VISCOSITY AND DENSITIES OF BINARY MIXTURES OF ACETONITRILE WITH SUBSTITUTED ANILINES. PART 4

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(Received 1 January 1987)

ABSTRACT

Viscosity and density data are presented for five binary liquid mixtures of acetonitrile with aniline and substituted anilines at five different temperatures. The experimental data are fitted to semitheoretical equations proposed by McAllister and Heric. Excess viscosity, excess volume and the excess Gibbs energy of activation of flow have been calculated from the experimental data. Various thermodynamic parameters of activation of flow are calculated from the dependence of viscosity on temperature. The deviations from ideality of thermodynamic and transport functions are explained on the basis of molecular interactions between the components of the mixture.

INTRODUCTION

As part of a study of thermodynamic properties of binary liquid mixtures, we reported excess volumes, viscosities and activation parameters of flow for the systems *o*-chlorophenol and *m*-cresol with substituted anilines [1,2].

In the present investigation we report the excess volumes (V^E), excess viscosity (η^E), thermodynamic parameters of activation of flow and partial molar quantities ($\bar{V_i}$) for the binary systems: acetonitrile (ACN) + aniline (ANL), ACN + *N*-methylaniline (MEA), ACN + *N,N*-dimethylaniline (DMA), ACN + *N*-ethylaniline (EAN) and ACN + *N,N*-diethylaniline (DEA). The experimental viscosity values of the solution are analysed in terms of theoretical equations proposed by McAllister [3] and Heric [4,5] in order to examine the closeness of the fit between each of the above relations and the experimental values.

EXPERIMENTAL

All the reagents used were of reagent grade and were purified by standard procedures [6]. All the solutions were prepared by mixing weighed amounts

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of pure liquids. Densities of pure liquids and binary mixtures at different temperatures were measured with an Anton-Parr DMA 45 densimeter with an accuracy in density measurement of 0.0001 g ml^{-1}. The viscosities were obtained with modified Ostwald or Cannon-Fenske viscometers by comparing the flowtimes of pure liquids or binary mixtures with that of water at different temperatures and the accuracy in the viscosity measurements was found to be ± 0.005 cP. The density and viscosity values of the pure compounds agree very well with the available data in the literature [1,2,6].

RESULTS

The experimental mole fractions, densities and viscosities at different temperatures for all systems * were used to calculate the excess thermodynamic functions with the following equations

$$\eta^E = \eta - (x_1\eta_1 + x_2\eta_2) \tag{1}$$

$$V^E = V - (x_1 V_1^0 + x_2 V_2^0) \tag{2}$$

$$G^{\star E} = RT\left[\ln \eta V - (x_1 \ln \eta_1 V_1^0 + x_2 \ln \eta_2 V_2^0)\right] \tag{3}$$

where η and V are the viscosity and molar volume respectively of the mixtures, η_1, η_2 and V_1^0, V_2^0 are viscosities and molar volumes of the pure components 1 and 2, respectively. The excess functions were fitted with a Redlich-Kister [7] form of the type

$$x^E = x_1(1 - x_1) \sum_{j=1}^{n} a_j(1 - 2x_1)^{j-1} \tag{4}$$

where x^E represents the excess property under consideration. The a_j values are evaluated by the method of least-squares and are given in Tables 1–3 together with the standard deviation. Figures 1–3 show the values of η^E, V^E and $G^{\star E}$ as a function of mole fraction of acetonitrile at 298 K. Activation parameters ($\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$) of flow were calculated from the variation of viscosity of the liquids with temperature using Eyring's equation [8] and are presented in Table 4. Partial molar excess volumes and partial molar volumes were respectively calculated from the following equations

$$\left(V_1^E\right)_{1,2} = (V^E)_{1,2} + (1 - x_1)\left[\frac{\partial (V^E)_{1,2}}{\partial x_1}\right]_{P,T} \tag{5}$$

$$\overline{V}_1 = V_1^0 + \left(V_1^E\right)_{1,2} \tag{6}$$

where $(V_1^E)_{1,2}$ is the partial molar excess volume of component 1 in solution.

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* A complete set of tabular data on viscosity and density is available from the authors on request.

TABLE I

Coefficients for least-squares fit of results by eqn. (1) for excess viscosity (cP)

System	T (K)	$A1$	$A2$	$A3$	$A4$	$A5$	$A6$	RMS deviation
Acetonitrile + aniline	298	−3.703	−1.231	−0.440	−0.767			0.0160
	303	−2.911	−0.890	−0.285	−0.396			0.0140
	308	−2.308	−0.570					0.0190
	313	−1.791	−0.246					0.0310
	318	−1.451	−0.162					0.0220
Acetonitrile + N-methylaniline	298	−1.050	0.074	0.227				0.0062
	303	−0.798	0.240	0.347				0.0050
	308	−0.638	0.204	0.249				0.0054
	313	−0.508	0.187	0.276	0.143			0.0040
	318	−0.406	0.184	0.264	0.153			0.0030
Acetonitrile + N,N-dimethylaniline	298	−0.220	0.157	0.082	0.048			0.0014
	303	−0.156	0.238	−0.361	−1.033	1.389	2.485	0.0043
	308	−0.150	0.111	0.055	0.089			0.0018
	313	−0.129	0.147	0.062				0.0024
	318	−0.110	0.129	0.056				0.0019
Acetonitrile + N-ethylaniline	298	−0.743	0.258	−0.310	−0.617			0.0056
	303	−0.549	0.252	−0.267	−0.506			0.0093
	308	−0.452	0.189	−0.368	−0.511			0.0062
	313	−0.306	0.241	−0.195	−0.312			0.0036
	318	−0.223	0.222	−0.209	−0.164	0.251		0.0025
Acetonitrile + N,N-diethylaniline	298	−0.552	0.105	0.334	−0.047	0.546		0.0056
	303	−0.447	0.121	0.350	−0.784			0.0047
	308	−0.337	0.212	0.267	−0.048	−0.530	1.063	0.0038
	313	−0.268	0.120	0.267	−0.048	−0.465		0.0051
	318	−0.206	0.114	0.222	−0.013	−0.357		0.0035

TABLE 2

Coefficients for least-squares fit of results by eqn. (2) for excess volume (cm^3 mol^{-1})

System	T (K)	$A1$	$A2$	$A3$	$A4$	$A5$	$A6$	RMS deviation
Acetonitrile + aniline	298	−2.579	0.021	0.122	0.111			0.0140
	303	−3.100	−0.096	0.238	0.547			0.0035
	308	−3.623	0.003	2.574	2.647			0.0018
	313	−3.989	1.249	1.377	−1.711	−0.368		0.0050
	318	−4.008	0.889	0.602	0.074	−0.277		0.0023
Acetonitrile + N-methylaniline	298	−1.823	−0.214	−0.485	−0.853	−0.830	1.061	0.0050
	303	−2.081	−0.028	0.841	0.197			0.0043
	308	−2.781	−0.208	−0.120	2.200			0.0930
	313	−2.524	0.750	−1.006	0.994	0.151		0.0018
	318	−2.791	0.828	−1.163				0.0870
Acetonitrile + N,N-dimethylaniline	298	−1.175	−0.932	−0.048	0.871	−1.182	1.539	0.0048
	303	−1.851	−2.786	−0.866	3.843			0.0061
	308	−1.278	1.633	0.811	−2.016	−0.532		0.0022
	313	−1.781	0.361	−0.650	−0.859	0.459		0.0051
	318	−2.366	0.686	1.628	0.362			0.0070
Acetonitrile + N-ethylaniline	298	−1.564	−0.554	1.716	−0.512	−0.846	2.354	0.0082
	303	0.026	0.093	0.299	0.250	0.544		0.0062
	308	−1.900	−0.197	0.182	1.597			0.0066
	313	−2.194	−0.126	0.165	1.610	−0.067	0.461	0.0055
	318	−2.601	−0.299	1.395	1.579			0.0012
Acetonitrile + N,N-diethylaniline	298	−0.502	1.148	−1.153	−3.327	−0.624		0.0098
	303	−1.171	0.803	−1.067	−1.335	0.501		0.0043
	308	−1.442	1.228	−0.526	−2.343			0.0031
	313	−1.853	1.864	−0.130	−3.220			0.0040
	318	−2.319	2.148	−0.403	−3.602			0.0290

TABLE 3

Coefficients for least-squares fit of results by eqn. (3) for excess molar free energy of activation flow (J mol^{-1})

| System	T (K)	A1	A2	A3	A4	A5	A6	RMS deviation
Acetonitrile + aniline	298	-20.6	677.3	-424.4	-1890.0	1538.0		39
	303	115.1	164.5					33
	308	364.1	547.1					48
	313	603.3	761.8					73
	318	733.0	654.6					64
Acetonitrile + N-methylaniline	298	1396.0	338.2	149.3				18
	303	1550.0	597.2	320.4				15
	308	1609.0	473.7	276.8				17
	313	1671.0	542.3	366.0				14
	318	1731.0	435.5	366.4	321.4			11
Acetonitrile + N,N-dimethylaniline	298	2220.0	-156.5	100.5	152.6			7
	303	2263.0	164.6	-688.4	-3519.0	2733.0	7524.0	10
	308	2257.0	-78.8	75.1	-626.5	4.7	1243.0	8
	313	2225.0	15.8	196.4				16
	318	2211.0	-64.7	197.5				10
Acetonitrile + N-ethylaniline	298	2456.0	100.5	-734.0	-905.2			9
	303	2549.0	35.8	-733.3	-741.1			21
	308	2577.0	-139.7	-982.0	-682.6			19
	313	2705.0	2.2	-1023.0	-497.3	625.3		13
	318	2736.0	2.7	-977.9	-366.1	1137.0		9
Acetonitrile + N,N-diethylaniline	298	3484.0	-930.3	186.6				24
	303	3464.0	-937.7	339.6				26
	308	3480.0	-639.2	1494.0	-2706.0	-1878.0	3637.0	24
	313	3514.0	-921.7	304.6				30
	318	3517.0	-880.2	333.4				23
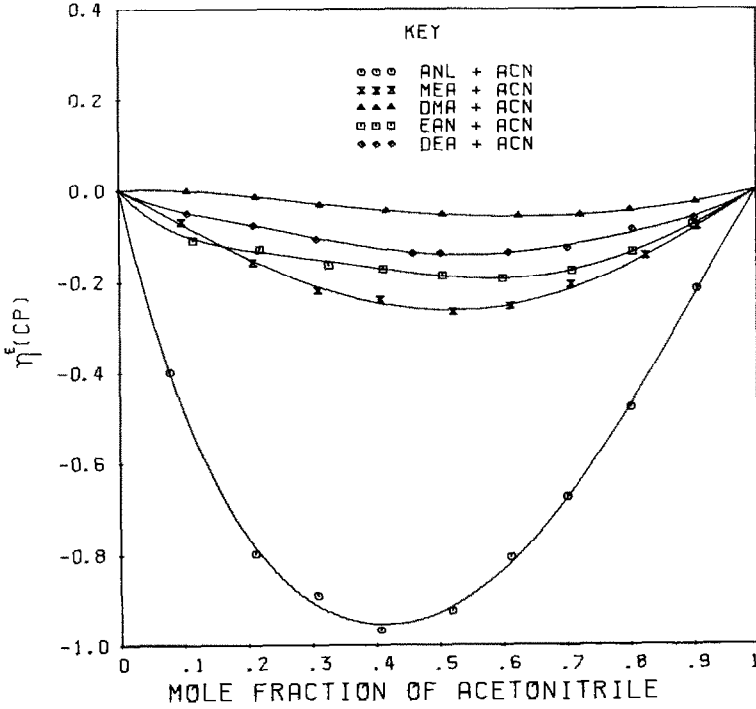
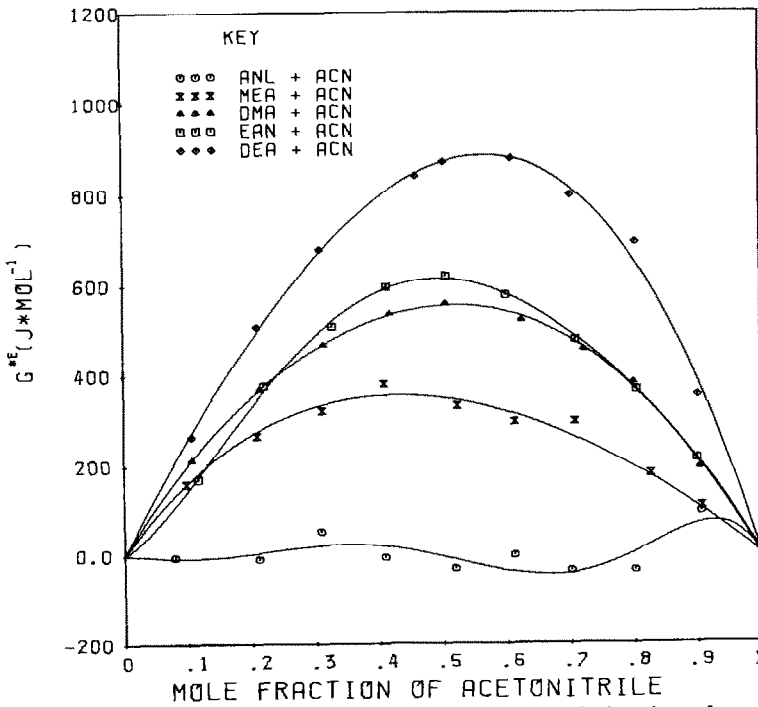Fig. 1. Plot of excess viscosity vs. mole fraction of acetonitrile.

Fig. 2. Plot of excess Gibbs energy of activation vs. mole fraction of acetonitrile.
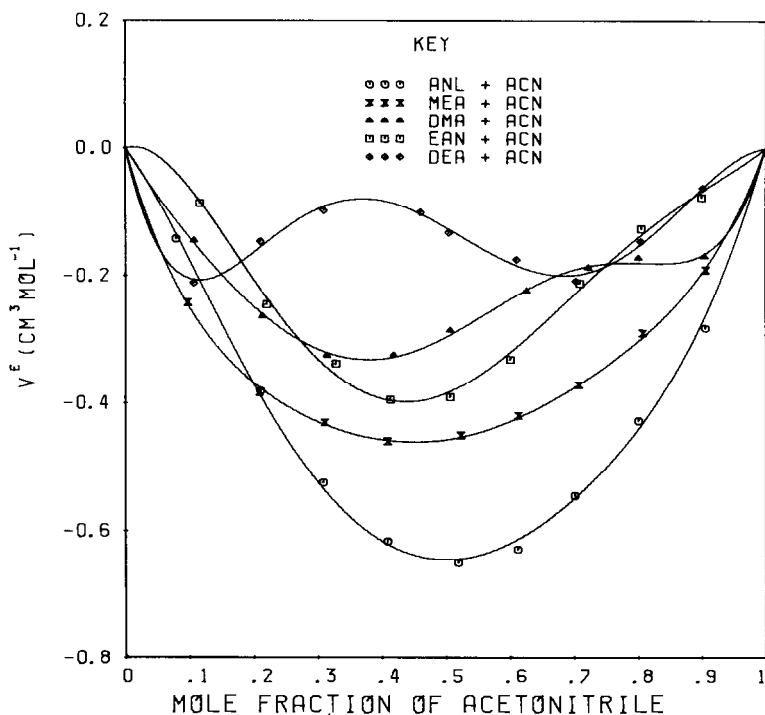
Fig. 3. Plot of excess volume vs. mole fraction of acetonitrile.

Figure 4 shows the values of $\overline{V}_1$ as a function of the mole fraction of acetonitrile. In the theoretical analysis of our data, the following predictive equations of McAllister [3] and Heric [4,5] respectively have been tested

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 + D \qquad (7)$$

$$D = \ln\left[x_1 + \left(\frac{x_2 M_2}{M_1}\right)\right] + 3x_1^2 x_2 \ln\left[\frac{2}{3} + \left(\frac{M_2}{3M_1}\right)\right] + 3x_1 x_2^2 \ln\left[\frac{1}{3} + \left(\frac{2M_2}{3M_1}\right)\right]$$

$$+ x_2^3 \ln\left[\frac{M_2}{M_1}\right] \qquad (7a)$$

where ν is the kinematic viscosity and M is the molecular mass. The adjustable interaction parameters η_{12} and η_{21} were determined from the experimental values using a non-linear least-squares method and are presented in Table 5.

$$\ln \nu = x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln\left[x_1 M_1 + x_2 M_2\right] + \Delta_{12} \qquad (8)$$

TABLE 4

Activation parameters for viscous flow [a]

System	X	ΔH	ΔS	ΔG
Acetonitrile and aniline	0.0000	22.35	19.28	16.60
	0.0792	19.17	10.57	16.02
	0.2110	16.60	5.16	15.06
	0.3090	13.17	−4.16	14.41
	0.4086	13.14	−4.65	13.64
	0.5188	11.32	−4.98	12.81
	0.6119	9.94	−7.45	12.16
	0.7011	9.19	−7.72	11.49
	0.8014	8.02	−9.18	10.75
	0.9061	5.66	−14.72	10.05
	1.0000	5.92	−11.53	9.36
Acetonitrile and N-methylaniline	0.0000	16.98	5.05	15.47
	0.0979	15.22	0.58	15.04
	0.2096	13.79	−2.32	14.48
	0.3118	12.65	−4.20	13.90
	0.4093	11.71	−5.56	13.36
	0.5235	10.33	−7.66	12.61
	0.6138	9.22	−9.38	12.02
	0.7084	8.75	−9.03	11.44
	0.8079	7.64	−10.34	10.72
	0.8262	7.46	−10.53	10.60
	0.9069	6.69	−11.23	10.03
	1.0000	5.92	−11.53	9.36
Acetonitrile and N,N-dimethylaniline	0.0000	11.01	−12.71	14.80
	0.1068	11.41	−10.31	14.48
	0.2140	10.11	−13.07	14.00
	0.3144	9.81	−12.59	13.56
	0.4189	9.38	−12.34	13.06
	0.5068	9.14	−11.62	12.61
	0.6192	8.19	−12.64	11.96
	0.7227	8.00	−11.19	11.33
	0.8012	7.29	−11.87	10.82
	0.9046	6.67	−11.41	10.07
	1.0000	5.92	−11.53	9.36
Acetonitrile and N-ethylaniline	0.0000	16.64	2.70	15.85
	0.1162	14.50	−2.49	15.24
	0.2206	13.90	−2.98	14.78
	0.3290	12.63	−5.28	14.20
	0.4137	11.92	−6.16	13.75
	0.5068	10.76	−8.14	13.18
	0.6008	9.77	−9.24	12.52
	0.7099	8.65	−10.28	11.72
	0.8061	7.76	−10.80	10.98
	0.9004	6.69	−11.83	10.23
	1.0000	5.92	−11.53	9.36

TABLE 4 (continued)

System	X	ΔH	ΔS	ΔG
Acetonitrile and N,N-diethyl-	0.0000	15.35	− 3.49	16.39
aniline	0.1071	14.40	− 5.05	15.90
	0.2109	13.61	− 6.05	15.42
	0.3097	12.85	− 6.87	14.89
	0.4608	11.62	− 7.94	13.99
	0.5044	11.25	− 8.27	13.71
	0.6106	10.46	− 8.44	12.97
	0.7034	9.31	− 9.85	12.25
	0.8049	8.31	− 10.48	11.43
	0.9020	7.10	− 11.07	10.40
	1.0000	5.92	− 11.53	9.36

[a] X is the mole fraction of acetonitrile. Units: ΔH, ΔG, kJ mol^{-1}; ΔS, J mol^{-1}.

where $\Delta_{12} = \alpha_{12}x_1x_2$ is a term representing departure from a noninteracting system, α_{12} is the interaction parameter and is a linear function of composition

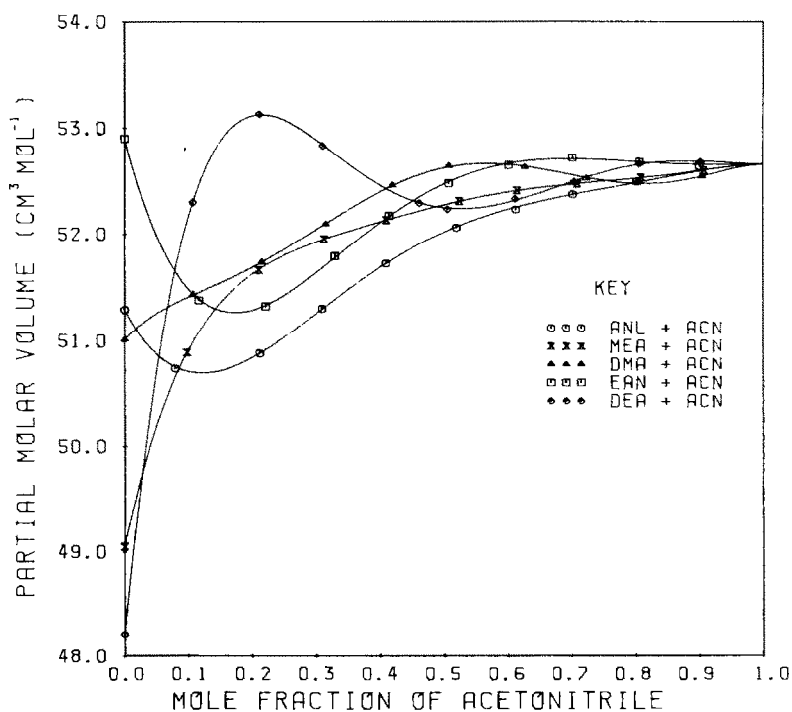$$\alpha_{12} = \beta'_{12} + \beta''_{12}(x_1 - x_2) \tag{8a}$$

Fig. 4. Plot of partial molar volume of acetonitrile vs. mole fraction of acetonitrile.

TABLE 5

Computer analysis of parameters of eqns. (7) and (8)

System	T (K)	McAllister formula (eqn. 7)		Heric formula (eqn. 8)		Average
		η_{12}	η_{21}	β'_{12}	β''_{12}	% error
Acetonitrile and	298	1.7048	0.8065	-0.0111	0.0498	0.604
aniline	303	1.5464	0.7412	0.0492	0.0900	0.767
	308	1.5310	0.6718	0.1633	0.2790	1.120
	313	1.4467	0.6328	0.2245	0.3337	0.730
	318	1.3052	0.6125	0.2634	0.2690	0.660
Acetonitrile and	298	1.4053	0.7518	0.5686	0.1527	0.461
N-methylaniline	303	1.3302	0.6883	0.6166	0.2391	0.461
	308	1.2047	0.6626	0.6227	0.1823	0.422
	313	1.1195	0.6318	0.6233	0.1759	0.334
	318	1.0354	0.5996	0.6322	0.1659	0.306
Acetonitrile and	298	1.1087	0.7559	0.8986	-0.0321	0.170
N,N-dimethylaniline	303	1.0654	0.6849	0.8825	0.0775	0.961
	308	0.9144	0.6938	0.8233	-0.1574	1.060
	313	0.9291	0.6355	0.8649	0.0197	0.304
	318	0.8361	0.6156	0.7910	-0.0858	0.250
Acetonitrile and	298	1.4284	0.9311	0.9621	-0.1663	0.974
N-ethylaniline	303	1.2644	0.8831	0.9434	-0.2399	1.200
	308	1.1830	0.8331	0.9763	-0.2148	1.020
	313	1.1340	0.7730	1.0023	-0.1267	0.778
	318	1.0530	0.7227	0.9872	-0.1114	0.550
Acetonitrile and	298	1.5384	1.0780	1.4340	-0.3057	0.448
N,N-diethylaniline	303	1.3737	0.9992	1.3887	-0.3335	0.493
	308	1.2888	0.9411	1.4108	-0.3058	0.668
	313	1.1937	0.8829	1.3742	-0.2956	0.510
	318	1.0988	0.8272	1.3418	-0.2984	0.427

The two adjustable parameters β'_{12} and β''_{12} were determined using non-linear least-squares methods and are presented in Table 5.

DISCUSSION

Analysis of the adjustable parameters together with the mean percentage deviation indicate that equations of both McAllister and Heric with two adjustable parameters are found to be effective in fitting our binary data. The selection of cubic equation (McAllister) is justified, since for each solution in this work the ratio of radius $(r_2/r_1) = [V_2^0/V_1^0]^{1/3}$ is found to be smaller than 1.5. The viscosities of the mixtures increase regularly with the mole fraction of ACN, and their deviations from linear dependency on composition as expressed in terms of the excess viscosity are negative (Fig.

1). The values of η^E vary approximately from 0.0 to 1.0 cP for ACN + DEA to ACN + ANL systems. Similarly, the excess Gibbs energies of activation of flow are positive over the whole composition range (Fig. 2). The $G^{\star E}$ values increase in the sequence DEA > EAN > DMA > MEA > ANL with the mixtures of ACN. Excess viscosities and values of $G^{\star E}$ suggest that the specific interactions significant enough to cause notable changes in the degree of association are not present in the mixtures [9–12].

All mixtures exhibit negative excess volumes over the entire composition range with a minimum, in no case exceeding -1.0 cm^3 mol^{-1}, and the magnitude of the minimum increases steadily with temperature. The negative values of V^E in Fig. 3 for the five systems are explained in terms of different sizes of the molecules or dipole–dipole interaction between them [13]. The molar volume of acetonitrile 52.85 cm^3 mol^{-1} (298 K) is smaller than the molar volumes of ANL (91.54), MEA (109.16), DMA (127.29), EAN (126.70) and DEA (160.49 cm^3 mol^{-1}). Accordingly, it seems reasonable to ascribe the contraction in volume in the case of mixtures of ACN with ANL, MEA and EAN to weak N–H---N hydrogen bonding and geometrical effects. In the case of DEA and DMA mixtures with ACN, the volume contraction is mainly due to geometrical effects.

Examination of Fig. 4 reveals that the addition of 1 mole of acetonitrile in a large volume of the different bases produces a volume contraction in the order DEA > MEA > DMA > ANL > EAN.

In the temperature range investigated, the values of $\Delta H^{\#}$ are positive and vary in the order ANL > EAN > MEA > DEA > DMA > ACN, indicating that the dipole–dipole interactions and association increase with the value of $\Delta H^{\#}$ (Table 4). The values of $\Delta S^{\#}$ are positive except for DEA, DMA and ACN. Negative values of $\Delta S^{\#}$ indicate very little association in these liquids. The $\Delta H^{\#}$ and $\Delta G^{\#}$ values for the mixtures are positive for all the binary systems. The $\Delta S^{\#}$ values are negative for the entire range for DEA and DMA mixtures and become negative for the other systems with increase in acetonitrile composition.

In conclusion, the study indicates that the strength of specific interactions between acetonitrile and anilines vary in the order ACN + ANL > ACN + MEA > ACN + EAN > ACN + DEA > ACN + DMA. The interactions occurring between the systems are mainly due to dispersion forces and weak (N–H---N) hydrogen bonding.

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