

Ultrasonic and Viscometric Studies of Molecular Interactions in Binary Mixtures of Acetonitrile with Some Amides at Different Temperatures

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Ultrasonic speeds (u) and viscosities (η) of binary mixtures of acetonitrile (ACN) with formamide (FA), *N*,*N*-dimethylformamide (DMF), *N*-methylacetamide (NMA), and *N*,*N*-dimethylacetamide (DMA), including those of pure liquids, over the entire composition range expressed by mole fraction x_1 of ACN ($0 \leq x_1 \leq 1$) were measured at 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15 K. From the experimental data, the deviations in isentropic compressibility (Δk_s), in ultrasonic speed (Δu), and in viscosity ($\Delta\eta$), and partial molar compressibilities, ($\bar{K}^{o}_{\phi,1}$ and $\bar{K}^{o}_{\phi,2}$) for ACN in amide and amide in ACN at infinite dilution, respectively, were calculated. The variation of these parameters with composition and temperature of the mixtures are discussed in terms of the molecular interactions in these mixtures. It was observed that the ACN–amide interaction in these mixtures follows the order: FA > NMA > DMA > DMF. The effect of the number and position of the methyl group on the amide on the molecular interactions in these mixtures is also discussed. Finally, the free energy (ΔG^*), enthalpies (ΔH^*), and entropies (ΔS^*) of activation of viscous flow have also been obtained by using Eyring's viscosity equation, and the dependence of ΔG^*, ΔH^*, and ΔS^* on composition of the mixtures is also discussed.

The physicochemical properties of non-aqueous binary liquid mixtures have relevance in theoretical and applied areas of research, and the information is frequently used in design process (flow, mass transfer or heat transfer calculations) in many chemical and industrial processes. Mixed solvents are frequently used as media for many chemical, industrial, and biological processes, because they provide a wide range of desired properties. Moreover, amides are convenient model systems for the investigation of peptide and protein interactions in biological systems.[1] In continuation of our earlier studies[2–6] on the acoustics, volumetric and transport properties of binary liquid mixtures containing amides, we report here the qualitative results of our study on the binary mixtures of acetonitrile (ACN) with four amides [formamide (FA), *N*,*N*-dimethylformamide (DMF), *N*-methylacetamide (NMA), and *N*,*N*-dimethylacetamide (DMA)], over the entire composition range expressed by mole fraction x_1 of ACN ($0 \leq x_1 \leq 1$) at different temperatures. ACN molecules are aprotic but highly polar ($\mu = 3.7$ D)[7] with their dipoles oriented anti-parallel to each other, and the strongly ordered structure in ACN is due to dipole–dipole interactions.[7–9] FA, DMF, NMA, and DMA ($\mu = 3.37$, 3.86, 4.39, and 3.72 D, respectively)[7] are also highly polar, and pure FA and NMA are strongly associated through hydrogen bonding.[8] However, this association decreases with an increase in the number of methyl groups on the molecule. Thus, DMF and DMA are practically unassociated,[10,11] because they are unable to hydrogen bond with themselves. To the best of our knowledge, there has been no temperature-dependent study of these systems from the point of view of their ultrasonic and viscometric behaviour.

The present paper reports the ultrasonic speeds (u) and viscosities (η) of the binary mixtures of ACN with FA, DMF, NMA, and DMA, including those of the pure liquids at 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15 K, covering the entire composition range expressed by mole fraction x_1 of ACN ($0 \leq x_1 \leq 1$). The density (ρ) data for the calculations was taken from our previous work.[12] The experimental values of ρ, u, and η were used to calculate the deviations in isentropic compressibility (Δk_s), deviations in ultrasonic speed (Δu), deviations in viscosity ($\Delta\eta$), and partial molar compressibilities ($\bar{K}^{o}_{\phi,1}$ and $\bar{K}^{o}_{\phi,2}$) of ACN in amide and amide in ACN at infinite dilution, respectively. The changes in these parameters with composition and temperature of the mixtures are discussed in terms of molecular interactions. The effect of the number and position of the methyl group in these amides on molecular interactions in these mixtures is also discussed. Finally, the free energy (ΔG^*), enthalpy (ΔH^*), and entropy (ΔS^*) of activation of viscous flow were also obtained by using Eyring's viscosity equation,[13] and their dependence on the composition of the mixtures is discussed.

Experimental

Materials. ACN, FA, DMF, NMA, and DMA (all s.d. fine chemicals, India) were purified by using the methods described in the literature.[14,15] The mass fraction purities as determined by gas chromatography are: ACN > 0.996, FA > 0.995, NMA > 0.995, DMF > 0.997, and DMA > 0.997. Before use, the chemicals were stored over 0.4 nm molecular sieves to reduce water content, as much as possible, and were degassed at low pressure. The mixtures were prepared by mass and were kept in special air-tight glass bottles to avoid evaporation. The weighings were done on an electronic balance with a precision of ±0.1 mg. The probable error in the mole fraction was estimated to be less than ±0.0001.

Instrumentation. The ultrasonic speeds in the pure liquids and in the mixtures were measured using a single-crystal variable-path interferometer operating at 3 MHz by the method describ-

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ed elsewhere.[3–6] The ultrasonic speed data were reproducible within $\pm 0.5\,\mathrm{ms}^{-1}$. The viscosities of the pure liquids and their binary mixtures were measured by using 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 the viscometer were minimized. The time of flow was recorded in triplicate with a digital stopwatch with an accuracy of ± 0.01 second. The viscosity data were reproducible within $\pm 5 \times 10^{-7}\,\mathrm{N\,s\,m}^{-2}$. The temperature of the test liquids during the measurements was maintained to an accuracy of ± 0.02 K in an electronically controlled thermostatic water bath (JULABO, Model-MD, Germany). The reliability of experimental measurements of u and η were ascertained by comparing the experimental data of the pure liquids with the corresponding reported values at the studied temperatures.[16–22] For instance, the experimental values of ultrasonic speeds in ACN, FA, DMF, NMA, DMA are: 1282.9, 1601.0, and 1468.3 m s^{-1} at 298.15 K, 1350.1 and 1420.2 m s^{-1} at 308.15 K, respectively, (literature values: 1283.0,[16] 1599.05,[17] 1469.3,[18] 1351.1,[2] and 1420.2[2]/1418.9[19] m s^{-1}). The experimental values of viscosities of FA, DMF, and DMA are: 3.322, 0.8125, and 0.9436 cP at 298.15 K, respectively (literature values: 3.34[20]/3.302,[20] 0.8136,[21] and 0.9437[22] cP).

Results and Discussion

The ultrasonic speeds and viscosities of binary mixtures of ACN, FA, DMF, NMA, and DMA, with ACN as a common component, with respect to the mole fraction, x_1 of ACN at different temperatures are listed in Tables 1 and 2. Excess functions, such as Δk_s, $\Delta\eta$, and Δu, have been calculated by using the following standard relations

$$\Delta k_s = k_s - (\phi_1 k_{s1} + \phi_2 k_{s2}), \quad (1)$$

$$\Delta u = u - (x_1 u_1 + x_2 u_2), \quad (2)$$

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2), \quad (3)$$

where ϕ and x are the volume fraction and mole fraction, respectively; subscripts 1 and 2 stand for pure ACN and amide (FA/DMF/NMA/DMA), respectively; k_s is the isentropic compressibility, calculated by using the relation

$$k_s = 1/u^2\rho. \quad (4)$$

The values of k_s are listed in Table 3. The excess functions Δk_s, Δu, and $\Delta\eta$ were fitted to a Redlich–Kister type[23] polynomial equation

$$Y^E = x_1(1-x_1)\sum_{i=1}^{5} A_i(1-2x_1)^{i-1}, \quad (5)$$

where Y^E is Δk_s or Δu or $\Delta\eta$. The values of coefficients (A_i) were evaluated using the least-squares method with all points weighted equally, together with the corresponding standard deviation, $\sigma(Y^E)$ calculated by using the relation

$$\sigma(Y^E) = \left[\frac{\sum(Y^E_{\mathrm{Expt}} - Y^E_{\mathrm{cal}})^2}{(m-n)}\right]^{1/2}, \quad (6)$$

where m is the number of experimental data points and n is the number of coefficients considered ($n = 5$ in the present calculation), are listed in Table 4. Y^E_{cal} has been obtained from Eq. 5 by using the best-fit values of coefficient A_i. Plots of Δk_s, Δu, and $\Delta\eta$ vs x_1, along with smoothed values using Eq. 5, at 298.15 and 318.15 K are shown in Figs. 1–3.

Table 1. Values of Ultrasonic Speeds (u/m s^{-1}) as a Function of Mole Fraction (x_1) of ACN for the Binary Mixtures at Different Temperatures

x_1	Temperature/K					
	293.15	298.15	303.15	308.15	313.15	318.15
			ACN + FA			
0.0000	1615.8	1601.0	1589.2	1577.2	1565.1	1553.1
0.0764	1605.8	1591.3	1580.1	1568.6	1557.3	1545.8
0.1610	1594.5	1581.3	1570.8	1559.2	1547.1	1535.5
0.2485	1578.3	1564.9	1553.8	1542.2	1531.1	1519.5
0.3444	1553.2	1539.0	1526.5	1515.2	1503.9	1492.6
0.4120	1530.7	1516.8	1504.5	1494.9	1483.2	1473.6
0.5336	1490.8	1475.1	1461.9	1449.2	1437.2	1424.5
0.6388	1450.2	1434.5	1421.3	1407.9	1394.6	1381.2
0.7554	1404.3	1387.9	1373.6	1358.6	1343.9	1328.9
0.8754	1355.9	1336.9	1320.3	1305.1	1289.2	1274.0
1.0000	1304.9	1282.9	1263.4	1245.1	1226.3	1208.0
			ACN + DMF			
0.0000	1484.5	1468.3	1448.2	1428.2	1411.2	1391.2
0.1303	1466.5	1450.8	1431.8	1413.5	1397.5	1379.2
0.2586	1447.3	1431.7	1413.6	1396.3	1380.6	1363.3
0.3851	1427.4	1411.1	1393.2	1376.2	1360.5	1343.5
0.5125	1405.7	1388.4	1371.0	1354.1	1338.1	1321.2
0.5925	1391.1	1373.3	1355.8	1339.2	1323.3	1306.7
0.6899	1372.1	1354.0	1336.5	1319.9	1303.5	1286.9
0.7736	1355.2	1336.5	1318.8	1302.3	1285.6	1269.1
0.8522	1338.7	1319.2	1301.2	1284.6	1267.2	1250.6
0.9359	1320.5	1299.8	1281.4	1264.2	1246.5	1229.3
1.0000	1304.9	1282.9	1263.4	1245.1	1226.3	1208.0
			ACN + NMA			
0.0000	1417.6	1398.8	1371.0	1350.1	1329.9	1309.0
0.1232	1414.1	1396.5	1370.3	1350.4	1331.6	1311.7
0.2665	1407.3	1389.6	1365.3	1346.8	1328.7	1310.2
0.3702	1402.2	1384.2	1361.0	1343.1	1326.3	1308.4
0.4925	1391.9	1373.2	1351.6	1334.1	1317.3	1299.8
0.5800	1383.7	1365.1	1344.1	1326.7	1309.7	1292.3
0.6766	1372.2	1353.2	1332.9	1315.7	1298.7	1281.5
0.7613	1360.2	1340.8	1320.6	1303.4	1286.3	1269.1
0.8305	1347.1	1327.1	1307.4	1289.8	1272.4	1254.8
0.9203	1327.3	1306.4	1287.2	1269.6	1251.5	1233.9
1.0000	1304.9	1282.9	1263.4	1245.1	1226.3	1208.0
			ACN + DMA			
0.0000	1482.2	1462.6	1438.1	1420.2	1402.4	1384.5
0.1674	1462.3	1443.5	1421.1	1404.5	1388.1	1371.5
0.3133	1445.8	1426.7	1405.5	1389.2	1372.4	1356.1
0.4223	1432.3	1413.7	1392.4	1376.7	1360.2	1344.5
0.5387	1414.5	1396.1	1375.9	1359.8	1342.5	1326.4
0.6379	1397.2	1377.9	1358.2	1341.5	1324.9	1308.8
0.7236	1380.4	1361.2	1342.2	1325.4	1308.5	1291.7
0.8071	1361.5	1342.2	1323.5	1306.4	1289.5	1272.4
0.8776	1343.5	1323.8	1305.5	1288.5	1270.9	1253.9
0.9424	1324.3	1303.7	1285.3	1267.9	1250.2	1232.8
1.0000	1304.9	1282.9	1263.4	1245.1	1226.3	1208.0

The results shown in Fig. 1 indicate that Δk_s values are neg-

Table 2. Values of Viscosities ($\eta/10^{-3}$ N s m^{-2}) as a Function of Mole Fraction (x_1) of ACN for the Binary Mixtures at Different Temperatures

x_1	Temperature/K					
	293.15	298.15	303.15	308.15	313.15	318.15
			ACN + FA			
0.0000	3.6542	3.3220	2.9663	2.6531	2.4039	2.2187
0.0764	3.4804	3.1961	2.8915	2.6200	2.4180	2.2855
0.1610	3.2658	3.0225	2.7758	2.5725	2.4170	2.3093
0.2485	3.0356	2.8401	2.6352	2.4771	2.3697	2.3130
0.3444	2.7640	2.6040	2.4468	2.3301	2.2504	2.2077
0.4120	2.5668	2.4261	2.2951	2.2059	2.1358	2.1048
0.5336	2.1755	2.0764	1.9810	1.9282	1.8758	1.8538
0.6388	1.7964	1.7305	1.6722	1.6359	1.6089	1.5912
0.7554	1.3547	1.3141	1.2785	1.2554	1.2468	1.2427
0.8754	0.8852	0.8604	0.8387	0.8217	0.8154	0.8098
1.0000	0.3775	0.3693	0.3565	0.3420	0.3252	0.3061
			ACN + DMF			
0.0000	0.8686	0.8125	0.7645	0.7190	0.6856	0.6643
0.1303	0.8014	0.7512	0.7073	0.6654	0.6337	0.6122
0.2586	0.7358	0.6916	0.6521	0.6142	0.5845	0.5630
0.3851	0.6720	0.6338	0.5987	0.5646	0.5370	0.5159
0.5125	0.6084	0.5763	0.5458	0.5156	0.4902	0.4694
0.5925	0.5688	0.5405	0.5128	0.4851	0.4610	0.4405
0.6899	0.5212	0.4977	0.4734	0.4487	0.4262	0.4059
0.7736	0.4810	0.4615	0.4401	0.4180	0.3968	0.3765
0.8522	0.4438	0.4280	0.4096	0.3902	0.3704	0.3502
0.9359	0.4052	0.3936	0.3784	0.3616	0.3434	0.3238
1.0000	0.3775	0.3693	0.3565	0.3420	0.3252	0.3061
			ACN + NMA			
0.0000	4.9230	4.2086	3.6569	3.2692	2.8604	2.4306
0.1232	4.4065	3.7878	3.3133	2.9797	2.6283	2.2591
0.2665	3.7990	3.2874	2.8932	2.6153	2.3213	2.0112
0.3702	3.3634	2.9256	2.5870	2.3503	2.0970	1.8319
0.4925	2.8285	2.4782	2.2037	2.0135	1.8102	1.5938
0.5800	2.4389	2.1483	1.9231	1.7645	1.5957	1.4168
0.6766	1.9928	1.7716	1.5978	1.4759	1.3447	1.2041
0.7613	1.5910	1.4294	1.3026	1.2108	1.1139	1.0108
0.8305	1.2511	1.1362	1.0457	0.9779	0.9060	0.8301
0.9203	0.7970	0.7430	0.6966	0.6601	0.6221	0.5826
1.0000	0.3775	0.3693	0.3565	0.3420	0.3252	0.3061
			ACN + DMA			
0.0000	1.0376	0.9436	0.8788	0.8174	0.7692	0.7342
0.1674	0.9220	0.8420	0.7854	0.7314	0.6876	0.6545
0.3133	0.8223	0.7545	0.7054	0.6580	0.6188	0.5879
0.4223	0.7480	0.6895	0.6461	0.6037	0.5680	0.5390
0.5387	0.6702	0.6218	0.5843	0.5474	0.5154	0.4883
0.6379	0.6049	0.5650	0.5328	0.5006	0.4718	0.4462
0.7236	0.5497	0.5171	0.4893	0.4611	0.4349	0.4107
0.8071	0.4966	0.4712	0.4478	0.4235	0.4000	0.3773
0.8776	0.4523	0.4330	0.4133	0.3925	0.3714	0.3500
0.9424	0.4123	0.3988	0.3826	0.3650	0.3460	0.3256
1.0000	0.3775	0.3693	0.3565	0.3420	0.3252	0.3061

Table 3. Values of Isentropic Compressibilities ($k_s/10^{-10}$ m^2 N^{-1}) as a Function of Mole Fraction (x_1) of ACN for the Binary Mixtures at Different Temperatures

x_1	Temperature/K					
	293.15	298.15	303.15	308.15	313.15	318.15
			ACN + FA			
0.0000	3.3806	3.4556	3.5196	3.5861	3.6548	3.7248
0.0764	3.5118	3.5911	3.6574	3.7269	3.7972	3.8703
0.1610	3.6650	3.7442	3.8126	3.8882	3.9684	4.0482
0.2485	3.8559	3.9427	4.0202	4.1032	4.1850	4.2717
0.3444	4.1229	4.2233	4.3174	4.4073	4.4997	4.5948
0.4120	4.3546	4.4612	4.5616	4.6482	4.7504	4.8419
0.5336	4.8076	4.9417	5.0634	5.1857	5.3067	5.4369
0.6388	5.2897	5.4419	5.5803	5.7244	5.8735	6.0286
0.7554	5.9025	6.0832	6.2523	6.4344	6.6207	6.8191
0.8754	6.6333	6.8693	7.0910	7.3068	7.5397	7.7743
1.0000	7.5090	7.8218	8.1205	8.4177	8.7382	9.0681
			ACN + DMF			
0.0000	4.7811	4.9105	5.0719	5.2394	5.3924	5.5755
0.1303	4.9752	5.1081	5.2700	5.4332	5.5856	5.7631
0.2586	5.1948	5.3347	5.4999	5.6644	5.8235	6.0023
0.3851	5.4413	5.5963	5.7712	5.9446	6.1143	6.3028
0.5125	5.7307	5.9058	6.0899	6.2759	6.4626	6.6653
0.5925	5.9397	6.1285	6.3228	6.5161	6.7113	6.9219
0.6899	6.2299	6.4338	6.6418	6.8489	7.0636	7.2899
0.7736	6.5123	6.7361	6.9600	7.1801	7.4121	7.6520
0.8522	6.8140	7.0600	7.3016	7.5381	7.7950	8.0537
0.9359	7.1785	7.4565	7.7218	7.9850	8.2672	8.5562
1.0000	7.5090	7.8218	8.1205	8.4177	8.7382	9.0681
			ACN + NMA			
0.0000	5.1921	5.3561	5.5996	5.7999	6.0041	6.2245
0.1232	5.2930	5.4532	5.6904	5.8876	6.0838	6.2997
0.2665	5.4457	5.6138	5.8452	6.0378	6.2355	6.4462
0.3702	5.5695	5.7461	5.9759	6.1697	6.3617	6.5730
0.4925	5.7691	5.9613	6.1888	6.3891	6.5913	6.8089
0.5800	5.9365	6.1357	6.3667	6.5742	6.7868	7.0132
0.6766	6.1640	6.3775	6.6142	6.8308	7.0550	7.2916
0.7613	6.4055	6.6347	6.8835	7.1117	7.3500	7.6005
0.8305	6.6569	6.9041	7.1608	7.4065	7.6614	7.9310
0.9203	7.0530	7.3287	7.5994	7.8650	8.1499	8.4423
1.0000	7.5090	7.8218	8.1205	8.4177	8.7382	9.0681
			ACN + DMA			
0.0000	4.8372	4.9916	5.1881	5.3449	5.5082	5.6792
0.1674	5.0487	5.2063	5.3981	5.5537	5.7139	5.8815
0.3133	5.2501	5.4184	5.6109	5.7722	5.9442	6.1180
0.4223	5.4264	5.5982	5.7999	5.9632	6.1399	6.3165
0.5387	5.6634	5.8442	6.0487	6.2249	6.4203	6.6116
0.6379	5.9090	6.1088	6.3210	6.5151	6.7156	6.9202
0.7236	6.1632	6.3742	6.5933	6.8003	7.0173	7.2428
0.8071	6.4692	6.6959	6.9274	7.1525	7.3854	7.6311
0.8776	6.7811	7.0275	7.2706	7.5103	7.7682	8.0306
0.9424	7.1329	7.4073	7.6702	7.9334	8.2130	8.5022
1.0000	7.5090	7.8218	8.1205	8.4188	8.7393	9.0693

ative over the entire range of x_1 and at each temperature for all the four binary systems under study. The observed negative values of Δk_s for ACN + amide mixtures indicate the presence of specific interactions between ACN and amide molecules in these mixtures. The observed Δk_s values depend on several factors, which are of physical and/or chemical

Table 4. Coefficients (A_i) of Eq. 5 and Standard Deviations $\sigma(Y^E)$ for the Binary Mixtures at Different Temperatures

T/K	A_1	A_2	A_3	A_4	A_5	$\sigma(Y^E)$
			ACN + FA			
$\Delta k_s/10^{-10}$ m^2 N^{-1}						
293.15	−4.1301	1.2395	−0.4276	0.3125	0.3580	0.0048
298.15	−4.4562	1.3829	−0.6129	0.4713	0.4357	0.0029
303.15	−4.7624	1.5620	−0.8857	0.5650	0.5738	0.0022
308.15	−5.1044	1.6922	−0.6880	0.7861	0.0082	0.0037
313.15	−5.4678	1.8822	−0.7302	0.9352	−0.2244	0.0036
318.15	−5.8618	2.0205	−0.4498	1.2390	−0.9723	0.0080
$\Delta u/10^2$ m s^{-1}						
293.15	1.6487	0.8817	0.5923	−0.4403	−1.2027	0.0083
298.15	1.7786	0.8962	0.8424	−0.5069	−1.5084	0.0044
303.15	1.8771	0.8041	1.2009	−0.3508	−1.9057	0.0028
308.15	2.0354	0.9136	0.7804	−0.6599	−1.1410	0.0062
313.15	2.1826	0.9163	0.6097	−0.7212	−0.7831	0.0060
318.15	2.3393	1.0369	0.1738	−1.0500	0.0116	0.0119
$\Delta\eta/10^{-3}$ N s m^{-2}						
293.15	1.0781	0.0991	−0.4744	−0.0214	0.5193	0.0015
298.15	1.3253	0.0704	−0.2739	0.1519	0.2367	0.0032
303.15	1.6532	0.0862	−0.0999	0.2047	−0.0222	0.0007
308.15	2.0436	0.1950	0.0621	0.0513	−0.4808	0.0009
313.15	2.3605	0.3004	0.5096	−0.0280	−0.9922	0.0014
318.15	2.6796	0.5238	0.5003	−0.2112	−0.7117	0.0068
			ACN + DMF			
$\Delta k_s/10^{-10}$ m^2 N^{-1}						
293.15	−0.8010	0.1046	0.0433	0.1052	−0.1628	0.0005
298.15	−0.9315	0.1382	−0.1084	0.1055	−0.0664	0.0002
303.15	−1.0756	0.1577	−0.1140	0.1751	−0.1878	0.0009
308.15	−1.2274	0.1844	−0.2222	0.1987	−0.1997	0.0006
313.15	−1.3862	−0.2034	−0.2617	0.2502	−0.3105	0.0012
318.15	−1.5640	0.2372	−0.4033	0.2933	−0.3289	0.0020
$\Delta u/10^2$ m s^{-1}						
293.15	0.5319	−0.0564	−0.1806	−0.0495	0.3517	0.0002
298.15	0.6076	−0.0315	0.0020	−0.1350	0.1895	0.0001
303.15	0.7002	−0.0521	−0.0349	−0.1626	0.3430	0.0007
308.15	0.7952	−0.0438	0.0250	−0.2154	0.4010	0.0005
313.15	0.8799	−0.0470	−0.0120	−0.2242	0.5691	0.0011
318.15	0.9720	−0.0297	0.1075	−0.3020	0.5433	0.0019
$\Delta\eta/10^{-4}$ N s m^{-2}						
293.15	−0.3422	0.1111	−0.0156	0.1046	−0.1891	0.0003
298.15	−0.3660	0.1111	0.0143	0.1042	−0.2829	0.0005
303.15	−0.3873	0.1005	−0.0806	0.1306	−0.1639	0.0007
308.15	−0.0409	0.1084	−0.0973	0.1110	−0.1996	0.0005
313.15	−0.4306	0.1059	−0.1508	−0.1275	−0.1641	0.0006
318.15	−0.4511	0.0929	−0.2275	0.1621	−0.1217	0.0007

T/K	A_1	A_2	A_3	A_4	A_5	$\sigma(Y^E)$
			ACN + NMA			
$\Delta k_s/10^{-10}$ m^2 N^{-1}						
293.15	−1.5462	0.4690	−0.3010	−0.0474	0.2372	0.0025
298.15	−1.6919	0.5239	−0.3753	−0.1291	0.2076	0.0035
303.15	−1.8535	0.5133	−0.2678	−0.0199	−0.0149	0.0030
308.15	−2.0138	0.5259	−0.3838	0.0180	0.1207	0.0029
313.15	−2.2100	0.5367	−0.5076	0.0033	0.2443	0.0044
318.15	−2.4015	0.5427	−0.6016	0.0701	0.3251	0.0043
$\Delta u/10^2$ m s^{-1}						
293.15	1.2014	−0.4207	0.4962	−0.1956	−0.3795	0.0023
298.15	1.2851	−0.4882	0.3863	−0.0158	−0.0839	0.0055
303.15	1.3633	−0.5024	0.3433	−0.0654	0.0122	0.0041
308.15	1.4482	−0.4922	0.3513	−0.1414	0.0049	0.0042
313.15	1.5520	−0.4866	0.3912	−0.1546	−0.0483	0.0066
318.15	1.6367	−0.4743	0.4051	−0.2343	−0.0645	0.0067
$\Delta\eta/10^{-3}$ N s m^{-2}						
293.15	0.5857	−0.2525	−0.0593	0.0348	0.0837	0.0018
298.15	0.6481	−0.2445	−0.0222	−0.0246	0.1314	0.0017
303.15	0.6965	−0.2448	0.1073	−0.0455	0.0869	0.0020
308.15	0.7533	−0.2478	0.0750	−0.0499	0.2156	0.0022
313.15	0.7989	−0.2628	0.1314	−0.0618	0.2628	0.0019
318.15	0.8512	−0.2603	0.1003	−0.1001	0.5076	0.0032
			ACN + DMA			
$\Delta k_s/10^{-10}$ m^2 N^{-1}						
293.15	−1.0612	0.2971	−0.0693	0.1778	0.2564	0.0017
298.15	−1.2060	0.3502	−0.1859	0.2133	0.3059	0.0026
303.15	−1.3495	0.4067	−0.2286	0.2471	0.1581	0.0028
308.15	−1.4871	0.3773	−0.3477	0.3548	0.1952	0.0041
313.15	−1.6422	0.4427	−0.3931	0.3308	0.0375	0.0036
318.15	−1.8207	0.4082	−0.4035	0.4563	−0.1184	0.0045
$\Delta u/10^2$ m s^{-1}						
293.15	1.0844	−0.4402	0.0731	−0.3394	−0.1201	0.0014
298.15	1.1679	−0.4310	0.1620	−0.4650	−0.1418	0.0024
303.15	1.2288	−0.4713	0.1463	−0.4520	0.1676	0.0029
308.15	1.3128	−0.3993	0.1276	−0.5950	0.2527	0.0035
313.15	1.3654	−0.3357	0.3735	−0.7841	0.0761	0.0030
318.15	1.4649	−0.4294	−0.0135	−0.5114	0.8251	0.0035
$\Delta\eta/10^{-4}$ N s m^{-2}						
293.15	−0.9275	0.3742	−0.0242	0.2164	−0.1384	0.0012
298.15	−0.9549	0.3395	−0.0891	0.3461	−0.0397	0.0018
303.15	−0.9801	0.3726	−0.0319	0.2580	−0.2382	0.0010
308.15	−1.0121	0.3697	−0.0512	0.3019	−0.2337	0.0010
313.15	−1.0413	0.3406	−0.1093	0.3371	−0.2381	0.0004
318.15	−1.0730	0.3542	−0.0667	0.2848	−0.3966	0.0005

nature.[8,24] The physical contributions, i.e., dispersion forces and non-specific physical (weak) interactions that lead to positive Δk_s values; physical contributions are also due to geometrical effects which allow molecules with very different sizes to fit into each other's structure resulting in negative Δk_s values. Chemical contributions involve breaking up of the hydrogen-bonded structure(s), resulting in positive Δk_s values, and specific interactions, such as the formation of hydrogen bonds, formation of charge-transfer complexes and strong dipole–dipole interactions between component molecules, result in negative Δk_s values.

A plausible qualitative interpretation of the behavior of these mixtures with composition has been suggested. As stated earlier, the ACN molecules have a strongly ordered structure due to dipole–dipole interactions, and molecules of FA and NMA are associated through hydrogen bonding due presence of a strong proton-acceptor[25] group (C=O) and proton-donor group (–NH_2/–NH) in their molecules. Mixing of ACN with FA/NMA induces dissociation of the dipole–dipole association in ACN and breaking of H-bonding in FA/NMA, and

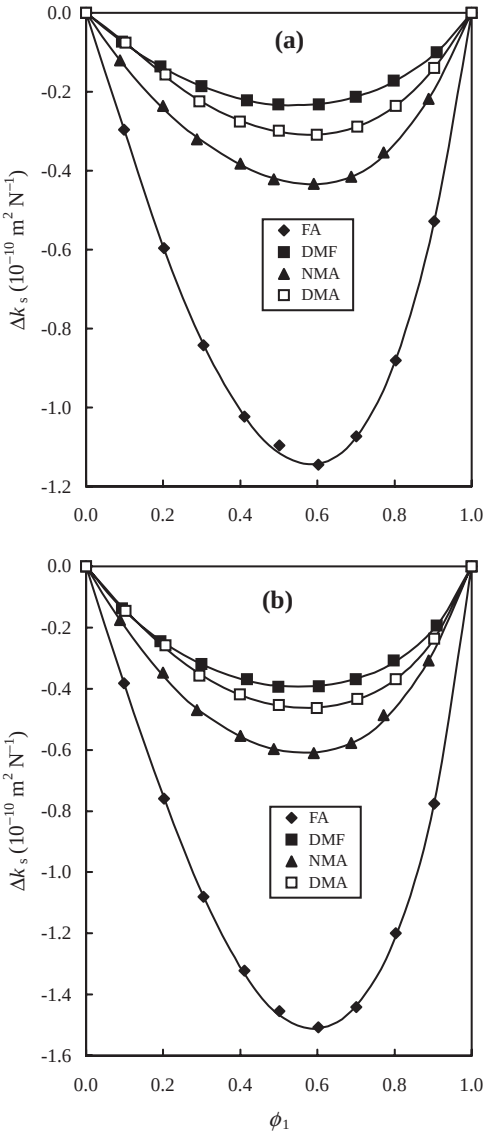

Fig. 1. Plots of deviations in isentropic compressibility (Δk_s) vs volume fraction (ϕ_1) of acetonitrile (ACN) for the binary mixtures (a) at 298.15 K, and (b) at 318.15 K. Points show experimental values and curves show smoothed values using Eq. 5.

subsequent formation of different H-bonding (C≡N···H–N) between nitrogen atom of –CN group of ACN and hydrogen atom(s) of the amino group of FA/NMA occurs. This leads to a decrease in volume and, hence compressibility of the mixture, resulting in negative Δk_s values (Fig. 1). The Δk_s values for ACN + FA are more negative than those for ACN + NMA mixtures (Fig. 1), which is due to the fact that the proton-donating ability of FA is greater than that of NMA[26] due to the presence of $-CH_3$ group at the nitrogen atom of amino group in NMA. Thus, there are stronger H-bonding interactions in the ACN + FA mixtures. In case of ACN + DMF/DMA mixtures, the negative Δk_s values (Fig. 1) are attributed to strong dipole–dipole interactions between unlike molecules in the mixture. Also, the Δk_s values are more negative for ACN + DMA than those for ACN + DMF. This is due to the fact that electron density of the oxygen atom of the carbonyl moiety of DMA is greater than that of DMF[2,26] because of the $-CH_3$ group on the carbonyl group of DMA. Furthermore, the magnitude of the negative Δk_s values for mixtures with equimolar composition at 298.15 K follow the order: FA > NMA > DMA > DMF, which, in turn, indicates the order of interactions between ACN and amide molecules in these mixtures.

From the above discussion, we conclude that the interaction between ACN and amide molecules in the mixtures decreases when a $-CH_3$ group is attached to the nitrogen atom of the amide (as evident from the comparison of Δk_s values of the mixtures: ACN + FA > ACN + DMF/NMA and ACN + NMA > ACN + DMA) and increases when a $-CH_3$ group is attached to the carbon atom of the carbonyl group of the amide (as evident from more negative Δk_s values for ACN + DMA than those for ACN + DMF mixtures). This clearly suggests that the magnitude of Δk_s depends upon the position of methyl groups in these amides.

As expected, the Δu values are positive (Fig. 2) over entire mole fraction range and at all temperatures investigated for all the four binary system under study, and thus follow the order: FA > NMA > DMA > DMF. In general, positive deviations in Δu indicate the presence of significant interactions between the component molecules in the present mixtures. Kawaizumi et al.[19] and Prakash and Sinha[27] suggested that the concentration at which the Δu versus x_1 curve reaches a maximum indicates strong interaction between the component molecules, leading to the formation of complex. Thus, the trends of Δu vs x_1 (Fig. 2) strongly support the behaviour of Δk_s for these mixtures.

It is worth mentioning that the Δk_s values decrease (become more negative) whereas Δu values increase (become more positive) with increase in temperature of the mixture for all the four systems under study. The rise in temperature induces dissociation in the mixture releasing an increased number of free ACN dipoles, and also leads to an expansion in volume, which allows more favourable fitting of smaller ACN molecules into the larger voids created by associates of FA and bigger NMA/DMF/DMA molecules.[15] This leads to a contraction in volume, which causes a decrease in the compressibility of the mixture, and hence, large negative Δk_s values or large positive Δu values are observed.

The curves in Fig. 3 indicate that $\Delta\eta$ values are positive for ACN + FA/NMA mixtures and negative for ACN + DMF/DMA mixtures over the entire range of x_1 at each temperature. The positive $\Delta\eta$ values for ACN + FA/NMA indicate the presence of strong H-bonding interactions between unlike molecules in these mixtures. The small negative $\Delta\eta$ values for ACN + DMF/DMA mixtures suggest the presence of dipole–dipole interactions between unlike molecules.[28,29] Also, negative $\Delta\eta$ values are observed for the mixtures having component molecules that are greatly different in sizes,[6,29] as in ACN + DMF/DMA mixtures.

The apparent molar compressibilities, $K_{\phi,1}$ and $K_{\phi,2}$, for ACN and amides, respectively, in these mixtures at each temperature, have been calculated by using the following relations[30,31]

$$K_{\phi,1} = K^*_{\phi,1} + K^E_s/x_1, \tag{7}$$

$$K_{\phi,2} = K^*_{\phi,2} + K^E_s/x_2, \tag{8}$$

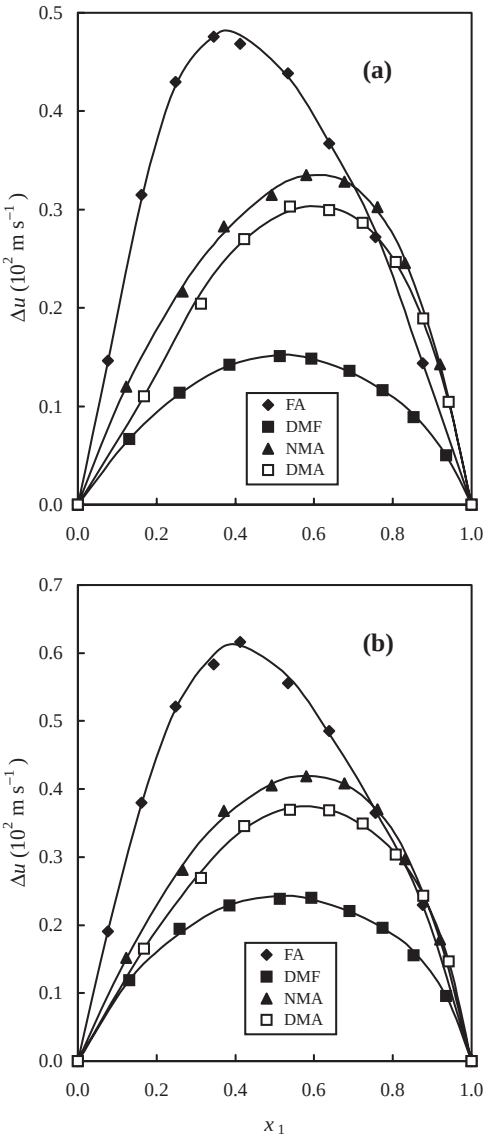

Fig. 2. Plots of deviations in ultrasonic speed (Δu) vs mole fraction (x_1) of acetonitrile (ACN) for the binary mixtures (a) at 298.15 K, and (b) at 318.15 K. Points show experimental values and curves show smoothed values using Eq. 5.

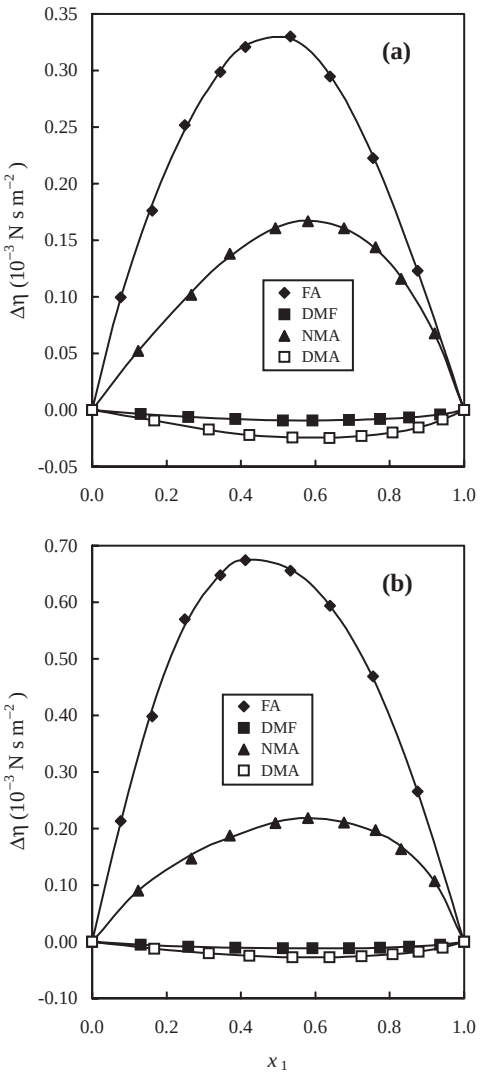

Fig. 3. Plots of deviations in viscosity ($\Delta\eta$) vs mole fraction (x_1) of acetonitrile (ACN) for the binary mixtures (a) at 298.15 K, and (b) at 318.15 K. Points show experimental values and curves show smoothed values using Eq. 5.

where K_s^E [$=(k_sV)^E$] is the excess molar compressibility of the mixture; $K^*_{\phi,1}$ and $K^*_{\phi,2}$ are the molar isentropic compressibilities of pure ACN and amide, respectively. $\bar{K}^o_{\phi,1}$ and $\bar{K}^o_{\phi,2}$ of ACN in amides and amides in ACN, respectively, at infinite dilution were obtained by using a method described elsewhere.[3,30,32] The deviations in K_ϕ at infinite dilution ΔK_1 and ΔK_2, for ACN and amide, respectively, were calculated by using the following relations[30]

$$\Delta K_1 = \bar{K}^o_{\phi,1} - K^*_{\phi,1}, \quad (9)$$

$$\Delta K_2 = \bar{K}^o_{\phi,2} - K^*_{\phi,2}. \quad (10)$$

The values of $\bar{K}^o_{\phi,1}$, $K^*_{\phi,1}$, ΔK_1, $\bar{K}^o_{\phi,2}$, $K^*_{\phi,2}$, and ΔK_2 for the binary systems under study at different temperatures are listed in Table 5. Table 5 indicates that the deviations, ΔK_1 and ΔK_2 are negative (Table 5) for all four binary systems under study at each temperature. This suggests that $\bar{K}^o_{\phi,1}$ and $\bar{K}^o_{\phi,2}$ of ACN and amides, respectively, at infinite dilution are less than their corresponding values in pure state, at each temperature, again, suggesting a contraction in the volume of the mixture. The observed trends in the values of ΔK_1 and ΔK_2 suggest that ACN–amide interactions in these mixtures follow the order: FA > NMA > DMA > DMF, and decrease with an increase in temperature for each mixture. This further supports our earlier conclusion regarding interactions in these mixtures.

In addition, the thermodynamics of viscous flow were investigated by using the Eyring viscosity equation[13]

$$\eta = \left(\frac{hN}{V}\right)\exp\left(\frac{\Delta G^*}{RT}\right), \quad (11)$$

where h is Planck's constant, N is Avogadro number, and ΔG^* is the free energy of activation of viscous flow. Combining Eq. 11 with $\Delta G^* = \Delta H^* - T\Delta S^*$ gives the equation

Table 5. Values of $\bar{K}^{o}_{\phi,1}$, $K^{*}_{\phi,1}$, ΔK_1, $\bar{K}^{o}_{\phi,2}$, $K^{*}_{\phi,2}$, and ΔK_2 for the Binary Mixtures at Different Temperatures

T/K	$\bar{K}^{o}_{\phi,1}$	$K^{*}_{\phi,1}$	ΔK_1	$\bar{K}^{o}_{\phi,2}$	$K^{*}_{\phi,2}$	ΔK_2
	10^{-14} m^5 N^{-1} mol^{-1}			10^{-14} m^5 N^{-1} mol^{-1}		
			ACN + FA			
293.15	2.2404	3.9413	−1.7009	−0.4653	1.3439	−1.8092
298.15	2.3033	4.1334	−1.8301	−0.6150	1.3786	−1.9936
303.15	2.3618	4.3208	−1.9590	−0.7693	1.4091	−2.1784
308.15	2.4244	4.5093	−2.0849	−0.9216	1.4408	−2.3624
313.15	2.4847	4.7136	−2.2269	−1.0981	1.4737	−2.5718
318.15	2.5519	4.9258	−2.3739	−1.2841	1.5073	−2.7914
			ACN + DMF			
293.15	3.5771	3.9413	−0.3641	2.9971	3.6819	−0.6848
298.15	3.6941	4.1334	−0.4393	2.9773	3.7996	−0.8222
303.15	3.8091	4.3208	−0.5117	2.9724	3.9432	−0.9709
308.15	3.9089	4.5093	−0.6004	2.9617	4.0927	−1.1309
313.15	4.0248	4.7136	−0.6888	2.9352	4.2325	−1.2973
318.15	4.1320	4.9258	−0.7938	2.8986	4.3974	−1.4988
			ACN + NMA			
293.15	3.2333	3.9413	−0.7079	2.6472	3.9597	−1.3124
298.15	3.3426	4.1334	−0.7908	2.6643	4.1027	−1.4383
303.15	3.4572	4.3208	−0.8635	2.7404	4.3077	−1.5673
308.15	3.5659	4.5093	−0.9434	2.7866	4.4816	−1.6950
313.15	3.6636	4.7136	−1.0500	2.8112	4.6601	−1.8489
318.15	3.7798	4.9258	−1.1461	2.8459	4.8523	−2.0064
			ACN + DMA			
293.15	3.5049	3.9413	−0.4364	3.3300	4.4784	−1.1484
298.15	3.6260	4.1334	−0.5074	3.2957	4.6436	−1.3479
303.15	3.7362	4.3208	−0.5846	3.2918	4.8496	−1.5578
308.15	3.8426	4.5093	−0.6667	3.2945	5.0199	−1.7354
313.15	3.9572	4.7136	−0.7564	3.2460	5.1985	−1.9525
318.15	4.0638	4.9258	−0.8620	3.2064	5.3862	−2.1797

$$R\ln\left(\frac{\eta V}{hN}\right) = \left(\frac{\Delta H^*}{T}\right) - \Delta S^*, \tag{12}$$

where ΔH^* and ΔS^* are the enthalpy and entropy of activation of viscous flow, respectively. The plots of the left hand side of Eq. 12, i.e., $R\ln(\eta V/hN)$ vs $1/T$ for all four binary systems were found to be almost linear for each x_i. This indicates that ΔH^* is independent of temperature in the temperature range from 293.15 to 318.15 K. The values of ΔH^* and ΔS^* were obtained as the slope and intercept, respectively, from the linear plots of $R\ln(\eta V/hN)$ versus $1/T$ at each x_i by using a linear regression.

The values of ΔG^*, ΔH^*, and ΔS^* along with the linear regression coefficient, r, are given in Table 6. Table 6 indicates that for each binary mixture, the values of ΔG^* and ΔH^* decrease with increase in x_i of ACN in the mixtures. This suggests that the formation of an activated species that is necessary for viscous flow is easier in ACN-rich region in comparison to that in amide-rich region. The values of ΔS^* increase for ACN + FA/NMA mixtures, whereas they initially decrease and then increase to a maximum for ACN + DMF/DMA mixtures, as x_i of ACN increases in the mixture. The decrease in ΔS^* values for ACN + FA/NMA mixtures with

Table 6. The Values of Free Energy (ΔG^*), Enthalpy (ΔH^*), and Entropy, (ΔS^*) of Activation of Viscous Flow along with the Linear Regression Coefficient (r) as a Function of Mole Fraction (x_1) of ACN for the Binary Mixtures

x_1	ΔG^* /kJ mol^{-1} (at 298.15 K)	ΔH^* /kJ mol^{-1}	ΔS^* /J mol^{-1} K^{-1}	r
		ACN + FA		
0.0000	14631.8	15304.9	3.14	0.998
0.0764	14583.6	12828.2	−5.01	0.995
0.1610	14497.2	10262.3	−13.37	0.993
0.2485	14398.1	7911.5	−20.92	0.976
0.3444	14246.5	6271.9	−25.94	0.967
0.4120	14117.4	5362.3	−28.58	0.959
0.5336	13814.1	4045.5	−32.00	0.948
0.6388	13432.3	2741.6	−35.13	0.928
0.7554	12825.1	1660.6	−36.75	0.789
0.8754	11846.4	1736.1	−33.26	0.861
1.0000	9803.8	5429.7	−14.09	0.957
		ACN + DMF		
0.0000	12752.2	7750.3	−16.07	0.990
0.1303	12445.3	7763.4	−15.01	0.993
0.2586	12124.5	7673.3	−14.26	0.995
0.3851	11789.3	7528.4	−13.63	0.998
0.5125	11428.3	7314.3	−13.16	0.999
0.5925	11188.3	7162.6	−12.87	0.999
0.6899	10881.7	6937.9	−12.61	0.998
0.7736	10605.4	6724.4	−12.41	0.995
0.8522	10333.2	6408.2	−12.57	0.989
0.9359	10032.9	5956.5	−13.08	0.976
1.0000	9803.8	5429.7	−14.09	0.957
		ACN + NMA		
0.0000	16872.2	20580.2	13.30	0.997
0.1232	16503.7	19391.2	10.52	0.997
0.2665	16021.6	18367.2	8.68	0.997
0.3702	15633.7	17471.3	6.96	0.997
0.4925	15101.1	16392.3	5.10	0.997
0.5800	14657.4	15441.6	3.37	0.997
0.6766	14077.5	14213.8	1.17	0.997
0.7613	13453.2	12691.4	−1.87	0.997
0.8305	12805.8	11371.7	−4.15	0.998
0.9203	11645.3	8492.9	−9.95	0.999
1.0000	9803.8	5429.7	−14.09	0.957
		ACN + DMA		
0.0000	13593.5	9978.9	−11.43	0.991
0.1674	13113.2	9860.6	−10.24	0.994
0.3133	12655.6	9621.5	−9.52	0.996
0.4223	12284.3	9363.9	−9.15	0.998
0.5387	11861.3	8995.7	−8.98	0.999
0.6379	11473.4	8573.8	−9.11	0.999
0.7236	11117.0	8134.5	−9.40	0.999
0.8071	10747.5	7579.7	−10.03	0.997
0.8776	10417.7	6972.9	−10.96	0.992
0.9424	10099.2	6301.9	−12.15	0.980
1.0000	9803.8	5429.7	−14.09	0.957

increase in ACN concentration indicates that, during viscous flow, there is less structuredness in ACN-rich regions as a result of the ease in which the activated species forms as compared to that in amide-rich region where ΔS^* values are large. Similar results for ΔH^* and ΔS^* values have also been observed for DMF + ethanediol binary systems, wherein the ΔS^* values were reported to increase as the amount of the self-associated component (ethanediol) increased in the mixture,[21] as in the FA/NMA rich region in the present systems. The maxima in ΔS^* values for ACN + DMF/DMA mixtures indicate that during viscous flow there is less structuredness in the region of equimolar composition as compared to ACN or DMF/DMA rich regions.

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