Short Articles

Density and Viscosity of Anhydrous Mixtures of Dimethylsulfoxide with Acetonitrile in the Range (298.15 to 318.15) K†

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The density and viscosity of dimethylsulfoxide (DMSO) + acetonitrile (AN) mixtures were determined over the whole composition range at T = (298.15, 303.15, 308.15, 313.15, and 318.15) K. Since experimental density values showed to be very sensitive to water content, the water-free values of these magnitudes were determined by extrapolation from data obtained on ternary mixtures with small, well-determined, amounts of water and constant x_{DMSO}/x_{AN}. Excess volumes of the anhydrous mixtures show positive values with a quite symmetrical behavior. Viscosity data were satisfactorily fitted with a sixth degree polynomial. Excess viscosities as well as activation parameters for viscous flow in the mixtures were calculated.

1. Introduction

The use of highly polar solvents for industrial applications is continuously increasing insomuch as they provide an ample choice of physicochemical properties. Moreover, the possibility of employing mixtures of these solvents, with or without water in them, opens a wide spectrum of alternatives for finding better conditions for carrying out different processes. Thus, it is not surprising that a significant amount of work is being devoted to studying basic thermodynamic properties in such mixtures, and in this respect, the literature shows several studies of phase equilibria in ternary and quaternary systems that involve at least two highly polar solvents and water. However, information is scant for the case of pure binary systems in which both components are highly polar solvents.

Taking this into account, we thought it of interest to carry out experimental work for measuring some fundamental properties of binary mixtures of two highly polar solvents of industrial interest. In this paper, we report results obtained when density and viscosity measurements were performed on dimethylsulfoxide (DMSO) + acetonitrile (AN) mixtures.

2. Experimental

Spectroscopic grade AN (Aldrich) and DMSO (Baker), in both cases purity > 0.999 mass fraction, were employed throughout the experiments. Chromatographic analysis of both substances showed no detectable impurities, besides water. Water content was determined as in previous work,[1] and its mole fraction was found to be 0.0010 ± 0.0002 in the case of AN and 0.0015 ± 0.0002 in the provided DMSO. Density and viscosity measurements were performed at T = (298.15, 303.15, 308.15, 313.15, and 318.15) K.

A serious experimental problem with this mixture is to avoid water (W) absorption from the environment during manipulation, even when stringent purification methods are applied and utmost care is taken in transfer operations, because of the highly hydrophilic nature of both solvents. Thus, according to the results obtained in preliminary measurements, it was decided to perform density measurements on ternary mixtures of DMSO + AN + W with constant mass relation between DMSO and AN and varying water content. Viscosity measurements showed no fluctuations on binary mixtures of DMSO + AN prepared with solvents as received. In all experiments, bidistilled deionized water with specific conductance below 1 $\mu S \cdot cm^{-1}$ was employed.

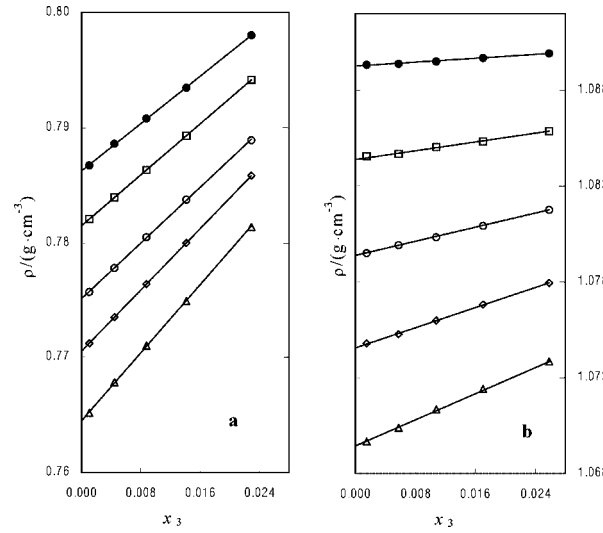

Figure 1. Linear extrapolation, from experimental density values ρ, for the DMSO (1) + AN (2) + W (3) system, obtained on solutions with constant x_1/x_2, when controlled amounts of water were added, at different temperatures: ●, 298.15 K; □, 303.15 K; ○, 308.15 K; ◇, 313.15 K; △, 318.15 K. (a) x_1/x_2 = 0.0235; (b) x_1/x_2= 39.18.

All samples were prepared by weight, employing a Mettler H20-332131 balance with an uncertainty of 10^{-5} g. Density and viscosity measurements were performed at controlled temperatures as already described[2] with repeatability below $5 \cdot 10^{-5}$ g·cm^{-3} and $2 \cdot 10^{-4}$ mPa·s, respectively. The uncertainty was better than $1 \cdot 10^{-4}$ g·cm^{-3} and $5 \cdot 10^{-4}$ mPa·s for density and viscosity measurements.

In reporting our results, subindeces **1**, **2**, and **3** correspond, respectively, to DMSO, AN, and water. Twenty-two solutions with constant x_1/x_2 ratio were prepared as detailed in the first column in Table 1. Controlled amounts of water were added to

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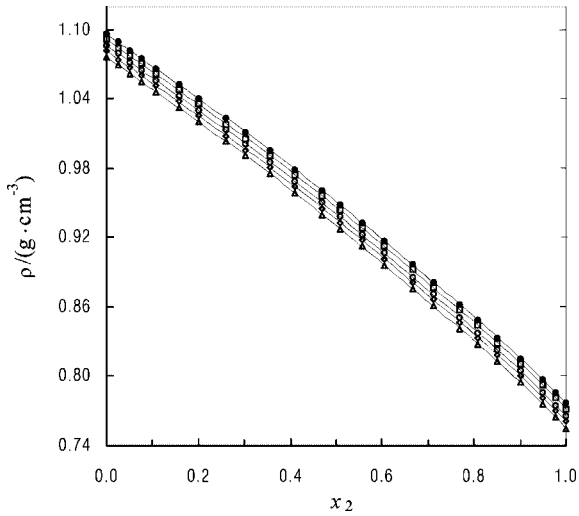

Figure 2. Experimental density values, ρ, for the DMSO (1) + AN (2) system, at different temperatures: ●, 298.15 K; □, 303.15 K; ○, 308.15 K; ◇, 313.15 K; △, 318.15 K.

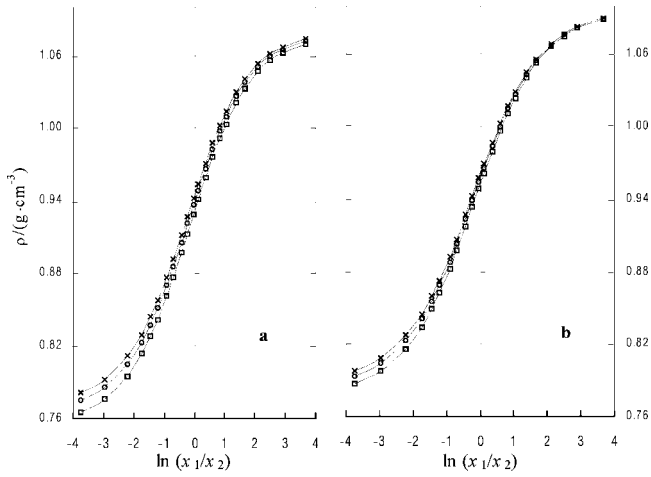

Figure 3. Experimental density values, ρ, for the DMSO (1) + AN (2) + W (3) system, as a function of $\ln(x_1/x_2)$, at different values of x_3: □, 0.0015; ○, 0.015; ×, 0.025. (a) $T = 318.15$ K; (b) $T = 298.15$ K.

weighed samples of each solution, and density measurements were performed on five series of experiments.

3. Results and Discussion

3.1. Density Measurements. Experimental data obtained on the different samples are reported in Table 1. Density values for the mixtures at $x_3 = 0$ were obtained by linear extrapolation from these data, as shown for two cases in Figure 1. The extrapolated values, corresponding to pure DMSO + AN mixtures, are shown in Table 2 and in Figure 2.

In Figure 3, densities of mixtures with different water content are plotted as a function of $\ln(x_1/x_2)$ at (318.15 and 298.15) K. As it is clearly seen, the AN-rich mixtures are the most affected by water content.

Excess volumes of mixing were calculated according to

$$V_M^E = \sum_i x_i M_i (\rho^{-1} - \rho_i^{o-1}) \quad (1)$$

where M_i is the molecular weight and ρ_i° is the density of component i. In Table 3, the resulting values for V_M^E are listed, and the dependence with x_2 is shown in Figure 4.

As can be seen therefrom, the excess volume shows positive deviation from ideality with a rather symmetrical behavior. This

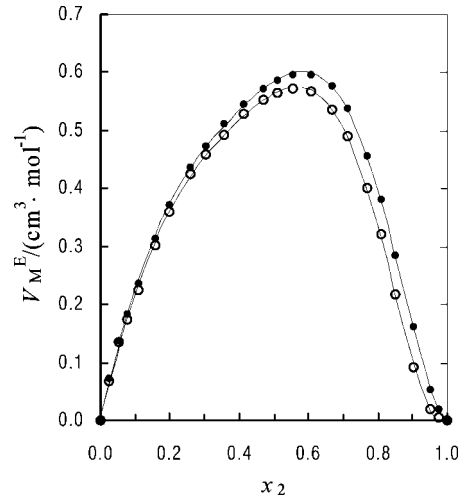

Figure 4. Excess molar volumes, V_M^E, for the DMSO (1) + AN (2) system: ●, 298.15 K; ○, 318.15 K.

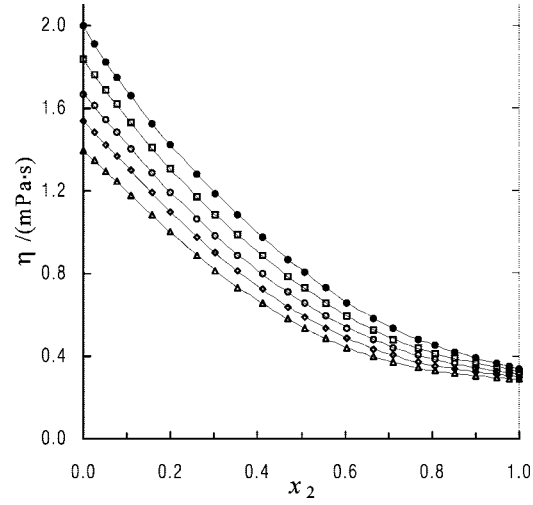

Figure 5. Experimental viscosity values, η, for the DMSO (1) + AN (2) system at different temperatures: ●, 298.15 K; □, 303.15 K; ○, 308.15 K; ◇, 313.15 K; △, 318.15 K. Curves calculated from eq 2.

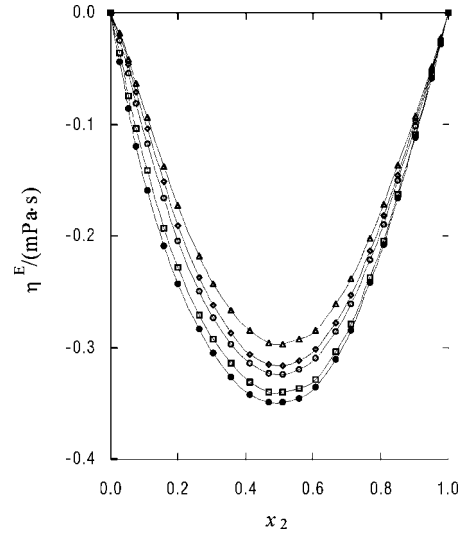

Figure 6. Excess viscosities, η^E, for the DMSO (1) + AN (2) system at different temperatures: ●, 298.15 K; □, 303.15 K; ○, 308.15 K; ◇, 313.15 K; △, 318.15 K.

can be explained if it is considered that both solvents are aprotic, and hence, their liquid state structure will mainly depend on

Table 1. Experimental Density Values, ρ, for the DMSO (1) + AN (2) + W (3) System from T = (298.15 to 318.15) K, Obtained on Solutions with Constant x_1/x_2, when Controlled Amounts of Water Were Added

				ρ/(g·cm^{-3})				
x_1/x_2	x_1	x_2	x_3	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15
				Series 1				
39.18	0.9736	0.0249	0.0015	1.08932	1.08453	1.07950	1.07480	1.06966
18.29	0.9467	0.0518	0.0015	1.08182	1.07698	1.07198	1.06718	1.06208
12.17	0.9227	0.0758	0.0015	1.07522	1.07049	1.06537	1.06066	1.05565
8.266	0.8907	0.1078	0.0015	1.06650	1.06166	1.05655	1.05196	1.04681
5.367	0.8418	0.1568	0.0014	1.05283	1.04810	1.04286	1.03814	1.03308
4.006	0.7991	0.1995	0.0014	1.04092	1.03610	1.03091	1.02616	1.02098
2.834	0.7381	0.2605	0.0014	1.02357	1.01884	1.01346	1.00877	1.00355
2.296	0.6956	0.3030	0.0014	1.01138	1.00658	1.00115	0.99654	0.99118
1.819	0.6444	0.3543	0.0013	0.99623	0.99148	0.98605	0.98135	0.97601
1.433	0.5883	0.4104	0.0013	0.97939	0.97461	0.96909	0.96438	0.95897
1.130	0.5297	0.4690	0.0013	0.96129	0.95653	0.95094	0.94623	0.94078
0.9668	0.4909	0.5078	0.0013	0.94908	0.94428	0.93859	0.93398	0.92850
0.7967	0.4429	0.5559	0.0012	0.93356	0.92879	0.92308	0.91843	0.91291
0.6520	0.3942	0.6046	0.0012	0.91765	0.91284	0.90704	0.90253	0.89693
0.5002	0.3330	0.6658	0.0012	0.89720	0.89244	0.88662	0.88210	0.87662
0.4057	0.2882	0.7106	0.0012	0.88207	0.87740	0.87159	0.86712	0.86147
0.3008	0.2310	0.7679	0.0011	0.86256	0.85786	0.85194	0.84745	0.84189
0.2375	0.1917	0.8072	0.0011	0.84901	0.84434	0.83848	0.83403	0.82839
0.1751	0.1489	0.8500	0.0011	0.83399	0.82931	0.82344	0.81902	0.81338
0.1100	0.0990	0.9000	0.0010	0.81606	0.81138	0.80535	0.80097	0.79535
0.05245	0.0498	0.9492	0.0010	0.79749	0.79283	0.78669	0.78223	0.77626
0.02345	0.0229	0.9761	0.0010	0.78673	0.78207	0.77570	0.77122	0.76518
				Series 2				
39.18	0.9695	0.0247	0.0058	1.08938	1.08469	1.07993	1.07530	1.07040
18.29	0.9429	0.0515	0.0056	1.08193	1.07731	1.07240	1.06783	1.06296
12.17	0.9191	0.0755	0.0054	1.07552	1.07078	1.06591	1.06140	1.05651
8.266	0.8870	0.1073	0.0057	1.06676	1.06213	1.05725	1.05281	1.04805
5.367	0.8383	0.1562	0.0055	1.05342	1.04870	1.04370	1.03921	1.03444
4.006	0.7960	0.1987	0.0053	1.04156	1.03694	1.03178	1.02731	1.02256
2.834	0.7354	0.2595	0.0051	1.02445	1.01974	1.01458	1.01007	1.00514
2.296	0.6933	0.3019	0.0048	1.01224	1.00762	1.00231	0.99781	0.99280
1.819	0.6421	0.3530	0.0049	0.99732	0.99272	0.98731	0.98287	0.97774
1.433	0.5861	0.4089	0.0050	0.98051	0.97597	0.97053	0.96606	0.96083
1.130	0.5275	0.4671	0.0054	0.96275	0.95810	0.95259	0.94815	0.94299
0.9668	0.4893	0.5060	0.0047	0.95026	0.94563	0.94006	0.93567	0.93037
0.7967	0.4411	0.5538	0.0051	0.93508	0.93042	0.92478	0.92039	0.91526
0.6520	0.3928	0.6024	0.0048	0.91906	0.91438	0.90877	0.90440	0.89919
0.5002	0.3318	0.6633	0.0049	0.89870	0.89413	0.88846	0.88417	0.87898
0.4057	0.2873	0.7081	0.0046	0.88360	0.87896	0.87328	0.86905	0.86376
0.3008	0.2301	0.7651	0.0048	0.86416	0.85960	0.85395	0.84968	0.84447
0.2375	0.1909	0.8039	0.0052	0.85083	0.84637	0.84077	0.83655	0.83117
0.1751	0.1483	0.8468	0.0049	0.83580	0.83119	0.82551	0.82137	0.81609
0.1100	0.0986	0.8967	0.0047	0.81782	0.81329	0.80753	0.80334	0.79806
0.05245	0.0496	0.9456	0.0048	0.79942	0.79485	0.78889	0.78466	0.77908
0.02345	0.0228	0.9727	0.0045	0.78855	0.78395	0.77781	0.77349	0.76780
				Series 3				
39.18	0.9645	0.0246	0.0109	1.08949	1.08501	1.08033	1.07596	1.07131
18.29	0.9382	0.0513	0.0106	1.08216	1.07760	1.07298	1.06865	1.06396
12.17	0.9144	0.0751	0.0105	1.07578	1.07124	1.06662	1.06231	1.05779
8.266	0.8824	0.1068	0.0108	1.06717	1.06274	1.05806	1.05389	1.04943
5.367	0.8342	0.1554	0.0104	1.05398	1.04950	1.04470	1.04043	1.03610
4.006	0.7920	0.1977	0.0103	1.04243	1.03787	1.03299	1.02882	1.02457
2.834	0.7318	0.2582	0.0100	1.02547	1.02101	1.01608	1.01177	1.00729
2.296	0.6899	0.3005	0.0096	1.01352	1.00910	1.00391	0.99967	0.99500
1.819	0.6391	0.3514	0.0095	0.99871	0.99425	0.98903	0.98473	0.97999
1.433	0.5833	0.4069	0.0098	0.98207	0.97764	0.97243	0.96823	0.96329
1.130	0.5250	0.4648	0.0102	0.96438	0.95992	0.95454	0.95038	0.94567
0.9668	0.4868	0.5035	0.0097	0.95211	0.94752	0.94220	0.93813	0.93318
0.7967	0.4392	0.5513	0.0096	0.93682	0.93228	0.92679	0.92264	0.91794
0.6520	0.3910	0.5997	0.0093	0.92090	0.91635	0.91088	0.90683	0.90192
0.5002	0.3303	0.6603	0.0094	0.90062	0.89610	0.89064	0.88672	0.88191
0.4057	0.2860	0.7049	0.0091	0.88558	0.88110	0.87560	0.87173	0.86673
0.3008	0.2291	0.7615	0.0094	0.86628	0.86181	0.85631	0.85252	0.84765
0.2375	0.1901	0.8007	0.0092	0.85272	0.84830	0.84298	0.83907	0.83396
0.1751	0.1476	0.8431	0.0093	0.83787	0.83346	0.82800	0.82421	0.81918
0.1100	0.0982	0.8928	0.0091	0.82001	0.81557	0.80996	0.80622	0.80121
0.05245	0.0494	0.9416	0.0090	0.80153	0.79716	0.79141	0.78747	0.78212
0.02345	0.0227	0.9685	0.0088	0.79073	0.78633	0.78047	0.77640	0.77098

the dipole−dipole interaction. Thus, since dipole moments for DMSO and AN are almost the same [(3.96 and 3.92) D, respectively], it is to be expected that as AN content increases the original DMSO structure is partially destroyed and mixture

Table 1 Continued

				ρ/(g·cm^{-3})				
x_1/x_2	x_1	x_2	x_3	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15
				Series 4				
39.18	0.9584	0.0245	0.0171	1.08965	1.08533	1.08094	1.07683	1.07240
18.29	0.9325	0.0510	0.0165	1.08237	1.07806	1.07373	1.06959	1.06516
12.17	0.9086	0.0746	0.0168	1.07622	1.07187	1.06746	1.06336	1.05927
8.266	0.8777	0.1062	0.0161	1.06765	1.06333	1.05884	1.05496	1.05100
5.367	0.8291	0.1545	0.0164	1.05483	1.05055	1.04592	1.04189	1.03812
4.006	0.7873	0.1966	0.0161	1.04340	1.03911	1.03442	1.03051	1.02678
2.834	0.7274	0.2567	0.0159	1.02685	1.02264	1.01785	1.01370	1.00984
2.296	0.6858	0.2986	0.0156	1.01519	1.01092	1.00581	1.00194	0.99782
1.819	0.6354	0.3494	0.0152	1.00046	0.99612	0.99109	0.98714	0.98291
1.433	0.5800	0.4047	0.0153	0.98379	0.97967	0.97472	0.97075	0.96622
1.130	0.5221	0.4622	0.0157	0.96635	0.96204	0.95694	0.95297	0.94868
0.9668	0.4839	0.5005	0.0156	0.95422	0.94988	0.94474	0.94107	0.93664
0.7967	0.4367	0.5481	0.0152	0.93902	0.93463	0.92939	0.92549	0.92135
0.6520	0.3886	0.5961	0.0153	0.92344	0.91896	0.91375	0.91006	0.90570
0.5002	0.3284	0.6566	0.0150	0.90299	0.89868	0.89342	0.88990	0.88567
0.4057	0.2844	0.7010	0.0146	0.88802	0.88365	0.87850	0.87494	0.87043
0.3008	0.2278	0.7574	0.0148	0.86870	0.86444	0.85923	0.85580	0.85139
0.2375	0.1892	0.7966	0.0142	0.85502	0.85078	0.84574	0.84216	0.83750
0.1751	0.1468	0.8383	0.0149	0.84052	0.83627	0.83120	0.82776	0.82318
0.1100	0.0977	0.8879	0.0144	0.82262	0.81841	0.81311	0.80968	0.80511
0.05245	0.0491	0.9369	0.0140	0.80405	0.79984	0.79446	0.79075	0.78581
0.02345	0.0226	0.9633	0.0141	0.79349	0.78932	0.78369	0.77991	0.77493
				Series 5				
39.18	0.9499	0.0242	0.0259	1.08993	1.08588	1.08175	1.07797	1.07382
18.29	0.9241	0.0505	0.0254	1.08281	1.07871	1.07474	1.07089	1.06690
12.17	0.9009	0.0740	0.0251	1.07677	1.07258	1.06850	1.06487	1.06135
8.266	0.8692	0.1052	0.0256	1.06838	1.06432	1.06039	1.05704	1.05366
5.367	0.8216	0.1531	0.0253	1.05596	1.05199	1.04770	1.04417	1.04123
4.006	0.7802	0.1948	0.0250	1.04500	1.04087	1.03656	1.03306	1.03035
2.834	0.7211	0.2545	0.0244	1.02871	1.02481	1.02034	1.01664	1.01362
2.296	0.6796	0.2959	0.0245	1.01758	1.01356	1.00878	1.00543	1.00193
1.819	0.6296	0.3461	0.0243	1.00314	0.99922	0.99455	0.99089	0.98743
1.433	0.5745	0.4008	0.0247	0.98689	0.98302	0.97851	0.97495	0.97111
1.130	0.5172	0.4579	0.0249	0.96954	0.96548	0.96075	0.95720	0.95387
0.9668	0.4794	0.4958	0.0248	0.95764	0.95344	0.94867	0.94556	0.94185
0.7967	0.4327	0.5432	0.0241	0.94249	0.93835	0.93338	0.92999	0.92671
0.6520	0.3849	0.5905	0.0246	0.92724	0.92288	0.91810	0.91505	0.91145
0.5002	0.3254	0.6504	0.0242	0.90686	0.90279	0.89787	0.89497	0.89169
0.4057	0.2817	0.6945	0.0238	0.89201	0.88780	0.88321	0.88034	0.87653
0.3008	0.2257	0.7504	0.0239	0.87281	0.86878	0.86399	0.86120	0.85761
0.2375	0.1873	0.7887	0.0240	0.85954	0.85555	0.85110	0.84810	0.84429
0.1751	0.1455	0.8310	0.0235	0.84450	0.84047	0.83602	0.83323	0.82925
0.1100	0.0967	0.8795	0.0238	0.82723	0.82332	0.81847	0.81567	0.81187
0.05245	0.0487	0.9282	0.0231	0.80854	0.80464	0.79987	0.79674	0.79245
0.02345	0.0224	0.9547	0.0229	0.79799	0.79416	0.78891	0.78577	0.78138

Table 2. Experimental Density Values, ρ, for the DMSO (1) + AN (2) System from T = (298.15 to 318.15) K

	ρ/(g·cm^{-3})				
x_2	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15
0.0000	1.09629	1.09144	1.08641	1.08159	1.07646
0.0249	1.08925	1.08441	1.07937	1.07457	1.06943
0.0518	1.08172	1.07688	1.07178	1.06698	1.06181
0.0759	1.07514	1.07033	1.06520	1.06043	1.05525
0.1079	1.06634	1.06151	1.05633	1.05161	1.04639
0.1570	1.05266	1.04783	1.04260	1.03781	1.03257
0.1998	1.04065	1.03583	1.03053	1.02577	1.02045
0.2609	1.02327	1.01844	1.01306	1.00831	1.00291
0.3034	1.01097	1.00618	1.00071	0.99597	0.99054
0.3548	0.99586	0.99106	0.98553	0.98082	0.97532
0.4110	0.97894	0.97415	0.96853	0.96381	0.95825
0.4696	0.96084	0.95606	0.95036	0.94565	0.94003
0.5084	0.94858	0.94378	0.93805	0.93336	0.92772
0.5566	0.93309	0.92829	0.92251	0.91782	0.91219
0.6053	0.91712	0.91234	0.90649	0.90186	0.89619
0.6666	0.89667	0.89191	0.88605	0.88145	0.87579
0.7114	0.88156	0.87687	0.87094	0.86639	0.86068
0.7688	0.86203	0.85732	0.85138	0.84681	0.84115
0.8081	0.84847	0.84381	0.83789	0.83337	0.82759
0.8510	0.83349	0.82878	0.82279	0.81829	0.81261
0.9009	0.81555	0.81084	0.80479	0.80034	0.79464
0.9502	0.79701	0.79231	0.78606	0.78154	0.77555
0.9771	0.78622	0.78149	0.77512	0.77053	0.76446
1.0000	0.77669	0.77189	0.76546	0.76086	0.75476

Table 3. Excess Molar Volumes, V_M^E, for the DMSO (1) + AN (2) System from T = (298.15 to 318.15) K

	V_M^E/(cm^3·mol^{-1})				
x_2	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15
0.0000	0.000	0.000	0.000	0.000	0.000
0.0249	0.072	0.071	0.069	0.068	0.067
0.0518	0.138	0.137	0.136	0.135	0.134
0.0759	0.182	0.180	0.178	0.176	0.173
0.1079	0.236	0.235	0.233	0.227	0.225
0.1570	0.314	0.312	0.309	0.308	0.303
0.1998	0.371	0.368	0.365	0.362	0.359
0.2609	0.437	0.434	0.430	0.427	0.424
0.3034	0.474	0.469	0.466	0.462	0.458
0.3548	0.511	0.506	0.501	0.496	0.493
0.4110	0.545	0.539	0.535	0.531	0.528
0.4696	0.572	0.566	0.561	0.557	0.554
0.5084	0.586	0.581	0.575	0.570	0.565
0.5566	0.596	0.592	0.584	0.580	0.571
0.6053	0.596	0.590	0.583	0.575	0.566
0.6666	0.576	0.569	0.557	0.549	0.535
0.7114	0.537	0.526	0.514	0.503	0.490
0.7688	0.456	0.446	0.430	0.421	0.401
0.8081	0.381	0.368	0.347	0.335	0.320
0.8510	0.284	0.274	0.254	0.242	0.217
0.9009	0.162	0.153	0.133	0.118	0.092
0.9502	0.054	0.045	0.034	0.026	0.018
0.9771	0.018	0.013	0.009	0.007	0.005
1.0000	0.000	0.000	0.000	0.000	0.000

Table 4. Experimental Viscosity Values, η, for the DMSO (1) + AN (2) System from T = (298.15 to 318.15) K

	η/(mPa·s)				
x_2	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15
0.0000	1.9960	1.8357	1.6689	1.5351	1.3935
0.0249	1.9111	1.7620	1.6101	1.4836	1.3477
0.0518	1.8244	1.6835	1.5439	1.4245	1.2947
0.0759	1.7503	1.6169	1.4847	1.3707	1.2465
0.1079	1.6581	1.5313	1.4053	1.2982	1.1801
0.1570	1.5269	1.4060	1.2901	1.1894	1.0823
0.1998	1.4221	1.3061	1.1938	1.0981	1.0004
0.2609	1.2812	1.1712	1.0659	0.9759	0.8875
0.3034	1.1885	1.0854	0.9838	0.8980	0.8161
0.3548	1.0824	0.9867	0.8905	0.8098	0.7348
0.4110	0.9742	0.8848	0.7978	0.7219	0.6547
0.4696	0.8699	0.7875	0.7092	0.6398	0.5794
0.5084	0.8053	0.7285	0.6554	0.5910	0.5348
0.5566	0.7292	0.6595	0.5949	0.5366	0.4864
0.6053	0.6586	0.5945	0.5379	0.4862	0.4403
0.6666	0.5821	0.5266	0.4786	0.4350	0.3971
0.7114	0.5345	0.4841	0.4428	0.4044	0.3700
0.7688	0.4819	0.4392	0.4048	0.3727	0.3423
0.8081	0.4514	0.4129	0.3833	0.3554	0.3298
0.8510	0.4225	0.3905	0.3645	0.3396	0.3178
0.9009	0.3934	0.3680	0.3459	0.3257	0.3062
0.9502	0.3658	0.3478	0.3285	0.3119	0.2967
0.9771	0.3517	0.3363	0.3194	0.3050	0.2927
1.0000	0.3417	0.3280	0.3129	0.3009	0.2899

molar volume increases. A similar effect is to be expected when DMSO is added on pure AN, and hence, the maximum deviation should occur near equimolar composition. This argument is cogent with the fact that V_M^E increases when temperature decreases from (318.15 to 298.15) K.

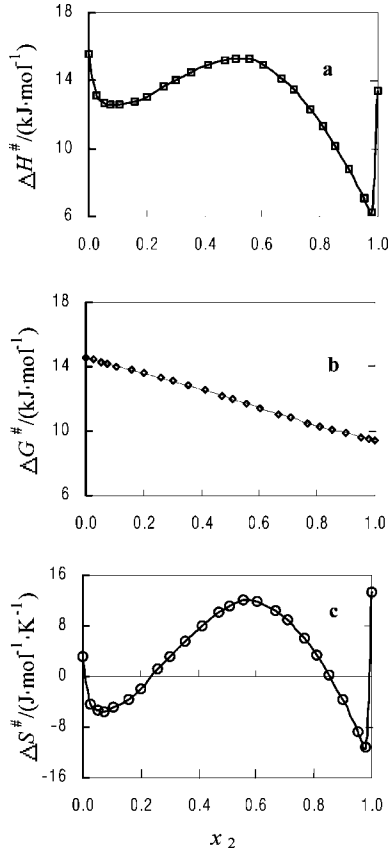

Figure 7. (a) Standard activation entalphy $\Delta H^{\#}$; (b) standard activation free entalphy $\Delta G^{\#}$; and (c) standard activation entropy $\Delta S^{\#}$, for viscous flow in the system DMSO (1) + AN (2).

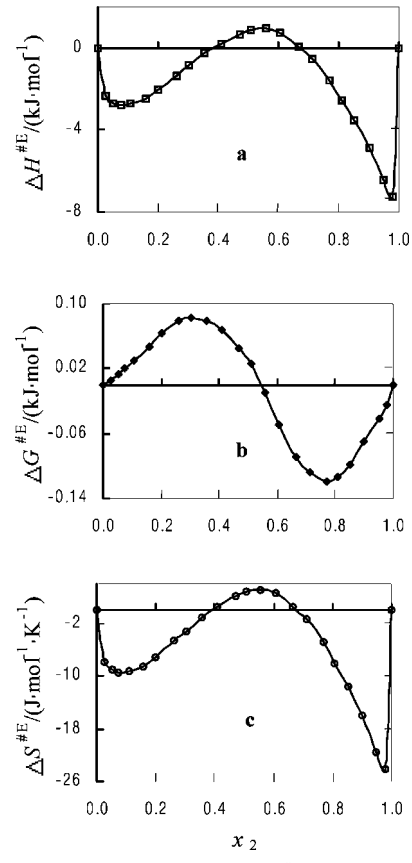

Figure 8. (a) Excess activation entalphy $\Delta H^{\#E}$; (b) excess activation free entalphy $\Delta G^{\#E}$; and (c) excess activation entropy $\Delta S^{\#E}$, for viscous flow in DMSO (1) + AN (2) mixtures.

3.2. Viscosity Measurements. Viscosity data obtained on the different samples are reported in Table 4. These data were fitted by the polynomial

$$\eta = \sum_{j=0,n} c_j x_2^j \tag{2}$$

In Table 5, the values obtained for the fitting coefficients are given together with the root-mean-square deviation

$$\sigma = \left[\sum (\eta_{exptl} - \eta_{calcd})^2 N^{-1}\right]^{1/2} \tag{3}$$

The corresponding curves are shown in Figure 5, together with experimental data.

Deviations from linear additive behavior are calculated as an "excess viscosity" from

$$\eta^E = \eta - (x_1\eta^o{}_1 + x_2\eta^o{}_2) \tag{4}$$

and are reported in Table 6 and shown in Figure 6 as a function of composition.

As seen from these results, negative excess viscosities are observed which are, also, symmetric with respect to mixture composition with a minimum at $x_2 = 0.51$. Excess viscosities become less negative as temperature is increased.

By its hand, in terms of the absolute rate theory, the viscosity of a liquid is given by

$$\eta = (hN_A/V)\exp(\Delta G^{\#}/RT) = (hN_A/V)\exp(\Delta H^{\#}/RT)\exp(-\Delta S^{\#}/R) \tag{5}$$

where h is Planck's constant; N_A is Avogadro's number; and V is the molar volume.

Table 5. Fitting Coefficients, c_i/(mPa·s), of the Experimental Viscosity Data and Root Mean Square Difference, σ, between Experimental and Calculated Viscosity Values with Equation 2, Employing a Sixth Grade Polynomial, for T = (298.15 to 318.15) K

T/K	c_0	c_1	c_2	c_3	c_4	c_5	c_6	σ
298.15	1.9964	−3.5532	4.6678	−8.0329	8.7758	−3.7390	0.22558	$67.145 \cdot 10^{-5}$
303.15	1.8363	−3.0601	2.1844	−0.25039	−3.5206	5.7893	−2.6520	$66.403 \cdot 10^{-5}$
308.15	1.6701	−2.4238	−0.9340	8.2444	−14.837	13.080	−4.4888	$79.612 \cdot 10^{-5}$
313.15	1.5361	−2.0907	−1.9417	9.9062	−15.418	12.245	−3.9373	$73.971 \cdot 10^{-5}$
318.15	1.3945	−1.8708	−1.7541	8.2629	−12.020	9.2088	−2.9329	$82.072 \cdot 10^{-5}$

Table 6. Excess Viscosities η^E of the DMSO (1) + AN (2) System for T = (298.15 to 318.15) K

	η^E/(mPa·s)				
x_2	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0249	−0.0437	−0.0362	−0.0250	−0.0208	−0.0183
0.0518	−0.0858	−0.0741	−0.0547	−0.0466	−0.0416
0.0759	−0.1202	−0.1044	−0.0813	−0.0707	−0.0633
0.1079	−0.1594	−0.1417	−0.1173	−0.1036	−0.0943
0.1570	−0.2093	−0.1929	−0.1659	−0.1519	−0.1379
0.1998	−0.2434	−0.2284	−0.2042	−0.1904	−0.1726
0.2609	−0.2833	−0.2712	−0.2493	−0.2373	−0.2181
0.3034	−0.3056	−0.2929	−0.2737	−0.2627	−0.2426
0.3548	−0.3267	−0.3141	−0.2973	−0.2874	−0.2672
0.4110	−0.3420	−0.3313	−0.3138	−0.3060	−0.2853
0.4696	−0.3493	−0.3402	−0.3229	−0.3157	−0.2959
0.5084	−0.3496	−0.3406	−0.3241	−0.3166	−0.2976
0.5566	−0.3460	−0.3370	−0.3193	−0.3116	−0.2928
0.6053	−0.3360	−0.3285	−0.3101	−0.3018	−0.2851
0.6666	−0.3112	−0.3041	−0.2864	−0.2774	−0.2608
0.7114	−0.2846	−0.2790	−0.2614	−0.2527	−0.2384
0.7688	−0.2423	−0.2374	−0.2216	−0.2136	−0.2028
0.8081	−0.2077	−0.2044	−0.1898	−0.1824	−0.1719
0.8510	−0.1657	−0.1622	−0.1505	−0.1452	−0.1366
0.9009	−0.1122	−0.1094	−0.1014	−0.0975	−0.0931
0.9502	−0.0584	−0.0554	−0.0520	−0.0505	−0.0482
0.9771	−0.0279	−0.0263	−0.0246	−0.0242	−0.0225
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 7. Activation Enthalphy $\Delta H^{\#}$, Activation Entropy $\Delta S^{\#}$, Activation Free Entalphies for Viscous Flow of Mixtures $\Delta G^{\#}$, Excess Activation Entalphy $\Delta H^{\#E}$, Excess Activation Entropy $\Delta S^{\#E}$, and Excess Activation Free Entalphies for Viscous Flow, $\Delta G^{\#E}$, for DMSO (1) + AN (2) Mixtures

	$\Delta H^{\#}$	$\Delta G^{\#}$	$\Delta S^{\#}$	$\Delta H^{\#E}$	$\Delta G^{\#E}$	$\Delta S^{\#E}$
x_2	(kJ·mol^{-1})	(kJ·mol^{-1})	(J·mol^{-1}·K^{-1})	(kJ·mol^{-1})	(kJ·mol^{-1})	(J·mol^{-1}·K^{-1})
0.0000	15.53	14.57	3.24	0.00	0.00	0.00
0.0249	13.17	14.45	−4.29	−2.32	0.01	−7.79
0.0518	12.71	14.32	−5.37	−2.71	0.01	−9.14
0.0759	12.57	14.20	−5.47	−2.81	0.02	−9.48
0.1079	12.58	14.05	−4.92	−2.73	0.03	−9.25
0.1570	12.73	13.81	−3.63	−2.47	0.05	−8.46
0.1998	13.06	13.61	−1.86	−2.06	0.06	−7.12
0.2609	13.66	13.31	1.18	−1.32	0.08	−4.70
0.3034	14.04	13.10	3.16	−0.86	0.08	−3.15
0.3548	14.51	12.83	5.64	−0.28	0.08	−1.19
0.4110	14.90	12.53	7.95	0.23	0.07	0.56
0.4696	15.23	12.21	10.13	0.68	0.05	2.14
0.5084	15.34	11.99	11.22	0.87	0.03	2.83
0.5566	15.30	11.71	12.03	0.93	−0.01	3.16
0.6053	14.96	11.42	11.88	0.70	−0.05	2.52
0.6666	14.15	11.07	10.34	0.02	−0.09	0.36
0.7114	13.50	10.82	8.98	−0.54	−0.11	−1.45
0.7688	12.33	10.51	6.09	−1.59	−0.12	−4.92
0.8081	11.30	10.32	3.28	−2.54	−0.11	−8.13
0.8510	10.19	10.11	0.26	−3.55	−0.10	−11.59
0.9009	8.81	9.89	−3.64	−4.83	−0.07	−15.98
0.9502	7.08	9.66	−8.67	−6.46	−0.04	−21.51
0.9771	6.23	9.54	−11.12	−7.25	−0.03	−24.24
1.0000	13.43	9.45	13.35	0.00	0.00	0.00

Thus, activation free enthalpies for viscous flow of the mixtures were obtained from

$$\Delta G^{\#} = RT \ln(\eta V/hN_A) \quad (6)$$

Activation enthalpy for the viscous flow was obtained by plotting $\ln(\eta V)$ as a function of T^{-1} and activation entropy calculated from

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \quad (7)$$

Excess activation quantities were calculated as

$$\Delta X^{\#E} = X^{\#} - (x_1 X_1^{\#} + x_2 X_2^{\#}) \quad (8)$$

Resulting values are listed in Table 7 and plotted in Figures 7 and 8.

The behavior observed for excess viscosities and activation parameters of viscous flow agrees with the idea that entropic effects are the main cause for deviation of ideality in these mixtures.

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