2)] BINARY MIXTURES IN THE TEMPERATURE RANGE 288.15 to 323.15 K

| $X_2$ | ρ | $V_m^E$ | ρ | $V_m^E$ | ρ | $V_m^E$ | ρ | $V_m^E$ |
|---|---|---|---|---|---|---|---|---|
| | T = 288.15 K | | T = 293.15 K | | T = 298.15 K | | T = 303.15 K | |
| 0.000000 | 0.78759 | 0.000000 | 0.78222 | 0.000000 | 0.77681 | 0.000000 | 0.77139 | 0.000000 |
| 0.022053 | 0.80561 | -0.044377 | 0.80025 | -0.046974 | 0.79486 | -0.050348 | 0.78944 | -0.052398 |
| 0.041422 | 0.82060 | -0.090827 | 0.81524 | -0.094929 | 0.80985 | -0.099866 | 0.80444 | -0.104186 |
| 0.059688 | 0.83411 | -0.142686 | 0.82876 | -0.148787 | 0.82338 | -0.155790 | 0.81798 | -0.162198 |
| 0.078070 | 0.84671 | -0.172968 | 0.84136 | -0.179927 | 0.83601 | -0.189941 | 0.83060 | -0.196537 |
| 0.104042 | 0.86362 | -0.226785 | 0.85828 | -0.235536 | 0.85292 | -0.245993 | 0.84754 | -0.255852 |
| 0.120895 | 0.87392 | -0.257151 | 0.86860 | -0.267838 | 0.86325 | -0.279566 | 0.85788 | -0.290690 |
| 0.144994 | 0.88780 | -0.294239 | 0.88251 | -0.307598 | 0.87717 | -0.320593 | 0.87182 | -0.333701 |
| 0.167709 | 0.90016 | -0.331385 | 0.89485 | -0.343626 | 0.88953 | -0.358437 | 0.88419 | -0.372604 |
| 0.203159 | 0.91801 | -0.380390 | 0.91273 | -0.395037 | 0.90743 | -0.411575 | 0.90210 | -0.426643 |
| 0.310848 | 0.96354 | -0.483572 | 0.95831 | -0.500823 | 0.95306 | -0.520025 | 0.94780 | -0.539103 |
| 0.386963 | 0.98961 | -0.526906 | 0.98442 | -0.545461 | 0.97921 | -0.565980 | 0.97397 | -0.584463 |
| 0.461545 | 1.01127 | -0.536056 | 1.00611 | -0.554535 | 1.00093 | -0.574949 | 0.99573 | -0.593949 |
| 0.552270 | 1.03388 | -0.542128 | 1.02901 | -0.584316 | 1.02381 | -0.599236 | 1.01854 | -0.607486 |
| 0.583221 | 1.04077 | -0.539465 | 1.03563 | -0.554709 | 1.03049 | -0.573714 | 1.02534 | -0.591839 |
| 0.659918 | 1.05574 | -0.465238 | 1.05063 | -0.479251 | 1.04550 | -0.495007 | 1.04037 | -0.510627 |
| 0.689491 | 1.06108 | -0.440520 | 1.05607 | -0.463231 | 1.05080 | -0.462867 | 1.04566 | -0.475638 |
| 0.752014 | 1.07154 | -0.380884 | 1.06644 | -0.390816 | 1.06134 | -0.404511 | 1.05622 | -0.415632 |
| 0.800934 | 1.07890 | -0.314616 | 1.07381 | -0.322649 | 1.06871 | -0.333328 | 1.06362 | -0.344561 |
| 0.831136 | 1.08322 | -0.276587 | 1.07814 | -0.283909 | 1.07305 | -0.293863 | 1.06796 | -0.303162 |
| 0.857042 | 1.08678 | -0.243557 | 1.08170 | -0.249309 | 1.07661 | -0.257659 | 1.07152 | -0.265263 |
| 0.879998 | 1.08979 | -0.209593 | 1.08471 | -0.213899 | 1.07963 | -0.221936 | 1.07454 | -0.227992 |
| 0.902871 | 1.09263 | -0.167906 | 1.08756 | -0.171854 | 1.08248 | -0.178363 | 1.07740 | -0.183979 |
| 0.940742 | 1.09728 | -0.114576 | 1.09221 | -0.116155 | 1.08714 | -0.121448 | 1.08206 | -0.124522 |
| 0.964432 | 1.09998 | -0.069916 | 1.09492 | -0.071103 | 1.08985 | -0.074793 | 1.08477 | -0.076162 |
| 0.985210 | 1.10225 | -0.026925 | 1.09725 | -0.033989 | 1.09205 | -0.020314 | 1.08698 | -0.021294 |
| 1.000000 | 1.10109 | 0.000000 | 1.09609 | 0.000000 | 1.09120 | 0.000000 | 1.08616 | 0.000000 |
| | T = 308.15 K | | T = 313.15 K | | T = 318.15 K | | T = 323.15 K | |
| 0.000000 | 0.76593 | 0.000000 | 0.76044 | 0.000000 | 0.75492 | 0.000000 | 0.74936 | 0.000000 |
| 0.022053 | 0.78400 | -0.058003 | 0.77851 | -0.058003 | 0.77300 | -0.060899 | 0.76745 | -0.063852 |
| 0.041422 | 0.79900 | -0.114423 | 0.79353 | -0.114423 | 0.78802 | -0.118969 | 0.78248 | -0.124329 |
| 0.059688 | 0.81255 | -0.175219 | 0.80707 | -0.175219 | 0.80158 | -0.182648 | 0.79605 | -0.190195 |
| 0.078070 | 0.82518 | -0.213497 | 0.81972 | -0.213497 | 0.81424 | -0.222568 | 0.80874 | -0.233272 |
| 0.104042 | 0.84213 | -0.277213 | 0.83669 | -0.277213 | 0.83122 | -0.288130 | 0.82572 | -0.299922 |
| 0.120895 | 0.85248 | -0.315305 | 0.84706 | -0.315305 | 0.84160 | -0.327481 | 0.83613 | -0.342074 |
| 0.144994 | 0.86643 | -0.360732 | 0.86102 | -0.360732 | 0.85558 | -0.374853 | 0.85011 | -0.389839 |
| 0.167709 | 0.87882 | -0.403177 | 0.87343 | -0.403177 | 0.86800 | -0.418281 | 0.86266 | -0.443733 |
| 0.203159 | 0.89675 | -0.460370 | 0.89138 | -0.460370 | 0.88598 | -0.477769 | 0.88055 | -0.495960 |
| 0.310848 | 0.94251 | -0.578555 | 0.93720 | -0.578555 | 0.93187 | -0.599352 | 0.92650 | -0.619819 |
| 0.386963 | 0.96873 | -0.625474 | 0.96345 | -0.625474 | 0.95816 | -0.646785 | 0.95286 | -0.670200 |
| 0.461545 | 0.99051 | -0.634479 | 0.98528 | -0.634479 | 0.98003 | -0.655709 | 0.97475 | -0.676953 |
| 0.552270 | 1.01340 | -0.628954 | 1.00799 | -0.628954 | 1.00291 | -0.661913 | 0.99781 | -0.695790 |
| 0.583221 | 1.02016 | -0.627431 | 1.01497 | -0.627431 | 1.00977 | -0.646642 | 1.00454 | -0.665358 |
| 0.659918 | 1.03522 | -0.542334 | 1.03006 | -0.542334 | 1.02488 | -0.558209 | 1.01969 | -0.575365 |

| $X_2$ | ρ | $V_m^E$ | ρ | $V_m^E$ | ρ | $V_m^E$ | ρ | $V_m^E$ |
|---|---|---|---|---|---|---|---|---|
| 0.689491 | 1.04068 | -0.514053 | 1.03545 | -0.514053 | 1.03039 | -0.540835 | 1.02511 | -0.546077 |
| 0.752014 | 1.05110 | -0.440512 | 1.04596 | -0.440512 | 1.04081 | -0.453040 | 1.03564 | -0.465392 |
| 0.800934 | 1.05850 | -0.363566 | 1.05337 | -0.363566 | 1.04824 | -0.374605 | 1.04309 | -0.385267 |
| 0.831136 | 1.06285 | -0.320172 | 1.05773 | -0.320172 | 1.05260 | -0.328919 | 1.04745 | -0.337137 |
| 0.857042 | 1.06642 | -0.280885 | 1.06131 | -0.280885 | 1.05618 | -0.287628 | 1.05105 | -0.296119 |
| 0.879998 | 1.06945 | -0.241424 | 1.06434 | -0.241424 | 1.05922 | -0.247542 | 1.05408 | -0.252910 |
| 0.902871 | 1.07230 | -0.193904 | 1.06720 | -0.193904 | 1.06209 | -0.199345 | 1.05696 | -0.203941 |
| 0.940742 | 1.07698 | -0.131326 | 1.07188 | -0.131326 | 1.06678 | -0.135032 | 1.06166 | -0.137723 |
| 0.964432 | 1.07969 | -0.080516 | 1.07460 | -0.080516 | 1.06949 | -0.080986 | 1.06438 | -0.082843 |
| 0.985210 | 1.08195 | -0.022168 | 1.07681 | -0.022168 | 1.07192 | -0.048826 | 1.06671 | -0.036107 |
| 1.000000 | 1.08125 | 0.000000 | 1.07850 | 0.000000 | 1.07341 | 0.000000 | 1.06721 | 0.000000 |

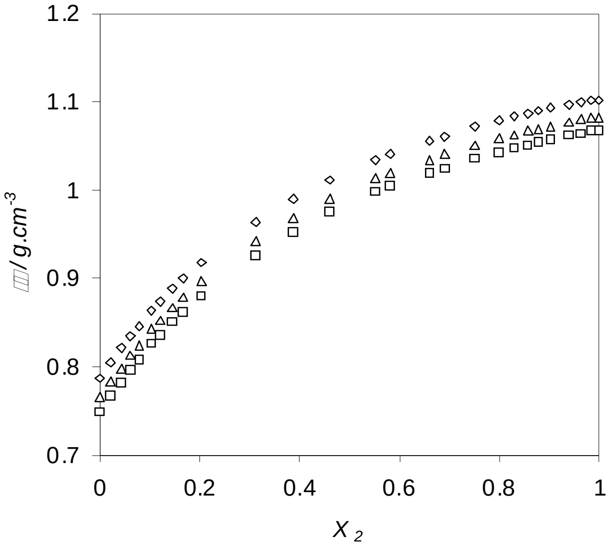

Fig. 1. Densities, ρ *vs.* $x_2$ for the [difurylmethane (2) + acetonitrile (1)] binary mixtures at: (◇) 288.15 K; (△) 308.15 K and (□) 323.15 K

Excess molar volumes, $V_m^E$, were calculated for each [difurylmethane + acetonitrile] binary composition from density measurements according to the following equation:

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

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, $V_m^{id}$ is the ideal molar volume, ρ is the density of the binary 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 $V_m^E$ values of each binary system were least-squares fitted to the Redlich-Kister[11] polynomial (2):

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

where $x_1$ and $x_2$ are the mole fractions of acetonitrile and difurylmethane. All points in this polynomial were weighted equally. For each [difurylmethane + acetonitrile] binary system at a specified temperature, the degree of the polynomial and the number of $A_k$ coefficients in eqn. 2 were fixed by testing the statistical significance of including each further term using an F-test[14] at the 95 % confidence level. The optimized number of regression coefficients $A_k$, for each [difurylmethane + acetonitrile] system at the temperatures studied are listed in Table-3 along with the corresponding standard deviation $\sigma(V_m^E)$ defined by eqn. 3,

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

where N is the number of data points and n the number of the regression coefficients. Fig. 2 displays the experimental $V_m^E$ *vs.* $x_2$ data and the fitted curves for the binary mixture at 288.15, 308.15 and 323.15 K as examples. For each curve the solid line represents the fitted curve calculated from the smoothing eqn. 2 of an appropriate degree.

TABLE-3
LEAST SQUARES FITTED $A_k$ ($cm^3\ mol^{-1}$) COEFFICIENTS OF THE REDLICH-KISTER EQUATION, CORRESPONDING STANDARD DEVIATIONS OF THE FITS AND $\sigma(V_m^E)$ FOR THE [DIFURYLMETHANE + ACETONITRILE] BINARY MIXTURES AT ALL TEMPERATURES OF STUDY

| T (K) | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $A_5$ | $A_6$ | $A_7$ | $\sigma(V_m^E)$ |
|---|---|---|---|---|---|---|---|---|---|
| 288.15 | -2.2961 | 0.0247 | 0.6272 | -2.1262 | -1.6495 | 3.6485 | 1.1242 | -1.7484 | 0.0010 |
| 293.15 | -2.3002 | -0.0438 | 0.6699 | -1.2799 | -1.7635 | 1.3255 | 1.2050 | – | 0.0010 |
| 298.15 | -2.3776 | -0.0257 | 0.8234 | -2.3383 | -2.4785 | 4.7366 | 1.8651 | -2.8079 | 0.0010 |
| 303.15 | -2.3777 | -0.0258 | 0.8234 | -2.3383 | -2.4786 | 4.7366 | 1.8651 | -2.8080 | 0.0010 |
| 308.15 | -2.5182 | -0.0714 | 0.4996 | -2.1495 | -1.4988 | 3.9121 | 1.0556 | -2.0907 | 0.0008 |
| 313.15 | -2.5754 | -0.1774 | 0.3292 | -1.7534 | -1.2540 | 3.2656 | 0.9711 | -1.7767 | 0.0006 |
| 318.15 | -2.6700 | -0.1777 | 0.2567 | -1.5518 | -0.7096 | 2.0014 | 0.2998 | -0.4493 | 0.0008 |
| 323.15 | -2.7763 | -0.1544 | 0.6443 | -2.3495 | -2.1248 | 4.1112 | 1.5656 | -2.0551 | 0.0010 |

The results presented in Table-2 as well as in Fig. 2 indicate that at each temperature investigated, $V_m^E$ values for the [difurylmethane + acetonitrile] system are negative over the entire composition range, with more negative values as temperature increases. At all temperatures investigated, the $V_m^E$ curves are symmetrical, the position of the minimum being at $x^2 \approx 0.5$, which corresponds to the formation of the 1:1, difurylmethane:acetonitrile associates.

As a result of mutual intermolecular interactions, many properties of liquid mixtures are not additive with respect to pure components and excess thermodynamic functions such as the $V_m^E$ values measure the extent of deviation from ideal behaviour. 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 which contribute positively to $V_m^E$. Physical effects comprise non-specific unfavourable interactions between unlike molecules which also contribute positively to $V_m^E$. Structural effects arise

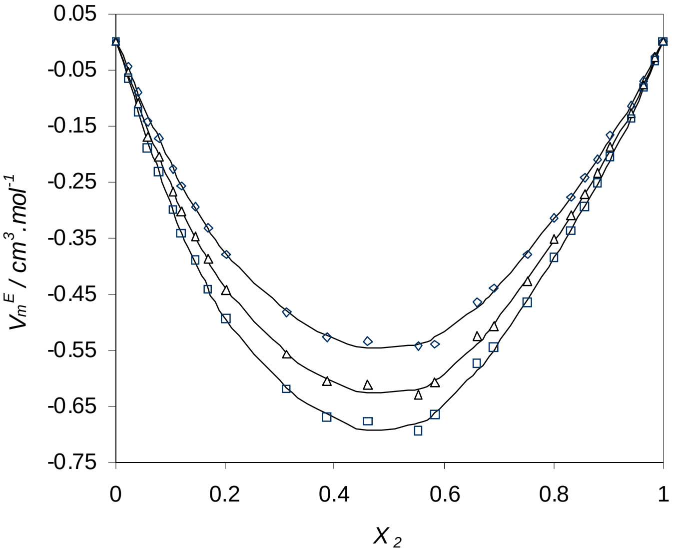

Fig. 2. Excess molar volume, $V_m^E$, *vs.* $X_2$ for the mixtures of [difurylmethane (2) + acetonitrile (1)] at: (◇) 288.15 K; (△) 308.15 K and (□) 323.15 K. The lines are from the appropriate Redlich-Kister fitting equations

from the restriction of the rotational degrees of freedom due to geometrical interstitial accommodation of liquid components into each other's cavities (clanthrate formation), due to differences in molar masses, shape and free volumes of pure components and they contribute negatively to $V_m^E$. Presence of specific dipole-dipole interactions between unlike component molecules also contribute negatively to $V_m^E$ values. The negative $V_m^E$-values observed at each temperature for the [difurylmethane + acetonitrile] system, indicate a completely miscible system and may suggest formation of strong dipole-dipole interactions between the -CN groups in acetonitrile and the polarized $\pi$-electron of the difurylmethane furan ring system. A further contribution to negative $V_m^E$-values would be due to the geometrical interstitial fitting of difurylmethane and acetonitrile into cavities of each other's liquid structure which more than offsets the positive contributions from the physical and chemical effects. The observed increase in the magnitude of negative $V_m^E$-values with temperature rise may suggest that the expansion in volume of the system results in more favourable mutual fitting of component molecules into the expanded cavities of component liquid structures, leading to a volume contraction.

Differential solution properties such as excess partial molar volumes ($\overline{V}_i^E$), provide valuable information on component response to intermolecular interactions[1-5,15,18]. In order to investigate individual component contribution to the excess molar volumes at each temperature, excess partial molar volumes of acetonitrile, ($\overline{V}_1^E$) and difurylmethane, ($\overline{V}_2^E$), in the binary system were obtained in accordance with eqns. 4 and 5[1,15-18], respectively,

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

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

The derivative $(\partial V_m^E / \partial x_2)_{p,T}$ in eqns. 4 and 5 was obtained by differentiation of eqn. 2 of an appropriate degree for the binary system at a specific temperature. Substituting for $(\partial V_m^E / \partial x_2)_{p,T}$ into eqns. 4 and 5 leads to the following expressions for $\overline{V}_1^E$ and $\overline{V}_2^E$, respectively:

$$\overline{V}_1^E = x_2^2\ \Sigma\ A_k(1-2x_2)^k + 2x_2^2\ (1-x_2)\ \Sigma\ A_k(k)(1-2x_2)k^{-1} \quad (6)$$

$$\overline{V}_2^E = (1-x_2)^2\ \Sigma A_k(1-2x_2)^k - 2x_2(1-x_2)^2\ \Sigma\ A_k(k)(1-2x_2\ )^{k-1} \quad (7)$$

Thus the regression coefficients $A_k$ (Table-3) of the Redlich-Kister eqn. 2 of an appropriate degree were used to calculate values of the derivative $(\partial V_m^E / \partial x_2)_{p,T}$ over the entire concentration range. Fig. 3 depicts the $\overline{V}_i^E$ *vs.* $x_2$ data for the binary mixture at 288.15, 308.15 and 323.15 K as examples. The slopes of all curves approach zero at $x_2 = 0$ for $\overline{V}_1^E$ and at $x_2 = 1$ for $\overline{V}_2^E$. This is consistent with the Gibbs-Duhem equation and has been suggested as a simple reliability test of partial molar volume curves[19]. The negative values of the $\overline{V}_i^E$ function for both components in the binary system at all the temperatures investigated and over the entire composition range suggest that molecules of both the components are more closely packed in the mixtures than in the pure liquid states. This observation renders further support to the $V_m^E$ data as depicted in Fig. 2. This behaviour may be attributed to the strong difurylmethane -acetonitrile, dipole-dipole interaction and structural effects arising from the mutual geometrical interstitial accommodation of acetonitrile and difurylmethane into cavities of each other's liquid structure which more than offset the positive contributions from the physical and chemical effects. The more negative $\overline{V}_i^E$-values observed with increase in temperature confirm the more effective mutual geometrical fitting of the component molecules into the expanded cavities of their liquid structure. It can further be inferred that in the difurylmethane rich region, the $\overline{V}_1^E$ function (Fig. 3a) does not exhibit significant changes with temperature, compared to a greater temperature dependence observed in $\overline{V}_2^E$-values (Fig. 3b) in the acetonitrile rich composition range.

Quantitative information about the solute-solvent intermolecular interactions and their dependence on temperature can be obtained from the limiting excess partial molar volumes ($\overline{V}_i^{E,\infty}$) of each component in the mixture. The optimized Redlich-Kister least squares fitting correlation coefficients for the binary system at a specific temperature (Table-3) have been used to obtain values of the limiting excess partial molar volumes for acetonitrile ($\overline{V}_1^{E,\infty}$) and difurylmethane ($\overline{V}_2^{E,\infty}$) using eqns. 8 and 9[15,16], respectively;

$$\overline{V}_1^{E,\infty} = \sum_{n=even} A_k - \sum_{n=odd} A_k (x_1 \rightarrow 0) \quad (8)$$

$$\overline{V}_2^{E,\infty} = \sum_k A_k \qquad (x_2 \rightarrow 0) \quad (9)$$

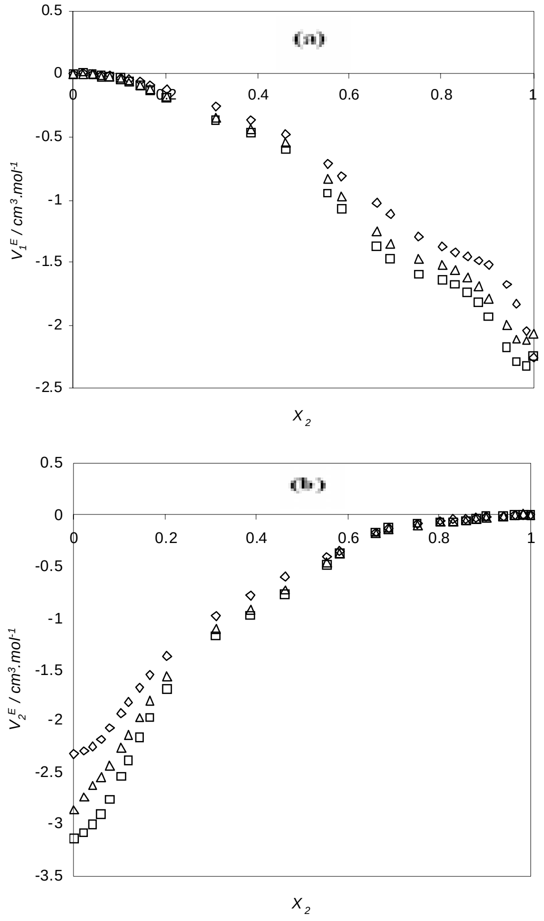

Fig. 3. Excess partial molar volume, $\overline{V}_1^E$ *vs.* $x_2$ for the [difurylmethane (2) + acetonitrile (1)] binary system at: (◇) 288.15 K; (△) 308.15 K and (□) 323.15 K

The $V_i^{E,\infty}$ values have also been calculated *via* apparent molar volumes, $V_{\phi,i}$. The apparent molar volumes of components 1 and 2 can be expressed by Ref.[9,15]:

$$V_{\phi,1} = V_{m,1}^* + (V_m^E/x_1) \tag{10}$$

$$V_{\phi,2} = V_{m,2}^* + (V_m^E/x_2) \tag{11}$$

The graphical extrapolation of $V_{\phi,1}$ to $x_1 = 0$ ($x_2 = 1$) leads to the limiting partial molar volume, $\overline{V}_1^\infty$ and the extrapolation of $V_{\phi,2}$ to $x_2 = 0$ ($x_1 = 1$) leads to the value of $\overline{V}_2^\infty$. Further, the limiting partial molar volume is expressed as $\overline{V}_i^\infty = \overline{V}_i^{E,\infty} + V_{m,i}^*$, from which the $\overline{V}_i^{E,\infty}$ can be derived. Table-4 presents the $V_i^{E,\infty}$ and $\overline{V}_i^\infty$ values at all temperatures investigated for each component in the binary system. It can be observed that the procedures of obtaining $V_i^{E,\infty}$ values by eqns. 8 and 9 or from the extrapolated $V_{\phi,i}$ values of eqns. 10 and 11, lead to comparable magnitudes of $\overline{V}_i^\infty$ values.

TABLE-4
LIMITING EXCESS ($\bar{V}_i^{E,\infty}$) AND PARTIAL ($\bar{V}_I^{\infty}$) MOLAR VOLUMES (cm$^3$ mol$^{-1}$) FOR THE COMPONENTS IN [DIFURYLMETHANE + ACETONITRILE] BINARY SYSTEM FROM 288.15 TO 323.15 K

| T (K) | $\bar{V}_1^{E,\infty}$ from eqn. 8 | $\bar{V}_1^{E,\infty}$ from eqn. 10 | $\bar{V}_1^{\infty}$ | $\bar{V}_2^{E,\infty}$ from eqn. 9 | $\bar{V}_2^{E,\infty}$ from eqn. 11 | $\bar{V}_2^{\infty}$ |
|---|---|---|---|---|---|---|
| 288.15 | -1.935 | -2.045 | 50.189 | -2.310 | -2.430 | 131.911 |
| 293.15 | -2.191 | -2.232 | 50.291 | -2.187 | -1.938 | 132.651 |
| 298.15 | -1.732 | -1.909 | 51.116 | -2.603 | -2.664 | 132.861 |
| 303.15 | -1.732 | -1.802 | 51.487 | -2.265 | -2.290 | 133.830 |
| 308.15 | -2.062 | -2.159 | 51.537 | -2.861 | -2.932 | 133.871 |
| 313.15 | -2.087 | -2.136 | 51.898 | -2.971 | -2.977 | 134.386 |
| 318.15 | -2.646 | -2.450 | 51.734 | -3.001 | -3.088 | 135.027 |
| 323.15 | -2.243 | -2.304 | 52.541 | -3.139 | -3.287 | 135.548 |

At all the temperatures studied negative $\bar{V}_i^{E,\infty}$ values were obtained, indicating that in the infinite diluted solutions of difurylmethane in acetonitrile or in the infinite diluted solutions of acetonitrile in difurylmethane, the solute-solvent interactions are stronger than the intermolecular interactions in the pure component. Such strong interactions would lead to a contraction in volume and therefore a better packing efficiency, on mixing difurylmethane with acetonitrile. Thus the negative $\bar{V}_i^{E,\infty}$ values are consistent with the stronger acetonitrile-difurylmethane dipole-dipole interaction and a more efficient interstitial accommodation of acetonitrile molecules into cavities of the difurylmethane liquid structure. These observations render further support to the observed negative $V_m^E$ values for this binary system.

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