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Densities and Viscosities of Binary Liquid Mixtures of Anisole or Methyl *tert*-Butyl Ether with Benzene, Chlorobenzene, Benzonitrile, and Nitrobenzene

S. Viswanathan and M. Anand Rao

Department of Chemistry, Osmania University, Hyderabad 500007, India

D. H. L. Prasad*

Chemical Engineering Laboratory, Indian Institute of Chemical Technology, Hyderabad 500007, India

Densities and viscosities for the binary liquid mixtures of anisole or methyl *tert*-butyl ether (MTBE) with benzene, chlorobenzene, benzonitrile, and nitrobenzene were measured at 288.15, 293.15, and 298.15 K. These were used to compute the excess volumes (V^E) and deviations in viscosity ($\Delta\eta$). These properties are discussed with reference to the nature of interactions between the unlike molecules.

Introduction

The nature of interactions in binary systems, similar to the ones used in the present study, have been explained on the basis of certain thermophysical properties, such as excess volumes V^E/(cm^3·mol^{-1}), deviations in viscosity $\Delta\eta$/(mPa·s), deviations in isentropic compressibility β, excess enthalpies H^E/(J·mol), etc.[1−4]

Excess volumes and deviations in isentropic compressibility for the systems anisole + benzonitrile and anisole + nitrobenzene are reported by Rajkumar et al.[3] According to them, charge-transfer complexes are formed in both systems, with anisole acting as the donor. Srivastava[5] also came to a similar conclusion for the above systems. Excess volumes and deviations in viscosity for the systems anisole + benzene, anisole + chlorobenzene, and anisole + nitrobenzene are reported by Joshi et al.,[1,2] who concluded that specific interactions leading to molecular complexes exist only in the anisole + nitrobenzene system. Our earlier conclusions, following experimental work on vapor−liquid equilibria[6,7] and excess enthalpies[8,9] on the systems anisole + benzene, anisole + chlorobenzene, anisole + benzonitrile, and anisole + nitrobenzene, are not in agreement with those of the above studies. Among these systems only anisole + benzonitrile shows maximum negative values of excess free energies G^E and excess enthalpies H^E. Anisole + nitrobenzene shows S-shaped curves for both these properties, and the G^E values are very close to zero. Anisole + chlorobenzene, though showing fairly high negative values of G^E, shows very small negative values of H^E. Anisole + benzene shows positive values of H^E. If specific interactions of the electron pair donor−electron pair acceptor (EPD/EPA) type are important in these systems, then anisole + nitrobenzene should show greater magnitude of negative excess enthalpies than anisole + benzonitrile, since nitro groups are better electron acceptors than cyano groups.[10]

We, therefore, in an attempt to resolve the disagreement found between different studies, took up the study of densities and viscosities of the aforementioned systems.

Table 1. Comparison of Refractive Index (*n*D) and Density (ρ) of the Pure Liquids with Literature Data

liquid	n_D (293.15 K)		ρ(303.15 K)/(kg·m^{-3})	
anisole	this work	1.5175	this work	994.0[a]
	Riddick et al.[12]	1.51700	Riddick et al.[12]	994.02[a]
MTBE	this work	1.3690	this work	742.5
	TRC[14]	1.3690	Timmermans[13]	741.8
benzene	this work	1.5010	this work	868.4
	Riddick et al.[12]	1.50112	Riddick et al.[12]	868.29
benzonitrile	this work	1.5290	this work	996.5
	Riddick et al.[12]	1.52823	Riddick et al.[12]	996.28
nitrobenzene	this work	1.5530	this work	1193.7
	Riddick et al.[12]	1.5526	Riddick et al.[12]	1193.41

[a] Data at 293.15 K.

Anisole is a well-known electron-pair donor and is shown[11] to be a better donor than the xylenes and mesitylene toward the acceptor chloranil. In order to obtain an insight into the electronic factors involved in the interactions between the components in each system, we employed another known electron-pair donor, namely, methyl *tert*-butyl ether (MTBE). Both anisole and MTBE are ethers, have the $-OCH_3$ group in common, and have similar dipole moments and dielectric constants. The excess enthalpies[8,9] for the binary systems of MTBE were reported by us previously.

This paper presents experimental densities and viscosities of the two sets of binary systems: anisole or MTBE + benzene, + chlorobenzene, + benzonitrile, and + nitrobenzene at 288.15, 293.15, and 298.15 K. The experimental data are used to compute excess volumes (V^E) and deviations in viscosity ($\Delta\eta$).

Experimental Section

Materials. All the chemicals, except benzene, were procured from Fluka with a guaranteed purity of >99% (GC). HPLC grade benzene is supplied by Spectrochem Pvt. Ltd. (Mumbai, India). No further purification of the chemicals was attempted. Refractive indices are measured for the sodium-D line, by means of an Abbe-type refractometer maintained within ±0.1 K of the chosen temperature, and the densities are measured using a carefully calibrated

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* To whom correspondence should be addressed.

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Table 2. Densities (ρ) and Viscosities (η) of Binary Mixtures of Anisole at Different Temperatures

	ρ/(kg·m^{-3})			η/(mPa·s)		
x_1	288.15 K	293.15 K	298.15 K	288.15 K	293.15 K	298.15 K
(A) Anisole (1)−Benzene (2)						
0.0000	883.6	878.9	873.8	0.7322	0.6862	0.6489
0.0945	897.7	893.0	887.0	0.7766	0.7297	0.6765
0.1951	912.0	907.0	900.8	0.8124	0.7551	0.7095
0.2984	924.4	919.4	914.7	0.8595	0.8001	0.7437
0.3942	936.7	931.0	926.0	0.9033	0.8413	0.7772
0.5178	949.2	944.6	940.0	0.9594	0.9017	0.8397
0.6157	962.0	957.2	952.7	1.0192	0.9434	0.8800
0.6574	966.5	961.8	957.1	1.0339	0.9641	0.9047
0.8116	981.7	977.1	972.6	1.1370	1.0524	0.9812
0.9060	990.2	985.6	981.2	1.1794	1.0969	1.0206
1.0000	999.0	994.0	990.0	1.2388	1.1429	1.0849
(B) Anisole (1)−Chlorobenzene (2)						
0.0000	1112.5	1107.2	1102.1	0.9132	0.8522	0.8131
0.0976	1100.6	1095.3	1090.2	0.9242	0.8705	0.8217
0.1922	1089.1	1083.9	1078.9	0.9557	0.8967	0.8474
0.2893	1077.8	1072.7	1067.7	0.9751	0.9253	0.8642
0.3873	1066.3	1061.6	1056.7	1.0107	0.9512	0.8824
0.4930	1054.6	1049.9	1045.0	1.0529	0.9898	0.9356
0.5987	1043.0	1038.1	1033.4	1.0404	0.9670	0.9051
0.7059	1030.9	1026.1	1021.5	1.0606	1.0073	0.9242
0.7916	1021.5	1016.7	1012.2	1.1502	1.0720	0.9965
0.9050	1009.4	1004.7	1000.4	1.1988	1.1070	1.0374
1.0000	999.0	994.4	990.0	1.2388	1.1429	1.0849
(C) Anisole (1)−Benzonitrile (2)						
0.0000	1010.1	1005.8	1001.7	1.4915	1.3817	1.2815
0.0923	1009.2	1005.0	1000.8	1.4350	1.3149	1.2261
0.1792	1008.4	1004.1	999.9	1.4211	1.2998	1.2011
0.2764	1007.5	1003.2	999.1	1.3789	1.2702	1.1809
0.3719	1006.5	1002.2	997.9	1.3510	1.2348	1.1423
0.4735	1005.4	1001.1	996.8	1.2811	1.1911	1.1222
0.6068	1004.0	999.7	995.4	1.2489	1.1644	1.0882
0.7036	1002.9	998.5	994.2	1.2354	1.1495	1.0787
0.8080	1001.7	997.4	993.1	1.2029	1.1340	1.0555
0.8989	1000.6	996.1	991.8	1.2001	1.1187	1.0362
1.0000	999.0	994.4	990.0	1.2388	1.1429	1.0849
(D) Anisole (1)−Nitrobenzene						
0.0000	1208.8	1204.0	1199.5	2.1873	2.0790	1.8733
0.0982	1187.6	1183.0	1178.3	2.0247	1.8637	1.7034
0.1946	1166.9	1162.3	1157.7	1.9037	1.7200	1.6132
0.2868	1147.6	1142.9	1138.4	1.7674	1.5973	1.4677
0.3929	1125.0	1120.4	1116.0	1.6178	1.4781	1.3707
0.5767	1099.2	1094.5	1990.0	1.5255	1.4073	1.2940
0.6086	1079.7	1075.1	1070.7	1.4542	1.2889	1.2007
0.7073	1059.5	1055.2	1050.7	1.3519	1.2297	1.1533
0.8086	1038.4	1033.9	1029.5	1.2649	1.1674	1.0741
0.9081	1081.1	1013.6	1009.4	1.2138	1.1166	1.0485
1.0000	999.0	994.4.	990.0	1.2388	1.1429	1.0849

Table 3. Densities (ρ) and Viscosities (η) of Binary Mixture of MTBE at Different Temperatures

	ρ/(kg·m^{-3})			η/(mPa·s)		
x_1	288.15 K	293.15 K	298.15 K	288.15 K	293.15 K	298.15 K
(A) MTBE (1)−Benzene (2)						
0.0000	883.6	878.9	873.8	0.7322	0.6858	0.6494
0.0933	868.3	863.2	858.2	0.6641	0.6290	9.5806
0.1906	852.5	847.5	842.5	0.6252	0.5805	0.5446
0.2994	835.4	830.5	825.5	0.5767	0.5449	0.5084
0.3965	821.5	816.4	811.4	0.5469	0.5122	0.4776
0.5143	805.7	800.6	795.6	0.5019	0.4813	0.4676
0.6083	793.1	788.1	783.3	0.4822	0.4593	0.4417
0.7015	781.7	776.8	771.7	0.4620	0.4466	0.4227
0.8071	769.1	764.1	759.0	1.4343	0.4160	0.4037
0.9024	758.1	753.1	748.2	1.4192	0.4052	0.3980
1.0000	747.6	742.5	7373.8	0.4008	0.3861	0.3687
(B) MTBE (1)−Chlorobenzene (2)						
0.0000	1112.5	1107.2	1102.1	0.9132	0.8522	0.8131
0.0948	1076.3	1071.1	1065.9	0.8318	0.7752	0.7335
0.1898	1041.1	1035.9	1030.8	0.7884	0.7379	0.6981
0.2929	1004.6	999.4	994.3	0.7248	0.6754	0.6506
0.3832	968.4	963.3	958.2	0.7041	0.6443	0.6036
0.4974	930.2	925.0	920.0	0.6149	0.5825	0.5697
0.6209	881.2	875.8	871.3	0.5680	0.5368	0.5019
0.7014	852.7	847.5	842.3	0.5303	0.4905	0.4658
0.8089	813.8	808.8	803.7	0.4883	0.4560	0.4246
0.9102	779.1	774.0	768.8	0.4337	0.4191	0.3945
1.0000	747.6	742.5	737.4	0.4008	0.3861	0.3687
(C) MTBE (1)−Benzonitrile (2)						
0.0000	1010.1	1005.8	1001.7	1.4915	1.3817	1.2815
0.1048	988.6	984.3	980.0	1.3772	1.2769	1.1854
0.2024	970.0	965.6	961.2	1.2707	1.1798	1.0964
0.3015	934.1	929.7	925.2	1.1627	1.0812	1.0060
0.3969	909.9	905.5	901.1	1.0586	0.9863	0.9189
0.4912	886.6	882.0	877.4	0.9557	0.8924	0.8329
0.6055	866.6	861.9 .	857.3	0.8311	0.7787	0.7286
0.7115	836.5	831.8	827.3	0.7155	0.6732	0.6319
0.7995	811.8.	807.1	802.5	0.6195	0.5856	0.5516
0.9050	780.0	775.2	770.3	0.5044	0.4806	0.4554
1.0000	747.6	742.5	737.4	0.4008	0.3861	0.3687
(D) MTBE (1)−Nitrobenzene (2)						
0.0000	1208.8	1204.0	1199.5	2.1873	2.0790	1.8733
0.0921	1168.1	1163.1	1158.4	1.9519	1.7449	1.6252
0.1852	1126.8	1121.9	1117.3	1.6867	1.5345	1.4022
0.2942	1074.9	1070.2	1065.5	1.3476	1.3449	1.2029
0.3906	1028.3	1023.5	1018.6	1.2202	1.0964	0.9995
0.4845	988.0	983.2	978.6	1.1328	1.0106	0.8725
0.6950	930.3	925.4	920.7	0.8747	0.7813	0.7032
0.7094	882.3	877.3	872.3	0.7043	0.6590	0.6043
0.8055	838.7	833.9	829.1	0.6091	0.5509	0.5070
0.9053	791.3	786.2	781.2	0.4308	0.4676	0.4335
1.0000	747.6	742.5	737.4	0.4008	0.3861	0.3687

pycnometer maintained within ±0.1 K of the chosen temperature. The purity of the chemicals was indicated by measuring some of the physical properties. From a comparison with the literature data[12−14] as shown in Table 1, the purity of the chemicals used in the present study is expected to be about 99.5%.

Measurements. The density of pure liquids and their mixtures are determined using a specially designed pycnometer, similar to the one used by Dahiya et al.[15] It consists of a small bulb of capacity around 25 mL. A capillary attached to its neck is calibrated using the masses of HPLC grade benzene, which is filled to a reference mark in the capillary. The level in the capillary is accurately read by a traveling microscope (least count = 0.001 cm) after the apparatus is immersed in a cryostat (Julabo F 20) and maintained at the required temperature to within ±0.01 K. The mass of the dried apparatus (along with a Teflon cap) is first taken. Subsequently the sample liquid or mixture is introduced into it by means of a hypodermic syringe, taking care that no air bubbles are entrapped. The apparatus is then capped and its mass determined on a precision balance (Sartorius RC 210 P), reproducible to within 10^{-5} g. The apparatus is then immnersed in the cryostat maintained at the desired temperature until no further change in the level of the liquid in the capillary is observed. This level is noted and used in the calculations for excess volume. Further readings on the same mixture are taken at the other two lower temperatures, achieved by lowering the setting of the cryostat temperature. The reliability of the apparatus and of the method is established by measuring the densities for the system anisole + nitrobenzene, and our results on the system agree with those of Joshi et al.,[2] within ±0.1 kg·m^{-3}.

The viscosities of the pure liquids and their mixtures are determined using a Höppler falling-ball viscometer which is connected to a cryostat (Julabo F 20) maintained at the required temperature to within ±0.01 K. The fall times are accurate within ±0.1 s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, is within ±0.2% of the reported value.

The mixture preparation is carried out in air-tight stoppered bottles whose dry masses were determined before filling. The more volatile component is introduced into the bottle, and the mass of this is measured. Subsequently the

Table 4. Parameters h_j and Standard Deviation $\sigma(V^E)$ for Different Binary Systems

system	h_0	h_1	h_2	h_3	h_4	$\sigma(V^E)$
			Temperature = 288.15 K			
anisole + benzene	−0.428000	−0.29480	−3.3490	+1.41200	+4.36500	0.0522
anisole + chlorobenzene	−0.009507	−0.25940	+0.6626	+0.01820	−1.13400	0.0089
anisole + benzonitrile	−0.313000	−0.02554	−0.1224	−0.29170	−0.07382	0.0021
anisole + nitrobenzene	−0.718200	−0.03019	+0.2670	−0.42220	−0.53670	0.0112
MTBE + benzene	−0.310700	+0.35870	−6.4240	−8.32800	−2.25200	0.4275
MTBE + chlorobenzene	−5.312000	+1.28700	+4.1350	−3.31300	−4.74900	0.1302
MTBE + benzonitrile	−8.039000	−7.90800	−20.6800	+6.75800	+15.67000	0.3375
NITBE + nitrobenzene	−7.821000	−1.79800	−5.2250	+1.68100	+5.46100	0.1055
			Temperature = 293.15 K			
anisole + benzene	−0.27580	−0.8180	−3.50100	+2.1370	+4.2710	0.0335
anisole + chlorobenzene	−0.09239	−0.1911	+1.09900	−0.1918	−1.5650	0.0037
anisole + benzonitrile	−0.37570	−0.1671	−0.17250	−0.1789	−0.1365	0.0046
anisole + nitrobenzene	−0.77360	−0.1638	−0.01198	−0.2623	−0.4919	0.0154
MTBE + benzene	−0.26570	+0.2070	−6.96800	−8.1680	−0.5492	0.4024
MTBE + chlorobenzene	−5.35900	+1.3490	+3.35300	−3.4650	−3.9480	0.1245
MTBE + benzonitrile	−8.27800	−8.0240	−21.00000	+6.4290	+15.6100	0.3381
MTBE + nitrobenzene	−8.09000	−1.8790	−5.79400	+1.5290	+6.5880	0.1113
			Temperature = 298.15 K			
anisole + benzene	−0.36470	−0.80440	−2.4730	+0.8998	+4.09700	0.0429
anisole + chlorobenzene	−0.06090	−0.17730	+1.0190	−0.4579	−1.74100	0.0060
anisole + benzonitrile	−0.37780	−0.12580	−0.3842	−0.3521	+0.04176	0.0067
anisole + nitrobenzene	−0.81520	−0.01532	+0.2611	−0.9279	−0.96950	0.0146
MTBE + benzene	−0.39860	+0.23740	−6.6310	−8.3650	−1.43400	0.4006
MTBE + chlorobenzene	−5.68100	+1.18200	+4.0100	−3.1700	−4.35300	0.1248
MTBE + benzonitrile	−8.52300	−8.43400	−21.7100	+6.6440	+16.36000	0.3379
MTBE + nitrobenzene	−8.37200	−2.01300	−6.0700	+1.4060	+7.00300	0.1241

Table 5. Parameters h_j and Standard Deviation $\sigma(\eta^E)$ for Different Binary Systems

system	h_0	h_1	h_2	h_3	h_4	$\sigma(\eta^E)$
			Temperature = 288.15 K			
anisole + benzene	−0.1241	+0.0468	−0.0015	−0.1229	+0.1397	0.0006
anisole + chlorobenzene	−0.1898	−0.3585	−0.0118	+0.7115	+0.0597	0.0030
anisole + benzonitrile	−0.3105	−0.2907	+0.0185	+0.0955	−0.5037	0.0010
anisole + nitrobenzene	−0.7278	+0.1010	+0.0454	−0.7805	−0.8351	0.0038
MTBE + benzene	−0.2265	+0.0399	+0.0588	+0.2495	−0.1437	0.0009
MTBE + chlorobenzene	−0.1221	−0.0123	+0.0074	+0.2454	−0.2945	0.0012
MTBE + benzonitrile	−0.2367	−0.3470	−0.0278	+0.5768	−0.3820	0.0024
MTBE + nitrobenzene	−1.0189	+0.8558	−0.0511	−1.9879	−0.5625	0.0092
			Temperature = 293.15 K			
anisole + benzene	−0.1013	+0.0658	−0.0035	−0.0997	+0.1898	0.0005
anisole + chlorobenzene	−0.1157	−0.2953	+0.0094	+0.5593	+0.0336	0.0024
anisole + benzonitrile	−0.2767	−0.1366	+0.0243	+0.1817	−0.5087	0.0012
anisole + nitrobenzene	−0.8994	+0.2001	+0.0302	−0.2363	−1.2210	0.0022
MTBE + benzene	−0.2048	+0.1193	+0.0221	+0.0914	−0.0319	0.0003
MTBE + chlorobenzene	−0.1428	−0.0365	+0.0039	+0.2841	−0.2353	0.0014
MTBE + benzonitrile	−0.2810	−0.3864	−0.0349	+0.7199	−0.5762	0.0030
MTBE + nitrobenzene	−1.1383	−0.0170	+0.0663	+1.1085	−1.0040	0.0055
			Temperature = 298.15 K			
anisole + benzene	−0.1599	+0.0606	+0.0127	−0.1891	−0.0996	0.0009
anisole + chlorobenzene	−0.1849	−0.3410	+0.0072	+0.5377	−0.1317	0.0023
anisole + benzonitrile	−0.2734	−0.0333	+0.0029	−0.2602	−0.7312	0.0016
anisole + nitrobenzene	−0.7732	+0.0312	+0.0328	−0.3972	−0.9578	0.0024
MTBE + benzene	−0.1949	+0.1290	+0.0717	+0.3024	−0.1657	0.0011
MTBE + chlorobenzene	−0.1385	−0.0839	+0.0085	+0.3518	−0.4167	0.0018
MTBE + benzonitrile	−0.3144	−0.2245	−0.0051	+0.0660	−0.2077	0.0004
MTBE + nitrobenzene	−1.0998	+0.1656	+0.0065	+0.1349	−0.0217	0.0006

second component is injected into the bottle through the stopper by means of a syringe, and the total mass is measured.

Treatment of the Data

The experimental values of ρ and η of all the binary mixtures studied at the three temperatures are given in Tables 2 and 3, respectively. The excess volumes are calculated using the relation

$$V^E = V - (x_1V_1 + x_2V_2) \tag{1}$$

where V is the molar volume of the mixture, defined as

$$V = (x_1M_1 + x_2M_2)/\rho \tag{2}$$

M_1 and M_2 are the molecular masses of the pure components 1 and 2, ρ is the density of the mixture, and V_1 and V_2 are the molar volumes of the pure components from

$$V_i = M_i/\rho_i \tag{3}$$

where ρ_i represents the density of component i.

The deviations in viscosity are calculated using the relation

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \tag{4}$$

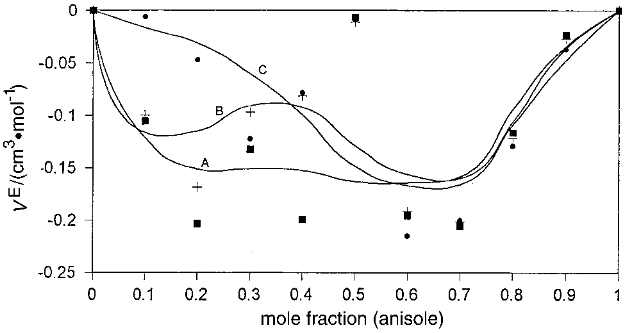

Figure 1. V^E for the anisole−benzene system at 15, 20, and 25 °C: (■) V^E at 15 °C; (+) V^E at 20 °C; (●) V^E at 25 °C. A = Calculated curve for V^E at 15 °C; B = calculated curve for V^E at 20 °C; C = calculated curve for V^E at 25 °C.

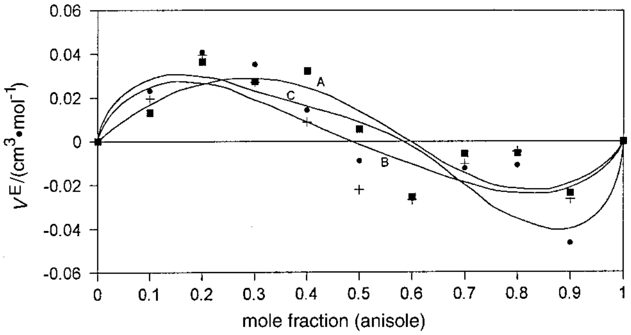

Figure 2. V^E for the anisole−chlorobenzene system at 15, 20, and 25 °C: (■) V^E at 15 °C; (+) V^E at 20 °C; (●) V^E at 25 °C. A = Calculated curve for V^E at 15 °C; B = calculated curve for V^E at 20 °C; C = calculated curve for V^E at 25 °C.

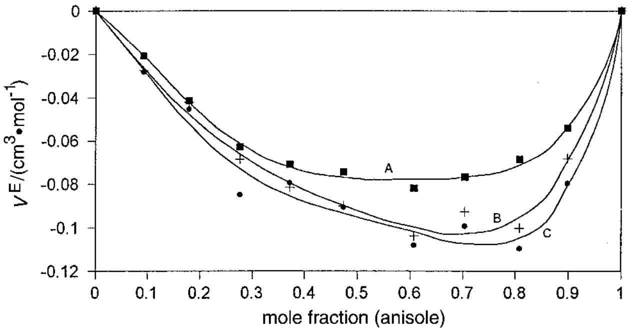

Figure 3. V^E for the anisole−benzonitrile system at 15, 20, and 25 °C: (■) V^E at 15 °C; (+) V^E at 20 °C; (●) V^E at 25 °C. A = Calculated curve for V^E at 15 °C; B = calculated curve for V^E at 20 °C; C = calculated curve for V^E at 25 °C.

where η, η_1, and η_2 are the viscosities of the mixture and pure components 1 and 2.

Experimental results of V^E and $\Delta\eta$ for each binary mixture at the three temperatures are shown in Figures 1−16. They are fitted by the method of least squares to a Redlich−Kister type of equation

$$V^E \text{ or } \Delta\eta = x(1 - x)\sum_j h_j(2x - 1)^j \qquad (5)$$

where the determined parameters, h_j, are given in Tables 4 and 5.

The standard deviation in each case is calculated using the relation

$$\sigma(X) = \left[\frac{\sum(X_{\text{expt}} - X_{\text{calc}})^2}{n - 1}\right]^{1/2} \qquad (6)$$

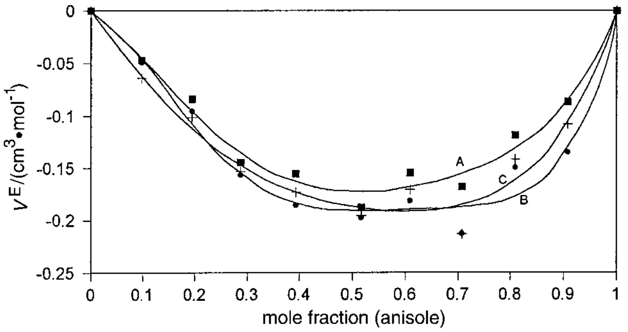

Figure 4. V^E for the anisole−nitrobenzene system at 15, 20, and 25 °C: (■) V^E at 15 °C; (+) V^E at 20 °C; (●) V^E at 25 °C. A = Calculated curve for V^E at 15 °C; B = calculated curve for V^E at 20 °C; C = calculated curve for V^E at 25 °C.

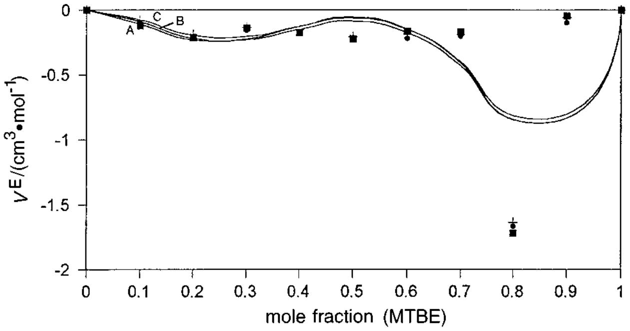

Figure 5. V^E for the MTBE−benzene system at 15, 20, and 25 °C: (■) V^E at 15 °C; (+) V^E at 20 °C; (●) V^E at 25 °C. A = Calculated curve for V^E at 15 °C; B = calculated curve for V^E at 20 °C; C = calculated curve for V^E at 25 °C.

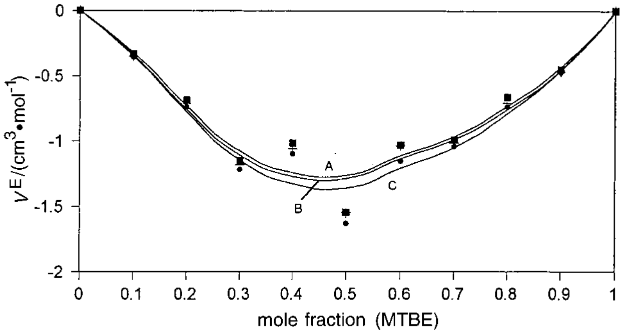

Figure 6. V^E for the MTBE−chlorobenzene system at 15, 20, and 25 °C: (■) V^E at 15 °C; (+) V^E at 20 °C; (●) V^E at 25 °C. A = Calculated curve for V^E at 15 °C; B = calculated curve for V^E at 20 °C; C = calculated curve for V^E at 25 °C.

where X represents V^E or $\Delta\eta$. n refers to the number of data points.

Results and Discussion

The excess volumes for all the anisole systems, except anisole + chlorobenzene, are negative at the three temperatures studied. The anisole + chlorobenzene system shows a sign change from positive to negative with increasing mole fraction of anisole at the three temperatures. The magnitude of V^E values for the three systems are in the order anisole + nitrobenzene > anisole + benzene > anisole + benzonitrile. The V^E values for all the MTBE systems are negative, and their magnitudes follow the order MTBE + benzonitrile > MTBE + nitrobenzene > MTBE + chlorobenzene > MTBE + benzene.

MTBE systems show greater magitude of V^E values than the anisole systems.

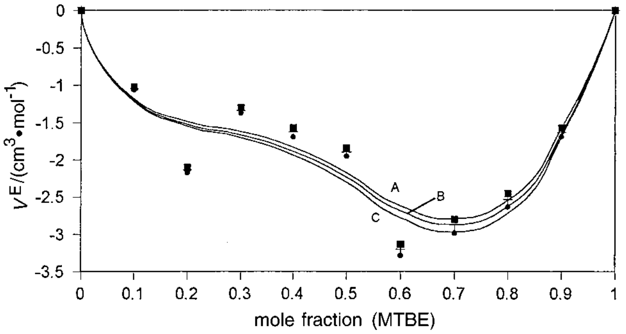

Figure 7. V^E for the MTBE−benzonitrile system at 15, 20, and 25 °C: (■) V^E at 15 °C; (+) V^E at 20 °C; (●) V^E at 25 °C. A = Calculated curve for V^E at 15 °C; B = calculated curve for V^E at 20 °C; C = calculated curve for V^E at 25 °C.

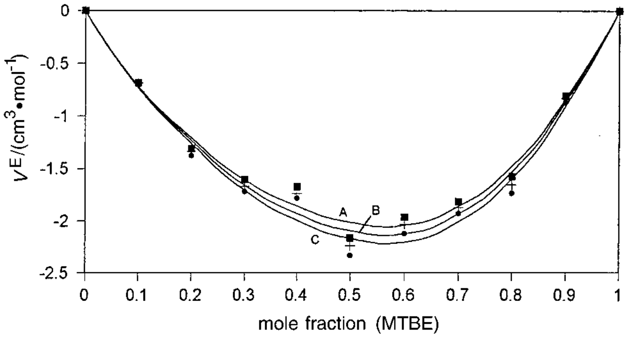

Figure 8. V^E for the MTBE−nitrobenzene system at 15, 20, and 25 °C: (■) V^E at 15 °C; (+) V^E at 20 °C; (●) V^E at 25 °C. A = Calculated curve for V^E at 15 °C; B = calculated curve for V^E at 20 °C; C = calculated curve for V^E at 25 °C.

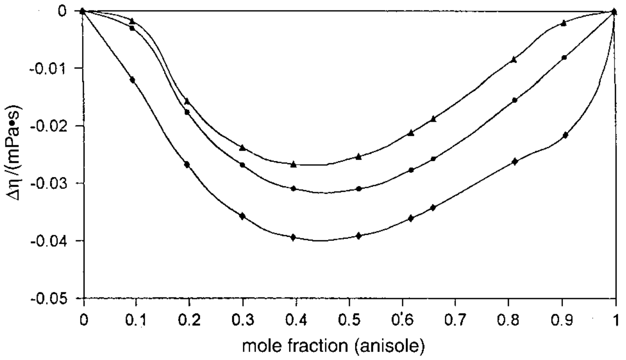

Figure 9. Deviations in viscosity, $\Delta\eta$, for anisole + benzene: (–•–) 288.15 K; (– ▲ –) 293.15 K; (– ♦ –) 298.15 K.

The deviations in viscosity, $\Delta\eta$, are negative for all eight systems studied at the three temperatures. Within the anisole systems the magnitudes are in the order anisole + nitrobenzene > anisole + chlorobenzene > anisole + benzonitrile > anisole + benzene. Within the MTBE systems the order is MTBE + nitrobenzene > MTBE + benzonitrile > MTBE + benzene > MTBE + chlorobenzene.

The $\Delta\eta$ values for MTBE + nitrobenzene are greater in magnitude than those for anisole + nitrobenzene while those for MTBE + chlorobenzene are slightly lesser than those for anisole + chlorobenzene. The other MTBE systems show marginally higher $\Delta\eta$ values when compared to the anisole systems. In general, therefore, MTBE systems show greater V^E and $\Delta\eta$ values than anisole systems, indicating that the former systems deviate more from ideality. The excess enthalpies of these systems are also in agreement with this. Except the systems involving benzene, which can be taken as a reference on account of being unsubstituted, the rest of the systems of anisole show less negative values of H^E than the corresponding systems of MTBE. This indicates that attractive interactions between the unlike molecules are stronger in MTBE systems. This provides support to the existence of electron-pair

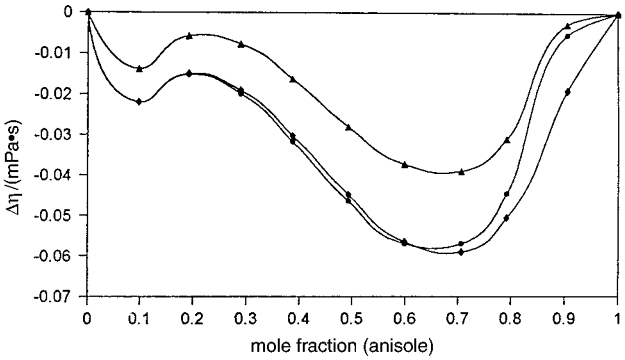

Figure 10. Deviations in viscosity, $\Delta\eta$, for anisole + chlorobenzene: (–•–) 288.15 K; (– ▲ –) 293.15 K; (– ♦ –) 298.15 K.

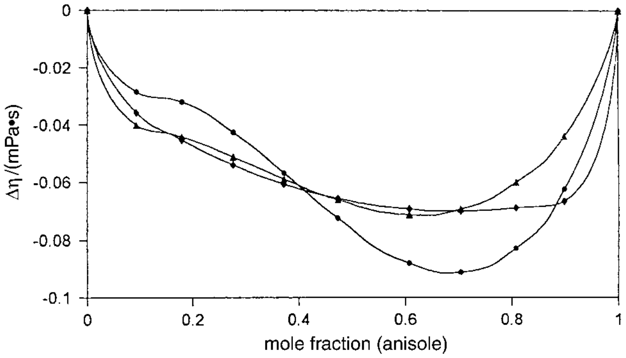

Figure 11. Deviations in viscosity, $\Delta\eta$, for anisole + benzonitrile: (–•–) 288.15 K; (– ▲ –) 293.15 K; (– ♦ –) 298.15 K.

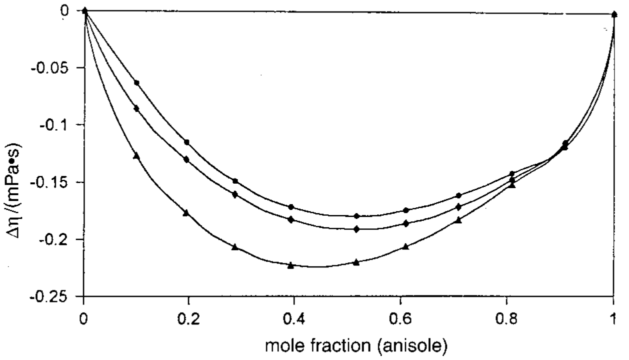

Figure 12. Deviations in viscosity, $\Delta\eta$, for anisole + nitrobenzene: (–•–) 288.15 K; (– ▲ –) 293.15 K; (– ♦ –) 298.15 K.

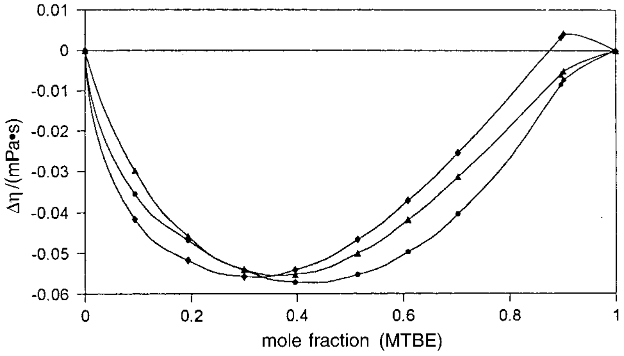

Figure 13. Deviations in viscosity, $\Delta\eta$, for MTBE + benzene: (–•–) 288.15 K; (– ▲ –) 293.15 K; (– ♦ –) 298.15 K.

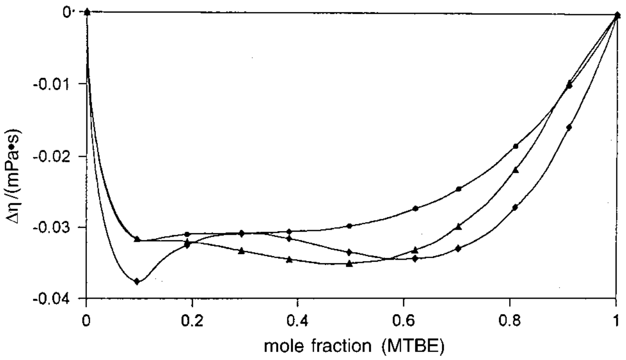

Figure 14. Deviations in viscosity, $\Delta\eta$, for MTBE + chlorobenzene: (–•–) 288.15 K; (– ▲ –) 293.15 K; (– ♦ –) 298.15 K.

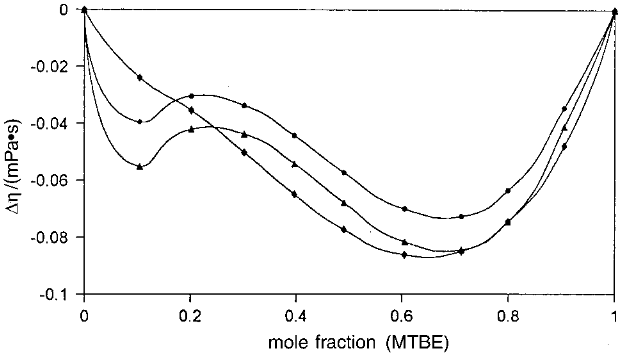

Figure 15. Deviations in viscosity, $\Delta\eta$, for MTBE + benzonitrile: (–•–) 288.15 K; (– ▲ –) 293.15 K; (– ♦ –) 298.15 K.

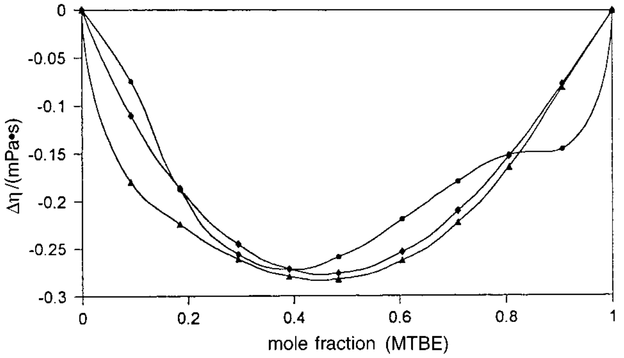

Figure 16. Deviations in viscosity, $\Delta\eta$, for MTBE + nitrobenzene: (–•–) 288.15 K; (– ▲ –) 293.15 K; (– ♦ –) 298.15 K.

donor–electron-pair acceptor types of interactions in all the systems studied, since MTBE is a better electron-pair donor than anisole. The better electron-donating capacity of MTBE is due to the fact that whenever the oxygen atom of an ether is attached to an unsaturated system, its donor properties are diminished due to delocalization of n electrons into the π-system.[4]

However, the $\Delta\eta$ values are negative in all the systems studied. According to Fort and Moore,[16] $\Delta\eta$ values are negative in systems of unequal molecular size in which dispersion forces are dominant. It is observed in many systems that there is no simple correlation between the strength of the interactions and the observed properties. Rastogi et al.,[17] therefore, suggested that the observed excess property is a combination of an interaction and a noninteraction part. Thus, we may write

$$X^{\mathrm{E}}(\text{observed}) = X^{\mathrm{E}}(\text{interaction}) + X^{\mathrm{E}}\ (\text{size effect}) \qquad (7)$$

where X^{E}(observed) refers to the excess or deviation in the property. The noninteraction part in the form of size effect can be comparable to the interaction part and may be sufficient to reverse the trend set by the latter.

Although the $\Delta\eta$ values are negative, the values of free energy of activation of flow, ΔG^*, defined as

$$\Delta G^* = RT[\ln(\eta V) - (x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2))] \qquad (8)$$

are positive in a few systems. According to Reed and Taylor[18] and Meyer et al.,[19] positive ΔG^* values indicate specific interactions while negative values indicate the dominance of dispersion forces. The positive ΔG^* values found in the systems MTBE + benzonitrile, MTBE + nitrobenzene, and MTBE + chlorobenzene are a fair indication of the presence of specific interactions. Further, both in $\Delta\eta$ and ΔG^*, temperature dependence is also found in the aforementioned systems, as also in anisole + benzonitrile. On comparison with H^{E} values for these systems,[8,9] we find that all of these, except MTBE + nitrobenzene, show greater magnitude of negative H^{E} values. The unfavorable H^{E} values (and G^{E} values) for both the nitrobenzene systems may be due to the large size effect associated with the somewhat nonplanar and extended nitrobenzene molecule.

Since temperature dependence is shown to be a good test for the presence of interactions,[20] we find that the following systems involve a fairly good amount of interactions: MTBE + benzonitrile, MTBE + chlorobenzene, MTBE + nitrobenzene, and anisole + benzonitrile. Anisole–benzene van der Waals complexes were studied[21] using a supersonic cooling technique, and the most stable conformation of the complex is also predicted. Presence of more stable complexes in the remaining seven binary systems is indicated by the more favourable excess volumes and deviations in viscosity for these systems.

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