Viscosities of Nonelectrolyte Liquid Mixtures Containing Acrylonitrile

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The measurements of viscosity η are reported for seven binary mixtures of acrylonitrile (AN) with ethanenitrile (EN), methyl acetate (MA), ethyl acetate (EA), *n*-butyl acetate (BA), dimethylformamide (DMF), dimethylacetamide (DMA), and dimethyl sulphoxide (DMSO) at 303.15 K temperature. The viscosity data have been correlated with the equations of Grunberg and Nissan; Hind, McLaughlin, and Ubbelohde; Tamura and Kurata; Katti and Chaudhri; McAllister; Heric and Brewer; and of Auslaender. The relations between the viscosity deviations $\Delta\eta$, excess Gibbs energy of activation ΔG^{*E} of viscous flow, and the intermolecular interaction in these mixtures are discussed.

KEY WORDS: acrylonitrile; alkyl acetate; binary liquid mixtures; correlating equations; dimethylformamide; dimethylacetamide; dimethyl sulphoxide; Gibbs energy of activation; molecular interactions; viscosities.

1. INTRODUCTION

The study of mixtures of acrylonitrile in various solvents is of considerable interest because of its wide use as an important industrial monomer for polyacrylonitrile, as well as investigating the effect of simultaneous presence of C=C double bond and polar nitrile –CN group on the molecular interactions. Therefore, in a previous paper [1] we have reported the isentropic compressibilities, excess isentropic compressibilities, and excess molar volumes of binary mixtures of acrylonitrile with ethanenitrile, methyl acetate, ethyl acetate, *n*-butyl acetate, dimethylformamide, dimethylacetamide, and dimethyl sulphoxide. The results indicated the specific interactions of

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dipole–dipole and π-n types between the unlike components. It was also observed that the polarity and free volumes of molecules involved in the mixture formation have a dominating effect on the results of excess properties of volume and isentropic compressibility. In order to confirm the earlier conclusions, in this paper we extend the studies to viscosity and related properties of the same binary mixtures. The viscosity measurements will also provide a test of various empirical equations to correlate viscosity data of binary mixtures containing only polar components.

2. EXPERIMENTAL

2.1. Method

The kinematic viscosities η/ρ were measured with a modified calibrated suspended level Ubbelohde viscometer [2]. The viscometer was designed so as to minimize surface tension effects [3]. The details of the method and technique used to determine viscosity have been described in previous publications [4–6]. The apparatus was submerged in a thermostatic bath maintained constant at 303.15 ± 0.05 K. The viscometer has been calibrated so as to determine the two constants C and B in the equation $\eta/\rho = Ct - B/t$, obtained by measuring the flow time t with pure water, benzene, and cyclo-hexane. The flow time of a definite volume of liquid through the capillary was measured with an accurate stop watch with a precision of ± 0.1 s. Four to five sets of readings for the flow times were taken for each pure liquid or liquid mixture, and the arithmetic mean was taken for the calculations. The error in viscosities η is estimated to be less than 0.002 mPa $\cdot$ s. The densities ρ required to convert kinematic viscosities into dynamic viscos-ities were taken from our previous paper [1]; they were obtained with an Anton Paar vibrating-tube digital densimeter (Model DMA 60/602). The densities ρ were accurate within $\pm 1 \times 10^{-5}$ g $\cdot$ cm^{-3}.

The mixtures were prepared by weight on an electronic balance (Mettler AE 163, Switzerland) with a precision of ± 0.01 mg. The possible error in the mole fraction is estimated to be $< 10^{-4}$.

2.2. Source and Purity of Samples

The source and purification process of pure liquids acrylonitrile (AN), ethanenitrile (EN), methyl acetate (MA), ethyl acetate (EA), n-butyl acetate (BA), dimethylformamide (DMF), dimethylacetamide (DMA), and dimethyl sulphoxide (DMSO) have been described in our earlier paper [1]. The middle fraction of the distillate was used.

Table I. Viscosity and Gibbs Energy of Activation of Viscous Flow of Binary Mixtures at 303.15 K[a]

x_1	η (mPa·s)	ΔG^{*E} (J·mol^{-1})	x_1	η (mPa·s)	ΔG^{*E} (J·mol^{-1})
(i)	AN + EN mixture		(ii)	AN + MA mixture	
0.0000	0.3244		0.0000	0.3442	
0.0965	0.3219	−4	0.1018	0.3427	16
0.2002	0.3193	−8	0.1999	0.3428	43
0.2977	0.3185	−2	0.3006	0.3407	54
0.3966	0.3178	4	0.4001	0.3380	60
0.4928	0.3169	7	0.4946	0.3357	68
0.5983	0.3154	6	0.6012	0.3319	66
0.6941	0.3147	8	0.6955	0.3283	62
0.7977	0.3136	7	0.8014	0.3242	55
0.8997	0.3124	4	0.8960	0.3198	43
1.0000	0.3111		1.0000	0.3111	
(iii)	AN + EA mixture		(iv)	AN + n-BA mixture	
0.0000	0.4026		0.0000	0.6438	
0.0974	0.3987	52	0.0988	0.6248	149
0.2010	0.3940	101	0.2033	0.5998	276
0.3020	0.3883	140	0.3022	0.5737	374
0.3997	0.3824	169	0.4010	0.5437	440
0.4964	0.3739	178	0.4962	0.5133	480
0.5946	0.3654	184	0.5941	0.4775	479
0.6974	0.3546	170	0.6991	0.4364	432
0.7978	0.3413	131	0.7966	0.3951	335
0.9018	0.3263	72	0.8992	0.3527	193
1.0000	0.3111		1.0000	0.3111	
(v)	AN + DMF mixture		(vi)	AN + DMA mixture	
0.0000	0.7675		0.0000	0.8769	
0.0990	0.7313	98	0.0998	0.8246	113
0.2027	0.6911	190	0.1982	0.7637	183
0.2977	0.6444	226	0.2970	0.7048	243
0.4005	0.5998	279	0.3941	0.6449	276
0.4970	0.5516	287	0.5009	0.5797	287
0.5957	0.5028	278	0.5995	0.5228	283
0.6984	0.4518	243	0.6984	0.4682	260
0.7980	0.4041	189	0.7976	0.4132	199
0.8950	0.3581	105	0.9005	0.3591	106
1.0000	0.3111		1.0000	0.3111	

[a] AN, acrylonitrile; EN, ethanenitrile; MA, methyl acetate; EA, ethyl acetate; n-BA, n-butyl acetate; DMF, dimethylformamide; DMA, dimethylacetamide; DMSO, dimethyl sulphoxide.

Table I. (*Continued*)

x_1	η (mPa $\cdot$ s)	ΔG^{*E} (J $\cdot$ mol^{-1})
(vii) AN + DMSO mixture		
0.0000	1.8034	
0.1020	1.5286	30
0.2051	1.2884	51
0.3025	1.0956	70
0.3994	0.9277	76
0.5057	0.7710	79
0.6018	0.6508	78
0.7045	0.5395	62
0.8066	0.4478	48
0.8999	0.3757	23
1.0000	0.3111	

The purity of the liquid samples was checked by gas-liquid chromatography and by measuring their physical properties. The estimated purity of all the samples was better than 99.8 mol%.

3. RESULTS

The experimental viscosity data of binary mixtures at 303.15 K are presented in Table I. For smooth representation, the values of η were fitted to a polynomial equation of the form,

$$\eta = \sum_{i=0}^{m} A_i x_1^i \tag{1}$$

where x_1 is the mole fraction of component 1. The coefficients A_i obtained from a least-squares fit with equal weights assigned to each point are listed in Table II together with the standard deviations σ. The viscosity deviations from a linear dependence on mole fraction are calculated from

$$\Delta \eta = \eta - \sum_{i=0}^{m} x_i \eta_i \tag{2}$$

where η and η_i represent the viscosities of the mixture and of the pure component i. On the basis of the theory of absolute reaction rates [7], the excess Gibbs energy of activation ΔG^{*E} of viscous flow was calculated from

$$\Delta G^{*E}/RT = \{\ln(\eta V/\eta_2 V_2) - x_1 \ln(\eta_1 V_1/\eta_2 V_2)\} \tag{3}$$

Table II. Coefficients A_i of Eq. (1) or (4) and Standard Deviations σ for Viscosities, Viscosity Deviations, and Gibbs Energies of Activation of Viscous Flow of Binary Mixtures at 303.15 K

Property	A_0	A_1	A_2	A_3	σ
(i) AN + EN mixture					
η (mPa · s)	0.3242	−0.0271	0.0322	−0.0184	0.0004
$\Delta\eta$ (mPa · s)	−0.0060	−0.0092			0.0004
$\Delta G^{*E}/RT$	0.0046	−0.0274			0.0013
(ii) AN + MA mixture					
η (mPa · s)	0.3437	−0.0008	0.0305		0.0008
$\Delta\eta$ (mPa · s)	0.0342	−0.0149			0.0010
$\Delta G^{*E}/RT$	0.1159	−0.0494			0.0029
(iii) AN + EA mixture					
η (mPa · s)	0.4017	−0.0206	−0.0694		0.0007
$\Delta\eta$ (mPa · s)	0.0672	−0.0095			0.0005
$\Delta G^{*E}/RT$	0.2879	−0.0594			0.0011
(iv) AN + BA mixture					
η (mPa · s)	0.6457	−0.2022	−0.1359		0.0021
$\Delta\eta$ (mPa · s)	0.1291	0.0386			0.0014
$\Delta G^{*E}/RT$	0.7568	−0.1216			0.0016
(v) AN + DMF mixture					
η (mPa · s)	0.7677	−0.3420	−0.2570	0.1426	0.0013
$\Delta\eta$ (mPa · s)	0.0451	0.0714			0.0013
$\Delta G^{*E}/RT$	0.4534	−0.0059			0.0023
(vi) AN + DMA mixture					
η (mPa · s)	0.8787	−0.5595	−0.1272	0.1197	0.0017
$\Delta\eta$ (mPa · s)	−0.0411	0.0732			0.0024
$\Delta G^{*E}/RT$	0.4733	−0.0048			0.0030
(vii) AN + DMSO mixture					
η (mPa · s)	1.8021	−2.8559	1.8645	−0.5008	0.0015
$\Delta\eta$ (mPa · s)	−1.1249	−0.2502			0.0021
$\Delta G^{*E}/RT$	0.1244	0.0125			0.0011

where V is the molar volume of the mixture and V_i is the molar volume of the pure component i. ΔG^{*E} data are included in Table I. The estimated uncertainty of ΔG^{*E} is about 15 J·mol^{-1}. The values $\Delta\eta$ and $\Delta G^{*E}/RT$ for each mixture have been fitted to the Redlich–Kister polynomial equation

$$\Delta\eta \quad \text{or} \quad \Delta G^{*E}/RT = x_1(1-x_1)\sum_{i=0}^{m} A_i(1-2x_1)^i \qquad (4)$$

The coefficients A_i of Eq. (4) and the standard deviations σ are also included in Table II.

4. CORRELATING EQUATIONS

Apart from expressing η as a polynomial fit, several semi-empirical relations have been proposed to estimate the dynamic viscosity η of liquid-mixtures in terms of pure-component data [8, 9]. We have examined equations proposed by Grunberg and Nissan [10], Tamura and Kurata [11], Hind, McLaughlin, and Ubbelohde [12], Katti and Chaudhri [13], McAllister [14], Heric and Brewer [15], and Auslaender [16]. These equations are presented in Ref. 17.

The correlating ability of each of Eqs. (5) to (11) in Ref. 17 was tested by calculating the standard percentage deviations $\sigma(\%)$ between the experimental and the calculated viscosity as

$$\sigma\% = \left[\frac{1}{n-k}\sum\left\{\frac{100(\eta_{\text{exp}}-\eta_{\text{cal}})}{\eta_{\text{exp}}}\right\}^2\right]^{1/2}$$

Table III. Values of the Parameters of Eqs. (5) to (8) in Ref. 17 and Percentage Standard Deviations $\sigma(\%)$ in Correlating Viscosity of Binary Mixtures at 303.15 K

Mixture	Eq. (5)		Eq. (6)		Eq. (7)		Eq. (8)	
	G_{12}	$\sigma(\%)$	C	$\sigma(\%)$	η_{12}	$\sigma(\%)$	W_{vis}/RT	$\sigma(\%)$
AN + EN	−0.02	0.25	0.32	0.24	0.31	0.25	0.00	0.24
AN + MA	0.11	0.37	0.34	0.29	0.34	0.34	0.12	0.36
AN + EA	0.22	0.44	0.39	0.15	0.39	0.25	0.29	0.49
AN + BA	0.53	0.64	0.52	1.52	0.54	0.68	0.76	1.00
AN + DMF	0.48	0.23	0.55	1.20	0.56	1.12	0.45	0.23
AN + DMA	0.44	0.33	0.54	0.97	0.57	0.99	0.47	0.30
AN + DMSO	0.15	0.09	0.47	3.66	0.50	3.10	0.12	0.12
Average $\sigma(\%)$		0.34		1.15		0.96		0.39

Table IV. Values of the Parameters of Eqs. (9) to (11) in Ref. 17 and Percentage Standard Deviations $\sigma(\%)$ in Correlating Viscosities of Binary Mixtures at 303.15 K

Mixture	Eq. (9)			Eq. (10)			Eq. (11)			
	Z_{12}	Z_{21}	$\sigma(\%)$	α_{12}	α_{21}	$\sigma(\%)$	B_{12}	A_{21}	B_{21}	$\sigma(\%)$
AN + EN	0.40	0.40	0.13	0.00	0.03	0.13	−0.14	−0.11	−6.91	0.32
AN + MA	0.40	0.38	0.29	0.12	0.05	0.29	−0.24	−0.61	−4.51	0.19
AN + EA	0.45	0.45	0.11	0.29	0.06	0.11	0.60	1.51	1.31	0.23
AN + BA	0.60	0.69	0.16	0.76	0.12	0.16	0.42	0.82	1.57	0.31
AN + DMF	0.58	0.73	0.24	0.45	0.01	0.24	0.29	0.41	2.47	0.38
AN + DMA	0.60	0.80	0.30	0.47	0.00	0.30	0.12	0.16	5.51	0.24
AN + DMSO	0.65	1.05	0.11	0.12	−0.01	0.11	1.00	0.51	0.77	0.09
Average $\sigma(\%)$			0.19			0.19				0.25
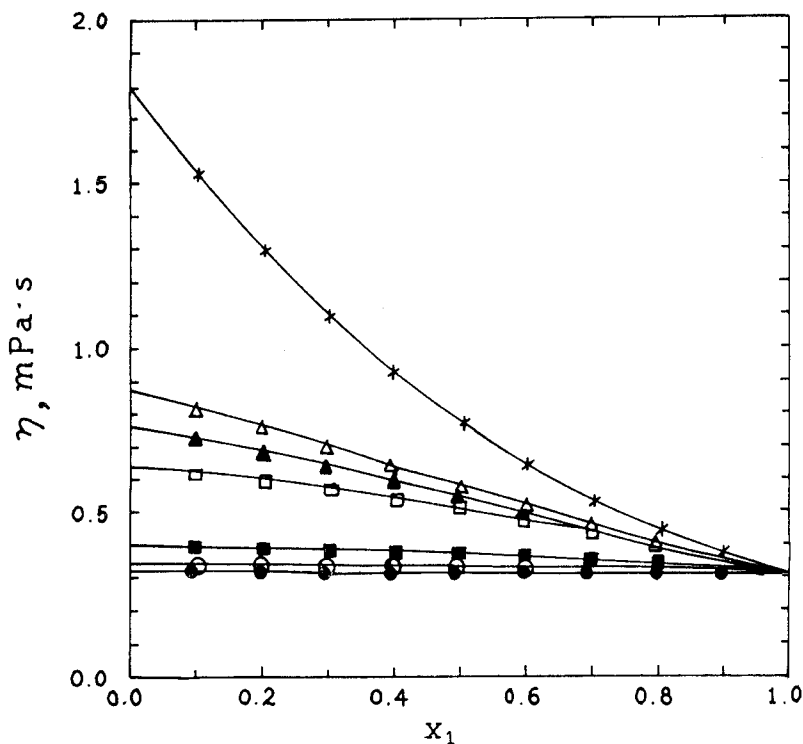
Fig. 1. Viscosity η for acrylonitrile binary mixtures at 303.15 K. Second component, ●, ethanenitrile (EN); ○, methyl acetate (MA); ■, ethyl acetate (EA); □, *n*-butyl acetate (BA); ▲, dimethylformamide (DMF); △, dimethylacetamide (DMA); ×, dimethyl sulphoxide (DMSO). (——) Calculated with Eq. (1).

where n represents the number of data points and k is the number of coefficients in the respective equation.

The results of the correlating equations, Eqs. (5)–(11) in Ref. 17, are compiled in Tables III and IV. The values of the different parameters and the percentage standard deviations $\sigma(\%)$ listed in Tables III and IV were obtained from the experimental viscosity data using the method of least squares.

5. DISCUSSION

No published viscosity measurements for the present systems were found in the literature for comparison with the present results. The experimental results for $\Delta\eta$, G_{12}, and ΔG^{*E} of the present mixtures are plotted in Figs. 1 to 4. The dependence of the viscosity on composition
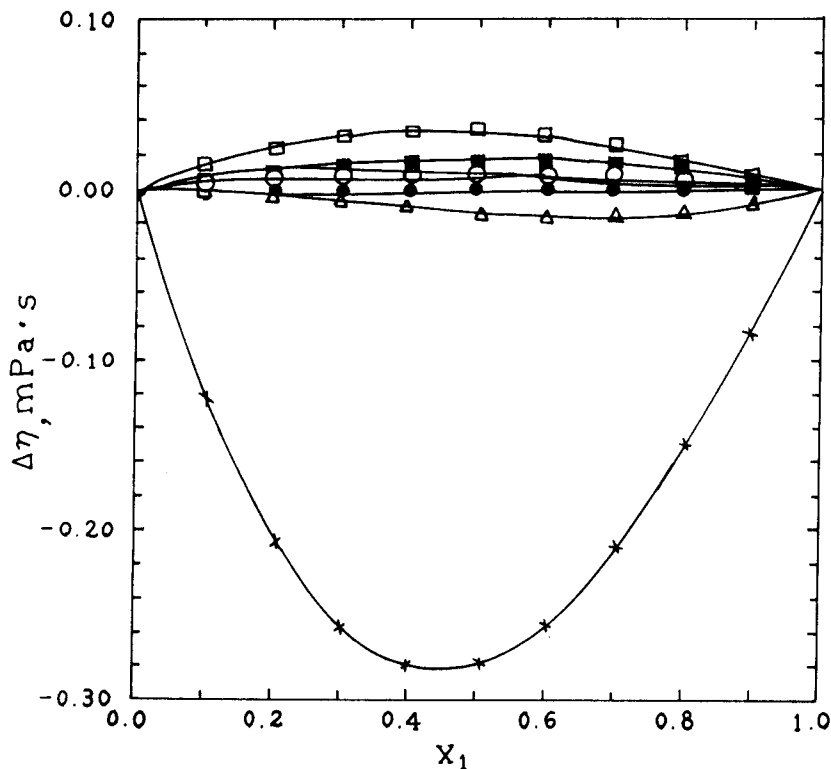
Fig. 2. Deviations of viscosity $\Delta\eta$ from linear additivity on mole fraction for acrylonitrile binary mixtures at 303.15 K. (——) Calculated with Eq. (4). Symbols same as in Fig. 1.

x_1 is shown in Fig. 1. It can be seen from Fig. 2 that the viscosities show very small and positive deviations from linearity on x_1 for AN + DMF, AN + MA, and AN + EA and very small and negative deviations for AN + DMA and AN + EN. For the mixture AN + BA, the deviations are significantly positive, while they are very large and negative for AN + DMSO.

The ΔG^{*E} values are positive for all the mixtures except for AN + EN (Fig. 3). For the latter mixture AN + EN, both small negative and small positive values of ΔG^{*E} are observed, but their magnitude is within the experimental error. The values of ΔG^{*E} for AN + EA, AN + BA, AN + DMF, and AN + DMA are large and positive; while for AN + MA and AN + DMSO they are small and positive. The values calculated for G_{12} in Eq. (5) in Ref. 17 as a function of composition x_1 for each of the binary mixtures are plotted in Fig. 4. The variation of G_{12} with composition depends on the type of second component. G_{12} is large and positive for
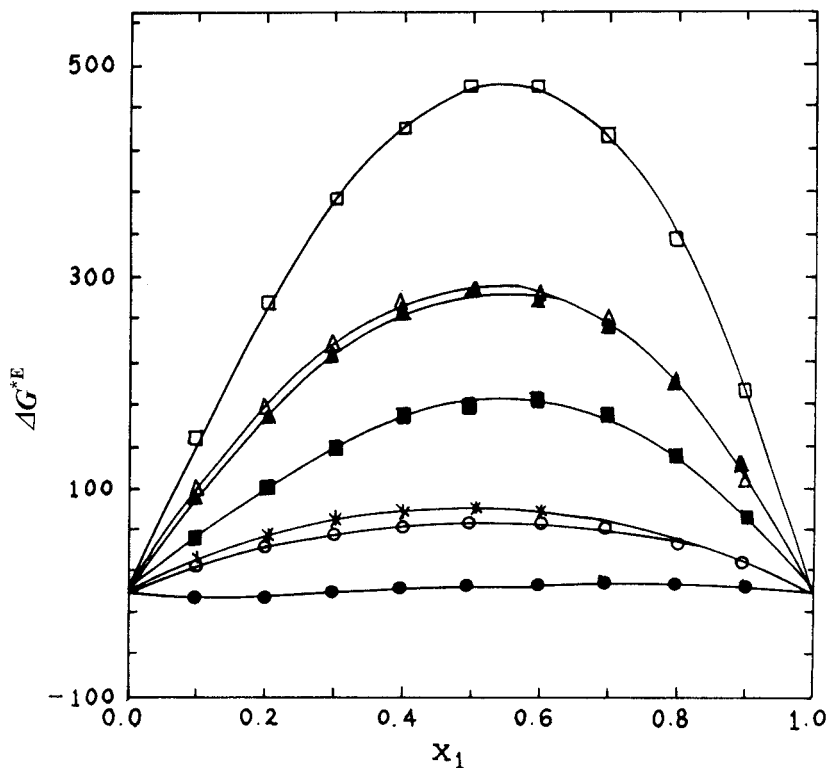

Fig. 3. Excess Gibbs Energy of activation ΔG^{*E} of viscous flow for acrylonitrile binary mixtures at 303.15 K. Symbols same as in Fig. 1. (———) Calculated with Eq. (4).
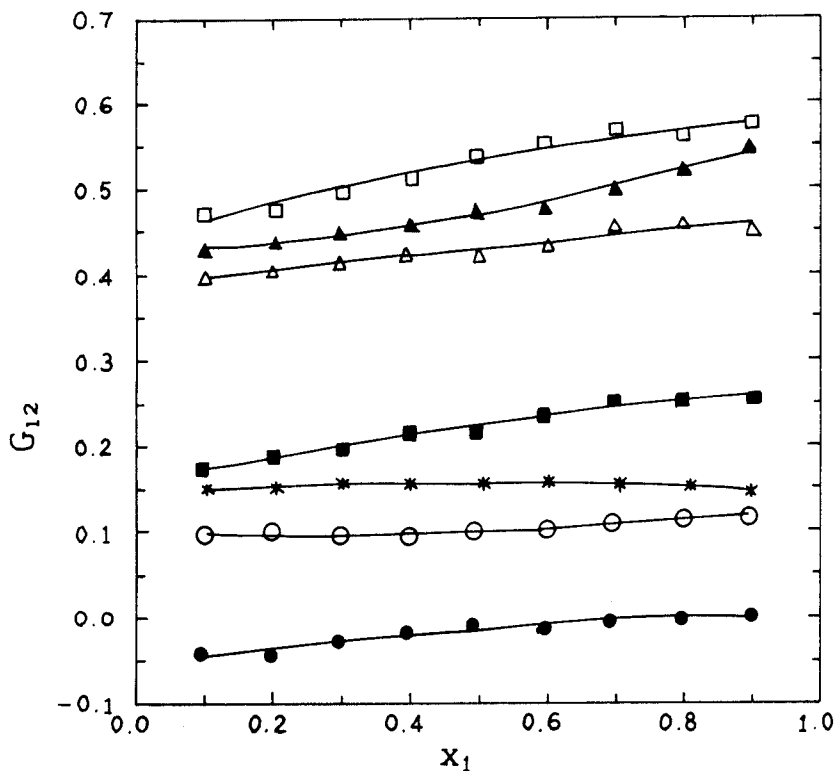
Fig. 4. Variation of Grunberg–Nissan parameter G_{12} of Eq. (5) from Ref. 17 with mole fraction x_1 of acrylonitrile. Symbols same as in Fig. 1.

AN + BA, AN + DMF, and AN + DMA and small and positive for AN + EA and AN + DMSO mixtures. For the AN + MA system, although the G_{12} values are positive, they have very small magnitude. The values of G_{12} for present mixtures are mostly composition dependent.

The values of G_{12} and ΔG^{*E} are positive over the entire range of composition for all mixtures of AN with EN, MA, EA, BA, DMF, DMA, and DMSO, except ΔG^{*E} for AN + EN. According to Fort and Moore [18], Nigam and Mahl [19], and Yadav and Yadav [20], such behaviour is indicative of specific interactions operating between unlike components. Thus, these results confirm the earlier findings [1] on the basis of excess molar volumes and isentropic compressibilities that the specific interactions dominate over the dispersion forces. For the AN + EN mixture both small negative and small positive values of ΔG^{*E} suggest that the combined effect of specific interactions and free volume contributions is counter balanced

by the dispersion interactions. The varying magnitudes of each of $\Delta\eta$, G_{12}, and ΔG^{*E} again suggest that the strength of interaction is dependent on the size and polarity of the second component [18, 19].

The values of $\sigma(\%)$ are in the range from 0.09 to 3.66% for the single-parameter Eqs. (5) to (8) in Ref. 17; from 0.11 to 0.30% for the two-parameter Eqs. (9) and (10) in Ref. 17; and from 0.09 to 0.38% for the three-parameter Eq. (11) in Ref. 17. Average percentage standard deviations $\langle\sigma(\%)\rangle$ for Eqs. (5) to (8) in Ref. 17 with a single parameter are 0.34, 1.15, 0.96, and 0.39, respectively; and for Eqs. (9) and (10) in Ref. 17 with two parameters $\langle\sigma(\%)\rangle$ is 0.19, while for the three-parameter Eq. (11) in Ref. 17, $\langle\sigma(\%)\rangle$ is 0.25. From an analysis of the results in Table IV, the Tamura and Kurata Eq. (6) in Ref. 17 and Hind et al. Eq. (7) in Ref. 17 have very large values of $\sigma(\%)$, whereas the other two Eqs. (5) and (8) in Ref. 17 of Grunberg and Nissan [10] and of Katti and Chaudhri [13], respectively, have comparatively low values of $\sigma(\%)$. However, the correlating ability for the two-parameter equations, Eqs. (9) and (10) in Ref. 17, proposed by McAllister [14] and by Heric and Brewer [15] is better than the other equations considered here.

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