Experimental and theoretical studies of transport and optical properties of binary mixtures of acetonitrile with some alkyl methacrylates at temperatures from 298.15 to 318.15 K

P Droliya[a], D Chand[b] & A K Nain[a]*

[a]Department of Chemistry, Dyal Singh College (University of Delhi), New Delhi 110 003, India
[b]Department of Chemistry, Amity University Dubai Campus, Dubai International Academic City, Dubai, UAE

Email: ak_nain@yahoo.co.in

The viscosities, η and refractive indices, n_D of pure acetonitrile, methyl methacrylate, ethyl methacrylate, *n*-butyl methacrylate and of their binary mixtures with acetonitrile as the common component, covering the entire composition range has been measured at temperatures (298.15, 303.15, 308.15, 313.15 and 318.15) K and atmospheric pressure. Using these experimental data, the deviations in viscosity $\Delta\eta$, deviations in refractive index, Δn_D, deviations in molar refraction, ΔR_M have been calculated. These excess properties are correlated by the Redlich-Kister polynomial equation. The variations of $\Delta\eta$, Δn_D and ΔR_M with composition and temperature has been discussed in terms of intermolecular interactions existing in these mixtures. Further, the viscosities and refractive indices of these binary mixtures have been calculated theoretically by using various empirical and semi-empirical relations and the results are compared with the experimental findings.

Keywords: Acetonitrile, Alkyl methacrylates, Excess properties, Intermolecular interactions, Refractive index, Viscosity

Many industrial formulations such as paints, cosmetics and foodstuff contain polymers. Their interactions with other molecules govern many of the properties.[1] The knowledge of excess properties gives important information about solution behaviour of solvents. Interactions between organic molecules are of interest in a number of pharmaceutical areas.[2] These include stability, solubility, compatibility, analysis, drug formulation and drug design.[3,4] The search for safer solvents has been the centre of research for decades now. An attempt is being made to find alternative solvents for replacing widely used compounds such as benzene, chloroform, dichloromethane, *etc*. Methacrylates are one such family that are primarily used for polymer synthesis with variety of applications in textiles, detergents, surface coatings, adhesives, paper treatments, *etc*.[5,6]

Acetonitrile is polar aprotic solvent with high dielectric constant. It is used in perfumes, rubber products, pesticides, acrylic nail removers and batteries.[7] It is also used to extract fatty acids from animal and vegetable oils. Pharmaceutical industry is the largest user of acetonitrile, as starting material for synthesis of Vitamin A and B1, some amino acids, carbonate drugs and as solvent in insulin and antibiotics.[8] The mixing behavior of liquid mixtures containing acetonitrile is interesting due to the presence of cyano group coupled with amide linkage resulting interactions in the liquid mixtures.[9] The use of chemicals is highly dependent upon the knowledge of their physicochemical properties and their molecular behaviour. The study can contribute to development of cost-effective and reliable process design to use these compounds in chemical processes.[10–13]

This work reports experimental viscosities, η and refractive indices, n_D data for binary mixtures of ACN with methyl methacrylate (MMA), ethyl methacrylate (EMA), *n*-butyl methacrylate (*n*-BMA), including those of pure liquids, over the entire composition range at temperatures (298.15, 303.15, 308.15, 313.15, 318.15 and 323.15) K and atmospheric pressure. From the experimental data, the excess properties, *viz.,* $\Delta\eta$, Δn_D and ΔR_M have been

calculated. Values of excess properties of the mixtures were correlated by Redlich-Kister equation. The variation of these parameters with the composition and temperature has been discussed in terms of intermolecular interactions existing in these mixtures.

Materials and Methods

Acetonitrile (RFLC Ltd., India, purity > 0.99), methyl methacrylate (Sigma, Germany, purity >0.99), ethyl methacrylate (Alfa Aesar, USA,purity > 0.98), n-butyl methacrylate (Alfa Aesar, USA, purity > 0.99) used in the study were purified by using the methods described in the literature.[14,15] The structures of the compounds are given in Fig. 1.The water content in the chemicals was <100 ppm (as stated by the manufacturer) and the final mass fraction purities of the purified chemicals as determined by gaschromatography are ACN> 0.997, MMA > 0.995, EMA > 0.994, n-BMA > 0.994. Before use, the chemicals were stored over 0.4 nm molecular sieves for 72 h to remove water content, if any, and were degassed at low pressure. The mixtures were prepared by mass and were kept in special airtight stopper glass bottles to avoid evaporation. The weighing were done by using an electronic balance (Model:GR-202, AND, Japan) with a precision of ±0.01 mg. The uncertainty in the mole fraction was estimated to be less than $\pm 1 \cdot 10^{-4}$.

The viscosities of pure liquids and their binary mixtures were measured by using a three-arm Ubbelohde type suspended level viscometer. The viscometer was calibrated with triply distilled water. The viscometer containing the test liquid was allowed to stand for about 30 min in a thermostatic water bath so that the thermal fluctuations in viscometer were minimized. The time of flow was recorded in triplicate with a digital stopwatch with an accuracy of ±0.01 sec. The uncertainty in viscosity measurements was within ±1%.
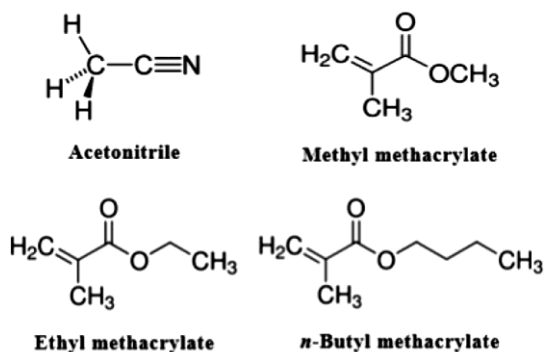

Fig. 1 — Structures of the compounds.

The refractive indices of pure liquids and their binary mixture were measured using a thermostated Abbe refractometer. The values of refractive index were obtained using sodium D light. The temperature of the test liquids between the prisms of refractometer during the measurements was maintained to an accuracy of ±0.2 K by circulating water through the jacket around the prisms from an electronically controlled thermostatic water bath and the temperature was measured with a digital thermometer connected with the prism jacket. The uncertainty in refractive index measurements was within ±0.0001. The temperature of the test liquids during the measurements was maintained to an uncertainty of ±0.1 K in an electronically controlled thermostatic water bath (JULABO, Model: ME-31A, Germany).

The reliability of experimental measurements of η and n_D was ascertained by comparing the experimental values of pure liquids with the corresponding literature[16–27] values at all investigated temperatures. This comparison is given in Table 1 and the agreement between the experimental and the literature values is found to be satisfactory.

Results and Discussion

The experimental values of viscosities, η and refractive indices, n_D of the binary mixtures of ACN with MMA, EMA and$n$-BMA over the entire composition range, expressed in terms of mole fraction, x_1 of ACN at different temperatures are given in Tables 2 and 3, respectively.

Excess properties

The deviations in viscosity, $\Delta\eta$, deviation in refractive index, Δn_D and deviations in molar refractions, ΔR_M have been calculated by using the following relations[28]

$$\Delta\eta = \eta - [x_1\eta_1 + (1-x_1)\eta_2] \qquad \ldots (1)$$

$$\Delta n_D = n_D - \left[\phi_1(n_{D,1})^2 + \phi_2(n_{D,2})^2 \right]^{1/2} \qquad \ldots (2)$$

$$\Delta R_M = R_M - [x_1 R_{M,1} + x_2 R_{M,2}]` \qquad \ldots (3)$$

where the subscript 1 and 2 refer to pure ACN and alkyl methacrylates, respectively. The values of volume fraction, ϕ and R_M have been calculated by using the following relations[29]

$$\phi_i = x_i V_{m,i} / \sum_{i=1}^{2} x_i V_{m,i} \qquad \ldots (4)$$

Table 1 — Comparison of experimental values viscosities, η and refractive indices, n_D of pure liquids along with the corresponding values available in the literature at the temperatures, $T = (293.15 - 318.15)$ K and at atmospheric pressure

Liquid	T (K)	η (10^{-3} N s m^{-2})		n_D	
		Expt.	Literature	Expt.	Literature
Acetonitrile	298.15	0.3462	0.370[12], 0.333[13], 0.346[14], 0.342[15]	1.3409	1.3412[17], 1.34163[11], 1.3416[18], 1.3411[19], 1.3407[20]
	303.15	0.3307	0.354[12], 0.325[13], 0.331[14], 0.334[15], 0.3307 [16]	1.3386	1.3397[18], 1.3390[19], 1.3391[20]
	308.15	0.3165	0.316[14], 0.314[15], 0.3005[16]	1.3364	1.3371[17], 1.3365[11], 1.3369[18], 1.3371[19], 1.3366[20]
	313.15	0.3035	0.327[12], 0.279[13], 0.304[14], 0.303[15]	1.3344	1.3342[18]
	318.15	0.2912	0.291[14]	1.3325	1.3327[17,11], 1.3314[18]
Methyl methacrylate	298.15	0.5625	0.584[21], 0.554[22], 0.585[23]	1.4118	1.412[21], 1.4161[23]
	303.15	0.5240	0.5248[22]	1.4090	1.4136[23]
	308.15	0.4932	0.492[21], 0.4956[22], 0.489[23]	1.4067	1.4068[21], 1.4094[23]
	313.15	0.4684	0.4719[22]	1.4047	-
	318.15	0.4498	0.4497[22]	1.4030	-
Ethyl methacrylate	298.15	0.6412	0.642[21]	1.4136	1.4134[21]
	303.15	0.5825	-	1.4110	
	308.15	0.5323	0.531[21]	1.4087	1.4085[21]
	313.15	0.4915	-	1.4068	-
	318.15	0.4586	-	1.4053	-
n-Butyl methacrylate	298.15	0.8768	0.877[21]	1.4238	1.424[21]
	303.15	0.8077	-	1.4219	-
	308.15	0.7483	0.748[21]	1.4203	1.4204[21]
	313.15	0.7012	-	1.4190	-
	318.15	0.6639	-	1.4180	-

Table 2 — Viscosity, η as function of mole fraction, x_1 of ACN for ACN + MMA/EMA/*n*-BMA mixtures at the temperatures $T = (298.15 - 318.15)$ K and atmospheric pressure

x_1	$10^3 \times \eta$ (N s m^{-2}) at T (K)				
	298.15	303.15	308.15	313.15	318.15
			ACN + MMA		
0.0000	0.5625	0.5240	0.4932	0.4684	0.4498
0.0688	0.5536	0.5171	0.4878	0.4643	0.4465
0.1376	0.5439	0.5091	0.4811	0.4585	0.4413
0.1957	0.5346	0.5013	0.4745	0.4526	0.4359
0.2716	0.5214	0.4899	0.4643	0.4435	0.4275
0.3344	0.5094	0.4795	0.4550	0.4350	0.4194
0.4135	0.4932	0.4651	0.4420	0.4230	0.4079
0.4916	0.4761	0.4498	0.4281	0.4100	0.3954
0.5649	0.4592	0.4344	0.4138	0.3967	0.3825
0.6386	0.4413	0.4183	0.3988	0.3825	0.3687
0.7084	0.4238	0.4023	0.3839	0.3683	0.3549
0.7927	0.4020	0.3823	0.3652	0.3505	0.3375
0.8550	0.3855	0.3672	0.3510	0.3367	0.3240
0.9073	0.3714	0.3541	0.3387	0.3249	0.3123

(*Contd.*)

Table 2 — Viscosity, η as function of mole fraction, x_1 of ACN for ACN + MMA/EMA/n-BMA mixtures at the temperatures $T = (298.15 – 318.15)$ K and atmospheric pressure (*Contd.*)

x_1	$10^3 \times \eta$ (N s m^{-2}) at T (K)				
	298.15	303.15	308.15	313.15	318.15
ACN + MMA					
0.9497	0.3599	0.3435	0.3286	0.3152	0.3028
1.0000	0.3462	0.3307	0.3165	0.3035	0.2912
ACN + EMA					
0.0000	0.6412	0.5825	0.5323	0.4915	0.4586
0.0556	0.6285	0.5725	0.5246	0.4857	0.4542
0.1112	0.6154	0.5620	0.5162	0.4790	0.4489
0.1631	0.6027	0.5516	0.5079	0.4722	0.4433
0.2147	0.5894	0.5408	0.4990	0.4649	0.4372
0.2795	0.5723	0.5266	0.4872	0.4550	0.4287
0.3446	0.5545	0.5115	0.4746	0.4443	0.4194
0.4132	0.5349	0.4950	0.4606	0.4322	0.4088
0.4819	0.5147	0.4777	0.4458	0.4194	0.3974
0.5597	0.4911	0.4574	0.4283	0.4040	0.3836
0.6375	0.4667	0.4364	0.4100	0.3878	0.3689
0.7251	0.4385	0.4119	0.3885	0.3686	0.3515
0.8113	0.4101	0.3870	0.3666	0.3490	0.3334
0.9014	0.3798	0.3604	0.3430	0.3277	0.3137
0.9542	0.3618	0.3445	0.3289	0.3148	0.3018
1.0000	0.3462	0.3307	0.3165	0.3035	0.2912
ACN + n-BMA					
0.0000	0.8768	0.8077	0.7483	0.7012	0.6639
0.0681	0.8436	0.7784	0.7223	0.6777	0.6423
0.1359	0.8101	0.7487	0.6958	0.6537	0.6202
0.1976	0.7793	0.7213	0.6713	0.6314	0.5995
0.2728	0.7411	0.6872	0.6407	0.6035	0.5735
0.3442	0.7043	0.6543	0.6111	0.5764	0.5483
0.4143	0.6677	0.6215	0.5815	0.5492	0.5229
0.4658	0.6405	0.5971	0.5594	0.5289	0.5039
0.5243	0.6094	0.5691	0.5340	0.5055	0.4820
0.5649	0.5876	0.5495	0.5162	0.4891	0.4665
0.6390	0.5475	0.5133	0.4834	0.4587	0.4379
0.7112	0.5080	0.4776	0.4508	0.4285	0.4095
0.7836	0.4680	0.4413	0.4178	0.3978	0.3805
0.8558	0.4277	0.4048	0.3844	0.3668	0.3512
0.9280	0.3871	0.3679	0.3506	0.3353	0.3214
1.0000	0.3462	0.3307	0.3165	0.3035	0.2912

Table 3 — Refractive index, n_D as function of mole fraction, x_1 of ACN for ACN + MMA/EMA/n-BMA mixtures at the temperatures $T = (298.15 – 318.15)$ K and atmospheric pressure

x_1	T (K)				
	298.15	303.15	308.15	313.15	318.15
ACN + MMA					
0.0000	1.4118	1.4090	1.4067	1.4047	1.4030
0.0688	1.4104	1.4077	1.4055	1.4036	1.4019
0.1376	1.4088	1.4061	1.4039	1.4020	1.4005
0.1957	1.4072	1.4046	1.4024	1.4006	1.3990
0.2716	1.4048	1.4022	1.4001	1.3983	1.3968
0.3344	1.4024	1.3999	1.3978	1.3961	1.3946

(*Contd.*)

Table 3 — Refractive index, n_D as function of mole fraction, x_1 of ACN for ACN + MMA/EMA/n-BMA mixtures at the temperatures $T = (298.15 - 318.15)$ K and atmospheric pressure (*Contd.*)

x_1	T (K)				
	298.15	303.15	308.15	313.15	318.15
ACN + MMA					
0.4135	1.3990	1.3965	1.3945	1.3928	1.3913
0.4916	1.3949	1.3925	1.3905	1.3888	1.3874
0.5649	1.3904	1.3880	1.3860	1.3843	1.3829
0.6386	1.3850	1.3827	1.3807	1.3790	1.3775
0.7084	1.3790	1.3767	1.3747	1.3730	1.3715
0.7927	1.3704	1.3681	1.3661	1.3644	1.3628
0.8550	1.3629	1.3606	1.3586	1.3568	1.3551
0.9073	1.3557	1.3535	1.3514	1.3495	1.3478
0.9497	1.3493	1.3470	1.3449	1.3430	1.3412
1.0000	1.3409	1.3386	1.3364	1.3344	1.3325
ACN + EMA					
0.0000	1.4136	1.4110	1.4087	1.4068	1.4053
0.0556	1.4126	1.4101	1.4079	1.4060	1.4044
0.1112	1.4114	1.4089	1.4067	1.4049	1.4035
0.1631	1.4101	1.4077	1.4056	1.4038	1.4024
0.2147	1.4086	1.4063	1.4042	1.4025	1.4011
0.2795	1.4065	1.4042	1.4022	1.4005	1.3992
0.3446	1.4041	1.4018	1.3998	1.3982	1.3969
0.4132	1.4011	1.3988	1.3968	1.3952	1.3939
0.4819	1.3975	1.3953	1.3933	1.3917	1.3904
0.5597	1.3928	1.3906	1.3886	1.3870	1.3856
0.6375	1.3871	1.3849	1.3829	1.3813	1.3798
0.7251	1.3794	1.3772	1.3751	1.3734	1.3719
0.8113	1.3701	1.3679	1.3658	1.3640	1.3624
0.9014	1.3580	1.3558	1.3537	1.3518	1.3501
0.9542	1.3494	1.3471	1.3450	1.3431	1.3413
1.0000	1.3409	1.3386	1.3364	1.3344	1.3325
ACN + n-BMA					
0.0000	1.4238	1.4219	1.4203	1.4190	1.4180
0.0681	1.4223	1.4205	1.4190	1.4178	1.4167
0.1359	1.4208	1.4190	1.4175	1.4163	1.4152
0.1976	1.4191	1.4174	1.4159	1.4147	1.4137
0.2728	1.4168	1.4150	1.4136	1.4124	1.4115
0.3442	1.4141	1.4123	1.4109	1.4097	1.4088
0.4143	1.4110	1.4092	1.4078	1.4066	1.4057
0.4658	1.4084	1.4066	1.4051	1.4039	1.4030
0.5243	1.4049	1.4031	1.4016	1.4004	1.3994
0.5649	1.4022	1.4004	1.3989	1.3976	1.3966
0.6390	1.3965	1.3946	1.3930	1.3917	1.3906
0.7112	1.3897	1.3878	1.3861	1.3847	1.3835
0.7836	1.3813	1.3793	1.3775	1.3760	1.3747
0.8558	1.3710	1.3689	1.3670	1.3654	1.3639
0.9280	1.3579	1.3557	1.3537	1.3519	1.3503
1.0000	1.3409	1.3386	1.3364	1.3344	1.3325

$$R_M = \left[\frac{n_D^2 - 1}{n_D^2 + 2} \right] V_m \qquad \ldots (5)$$

$$V_m = (x_1 M_1 + x_2 M_2) / \rho \qquad \ldots (6)$$

where V_m is the molar volume, M is the molar mass and ρ is the density of the mixture. The values of ρ used in the calculations of V_m have been taken from our earlier study.[30] The values of $\Delta\eta$, Δn_D and ΔR_M

with composition are listed in Supplementary Data, Tables S1–S3.

The values of $\Delta\eta$, Δn_D and ΔR_M have been fitting to Redlich-Kister equation[31] polynomial equation

$$Y^E = x_1 x_2 \sum_{i=0}^{j} A_i \left(1 - 2x_1\right)^i \qquad \dots (7)$$

where Y^E is $\Delta\eta$ or Δn_D or ΔR_M. The volume fraction, ϕ has been used in place of x for fitting of Δn_D. The values of A_i coefficients were evaluated by using the method of least squares regression, with all points weighted equally. The standard deviations, σ of fit have been calculated by using the relation,

$$\sigma = \left[\sum \left(Y_{\text{Calc.}}^E - Y_{\text{Expt.}}^E\right)^2 \Big/ (n-j) \right]^{1/2} \qquad \dots (8)$$

where n is the number of experimental data points and j is the number of A_i coefficients considered ($i+1$ in the present study). The coefficients, A_i and corresponding standard deviations, σ of fit for the mixtures are listed in Table 4. The variations of $\Delta\eta$, Δn_D and ΔR_M with composition along with smoothed values from Eqn (7) are shown graphically in Figs. 2–4 at 298.15 K and in Supplementary Data, Figs S1–S3 (at all studied temperatures), respectively.

The results presented in Fig. 2 and in Supplementary Data, Fig. S1 indicate that $\Delta\eta$ values are positive for all the three mixtures over the entire

Table 4 — Coefficients, A_i from Eq.(7) for $\Delta\eta$, Δn_D and ΔR_M along with standard deviations, σ for ACN + MMA/EMA/ n-BMA mixtures at the temperatures (T =298.15 to 318.15) K

$10^4 \times \Delta\eta$ (N s m^{-2})

T/K	A_0	A_1	A_2	A_3	A_4	σ
ACN + MMA						
298.15	0.7955	0.2180	-0.0198	-0.0218		0.0006
303.15	0.8292	0.2266	0.0005	-0.0274		0.0004
308.15	0.8624	0.2313	0.0126	-0.0196		0.0006
313.15	0.9008	0.2182	0.0240	0.0214		0.0004
318.15	0.9364	0.2276	0.0378	0.0152		0.0006
ACN + EMA						
298.15	0.6234	0.1246	-0.0234	0.0032		0.0005
303.15	0.6594	0.1303	-0.0071	0.0047		0.0004
308.15	0.6966	0.1330	0.0008	0.0045		0.0002
313.15	0.7346	0.1346	0.0142	0.0076		0.0004
318.15	0.7737	0.1366	0.0248	0.0134		0.0003
ACN +n-BMA						
298.15	0.4347	0.0470	0.0007	-0.0143		0.0003
303.15	0.4632	0.0472	0.0022	-0.0018		0.0003
308.15	0.4886	0.0525	0.0085	-0.0042		0.0003
313.15	0.5173	0.0565	0.0045	-0.0039		0.0003
318.15	0.5425	0.0590	0.0094	-0.0022		0.0003
$10^2 \times \Delta n_D$						
ACN + MMA						
298.15	2.2844	0.8530	-0.0050	0.0379		0.0021
303.15	2.3818	0.8744	0.0176	0.0311		0.0025
308.15	2.4932	0.8956	0.0502	0.0184		0.0030
313.15	2.6235	0.9184	0.0671	0.0937		0.0041
318.15	2.7524	0.9976	0.0784	0.0324		0.0034
ACN + EMA						
298.15	1.4647	0.8948	0.4551	0.1712		0.0030
303.15	1.5787	0.9250	0.5185	0.2977		0.0035
308.15	1.6598	1.0274	0.6785	0.2424		0.0043
313.15	1.7768	1.1825	0.7213	0.1031		0.0033
318.15	1.8631	1.2560	0.8268	0.1214		0.0039
ACN + n-BMA						
298.15	0.9183	0.8688	0.5045	0.0043		0.0045
303.15	0.9836	0.9117	0.5425	0.1557		0.0033
						(*Contd.*)

Table 4 — Coefficients, A_i from Eqn (7) for $\Delta\eta$, Δn_D and ΔR_M along with standard deviations, σ for ACN + MMA/EMA/ *n*-BMA mixtures at the temperatures (T =298.15 to 318.15) K (*Contd.*)

|			$10^4 \times \Delta\eta$ (N s m^{-2})			
308.15	1.0522	1.0012	0.7011	0.1916		0.0025
313.15	1.1453	1.0485	0.7456	0.2993		0.0025
318.15	1.2266	1.2070	0.8708	0.0095		0.0051
			$10^6 \times \Delta R_M$ (m^{3}mol^{-1})			
ACN + MMA						
T/K	A_0	A_1	A_2	A_3	A_4	σ
298.15	0.9049	-0.1758	-0.0531	0.0692	-0.0647	0.0008
303.15	0.9456	-0.1844	-0.0816	0.0801		0.0008
308.15	0.9942	-0.1920	-0.1158	0.0764	0.0681	0.0011
313.15	1.0489	-0.1906	-0.0717	0.0742		0.0019
318.15	1.1123	-0.1972	-0.1284	0.0909	0.0828	0.0011
ACN + EMA						
298.15	0.7729	0.0030	-0.0895	-0.0049	0.1179	0.0012
303.15	0.8254	0.0173	-0.0013			0.0014
308.15	0.8861	0.0637	-0.0734	-0.0452	0.1413	0.0021
313.15	0.9570	0.0837	-0.1129	-0.0759	0.1379	0.0016
318.15	1.0131	0.1419	-0.0623	-0.1997		0.0015
ACN +n-BMA						
298.15	0.7377	0.0105	-0.0448	-0.1286	-0.1090	0.0019
303.15	0.7889	0.0128	-0.0679	-0.0396		0.0019
308.15	0.8591	0.0674	-0.0677	-0.0714		0.0013
313.15	0.9287	0.0692	-0.1265	-0.0197	0.1423	0.0011
318.15	1.0038	0.1245	-0.1504	-0.2254		0.0017
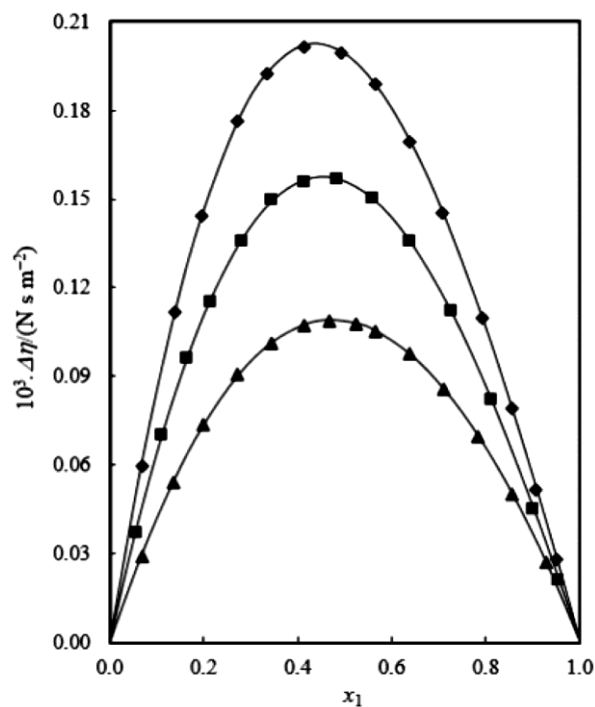
Fig. 2 — Plots of deviations in viscosity, $\Delta\eta$ *vs.* mole fraction, x_1 of ACN for ACN + alkyl methacrylate binary mixtures at 298.15 K, ACN + MMA, ♦; ACN + EMA,■; ACN + *n*-BMA, ▲. The points represent experimental values and lines represent values calculated from Eqn (7).

mole fraction range and at all investigated temperatures. The deviations in viscosity from ideal behaviour depends on intermolecular interactions, molecular size and shape,[32,33] and the magnitude of these deviations from the ideal behaviour can be negative or positive.The positive deviations from ideal behaviour indicate specific interactions between unlike molecules while negative deviations are indication of dispersion forces. It is known that the molecules of ACN are associated through dipolar interactions in pure state.[34] ACN presumably undergoes an appreciable amount of ACN-methacrylate (C≡N······C=O) association which proceeds in competition with the predominant dipolar association. The order of $\Delta\eta$ values is MMA > EMA >*n*-BMA (Supplementary Data, Fig. S1). As expected, the values of $\Delta\eta$ decreases with increase in bulkiness of the side groups. This is in agreement with the results obtained from the variations of excess molar volumes in our earlier study.[30]

From Fig. 3 and Supplementary Data, S2, it can be observed that the values of Δn_D for the binary mixtures are positive over the entire volume fraction range and at all investigated temperatures. In general, the negative deviations in Δn_D values from ideal
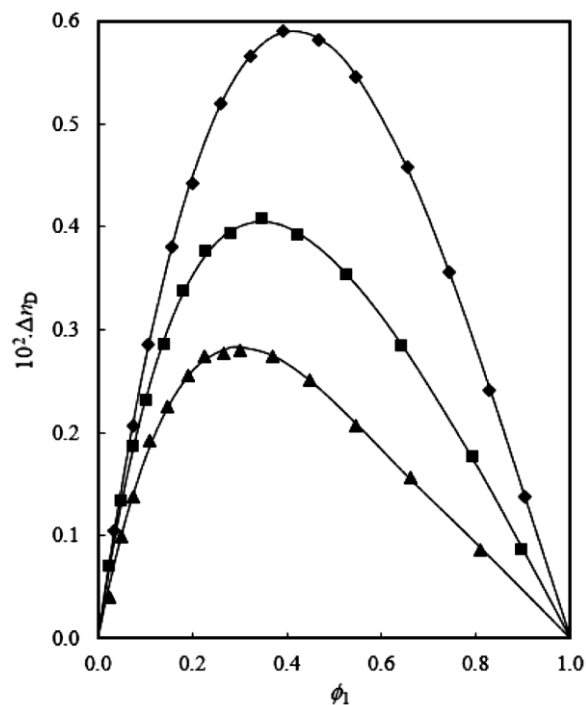
Fig. 3 — Plots of deviation in refractive index, Δn_D vs. volume fraction, ϕ_1 of ACN for ACN + alkyl methacrylate binary mixtures at 298.15 K, ACN + MMA, ♦; ACN + EMA,■; ACN + *n*-BMA, ▲. The points represent experimental values and lines represent values calculated from Eqn (7).
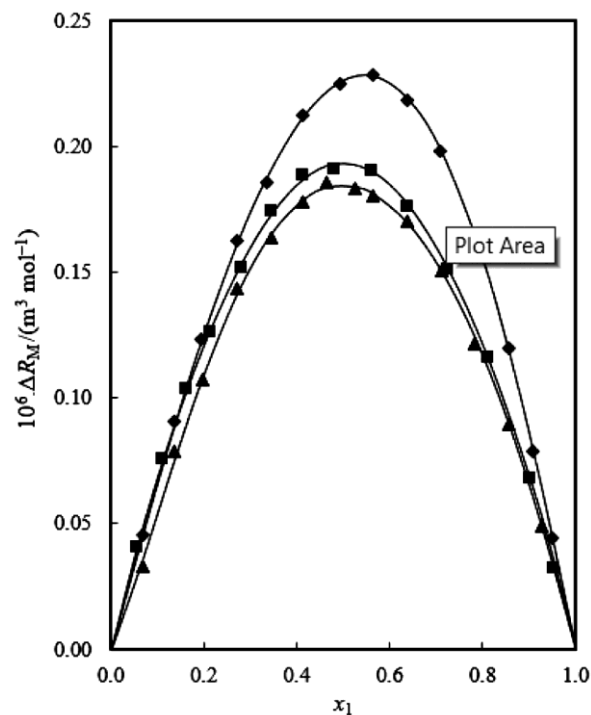

Fig. 4 — Plots of deviations in molar refractions, ΔR_M vs. mole fraction, x_1 of ACN for ACN + alkyl methacrylate binary mixtures at 298.15 K, ACN + MMA, ♦; ACN + EMA,■; ACN + *n*-BMA, ▲. The points represent experimental values and lines represent values calculated from Eqn (7).

behaviour indicate weak dispersion forces, whereas the positive deviations in Δn_D values are considered due to presence of specific interactions between the components of the mixture.[35] The observed positive Δn_D values indicate specific dipole-dipole interactions between ACN and methacrylate molecules in the mixture. Also, the Δn_D (positive) values are found opposite to the sign of excess molar volumes V_m^E (negative) for all the binary mixture,[30] which is in agreement with the view proposed by Brocos et al.[36] The Δn_D values increase with increase in temperature (Supplementary Data, Fig. S2). The increase could be result of increased physical interactions due to interstitial accommodation as opposed to weakening dipolar interactions with rise in temperature. The magnitudes of Δn_D at equimolar composition of these mixtures follow the order: MMA > EMA >*n*-BMA (Fig. 3), which in turn reflect the order of interactions in these mixtures. This further supports our earlier conclusions regarding the molecular interactions from the variations of V_m^E values of the mixture.[30]

The values of ΔR_M are found to be positive for the binary mixturesof ACN with methacrylates over the entire composition range and temperatures (Fig. 4 and Supplementary Data, Fig. S3). Generally, negative values of ΔR_M indicate the presence of weak dispersion forces or mutual loss of specific interactions in the system, and positive values of ΔR_M indicate strong significant interactions. The observed positive ΔR_M values indicate that specific interactions (mainly dipole-dipole interactions) are prevailing between unlike molecules. The formation of new interactions in the mixture and increase in free volume[37] are the primary contributors to the mixture effect for the system leading to positive values of ΔR_M. The order of variation of ΔR_M for binary systems is MMA > EMA >*n*-BMA. In terms of interactions, this can be interpreted as the weakening of interactions as we move from MMA to *n*-BMA.

Correlating models for viscosity

Several semi-empirical models[38–47] have been used to calculate the viscosities of the mixtures theoretically in terms of pure component data. The

experimental values of viscosity have been used to estimate viscosity of liquid mixtures using various empirical relations. The following semi-empirical models have been tested for the mixtures under study

The single parameter Grunberg-Nissan[38] model is a logarithmic function based on Arrhenius viscosity relation. The equation is stated as

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \qquad \dots (9)$$

Where G_{12} parameter is proportional to interchange energy.

Hind, McLaughlin and Ubbelohde[39] model also proposed a single parameter model

$$\eta = x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + 2x_1 x_2 H_{12} \qquad \dots (10)$$

Katti and Chaoudhri[40] proposed the following equation

$$\ln(\eta V) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + x_1 x_2 \frac{W_{\text{Vis}}}{RT} \qquad \dots (11)$$

Heric and Brewer[41,42] suggested a two-parameter model

$$\ln \nu = x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_1 \ln M_1 + x_2 \ln M_2$$
$$-\ln(x_1 M_1 + x_2 M_2) + x_1 x_2 \left[\alpha_{12} + \alpha_{21}(x_1 - x_2) \right] \qquad \dots (12)$$

McAllister[43] three-body interaction model is based on Eyring's theory of absolute reaction rates[44]
$$\ln \nu = x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + 3x_1^2 x_2 \ln Z_{12}$$

$$+3x_1 x_2^2 \ln Z_{21} - \ln\left(x_1 + x_2 \frac{M_2}{M_1} \right)$$

$$-3x_1^2 x_2 \ln\left(\frac{2}{3} + \frac{M_2}{3M_1} \right)$$

$$+3x_1 x_2^2 \ln\left(\frac{1}{3} + \frac{2M_2}{3M_1} \right) - x_2^3 \ln\left(\frac{M_2}{M_1} \right) \qquad \dots (13)$$

Lobe[45] model

$$\nu = \phi_1 \nu_1 \exp\left[\phi_2 \alpha_{12} \ln\left(\frac{\nu_2}{\nu_1} \right) \right]$$

$$+\phi_2 \nu_2 \exp\left[\phi_1 \alpha_{21} \ln\left(\frac{\nu_2}{\nu_1} \right) \right] \qquad \dots (14)$$

Heric and Brewer[41,42] three-parmeter model is of the form

$$\ln \nu = x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_1 \ln M_1 + x_2 \ln M_2$$
$$-\ln(x_1 M_1 + x_2 M_2)$$
$$+x_1 x_2 \left[a + b(x_1 - x_2) + c(x_1 - x_2)^2 \right] \qquad \dots (15)$$

McAllister[46] four-body interactions model
$$\ln \nu = \left(x_1^4 \ln \nu_1 + x_2^4 \ln \nu_2 \right) + 4x_1^3 x_2 \ln Z_{1112}$$

$$+6x_1^2 x_2^2 \ln Z_{1122} + 4x_1 x_2^3 \ln Z_{1222}$$

$$-\ln\left(x_1 + x_2 \frac{M_2}{M_1} \right) + 4x_1^3 x_2 \ln\left(\frac{3}{4} + \frac{M_2}{4M_1} \right)$$

$$+6x_1^2 x_2^2 \ln\left(\frac{1}{2} + \frac{M_2}{2M_1} \right)$$

$$+4x_1 x_2^3 \ln\left(\frac{1}{4} + \frac{3M_2}{4M_1} \right) + x_2^4 \ln\left(\frac{M_2}{M_1} \right) \qquad \dots (16)$$

Auslander[47] model

$$\eta = \frac{\eta_1 x_1 (x_1 + B_{12} x_2) + \eta_2 \left[(A_{21} x_2 (B_{21} x_1 + x_2)) \right]}{x_1 (x_1 + B_{12} x_2) + \left[A_{21} x_2 (B_{21} x_1 + x_2) \right]} \qquad \dots (17)$$

where ν ($=\eta/\rho$) is the kinematic viscosity. The terms and notation used in the relations (9)–(17) are the same as given in the literature.[38–47] The values of the parameters of the Eqns (9)–(17) were evaluated by using least-squares method, the standard deviations, σ and average percentage deviations (APDs) obtained by using experimental viscosity data, as described by Heric and Brewer,[43] are given in Table 5. The values of the calculated parameters, G_{12}, H_{12}, W_{Vis}/RT, α_{12}, α_{21}, Z_{12}, Z_{21}, a, b, c, Z_{1112}, Z_{1122}, Z_{1222}, A_{21}, B_{12}, B_{21} and viscosity of pure liquids are used to calculate theoretical viscosities of the mixtures.

From Table 5, it can be seen that the APD values for one-parameter relations are in the range 0.0936 to 0.4807 % for ACN + MMA, 0.1856 to 0.9241 % for ACN + EMA, and 0.0535 to 2.3673 % for ACN + *n*-BMA binary mixtures. The APD values for ACN + MMA are in the range 0.0455 to 0.8853%, 0.1205 to 0.9252 % for ACN + EMA, and 0.1493 to 0.3806 % for ACN + *n*-BMA binary mixtures. The APD values for three-parameter relations are in the range 0.0077 to 0.0107 % for ACN + MMA, 0.0158 to 0.0331 % for ACN + EMA, and 0.0042 to 0.5612 % for ACN + *n*-BMA binary mixtures.

The values of σ (%) for these binary systems under study (Table 5) indicate that for each system three-parameter models predict the data best followed by two-parameter models and then by one-parameter

Table 5 — Values of parameters calculated from various one-, two- and three-parameter models of viscosity, along with the standard deviation, σ and average percentage deviations, APD between theoretical and experimental η values for ACN + MMA/EMA/n-BMA binary mixture at T = 298.15 K

Model	Parameters			σ	APD
ACN + MMA					
Grunberg-Nissan	$G_{12} = 0.2873$			0.0004	0.0936
Hind et al.	$H_{12} = 0.4940$			0.0015	0.3076
Katti-Chaudhri	$W_{vis}/RT = 0.5102$			0.1670	0.4807
Heric-Brewer (2-parameter)	$\alpha_{12} = 0.5215$	$\alpha_{21} = 0.0683$		0.0003	0.0455
McAllister (3-body int.)	$Z_{12} = 1.1931$	$Z_{21} = 0.5844$		0.0003	0.0455
Lobe	$\alpha_{12} = -1.5693$	$\alpha_{21} = 0.6575$		0.0015	0.8853
Heric-Brewer (3-parameter)	$a = 0.5192$	$b = 0.0690$	$c = 0.0149$	0.0001	0.0111
McAllister (4-body int.)	$Z_{1112} = 0.5130$	$Z_{1122} = 0.5556$	$Z_{1222} = 0.5873$	0.0001	0.0107
Auslander	$A_{21} = 0.4915$	$B_{12} = 0.8993$	$B_{21} = 1.4058$	0.0001	0.0077
ACN + EMA					
Grunberg-Nissan	$G_{12} = 0.2964$			0.0012	0.2546
Hind et al.	$H_{12} = 0.4898$			0.0009	0.1854
Katti-Chaudhri	$W_{vis}/RT = 0.6318$			0.0368	0.9241
Heric-Brewer (2-parameter)	$\alpha_{12} = 0.6641$	$\alpha_{21} = 0.1392$		0.0007	0.1205
McAllister (3-body int.)	$Z_{12} = 1.4299$	$Z_{21} = 0.6030$		0.0007	0.1205
Lobe	$\alpha_{12} = 0.6751$	$\alpha_{21} = -1.1949$		0.0005	0.9252
Heric-Brewer (3-parameter)	$a = 0.6966$	$b = 0.0644$	$c = 0.1837$	0.0047	1.2331
McAllister (4-body int.)	$Z_{1112} = 0.5207$	$Z_{1122} = 0.5664$	$Z_{1222} = 0.6138$	0.0001	0.0158
Auslander	$A_{21} = 0.6990$	$B_{12} = 1.0086$	$B_{21} = 1.1916$	0.0001	0.0118
ACN + n-BMA					
Grunberg-Nissan	$G_{12} = 0.4573$			0.0051	0.8945
Hind et al.	$H_{12} = 0.5924$			0.0003	0.0535
Katti-Chaudhri	$W_{vis}/RT = 0.9857$			1.2701	2.3673
Heric-Brewer (2-parameter)	$\alpha_{12} = 1.0612$	$\alpha_{21} = 0.3317$		0.0026	0.3806
McAllister (3-body int.)	$Z_{12} = 2.4016$	$Z_{21} = 0.7787$		0.0026	0.3804
Lobe	$\alpha_{12} = 1.4103$	$\alpha_{21} = -2.3690$		0.0010	0.1493
Heric-Brewer (3-parameter)	$a = 1.0464$	$b = 0.3520$	$c = 0.1263$	0.0005	0.0644
McAllister (4-body int.)	$Z_{1112} = 0.6357$	$Z_{1122} = 0.7041$	$Z_{1222} = 0.8217$	0.0005	0.5612
Auslander	$A_{21} = 0.9241$	$B_{12} = 1.0340$	$B_{21} = 1.0510$	0.0001	0.0042

models. Therefore, it may be concluded that the predicting ability of these correlating relations increases as the number of adjustable parameters in the relation increases.

Prediction of refractive index

The refractive indices for the binary systems have been correlated using various mixing rules[48–50] such as Arago and Biot (A-B), Gladstone and Dale (G-D), Lorentz and Lorentz (L-L), Heller (H), Eykman (EK) and Weiner (W)

Arago-Biot (A-B) equation

$$n = n_1\phi_1 + n_2\phi_2 \qquad \qquad \dots (18)$$

Gladstone-Dale (G-D) equation

$$n - 1 = (n_1 - 1)\phi_1 + (n_2 - 1)\phi_2 \qquad \dots (19)$$

Lorentz-Lorentz (L-L) equation

$$\frac{n^2 - 1}{n^2 + 2} = \left(\frac{n_1^2 - 1}{n_1^2 + 2}\right)\phi_1 + \left(\frac{n_2^2 - 1}{n_2^2 + 2}\right)\phi_2 \qquad \dots (20)$$

Heller (H) equation

$$\frac{n - n_1}{n_1} = \frac{3}{2}\left[\frac{(n_2/n_1)^2 - 1}{(n_2/n_1)^2 + 2}\right]\phi_2 \qquad \dots (21)$$

Eykman (EK) equation

$$\frac{n^2 - 1}{n + 0.4} = \left(\frac{n_1^2 - 1}{n_1 + 0.4}\right)\phi_1 + \left(\frac{n_2^2 - 1}{n_2 + 0.4}\right)\phi_2 \qquad \dots (22)$$

Weiner (W) equation

$$\frac{n^2 - n_1^2}{n^2 + 2n_2^2} = \left(\frac{n^2 - n_1^2}{n_2^2 + 2n_1^2}\right)\phi_2 \qquad \dots (23)$$

The experimental indices were compared with the predicted results for the mixing rules and the corresponding average percentage deviations were calculated by using the following equation

$$APD = \frac{1}{m}\left[\sum \frac{(n_D^{Expt.} - n_D^{Calc.})}{n_D^{Expt.}} \times 100\right] \qquad \dots (24)$$

where m is the number of data points. The values of average percentage deviations (APDs) at each investigated temperature are presented in Table 6.

These refractive models are able to predict the values well. For all the systems studied, the Heller model best predicts the refractive index as suggested by the small APD values (Table 6). It has also been observed that Arago-Biot method and Gladstone-Dale equation give the same results which show the similar nature of these two methods. Heller model is followed by Eykwan, Weiner, Arago-Biot, Gladstone-Dale, Lorentz-Lorentz in order of best prediction of values. It can also be observed that these models are able to better predict the theoretical refractive indices for the systems with weak interactions. The APD values for all the systems are found to be increasing with rise in temperature.

Thermodynamic parameters of viscous flow

The temperature dependence of viscosity can be fitted to Arrhenius equation by using the Andrade relation[51]

$$\eta = A_s \exp\left(\frac{E_a}{RT}\right) \qquad \dots (25)$$

where A_s, is the Arrhenius entropic factor corresponding theoretically to the viscosity at infinite temperature, E_a is activation energy, R is gas constant. Taking logarithm of both sides the Eqn (25) can be re-written as

$$\ln \eta = \ln A_s + \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \qquad \dots (26)$$

The plots of the left hand side of Eqn (26), *i.e.*, $\ln \eta$ against the reciprocal of absolute temperature $1/T$ for all the binary systems were found to be almost linear for all composition. This indicates that E_a and $\ln(A_s)$ are independent of temperature in the studied temperature range. The values of E_a/R and A_s were obtained as slopes and intercepts, from linear regression of $\ln \eta$ versus $1/T$ at each composition. The values of E_a and A_s, alongwith linear regression coefficient, r^2 are provided in Supplementary Data, Table S4.

Partial molar activation energy

The Arrhenius activation energy, E_a indicated quasi-equality,[52,53] therefore, we can consider E_a as a thermodynamic property and the partial molar activation energies, $E_{a,1}$ and $E_{a,2}$ for acetonitrile and methacrylates in the mixtures, can be expressed by the

Table 6 — Average percentage deviations (APDs) in theoretically calculated refractive indices by using Arago-Biot (A-B), Gladstone-Dale (G-D), Lorentz-Lorentz (L-L), Heller (H), Eykman (EK), and Weiner (W) relations for ACN + MMA/EMA/ *n*-BMA binary mixtures at the temperatures, T = (298.15 – 318.15) K

| T/K	Average percentage deviations (APDs)					
	A-B	G-D	L-L	H	EK	W
ACN + MMA						
298.15	0.300	0.300	0.320	0.049	0.251	0.308
303.15	0.313	0.313	0.333	0.061	0.261	0.321
308.15	0.327	0.327	0.347	0.072	0.274	0.336
313.15	0.344	0.344	0.364	0.085	0.289	0.353
318.15	0.361	0.361	0.381	0.098	0.303	0.369
ACN + EMA						
298.15	0.211	0.211	0.231	0.007	0.183	0.219
303.15	0.227	0.227	0.247	0.022	0.197	0.235
308.15	0.242	0.242	0.262	0.034	0.211	0.250
313.15	0.258	0.258	0.278	0.047	0.225	0.266
318.15	0.272	0.272	0.292	0.058	0.237	0.280
ACN + n-BMA						
298.15	0.168	0.168	0.195	1.173	0.158	0.179
303.15	0.181	0.181	0.208	1.192	0.169	0.192
308.15	0.196	0.196	0.224	1.221	0.184	0.208
313.15	0.212	0.212	0.240	1.249	0.199	0.223
318.15	0.225	0.225	0.254	1.282	0.212	0.237
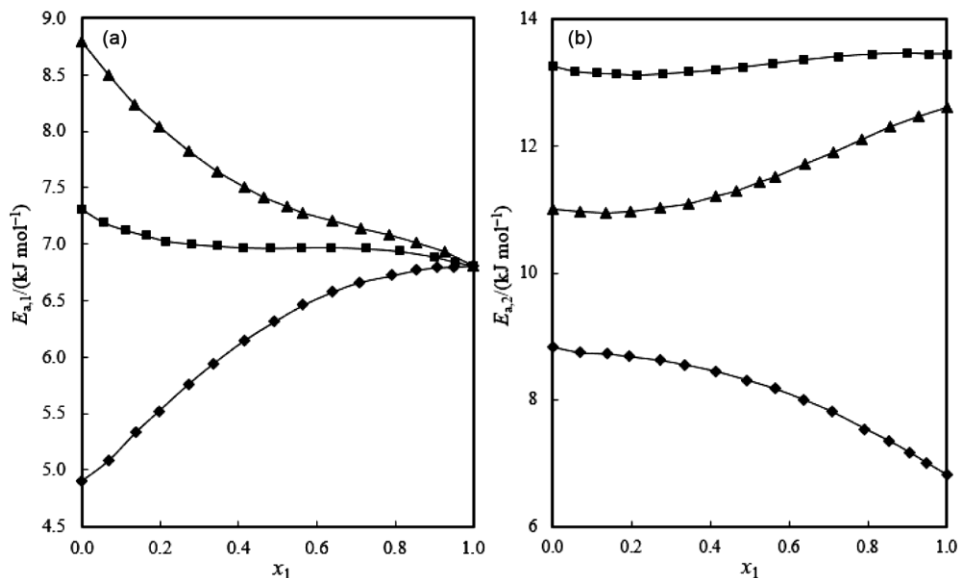
Fig. 5 — Variations of activation energy, $E_{a,1}$ and $E_{a,2}$ of the components (ACN and alkyl acrylates) vs. mole fraction x_1 of ACN for the binary mixtures at $T = 298.15$ K, ACN + MMA, ♦; ACN + EMA,■; ACN + n-BMA, ▲.

following relations[52]

$$E_{a,1} = E_a + x_2\left(\partial E_a / \partial x_1\right) \qquad \dots (27)$$

$$E_{a,2} = E_a - x_1\left(\partial E_a / \partial x_1\right) \qquad \dots (28)$$

The values of partial molar activation energies, $E_{a,1}$ and $E_{a,2}$, for acetonitrile and methacrylates are provided in Supplementary Data, Table S5 and shown graphically as function of mole fraction, x_1 of ACN in Fig. 5. The values of $E_{a,1}$ follows the order: n-BMA > EMA >MMA (Fig. 5) and those of $E_{a,2}$ follows the order: EMA >n-BMA >MMA (Fig. 5). The low value in ACN + MMA mixture suggests that the transition state is highly organized and solvation of the transition state by polar MMA molecules may also be involved. The increase in partial molar activation energies $E_{a,1}$ as EMA/n-BMA concentration increases and $E_{a,2}$ as n-BMA is probably an indication that more and more dipolar associations are to be ruptured before the activated complex has to be formed. It may also be inferred that a decreasing amount of solvent rearrangement takes place as activated complex is formed. That is, reactant (ACN) molecules are well solvated with alkyl acrylate molecules and formation of activated species, necessary for viscous flow requires mainly rearrangement of the solvent, and not the addition of new molecules. Similar trends for partial molar activation energies have been obtained by Lovering and Laidler[54] while studying alcohol-isocyanate reactions.

Conclusions

The measured values of viscosities and refractive indices of binary mixtures of ACN and methacrylates have been used to calculate various parameters, viz., $\Delta\eta$, Δn_D and ΔR_M. The results indicate that the presence of strong interactions through formations of dipole-dipole interactions between C≡N dipole in nitrile group of ACN and polar C=O group of methacrylate molecules. The dipole-dipole interactions in these systems follow the order: MMA > EMA >n-BMA. The refractive indices and viscosities of the mixtures were predicted from pure component data by using various mixing rules, the predicted n_D values compared well with the experimental findings. The Arrhenius activation energy approach was employed to discuss the thermodynamics of viscous flow.

Supplementary Data

Supplementary Data associated with this article are available in the electronic form http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A(10)1457 -1469_SupplData.pdf.

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