



Isentropic Compressibility and Volumetric Properties of [Difurylmethane + (Acetonitrile or Propionitrile or Benzonitrile)] Binary Mixtures at 298.15 K

WILFRED A.A. DDAMBA

Department of Chemistry, University of Botswana, Private Bag 0022, Gaborone, Botswana

Corresponding author: E-mail: ddambawa@mopipi.ub.bw

(Received: 5 October 2011;

Accepted: 15 June 2012)

AJC-11598

Densities (ρ) and speed sound (u) of binary systems of difurylmethane (DFM) with acetonitrile (ACN), benzonitrile (BCN) or propionitrile (PCN) have been measured over the entire composition range at 298.15 K and atmospheric pressure. Excess isentropic compressibilities (κ_s^E), and excess ultrasonic speeds, u^E , of [DFM + (ACN or BCN or PCN)] and excess molar volumes (V_m^E), of [DFM + (BCN or PCN)] binary systems were determined and correlated by the Redlich-Kister equation. The results have been discussed in terms of possible intermolecular interactions and structural effects.

Key Words: Difurylmethane, Acetonitrile, Propionitrile, Benzonitrile, Binary mixtures, Excess molar volume, Isentropic compressibilities, Excess isentropic compressibilities, Dipole-dipole interactions.

INTRODUCTION

In previous investigations¹⁻⁴, we have reported results of studies of the volumetric properties of the [difurylmethane + an alkan-1-ol]¹⁻³ and [difurylmethane + acetonitrile]⁴ binary systems in the temperature range between 288.15 and 308.15 K. Such studies contribute to the understanding of the intermolecular interactions existing between the various species in a solution and provide information about changes with respect to composition, in the packing efficiencies that take place in solution during the mixing process. As an extension of the studies on thermodynamic properties of binary systems containing difurylmethane as one of the components, we now report in this paper the measurements of density (ρ) and ultrasonic speeds (u), for [difurylmethane + (acetonitrile or benzonitrile or propionitrile)] binary systems, over the entire composition range at 298.15 K and atmospheric pressure. Acetonitrile, benzonitrile and propionitrile molecules are highly polar⁵⁻⁷ with their dipoles oriented antiparallel to each other. Therefore a strongly associated liquid structure results from the dipole-dipole interactions for each of these nitriles^{8,9}. Difurylmethane is an aprotic liquid which is assumed to be a typical example of a pure dipolar fluid³. Since hydrogen bonding is absent, the liquid structure of difurylmethane is determined by the dipole-dipole interactions between molecules. Therefore for solutions of difurylmethane dissolved in acetonitrile or benzonitrile or propionitrile, dipole-dipole association complexes may be expected to be formed. The present studies on [difurylmethane

+ (acetonitrile or benzonitrile or propionitrile)] binary systems are aimed at providing information on the mixtures with a view to understand the nature of possible intermolecular interactions in these solutions. Using these data, excess molar volumes (V_m^E), excess ultrasonic speeds (u^E) and excess isentropic compressibility (κ_s^E) have been calculated and correlated with the Redlich-Kister polynomial¹⁰ of an appropriate degree for each binary system. Trends in the excess functions: (V_m^E , u^E and κ_s^E) with changes in composition provided qualitative assessment of [difurylmethane + (acetonitrile or benzonitrile or propionitrile)] solution behaviour. A comparison of these excessive properties for the mixtures studied is presented in this paper.

EXPERIMENTAL

The three nitriles used in this study *i.e.*, acetonitrile (purity 99 %), benzonitrile (purity 99+%) and propionitrile (purity 99.5 %) were purchased from Aldrich. Each nitrile was first dried and distilled over anhydrous phosphorus pentoxide P_2O_5 (Merck, P.A.) as described elsewhere¹¹. The purity of the chemicals was assessed by measuring their densities and ultrasonic speeds. There was close agreement between the experimental values and values cited in literature (Table-1). Water required for the densimeter calibration was first deionized by means of ion exchange resins and then doubly distilled over $KMnO_4$ under nitrogen. Its conductivity was always less than $1.0 \times 10^{-6} S cm^{-1}$. Difurylmethane was prepared as described elsewhere¹² and its purity was confirmed by ¹H NMR, density

TABLE-1
VALUES OF DENSITY, ρ (g cm^{-3}), ULTRASONIC VELOCITIES, u (m s^{-1}), ISOBARIC EXPANSIVITY, α (10^{-4} K^{-1})
AND HEAT CAPACITY, C_p ($\text{J mol}^{-1} \text{ K}^{-1}$) FOR PURE LIQUIDS AT 298.15 K

Compound	ρ_{exptl}	ρ_{lit}	u_{exptl}	U_{lit}	α	C_p
Acetonitrile	0.77681	0.77649 ^a	1283.4	1283 ^b	1.4160 ^a	91.46 ^a
Propionitrile	0.77666	0.77682 ^a	1263.8	1265 ^c	12.9184 ^a	119.7 ^a
Benzonitrile	1.00041	1.00030 ^d	1402.3	1418 ^c	8.9972 ^a	190.3 ^a
Difurylmethane	1.09091	1.09088 ^c	1369.2	–	9.2733 ^f	256 ^g

^aRef. [11]; ^bRef. [13]; ^cRef. [16]; ^dRef. [14]; ^eRef. [15]; ^fCalculated from ρ data, Refs. [1,3]; ^gEstimated in this work from additivity rules.

measurements and elemental analyses. All purified organic liquids were stored in brown glass bottles and fractionally distilled shortly before use.

The [difurylmethane + (acetonitrile or benzonitrile or propionitrile)] binary mixtures were prepared by weighing appropriate amounts of the purified difurylmethane and nitrile on a Sartorius Supermicro balance (Fabr.-Nr., $\Delta m = \pm 10^{-6}$ g) by syringing each component into Teflon stoppered flasks in order to minimize preferential evaporation. Pure components were separately degassed by ultrasound shortly before sample preparations. This procedure eliminated possible changes in mixture composition that could occur during the degassing of already prepared binary mixtures. All mixtures were completely miscible over the entire composition range. The uncertainty in solution composition expressed as mole fraction was found to be less than 8×10^{-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 $10^{-5} \text{ g cm}^{-3}$). 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 $\pm 0.01 \text{ K}$. 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 $\pm 0.01 \text{ g m}^{-3}$.

The ultrasonic speeds were measured with uncertainty of $\pm 0.3 \%$ using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi, India), which was first calibrated with triply distilled water (Table-1). The temperature was maintained to within $\pm 0.01 \text{ K}$ by circulating thermostated water around a steel cell fitted with a quartz crystal of 1 MHz. In order to minimize the uncertainty in the wavelength measurements, the number of measured maxima, n , was recorded against the total distance (d), covered by the reflector. Each maximum was recorded with the highest swing of the needle on the micrometer scale for maximum sensitivity. The total distance (d), is given by:

$$d = n\lambda/2 \quad (1)$$

where λ is the wavelength. All plots of d vs. n generated were linear ($r^2 = 1$) with a slope of $\lambda/2$. The frequency of the cell

single-crystal, ν being accurately known (1 MHz), the speed of sound (u), is calculated by using the relation:

$$u = \lambda\nu \quad (2)$$

Each ultrasonic speed value presented in Tables 1 and 2 represents an average of u values deduced from four independently determined λ values for pure components and [difurylmethane + (acetonitrile or propionitrile or benzonitrile)] binary compositions.

RESULTS AND DISCUSSION

Experimental density, ρ and ultrasound speeds, u for pure ACN, PCN, BCN and DFM at 298.15 are listed in Table-1, together with the literature data. The agreement, within the experimental uncertainties between the measured and literature values at 298.15 K confirmed the purity of the chemicals used as well as the accuracy of the equipment and the experimental procedure. The experimental densities and ultrasound speeds for [DFM + (ACN or PCN or BCN)] binary mixtures, as a function of composition at 298.15 K are listed in Table-2.

To the best of our knowledge, no density measurements or ultrasound speeds of these binary systems have ever been published. These densities and ultrasound speeds cover the entire composition range of the binary mixtures, as expressed by the mole fraction x_2 of difurylmethane.

Excess molar volumes, V_m^E , were calculated for each of the [DFM + (PCN or BCN)] binary composition from density measurements according to the following equation:

$$V_m^E = V_m - V_m^{id} = M/\rho - \sum x_i M_i/\rho_i^* \quad (3)$$

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 ρ_i^* are respectively the mole fraction, the molar mass and the density of the pure liquid component 'i'.

The value of the excess isentropic compressibility, κ_s^E was calculated by using the following standard relation¹⁷⁻²¹:

$$\kappa_s^E = \kappa_s - \kappa_s^{id} \quad (4)$$

where the value of κ_s is calculated from Newton-Laplace equation¹⁸ using the experimental ρ and u -data:

$$\kappa_s = (r.u^2)^{-1} = -1/V_m(\partial V_m/\partial P)_s \quad (5)$$

The ideal isentropic compressibility, κ_s^{id} values are calculated from the following relations:

$$\kappa_s^{id} = \sum \phi_i [\kappa_{s,i}^* + T V_i^* (\alpha_{p,i}^*)^2 / C_{p,i}^*] - T(\sum x_i V_i^*) (\sum \phi_i \alpha_{p,i}^*)^2 / (\sum x_i C_{p,i}^*) \quad (6)$$

Here ϕ_i is the ideal volume fraction ($= x_i V_i^* / V_m^{id}$) of the component, $C_{p,i}^*$, $\alpha_{p,i}^*$, V_i^* are molar heat capacity at constant

TABLE-2
 EXPERIMENTAL DENSITIES, ρ , ULTRASONIC SPEEDS, u , ISENTROPIC COMPRESSIBILITY, κ_s , WITH EXCESS
 ULTRASONIC SPEED, u^E AND EXCESS ISENTROPIC COMPRESSIBILITY, κ_s^E FOR [DIFURYL METHANE +
 (ACETONITRILE or BENZONITRILE or PROPIONITRILE)] AND EXCESS MOLAR VOLUME, V_m^E , FOR
 [DIFURYL METHANE + (BENZONITRILE or PROPIONITRILE)] BINARY MIXTURES AT 298.15 K

x_2	ρ (kg m ⁻³)	u (m s ⁻¹)	u^E (m s ⁻¹)	κ_s (m ² N ⁻¹)	κ_s^E (m ² N ⁻¹)	V_m^E (cm ³ mol ⁻¹)
Difurylmethane + Benzonitrile						
0.00000	1000.41	1402.0	0.000	5.0854	0.000	0.000
0.01995	1003.06	1410.2	9.154	5.0131	-0.067	-0.030
0.03924	1005.41	1413.6	13.460	4.9774	-0.098	-0.039
0.06100	1008.11	1414.6	15.463	4.9571	-0.113	-0.058
0.08134	1010.55	1416.4	18.184	4.9325	-0.133	-0.072
0.10174	1013.23	1417.0	19.691	4.9153	-0.145	-0.113
0.15023	1019.18	1417.5	22.282	4.8832	-0.166	-0.177
0.19745	1024.62	1417.6	24.337	4.8566	-0.181	-0.220
0.25043	1030.31	1417.3	26.139	4.8318	-0.194	-0.242
0.30395	1035.90	1417.2	28.071	4.8064	-0.208	-0.266
0.35040	1040.58	1415.0	27.565	4.7997	-0.205	-0.284
0.39930	1045.35	1413.0	27.281	4.7913	-0.203	-0.298
0.45064	1050.01	1410.2	26.213	4.7890	-0.195	-0.291
0.51036	1055.13	1405.6	23.544	4.7970	-0.176	-0.267
0.55121	1058.45	1403.5	22.715	4.7963	-0.169	-0.241
0.59939	1062.14	1401.2	21.866	4.7953	-0.161	-0.195
0.65025	1066.15	1397.2	19.343	4.8047	-0.143	-0.172
0.69104	1069.25	1393.6	16.889	4.8155	-0.125	-0.149
0.75026	1073.56	1390.4	15.294	4.8183	-0.112	-0.107
0.80567	1077.47	1387.0	13.337	4.8244	-0.097	-0.067
0.85104	1080.36	1382.6	10.079	4.8422	-0.072	-0.007
0.89990	1083.58	1378.4	7.070	4.8572	-0.049	0.035
0.95014	1087.02	1373.8	3.655	4.8743	-0.024	0.053
0.97221	1088.73	1371.8	2.163	4.8809	-0.014	0.032
1.00000	1090.91	1369.0	0.000	4.8911	0.000	0.000
Difurylmethane + Propionitrile						
0.00000	776.71	1263.8	0.000	8.0609	0.000	0.000
0.03157	796.18	1266.8	3.073	7.8266	-0.048	-0.092
0.04658	805.07	1270.6	6.676	7.6940	-0.096	-0.136
0.07706	822.40	1277.0	12.273	7.4565	-0.167	-0.219
0.12989	850.25	1285.0	17.804	7.1227	-0.233	-0.344
0.17146	870.37	1291.8	21.882	6.8851	-0.276	-0.422
0.21666	890.63	1301.1	27.606	6.6325	-0.331	-0.489
0.24898	904.21	1306.0	29.624	6.4840	-0.346	-0.528
0.33733	937.94	1320.2	34.887	6.1171	-0.379	-0.606
0.41491	964.03	1333.6	39.509	5.8326	-0.403	-0.646
0.48568	985.31	1342.1	39.493	5.6345	-0.385	-0.652
0.55241	1003.38	1349.6	38.661	5.4717	-0.362	-0.625
0.67151	1031.53	1357.6	31.361	5.2599	-0.276	-0.504
0.77340	1052.53	1361.5	21.968	5.1254	-0.186	-0.381
0.84815	1066.57	1364.4	15.097	5.0365	-0.126	-0.298
0.90224	1075.72	1366.5	10.146	4.9783	-0.082	-0.196
0.93242	1080.51	1367.0	6.726	4.9526	-0.054	-0.129
0.95104	1083.41	1367.8	5.113	4.9336	-0.040	-0.089
0.98112	1088.02	1368.4	1.825	4.9084	-0.014	-0.029
1.00000	1090.91	1369.0	0.000	4.8911	0.000	0.000
Difurylmethane + Acetonitrile						
0.00000	776.81	1283.4	0.000	7.8156	0.000	-
0.02212	794.95	1283.8	1.169	7.6325	-0.022	-
0.04189	810.14	1286.0	3.562	7.4637	-0.056	-
0.05841	822.16	1288.6	6.023	7.3250	-0.088	-
0.07914	836.43	1292.0	8.921	7.1622	-0.124	-
0.10630	853.87	1298.4	14.205	6.9469	-0.184	-
0.14432	876.17	1305.0	18.560	6.7018	-0.229	-
0.20363	906.66	1314.3	23.234	6.3851	-0.271	-
0.31360	952.68	1330.3	28.645	5.9314	-0.305	-
0.38449	976.91	1339.9	30.802	5.7016	-0.312	-
0.46363	999.89	1346.8	29.252	5.5137	-0.285	-
0.57248	1026.02	1353.8	24.771	5.3178	-0.232	-
0.70015	1050.44	1358.7	16.769	5.1568	-0.152	-
0.79597	1065.49	1362.2	11.106	5.0579	-0.098	-
0.85779	1074.07	1364.6	7.847	4.9998	-0.068	-
0.88705	1077.87	1365.6	6.239	4.9749	-0.054	-
0.92571	1082.63	1366.6	3.861	4.9458	-0.034	-
0.94425	1084.82	1367.1	2.768	4.9322	-0.024	-
0.96253	1086.81	1367.7	1.816	4.9189	-0.016	-
0.98123	1088.81	1368.3	0.845	4.9055	-0.007	-
1.00000	1090.91	1369.0	0.000	4.8911	0.000	-

pressure, the thermal expansivity and the molar volume of a pure components. The corresponding mixing quantities $C_{p,m}^{id}$, α_p^{id} and V_m^{id} of the ideal mixtures are calculated from the following relations:

$$C_{p,m}^{id} = \sum x_i C_{p,i}^*; \alpha_p^{id} = \sum \phi_i \alpha_{p,i}^*; V_m^{id} = \sum x_i V_i^* \quad (7)$$

The values of α_p^* and C_p^* for pure ACN, BCN and PCN liquids at 298.15 K were taken from the literature¹¹. The value of α_p^* for difurylmethane was calculated from the temperature dependence of the density data by using the relation, $(-1/\rho)(\partial\rho/\partial T)_p$, while the corresponding value of heat capacity, C_p^* at 298.15 K was estimated using additivity rules²²⁻²⁴.

The value of the excess ultrasonic speed, u^E , was calculated by using the following relation:

$$u^E = u - u^{id} = u - (\rho^{id} \kappa_s^{id})^{-1/2} = [V_m^{id}/M_m \kappa_s^{id}]^{1/2} \quad (8)$$

where u^{id} is the ultrasonic speed in the ideal mixture and ρ^{id} is ideal density ($= \sum \phi_i \rho_i^*$) of ideal mixture, V_m^{id} is the ideal molar volume ($= \sum x_i V_i^*$) and M_m is molar mass of the binary mixture ($= \sum x_i M_i^*$).

The values of the functions (V_m^E , u^E and κ_s^E) for each of the [DFM + (ACN or BCN or PCN)] systems were least-squares fitted to the Redlich-Kister¹⁰ polynomial regressions of the type:

$$(V_m^E, u^E \text{ and } \kappa_s^E = x_1 x_2 \sum_{k=0}^n A_k (1 - 2x_2)^k \quad (9)$$

where the subscripts 1 and 2 stand for the pure nitrile and pure difurylmethane respectively. All points in these polynomial were weighted equally and the regression coefficients A_k in eqn. 9 were evaluated by the least-squares method and are listed in Table-3.

In each case, the optimum number, m , of the A_k coefficients ($m = n + 1$) was determined through an examination of the variation of standard deviation (σ) defined by the following equation:

$$\sigma(Y^E) = [\sum (Y_{exp}^E - Y_{calc}^E)^2 / (N-n)]^{1/2} \quad (10)$$

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

Fig. 1 displays the experimental V_m^E vs. x_2 data for each of the [DFM + (BCN or PCN)] binary systems at 298.15 K. Fig. 2(a) and (b) depict the κ_s^E vs. x_2 and u^E vs. x_2 data for [DFM + (ACN or BCN or PCN)] binary systems at 298.15 K.

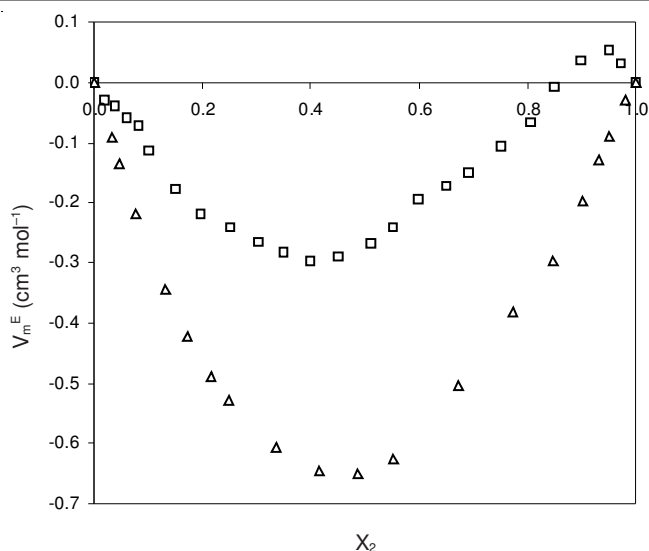


Fig. 1. Excess molar volumes, V_m^E vs. x_2 for the [DFM (2) + nitrile (1)] binary mixtures: (□) BCN; (△) PCN at 298.15 K

The magnitude and sign of excess thermodynamic functions such as V_m^E , κ_s^E and u^E measure the deviation from ideal behaviour and are sensitive to intermolecular interactions between component molecules of the mixture. These deviations arise from chemical, physical, structural and dipole-dipole interaction effects. The chemical effects involve the (entropy increasing) rupture of liquid order due to dipole-dipole association in the pure components, which contribute positively to V_m^E and κ_s^E and negatively to u^E . Physical contributions comprise non-specific unfavourable interactions between unlike molecules which also contribute positively to V_m^E and κ_s^E and negatively to u^E . Structural effects arise from the restriction of the rotational degrees of freedom due to geometrical interstitial accommodation of liquid components into each other's cavities (clathrate formation), due to differences in molar masses, shape and free volumes of pure components and they contribute negatively to V_m^E and κ_s^E and positively to u^E . Presence of specific dipole-dipole interactions between unlike component molecules also contribute negatively to V_m^E and κ_s^E and positively to u^E .

The V_m^E curve for [DFM + PCN] mixtures (Fig. 1) displays a negative deviation over the entire composition range, and is qualitatively similar to the V_m^E variation reported previously

TABLE-3
LEAST SQUARES FITTED A_i COEFFICIENTS FROM EQUATION (9) FOR κ_s^E ($10^{10} \text{ m}^2 \text{ N}^{-1}$) AND u^E (m s^{-1}) FOR [DIFURYLMETHANE + (ACETONITRILE or BENZONITRILE or PROPIONITRILE)], V_m^E ($\text{cm}^3 \text{ mol}^{-1}$) FOR [DIFURYLMETHANE + (BENZONITRILE or PROPIONITRILE)] BINARY MIXTURES AND CORRESPONDING STANDARD DEVIATIONS OF THE FITS, $\sigma(Y^E)$ AT 298.15 K

Y^E	A_0	A_1	A_2	A_3	A_4	A_5	$\sigma(Y^E)$
Difurylmethane + Benzonitrile							
V_m^E	-1.048	-0.888	0.033	0.800	1.475	-1.428	0.009
κ_s^E	-0.744	-0.567	-0.056	1.044	-0.807	-1.907	0.006
u^E	100.100	75.750	7.330	-145.080	118.530	260.860	0.830
Difurylmethane + Propionitrile							
V_m^E	-2.560	-0.662	0.120	0.398	-0.265	-0.377	0.009
κ_s^E	-1.526	-0.631	0.234	-0.600	-0.308	0.633	0.007
u^E	158.300	17.560	64.020	60.910	39.470	-68.470	0.670
Difurylmethane + Acetonitrile							
κ_s^E	-1.058	-1.019	-0.484	0.367	-0.566	—	0.008
u^E	110.600	82.300	9.790	-55.830	51.560	—	0.730

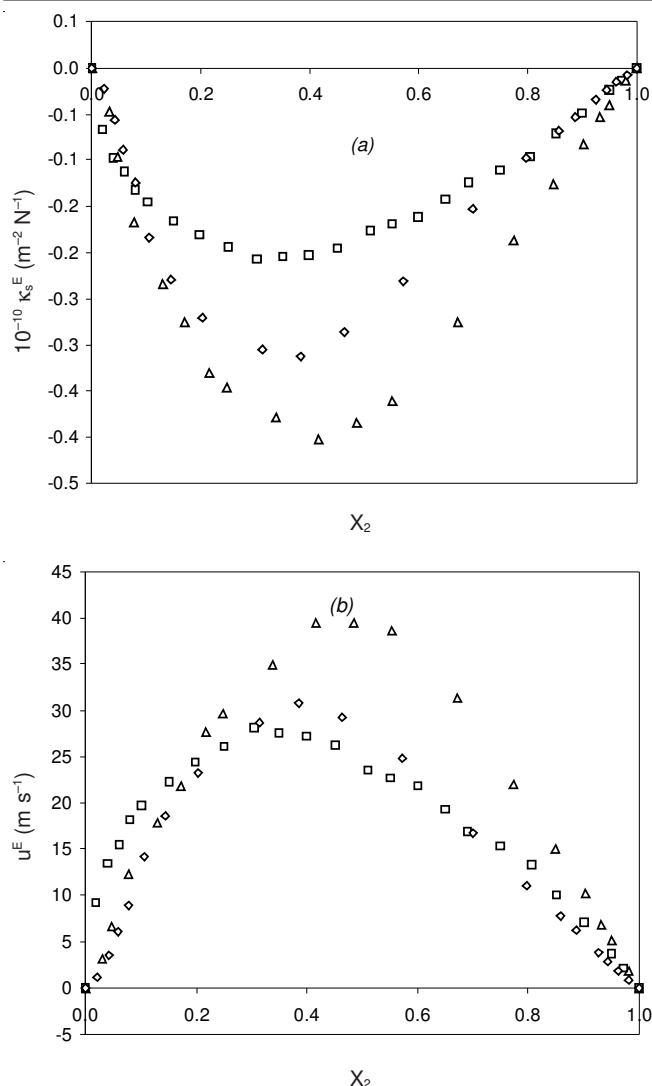


Fig. 2. Excess isentropic compressibility, κ_s^E vs. x_2 (a) and excess ultrasonic speeds, u^E vs. x_2 (b) for the [DFM (2) + nitrile (1)] binary mixtures: (\diamond) ACN; (\square) BCN; (\triangle) PCN at 298.15 K

for the [DFM + ACN] binary system⁴. The negative V_m^E -values indicate completely miscible systems and suggest formation of specific strong dipole-dipole interactions between the -CN groups in the nitrile and the polarized π -electron of the DFM furan ring system. A further contribution to negative V_m^E -values would be due to the geometrical interstitial fitting of DFM and the nitrile molecules into cavities of each other's liquid structure which more than offsets the positive contributions from the entropy increasing dispersive physical effects. The V_m^E values for [DFM + BCN] binary system present a sigmoidal shaped behaviour, with negative deviation limited to $0.00 \leq x_2 \leq 0.85$ and positive deviation over the remaining composition range. The sigmoidal behaviour in the excess thermodynamic function is the resultant of several opposing effects as was suggested by Treszczanowicz *et al.*²⁵. At lower DFM concentrations, negative V_m^E values can be attributed to predominance of DFM-BCN, dipole-dipole intermolecular interactions and geometrical interstitial accommodation of DFM molecules within the liquid structure of BCN. The positive V_m^E values observed at $x_2 \geq 0.85$ for this binary mixture, may be arising from the positive contributions from the

dispersive physical effects. The algebraic value of the minimum excess molar volume, $V_m^E(\text{min.})$, fall in the sequence: BCN > ACN⁴ > PCN and were $\approx -0.298 \text{ cm}^3 \text{ mol}^{-1}$ (at $x_2 = 0.40$), $-0.59 \text{ cm}^3 \text{ mol}^{-1}$ (at $x_2 = 0.55$)⁴ and $-0.652 \text{ cm}^3 \text{ mol}^{-1}$ (at $x_2 = 0.485$), respectively.

The experimental excess isentropic compressibility, κ_s^E vs. x_2 and excess ultrasonic speed, u^E vs. x_2 data are presented in Figs. 2(a) and 2(b), respectively. The κ_s^E values are negative over the entire x_2 -range, while u^E data show similar trend as observed in κ_s^E but with opposite sign for the three binary systems. Negative κ_s^E and positive u^E values suggest that the [DFM + (ACN or BCN or PCN)] binary mixtures are less compressible than the corresponding ideal mixtures. It is further observed that for each binary system, the mole fractions $x_2(\kappa_s^E)$, where the minima of κ_s^E occur are shifted to smaller values than the corresponding $x_2(V_m^E)$ for V_m^E -values. It is also noticeable that the sequence of the κ_s^E -curves is the same with that of V_m^E data (Fig. 1), with the algebraic value of the function, $\kappa_s^E(\text{min.})$, falling in the sequence: BCN > ACN > PCN and were $\approx -2.08 (10^{11} \text{ m N}^{-1})$ at $x_2 = 0.30$, $-3.12 (10^{11} \text{ m N}^{-1})$ at $x_2 = 0.38$ and $-4.03 (10^{11} \text{ m N}^{-1})$ at $x_2 = 0.41$, respectively. Thus the same sequence observed in the plots for the excess functions; (V_m^E , κ_s^E), (Figs. 1 and 2(a)), may suggest that similar factors contribute to the interactions between unlike molecules of these binary mixtures.

Conclusion

The densities (ρ) and ultrasonic speeds (u) for binary systems: [DFM + (ACN or BCN or PCN)], have been measured over the entire composition range at 298.15 K and atmospheric pressure. The excess of molar volume, V_m^E , for [DFM + (BCN or PCN)] and the excess ultrasonic properties; (κ_s^E , u^E) for [DFM + (ACN or BCN or PCN)] binary mixtures have been calculated and correlated to the Redlich-Kister polynomial. The three excess properties; (V_m^E , κ_s^E and u^E) suggest that there may be weak intermolecular interactions and that the interstitial accommodation play a role in the three studied binary mixtures.

ACKNOWLEDGEMENTS

The financial support by University of Botswana is gratefully acknowledged.

REFERENCES

- O. Mokate and W.A.A. Ddamba, *J. Sol. Chem.*, **34**, 1327 (2005).
- O. Mokate and W.A.A. Ddamba, *J. Sol. Chem.*, **35**, 1493 (2006).
- O. Mokate and W.A.A. Ddamba, *J. Sol. Chem.*, **37**, 331 (2008).
- W.A.A. Ddamba, *Asian J. Chem.*, **21**, 3057 (2009).
- A.D. Buckingham, E. Lippert and S. Bratos, *Organic Liquids: Structure, Dynamics and Chemical Properties*, Wiley Interscience, Chichester, UK, Ch. 17 (1978).
- Y. Marus, *Introduction to Liquid State*, Wiley Interscience, New York (1977).
- A.K. Nain, *J. Chem. Thermodyn.*, **38**, 1362 (2006).
- R.B. T6rres, M.I. Ortolan and P.L.O. Volpe, *J. Chem. Thermodyn.*, **40**, 442 (2008).
- A. Ali, A.K. Nain and Abida, *J. Chin. Chem. Soc.*, **51**, 477 (2004).
- O. Redlich and T.A. Kister, *Ind. Eng. Chem.*, **40**, 345 (1948).
- J.A. Riddick, W.B. Bunger and T.K. Sakano, *Organic Solvents: Physical Properties and Methods of Purification*, Wiley Interscience, New York, edn. 4 (1986); A.I. Vogel, *Text Book of Practical Organic Chemistry*, Longman & Green, London, edn. 5 (1989).

12. S.L. Buchwalter, *J. Polym. Sci.*, **23**, 2897 (1985).
13. S.J. Tangeda, S. Boodida and S. Nallani, *J. Chem. Thermodyn.*, **38**, 1438 (2006).
14. E.C. Iglesias, R. Bravo, M. Pinto, A. Amigo, A.H. Roux and G. Roux-Desgranges, *J. Chem. Thermodyn.*, **39**, 561 (2007).
15. D.G. Singh, R. Singh, H. Anand and J.K. Puri, *J. Molecul. Liq.*, **98-99**, 15 (2002).
16. S.K. Mehta and A.K. Sharma, *Fluid Phase Equilib.*, **205**, 37 (2003).
17. G. Douheret, M.I. Davis and H. Hoiland, *J. Molecul. Liq.*, **80**, 1 (1999).
18. G.C. Benson and O. Kiyohara, *J. Chem. Thermodyn.*, **11**, 1061 (1979).
19. G. Deuheret, M.I. Davis, J.C.R. Reis and M.J. Blandamer, *Chem. Phys. Chem.*, **2**, 149 (2001).
20. G. Deuheret, M.I. Davis and J.C.R. Reis, *Fluid Phase Equilib.*, **231**, 246 (2005).
21. A.F.S.S. Mendoca, F.A. Dias and I.M.S. Lampreia, *J. Sol. Chem.*, **36**, 13 (2007).
22. R. Shaw, *J. Chem. Eng. Data*, **14**, 461 (1969).
23. S.W. Sidney, F.R. Cruickshank, D.M. Golden, G.R. Haugen, H.E. O'Neal, A.S. Rodgers, R. Shaw and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).
24. T.M. Reid, J.M. Prausnitz and B.E. Poling, *The Properties of Gases and Liquids*, McGraw Hill, New York, edn. 4 (1987).
25. A.J. Treszczanowicz, O. Kiyohara and G.C. Benson, *J. Chem. Thermodyn.*, **13**, 253 (1981).