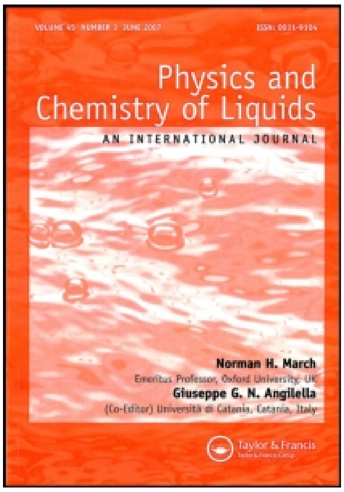

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Thermodynamic and acoustical studies of binary mixtures of diethyl malonate at 308.15K

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Thermodynamic and acoustical studies of binary mixtures of diethyl malonate at 308.15 K

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The density, viscosity, refractive index and speed of sound of binary mixtures of diethyl malonate with 1,4-dioxane, dimethyl formamide, tetrahydrofuran and hexane were measured at 308.15 K. Various acoustical and thermodynamic parameters were evaluated using these experimental data and the results have been explained on the basis of molecular interactions and geometric effects of the components in the mixture.

Keywords: Diethyl malonate; Viscosity; Refractive index; Ultrasonic velocity; Density

1. Introduction

Diethyl malonate is used in synthesis of vitamin B1 and B6, barbiturates and numerous other pharmaceuticals, agro chemicals and industry of flavours and fragrances compounds. A literature survey shows that although much work has been reported for various binary systems [1–5], no such data are available for binary mixtures of diethyl malonate. Thus, in the present work, acoustical properties of four binary solutions of diethyl malonate with 1,4-dioxane, dimethylformamide (DMF), tetrahydrofuran (THF) and hexane have been studied by measuring the density, viscosity, refractive index and ultrasonic velocity at 308.15 K over a wide range of compositions.

2. Experimental

All the liquids used in the present study were purified by standard methods [6]. The mole fraction of purity was better than 0.995 for all these liquids and they were stored in an inert atmosphere. The experimental values of density, refractive index and sound velocity of pure liquids were compared with those found in literature

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Table 1. Values of density (ρ), viscosity (η), ultrasonic velocity (U) and refractive index (RI) of various pure liquids at 308.15 K.

	Density ρ g cm^{-3}		Viscosity $\eta \times 10^3$ Pa s^{-1}		Velocity $U \times 10^{-5}$ cpm s^{-1}		RI	
Liquid	Obs.	Liter.	Obs.	Liter.	Obs.	Liter.	Obs.	Liter.
1,4-Dioxane	1.0277	1.0279 [6] 1.0280 [9]	0.7922	0.7917 [7]	1.3442	1.3439 [8]	1.4167	1.4191 [9] 1.4192 [10]
DMF	0.9440	0.9439 [6]	0.8130	0.8020 [6]	1.4680	1.4660 [6]	1.4282	1.4281 [6]
Hexane	0.6549	0.6550 [11,12] 0.6551 [14]	0.299	0.2968 [13]	1.0780	1.0768 [12]	1.3722	1.3723 [15]
THF	0.8818	0.8812 [16] 0.8823 [17]	0.463	0.4630 [18] 0.4540 [17]	1.2840	1.2660 [17]	1.4049	1.4047 [17] 1.4049 [9]
Diethyl malonate	1.0387	–	1.3767	–	1.2672	–	1.3950	–

at 308.15 K and are given in table 1. It is evident from table 1 that there is good agreement between the experimental and reported values.

Mixtures of different compositions (v/v) were prepared for each binary system in airtight bottles. The density, ultrasonic velocity, viscosity and refractive index of pure solvents and liquid mixtures were measured at 308.15 K by using a pyknometer, the single frequency interferometer operating at 2 MHz, an Ubbelohde viscometer and Abbe refractometer with an accuracy of 0.0001 g cm^{-3}, ±0.01%, ±0.06% and 0.0005, respectively. The uncertainty of temperature is ±0.1 K and that of concentration is 0.0001 mol dm^{-3}.

3. Results and discussion

From the experimental data, various acoustical parameters were evaluated using the following standard equations:

Adiabatic compressibility (κ_s): $\kappa_s = 1/(U^2\rho)$,
where U is the speed of sound and ρ the density of solution.
Intermolecular length (L_f): $L_f = K_j \kappa_s^{1/2}$,
where K_j is Jacobson's constant ($=6.0816 \times 10^4$).
Relaxation strength (r): $r = 1 - (U/U_\infty)^2$, where $U_\infty = 1.6 \times 10^5$ cm s^{-1}.
Rao's molar sound function (R_m): $R_m = (M/\rho)U^{1/3}$,
where M is the molecular weight of the solution.
Van der Waals constant (b): $b = (M/\rho)(1 - RT/MU^2(\sqrt{(1 + MU^2/3RT)} - 1))$,
where R is the gas constant and T is the absolute temperature.
Molar compressibility (W): $W = (M/\rho)\kappa_s^{-1/7}$.
Internal pressure (π): $\pi = bRT(K\eta/U)^{1/2}(\rho^{2/3}/M^{7/6})$,
where b is the packing constant (=2), K is also a constant ($=4.28 \times 10^9$), η is the viscosity of the solution and other symbols have their usual significance.
Free volume (V_f): $V_f = [(MU)/(K\eta)]^{3/2}$.

Some of these parameters are given in table 2. The plots of ultrasonic velocity (U) and adiabatic compressibility (κ_s) against X_{DEM} for these systems are shown in figures 1 and 2, respectively. Comparison of these two figures shows that ultrasonic

Table 2. Acoustical parameters for the four binary liquid mixtures at 308.15 K.

X_{DEM}	Viscosity $\eta \times 10^3$	L_f	r	R_m	b	$W \times 10^{-3}$	π	V_f
DO								
0.0000	9.6420	0.4565	0.3218	4387.372	79.9436	0.0674	494.8045	0.1492
0.0968	10.5074	0.4618	0.3386	4703.081	87.3703	2.6936	476.3576	0.1443
0.1943	10.7898	0.4629	0.3431	5035.144	93.7915	2.8851	445.5162	0.1535
0.2524	10.9958	0.4638	0.3460	5235.201	97.6738	3.0002	429.7647	0.1580
0.3601	11.7629	0.4632	0.3483	5578.892	104.3116	3.2004	411.5029	0.1583
0.4840	13.1800	0.4661	0.3576	5990.867	112.4412	3.4387	400.8136	0.1478
0.6280	13.8419	0.4675	0.3626	6478.576	121.9550	3.7201	374.8023	0.1542
0.7975	14.4792	0.4680	0.3661	7038.962	132.8674	4.0446	347.4250	0.1637
0.8941	14.9628	0.4695	0.3711	7353.837	139.1111	4.2273	335.4745	0.1661
DMF								
0.0000	6.2295	0.4293	0.1702	4109.443	68.4532	2.3140	490.1155	0.2526
0.1130	7.5979	0.4409	0.2276	4481.387	81.1663	2.5344	438.3392	0.2148
0.1935	8.1642	0.4467	0.2573	4766.960	86.9909	2.7034	421.0051	0.2114
0.3200	9.1358	0.4490	0.2799	5233.139	96.1824	2.9772	396.6999	0.2076
0.3935	9.6121	0.4555	0.3012	5509.281	101.8407	3.1389	382.8914	0.2062
0.4974	10.9020	0.4538	0.3054	5888.897	109.1553	3.3620	374.9165	0.1919
0.6175	11.0441	0.4571	0.3200	6552.954	118.3486	3.6322	344.6549	0.2107
0.7280	11.8982	0.4588	0.3321	6740.849	126.1022	3.8616	332.3552	0.2075
0.8210	12.5538	0.4644	0.3524	7058.844	132.8086	4.0504	323.0338	0.2040
0.9244	12.9720	0.4674	0.3640	7435.388	140.4460	4.2717	308.5314	0.2097
THF								
0.0000	3.8237	0.5205	0.3935	4112.881	75.3984	2.3065	365.1900	0.4068
0.0656	4.8717	0.5139	0.3921	4324.160	80.8804	2.4361	383.4714	0.3181
0.1514	5.5620	0.5074	0.3904	4640.071	86.9665	2.6223	373.1007	0.3002
0.2431	6.4471	0.5010	0.3889	4964.807	93.2335	2.8149	366.8947	0.2760
0.3486	7.6052	0.4945	0.3862	5345.092	100.5491	3.0396	361.5928	0.2497
0.4714	8.9278	0.4884	0.3838	5789.709	109.1143	3.3020	353.1392	0.2282
0.5777	10.2307	0.4840	0.3818	6177.004	116.5764	3.5301	347.8524	0.2100
0.7893	13.0336	0.4756	0.3773	6927.810	131.0261	3.9741	338.6006	0.1815
0.8892	13.8082	0.4728	0.3751	7301.208	138.2004	4.1930	326.3831	0.1826
HEX								
0.0000	2.5456	0.7055	0.5623	6134.216	117.9543	3.3344	218.7013	0.7662
0.1051	3.1226	0.6761	0.5553	6269.327	123.1232	3.4404	227.8974	0.6496
0.2137	3.8081	0.6527	0.5501	6430.535	126.3089	3.5575	237.1213	0.5503
0.3072	4.4591	0.6143	0.5150	6638.785	129.3089	3.6905	240.5609	0.5070
0.4035	4.6987	0.5921	0.4894	6978.377	135.1561	3.8868	229.7668	0.5357
0.5026	4.7727	0.5821	0.4718	7458.736	143.9802	4.1511	213.8218	0.5885
0.6048	5.7021	0.5683	0.4692	7591.533	146.6482	4.2504	224.0541	0.4946
0.7102	8.7991	0.5309	0.4571	7205.070	138.9234	4.0980	279.1009	0.2862
0.7979	12.4764	0.5095	0.4465	7104.446	136.7459	4.0754	327.0104	0.1842
0.9088	13.1529	0.4891	0.4031	7552.698	143.9764	4.3287	310.3350	0.1955

velocity is the reverse of adiabatic compressibility. On increasing X_{DEM}, the velocity increases for solutions of DEM + THF and DEM + hexane (DEM + HEX) systems, while adiabatic compressibility gives a proportional decrease. Table 2 shows a decrease in intermolecular free length (L_f) and free volume V_f, which may be caused by a closer packing of molecules in liquid mixtures. Thus, in these two systems, solute–solvent interactions predominate. However, in binary liquid mixtures DEM + dimethyl formamide (DMF) and DEM+ 1,4-dioxane (DO), it is observed that velocity decreases with increase in mole fraction of DEM (X_{DEM}), whereas adiabatic compressibility increases with X_{DEM}. This suggests loose packing of molecules in these systems, which is further confirmed by the increase in intermolecular free length (L_f) values with X_{DEM} in these

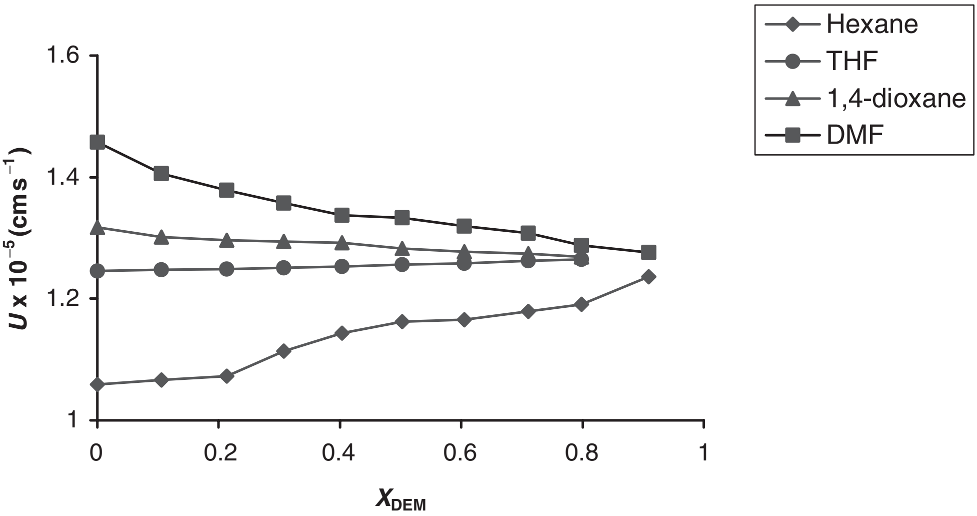

Figure 1. Variation of velocity (U) with composition X_{DEM}.

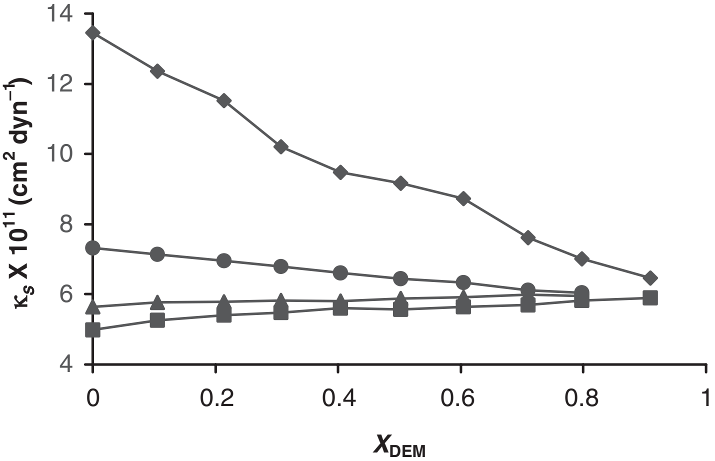

Figure 2. Variation of adiabatic compressibility (κ_s) with X_{DEM}.

two systems (table 2). The loose packing of molecules in these two systems is further supported by increase in free volume and decrease in internal pressure (π) in these two systems (table 2).

For some of the acoustical parameters, the correlation coefficient and correlation equations are given in table 3. The molar compressibility (W), Rao's molar function (R_m) and Van der Waal's constants (b) vary linearly with X_{DEM} for 1,4-dioxane, DMF and THF systems. This is confirmed by the correlation coefficients of these parameters in table 3. However, in the hexane system, non-linear behaviour was observed due to which correlation coefficients for the parameters in this system could not be calculated. The non-linear behaviour indicates the presence of complex formation in the DEM + HEX system.

Table 3. The correlation coefficients (γ) and correlation equations between acoustical parameters and compositions X_{DEM} (C) of the three binary liquid mixtures at 308.15 K.

Parameters	γ	Correlation equation
DEM + THF		
ρ (g cm^{-3})	0.9899	$\rho = 0.8994 + 0.1613C$
U (cm s^{-1})	0.9997	$U = 124596.8 + 2108.396C$
η (Pa s^{-1})	0.9982	$\eta = 0.0038 + 0.0112C$
κ_s (cm^2 dyn^{-1})	0.9876	$\kappa_s = 7.13 \times 10^{-11} - 1.3 \times 10^{-11}C$
L_{f} (A^0)	0.9894	$L_{\mathrm{f}} = 0.5139 - 0.0492C$
r	0.9996	$r = 0.3936 - 0.0207C$
W (cm$^{-19/7}$ dyn$^{1/7}$)	0.9999	$W = 2.2981 \times 10^3 + 2.1287 \times 10^3C$
R_{m} (cm$^{7/3}$ s$^{-1/3}$)	0.9999	$R_{\mathrm{m}} = 4089.77 + 3605.944C$
b (g$^{1/2}$cm^{2}erg$^{1/2}$ s^{-1})	0.9999	$b = 76.3761 + 69.4335C$
π	0.9917	$\pi = 384.0664 - 62.6351C$
DEM+DO		
ρ (g cm^{-3})	0.9804	$\rho = 1.0227 + 0.0228C$
U (cm s^{-1})	0.9921	$U = 130445.7 - 4039.54C$
η (Pa s^{-1})	0.9876	$\eta = 0.0098 + 0.0060C$
κ_s (cm^2 dyn^{-1})	0.9959	$\kappa_s = 5.75 \times 10^{-11} + 2.44 \times 10^{-12}C$
L_{f} (A^0)	0.9874	$L_{\mathrm{f}} = 0.4614 - 0.0091C$
r	0.9917	$r = 0.3354 + 0.0405C$
W (cm$^{-19/7}$ dyn$^{1/7}$)	0.9999	$W = 2.5105 \times 10^3 + 1.9224 \times 10^3$
R_{m} (cm$^{7/3}$ s$^{-1/3}$)	0.9999	$R_{\mathrm{m}} = 4387.459 + 3321.883C$
b (g$^{1/2}$cm^{2}erg$^{1/2}$ s^{-1})	0.9999	$b = 81.1399 + 64.8474C$
π	0.9902	$\pi = 479.4845 - 165.683C$
DEM + DMF		
ρ (g cm^{-3})	0.9918	$\rho = 0.9561 + 0.0990C$
U (cm s^{-1})	0.9905	$U = 141061.4 - 14698.0C$
η (Pas s^{-1})	0.9984	$\eta = 0.0069 + 0.0067C$
κ_s (cm^2 dyn^{-1})	0.9905	$\kappa_s = 5.22 \times 10^{-11} - 7.32 \times 10^{-12}C$‘
L_{f} (A^0)	0.9858	$L_{\mathrm{f}} = 0.4402 - 0.0295C$
r	0.9822	$r = 0.2256 - 0.1539C$
W (cm$^{-19/7}$ dyn$^{1/7}$)	0.9999	$W = 2.2923 \times 10^3 + 2.1486 \times 10^3C$
R_{m}(cm$^{7/3}$ s$^{-1/3}$)	0.9999	$R_{\mathrm{m}} = 4068.75 + 3656.213C$
b (g$^{1/2}$cm^{2}erg$^{1/2}$ s^{-1})	0.9999	$b = 72.9057 + 73.1044C$
π	0.9944	$\pi = 450.5106 - 158.88C$

The variation of refractive index of solutions of these four systems with X_{DEM} is shown in figure 3. It is clear from the figure that refractive index varies linearly with X_{DEM} except in the DEM + HEX system.

Some excess properties have also been calculated using the following equation:

$$A^{\mathrm{E}} = A_{\mathrm{mix}} - [X_1A_1 + X_2A_2]$$

where A^{E} can be any excess property such as excess volume, excess viscosity, refractive index, etc. A_{mix}, A_1 and A_2 are the volume, viscosity or refractive index of the mixture, of pure first constituent and pure second constituent, respectively. X_1 and X_2 are the mole fractions of the first and second constituents, respectively.

Figure 4 shows the variation of excess volume (V^{E}) with X_{DEM} for all the four systems. It can be observed from figure 4 that V^{E} is negative for DEM + THF, which again confirms the contraction of volume in the liquid mixture due to close packing. However, in the DEM + HEX system, initially V^{E} is observed to decrease, then it increases with X_{DEM}. It reaches its maximum around $X_{\mathrm{DEM}} = 0.5026$, and then

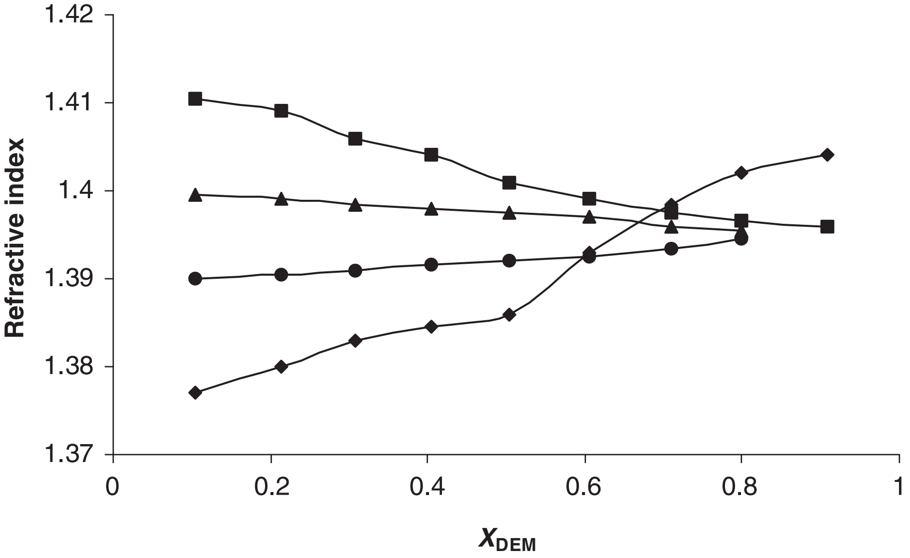

Figure 3. Variation of refractive index with X_{DEM}.

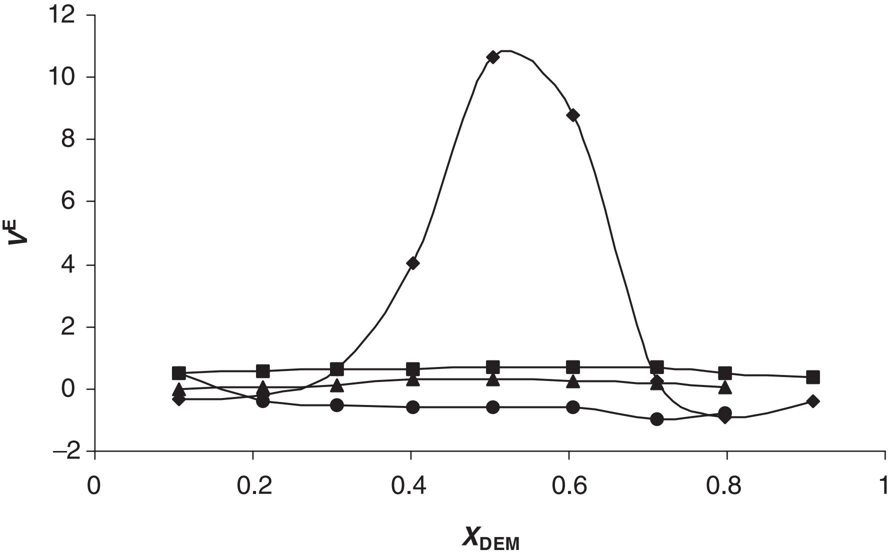

Figure 4. Variation of excess volume with X_{DEM}.

decreases continuously. Comparison of this plot with the velocity figure shows a sudden jump in velocity at around the same X_{DEM}. This is due to a complex formation, which causes an increase in volume in this system. The volume associated with loose structure makes V^{E} shift to the positive side as observed in DEM + DMF and DEM + DO systems due to expansion.

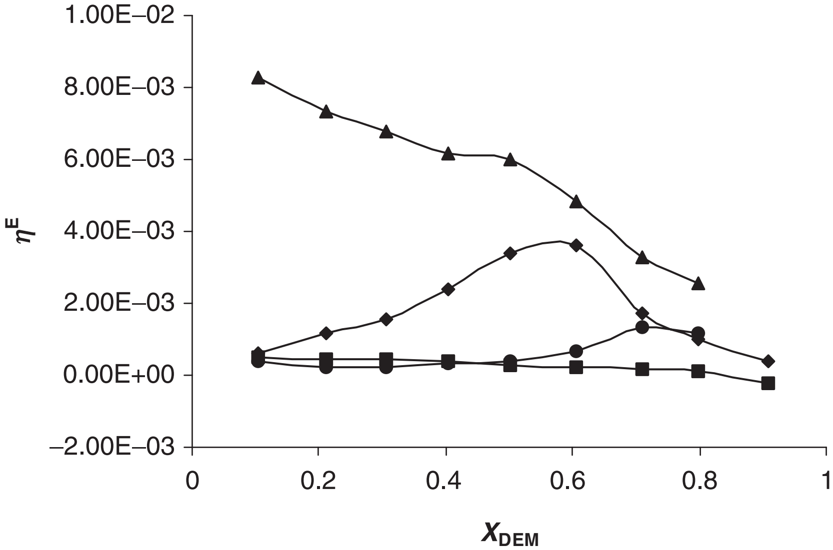

Figure 5. Variation of excess viscosity with X_{DEM}.

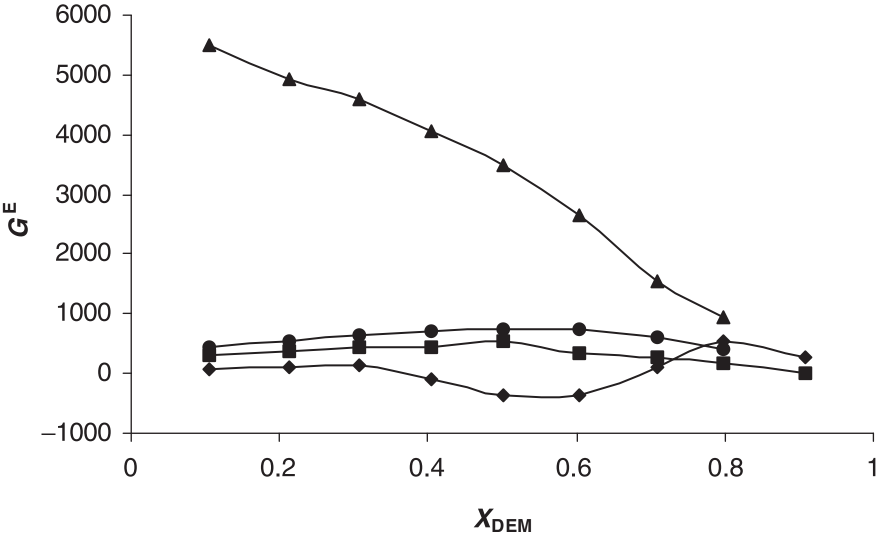

Figure 6. Variation of excess free energy with X_{DEM}.

The minimum and maximum in excess viscosity (η^{E}) curve (figure 5) gives evidence of greater interactions between two liquid molecules as observed in DEM + THF and DEM + HEX systems. The reverse is true for DEM + DO and DEM + DMSO systems in which there is a continuous decrease in excess viscosity values. The excess Gibb's free energy of activation (G^{E}) is positive for all the systems except DEM + HEX, where it becomes negative after $X_{\mathrm{DEM}} = 0.4$. The negative G^{E} i.e., decrease of G^{E} suggests that the process of complex formation is spontaneous and the complex starts dissociating as the free energy is increased (figure 6).

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