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Studies of viscous antagonism, excess molar volumes, viscosity deviation and isentropic compressibility of ternary mixtures containing *N,N*-dimethylformamide, benzene and some ethers at 298.15 K

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Abstract: The densities (ρ) and viscosities (η) for ternary liquid mixtures of *N,N*-dimethylformamide + benzene + an ether were measured as a function of composition at 298.15 K. From experimental measurements, the excess molar volumes (V^E), viscosity deviation ($\Delta\eta$), antagonistic interaction index (I_A) and Gibbs free energy of activation for viscous flow (ΔG^{*E}) were evaluated. The speeds of sound were also measured and excess isentropic compressibilities (K_s^E) were calculated at the experimental temperature. The results are discussed and interpreted in terms of molecular package and specific interaction predominated by hydrogen bonding.

Keywords: viscous antagonism; viscosity deviations; excess molar volumes; isentropic; compressibility; molecular interactions.

INTRODUCTION

The grouping of solvents into classes is often based on the nature of intermolecular forces because the manner in which solvent molecules are associated with each other has a marked effect on the resulting properties. Rheology is the branch of science¹ that studies material deformation and flow, and is increasingly applied to analyze the viscous behaviors of many pharmaceutical products,² and to establish their stability and even bio-availability, since it has been firmly established that viscosity influences the absorption rate of a drug in the body. The increasing use of the solvents: *N,N*-dimethylformamide (DMF), benzene, 1,3-dioxolane, 1,4-dioxane, tetrahydrofuran, 1,2-dimethoxyethane, di-isopropyl ether, diethyl ether, 2-methoxyethanol and 2-ethoxyethanol and their mixtures in many industrial processes, such as battery, pharmaceutical and cosmetics, has greatly stimulated the need for extensive information on their various properties. Hence,

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the present study gives extensive information on the various properties when these ethers are taken with DMF and benzene as mixed solvent systems.¹⁻⁷ The determination of density, viscosity and speed of sound are valuable tools to learn about the liquid state^{8,9} because of the close connection between liquid structure and macroscopic properties.

The viscosity and density of these ternary liquid mixtures were used to understand the molecular interactions between the components of the mixture to develop new theoretical models and also for engineering applications.^{10,11} In systematic investigations, the viscosities, densities and speeds of sound of different solvents and their mixtures were reported in previous papers.¹²⁻¹⁸

The present work contributes and extends the study of density (ρ), viscosity deviations ($\Delta\eta$), viscous antagonism, excess molar volumes (V^E) and isentropic compressibility (K_S^E) to mixtures of DMF and benzene with some ethers, where DMF is represented as A, benzene as B and the ethers as C.

EXPERIMENTAL

DMF (C₃H₇NO) was obtained from Merck and LR, and further purified by standard methods.¹⁹ Benzene (S. D. Fine Chemicals, purity > 99 %) was further purified by means of a simple distillation technique with the first and last 20 % of the distillate being discarded²⁰⁻²² and finally the density and viscosity value were compared with the literature.²³ The final purities of the obtained solvents were >99.5 %.

The experimental ethers, namely 1,3-dioxolane (1,3-DO), 1,4-dioxane (1,4-DO), tetrahydrofuran (THF), 1,2-dimethoxyethane(1,2-DME), di-isopropyl ether (DIE), diethyl ether (DEE), 2-methoxy ethanol (2-ME) and 2-ethoxyethanol (2-EE) were obtained from Merck and LR. These were further purified by standard methods.²⁴⁻²⁷ The purities of the liquids was ascertained by GLC and also by comparing the experimental values of densities, viscosities and sound velocities with those reported in the literature,^{24,27-35} as listed in Table I. The purities of the finally obtained solvents were >99 %.

TABLE I. Physical properties of the pure solvents at 298.15 K

Solvent	$\rho / \text{g cm}^{-3}$		$\eta / \text{mPa s}$		$u / \text{m s}^{-1}$	
	Experimental	Literature	Experimental	Literature	Experimental	Literature
DMF	0.94609	0.9447 ²⁷	0.8586	0.802 ²⁷	1465.2	1465.0 ²⁷
Benzene	0.8735	0.8735 ²³	0.5920	0.5920 ²³	1252.7	--
1,3-Dioxolane	1.0577	1.0586 ³³	0.5878	0.5873 ²¹	1338.2	1338.8 ³³
1,4-Dioxane	1.0287	1.0279 ³³	1.1779	1.196 ²⁵	1344.4	1345.5 ³³
Tetrahydrofuran	0.8807	0.8811 ²⁵	0.463	0.460 ²⁵	1292.2	1294.0 ²⁹
1,2-Dimethoxy ethane	0.8615	0.8611 ³⁵	0.4089	0.4089 ³⁵	1146.2	--
Di-isopropyl ether	0.7250	0.7250 ²¹	0.379	0.3791 ²¹	1050.1	--
Diethyl ether	0.7134	0.7134 ²⁵	0.224	0.22404 ²⁵	1080.8	--
2-Methoxy ethanol	0.95979	0.9600 ³⁴	1.543	1.5414 ³⁴	1339.4	--
2-Ethoxy ethanol	0.92497	0.9256 ²⁷	1.8277	1.851 ²⁷	1308.0	1308.0 ²⁷

Densities (ρ) were measured with an Ostwald–Sprengel type pycnometer having a bulb volume of 25 cm³ and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at the experimental temperature with triply distilled water and DMF. The measurements were realized in a thermostated water bath controlled to ± 0.01 K.² The weighings were performed on a Mettler electronic balance (AG-285) with a precision of ± 0.01 mg. The viscosities (η) were measured by means of a suspended Ubbelohde type viscometer⁷, which was calibrated at the desired temperature with triply distilled water and purified methanol using density and viscosity values from the literature. The ultrasonic speeds (u) were determined using a single-crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi) working at 5 MHz,^{32,36} which was calibrated with water, methanol and benzene. The temperature stability was maintained within ± 0.01 K by circulating thermostatic water around the cell with a circulating pump. The solutions were prepared by mixing known volumes of pure liquids in air-tight stoppered bottles at 298.15 K. The precisions of the speed of sound, density and viscosity measurements were ± 0.2 m s⁻¹, $\pm 3 \times 10^{-4}$ g cm⁻³ and $\pm 2 \times 10^{-4}$ mPa s, respectively. The estimated uncertainty for the excess molar volume (V^E), viscosity deviation ($\Delta\eta$), antagonistic interaction index (I_A) and excess isentropic compressibilities (K_s^E) were $\pm 0.5 \times 10^{-4}$ m³ mol⁻¹, ± 0.0004 mPa s, ± 0.002 and ± 0.2 Pa⁻¹, respectively.

RESULTS AND DISCUSSION

The measured density (ρ), viscosity (η) and the speeds of sound (u) data for mixtures of (DMF) (A), benzene (B), and the ethers (C), *i.e.*, 1,3-dioxolane, 1,4-dioxane, tetrahydrofuran, 1,2-dimethoxyethane, di-isopropyl ether, diethyl ether, 2-methoxy ethanol and 2-ethoxyethanol were used to calculate the excess molar volume (V^E), viscosity deviation ($\Delta\eta$) and excess isentropic compressibility (K_s^E).

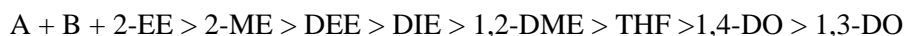
Viscous antagonism is the term used in respect to the interaction between the components of a system that cause the total viscosity of the latter to be less than the sum of the viscosities of the individual components in the system. The method compares the viscosity of the system determined experimentally, η_{exp} , with that expected in the absence of interaction, η_{calcd} . Viscous antagonism exists when, $\eta_{\text{exp}} < \eta_{\text{calcd}}$. This procedure is used when Newtonian fluids are involved.³⁷

Quantitatively, as per the absolute reaction rates theory,³⁸ the deviations of viscosities from the ideal mixture values for a three-component system can be calculated as:

$$\Delta\eta = \eta - \sum_{i=1}^3 x_i \eta_i \quad (1)$$

where η is the viscosity of the mixture, x_i and η_i are the mole fraction and viscosity of the pure components, respectively. The $\Delta\eta$ values for all the studied ternaries were found to be negative over the whole composition range at 298.15 K, as depicted by a representative plot in Fig. 1 as a function of the mole fraction of both DMF (x_A) and benzene (x_B). The $\Delta\eta$ values for the ternary mixtures (A) + (B) + 1,3-DO, 1,4-DO, THF, 1,2-DME, DIE, DEE, 2-ME and 2-EE (C) are plotted against the mole fraction of DMF (x_A) in Fig. 2, from which it can be

observed that $\Delta\eta$ increases as the mole fraction of DMF increases. The mixtures have a tendency of maximization, indicating a strong specific interaction between the unlike molecules. From the values of $\Delta\eta$, given in Table II, it can be concluded that the affinity of the molecules of the ethers towards benzene molecules in the presence of DMF is enhanced in the following order:



Here, dispersion and dipolar interactions between the DMF, benzene and 1,3-DO, 1,4-DO, THF, 1,2-DME, DIE, DEE, 2-ME and 2-EE molecules are operative, resulting in negative $\Delta\eta$ but with the increasing x_A , the dipolar interactions dominate giving rise to less negative values of $\Delta\eta$.³¹

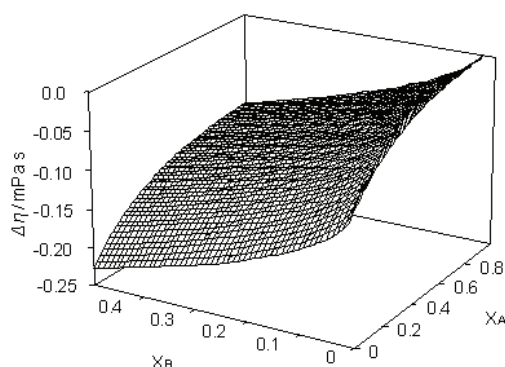


Fig. 1. 3D mesh plots of viscosity deviations ($\Delta\eta$) of DMF (A) + benzene (B) + 1,3-DO (C) mixtures with mole fraction of DMF (x_A) and benzene (x_B) at 298.15 K.

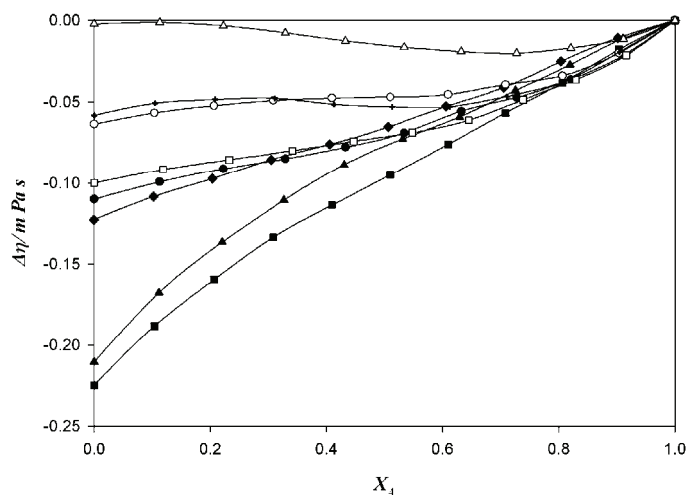


Fig. 2. Viscosity deviations ($\Delta\eta$) of: ■ DMF (A) + benzene (B) + 1,3-DO (C); ▲ DMF (A) + benzene (B) + 1,4-DO (C); ◆ DMF (A) + benzene (B) + THF (C); ● DMF (A) + benzene (B) + 1,2-DME (C); □ DMF (A) + benzene (B) + DIE (C); ○ DMF (A) + benzene (B) + DEE (C); + DMF (A) + benzene (B) + 2-ME (C); △ DMF (A) + benzene (B) + 2-EE (C) mixtures with mole fraction of DMF (x_A) at 298.15 K.

TABLE II. Experimental density (ρ), viscosity (η), viscosity deviations ($\Delta\eta$), antagonistic interaction index (I_A), excess molar volumes (V^E), Gibbs energy of activation (ΔG^{*E}) of viscous flow, experimental sound velocities (u), isentropic compressibility (K_s) and excess isentropic compressibility (K_s^E) of *N,N*-dimethylformamide (A) + benzene (B) + 1,3-DO, 1,4-DO, THF, 1,2-DME, DIE, DEE, 2-ME and 2-EE (C) at 298.15 K

x_A	x_B	ρ g cm ⁻³	η mPa s	$\Delta\eta$ mPa s	I_A	V^E cm ³ mol ⁻¹	ΔG^{*E} J mol ⁻¹	u m s ⁻¹	K_s 10 ⁻¹² Pa ⁻¹	K_s^E 10 ⁻¹² Pa ⁻¹
<i>N,N</i> -Dimethylformamide (A) + benzene (B) + 1,3-DO (C)										
0.0000	0.4868	0.9584	0.3650	-0.2248	0.38118	-0.1310	-1174.47	1302.1	615.4	340.2
0.1036	0.4363	0.9583	0.4296	-0.1881	0.30349	-0.2120	-871.83	1326.2	593.3	301.0
0.2064	0.3863	0.9578	0.4859	-0.1594	0.24506	-0.2630	-665.66	1336.7	584.3	275.0
0.3083	0.3367	0.9568	0.5393	-0.1334	0.19566	-0.2690	-504.20	1339.8	582.2	256.0
0.4095	0.2874	0.9557	0.5862	-0.1137	0.15942	-0.2600	-393.34	1339.8	583.0	240.0
0.5099	0.2386	0.9542	0.6320	-0.0949	0.12741	-0.2290	-301.30	1338.9	584.6	225.0
0.6094	0.1901	0.9527	0.6775	-0.0761	0.09797	-0.1890	-222.05	1344.1	581.0	205.0
0.7082	0.1420	0.9509	0.7235	-0.0567	0.07006	-0.1310	-151.39	1359.0	569.4	177.0
0.8062	0.0943	0.9492	0.7682	-0.0383	0.04552	-0.0840	-94.27	1387.0	547.6	139.0
0.9035	0.0470	0.9476	0.8148	-0.0179	0.02040	-0.0360	-39.35	1444.6	505.7	81.0
1.0000	0.0000	0.9461	0.8586	0.0000	0.00000	0.0000	0.00	1465.2	440.7	0.0
<i>N,N</i> -Dimethylformamide (A) + benzene (B) + 1,4-DO (C)										
0.0000	0.5301	0.9472	0.6569	-0.2104	0.25767	-0.2210	-548.86	1097.5	876.5	314.0
0.1118	0.4708	0.9479	0.6990	-0.1674	0.20782	-0.2770	-408.52	1130.9	824.9	276.0
0.2207	0.4131	0.9486	0.7290	-0.1364	0.17129	-0.3170	-317.23	1157.7	786.6	251.0
0.3268	0.3568	0.9487	0.7539	-0.1106	0.14044	-0.3130	-245.96	1181.8	754.7	232.0
0.4303	0.3020	0.9486	0.7750	-0.0886	0.11372	-0.2940	-189.09	1204.9	726.1	216.0
0.5311	0.2485	0.9484	0.7900	-0.0727	0.09381	-0.2540	-152.49	1226.6	700.8	203.0
0.6295	0.1964	0.9479	0.8027	-0.0591	0.07641	-0.2000	-123.44	1263.5	660.8	175.0
0.7255	0.1455	0.9474	0.8180	-0.0430	0.05598	-0.1430	-87.32	1301.5	623.1	149.0
0.8192	0.0958	0.9469	0.8329	-0.0273	0.03588	-0.0860	-53.23	1350.9	578.7	116.0
0.9107	0.0473	0.9464	0.8483	-0.0111	0.01500	-0.0380	-18.61	1435.8	512.6	61.0
1.0000	0.0000	0.9461	0.8586	0.0000	0.00000	0.0000	0.00	1465.2	440.7	0.0
<i>N,N</i> -Dimethylformamide (A) + benzene (B) + THF (C)										
0.0000	0.4800	0.8797	0.4022	-0.1227	0.23749	-0.2530	-645.90	1165.1	837.5	296
0.1023	0.4309	0.8868	0.4507	-0.1084	0.19612	-0.3150	-491.81	1210.0	770.1	268
0.2041	0.3820	0.8939	0.4957	-0.0973	0.16504	-0.3570	-382.37	1238.0	729.9	244
0.3054	0.3334	0.9009	0.5413	-0.0855	0.13641	-0.3840	-290.26	1263.2	695.7	226
0.4061	0.2851	0.9078	0.5843	-0.0761	0.11455	-0.3900	-225.66	1290.5	661.5	210
0.5064	0.2370	0.9145	0.6285	-0.0654	0.09315	-0.3790	-169.18	1322.2	625.4	190
0.6061	0.1891	0.9211	0.6744	-0.0528	0.07132	-0.3360	-117.21	1357.2	589.4	168
0.7053	0.1414	0.9276	0.7191	-0.0412	0.05294	-0.2860	-80.15	1392.0	556.4	140
0.8041	0.0941	0.9338	0.7681	-0.0251	0.03062	-0.2000	-37.14	1430.3	523.4	104
0.9023	0.0469	0.9400	0.8153	-0.0107	0.01235	-0.1090	-9.35	1484.8	482.5	58
1.0000	0.0000	0.9461	0.8586	0.0000	0.00000	0.0000	0.00	1465.2	440.7	0
<i>N,N</i> -Dimethylformamide (A) + benzene (B) + 1,2-DME (C)										
0.0000	0.5357	0.8702	0.3970	-0.1100	0.20674	-0.3050	-564.64	1137.8	887.7	285.0
0.1128	0.4752	0.8782	0.4473	-0.0994	0.16596	-0.3780	-418.36	1176.0	823.4	239.0
0.2225	0.4165	0.8862	0.4939	-0.0913	0.13661	-0.4290	-318.28	1203.8	778.6	212.0

TABLE II. Continued

x_A	x_B	ρ g cm ⁻³	η mPa s	$\Delta\eta$ mPa s	I_A	V^E cm ³ mol ⁻¹	ΔG^{*E} J mol ⁻¹	u m s ⁻¹	K_s 10 ⁻¹² Pa ⁻¹	K_s^E 10 ⁻¹² Pa ⁻¹
<i>N,N</i> -Dimethylformamide (A) + benzene (B) + 1,2-DME (C)										
0.3291	0.3594	0.8943	0.5376	-0.0851	0.11561	-0.4650	-250.96	1228.2	741.3	192.0
0.4329	0.3038	0.9022	0.5813	-0.0779	0.09698	-0.4760	-196.86	1243.8	716.5	184.0
0.5338	0.2498	0.9100	0.6257	-0.0690	0.07926	-0.4690	-150.92	1264.5	687.2	171.0
0.6320	0.1971	0.9177	0.6735	-0.0557	0.05849	-0.4320	-101.41	1282.7	662.3	162.0
0.7276	0.1459	0.9251	0.7155	-0.0473	0.04743	-0.3600	-81.04	1319.6	620.8	136.0
0.8208	0.0960	0.9324	0.7593	-0.0363	0.03519	-0.2690	-60.68	1367.3	573.7	104.0
0.9115	0.0474	0.9395	0.8061	-0.0214	0.02029	-0.1600	-36.31	1437.6	515.0	60.0
1.0000	0.0000	0.9461	0.8586	0.0000	0.00000	0.0000	0.00	1465.2	440.7	0.0
<i>N,N</i> -Dimethylformamide (A) + benzene (B) + DIE (C)										
0.0000	0.5668	0.7958	0.3997	-0.1000	0.17669	-0.4880	-441.50	1219.2	845.3	261.0
0.1186	0.4995	0.8103	0.4506	-0.0917	0.13814	-0.6450	-306.30	1261.7	775.3	208.0
0.2324	0.4350	0.8248	0.4975	-0.0856	0.11174	-0.7330	-217.97	1287.0	732.0	181.0
0.3417	0.3731	0.8394	0.5424	-0.0800	0.09219	-0.7680	-157.51	1301.5	703.3	168.0
0.4467	0.3136	0.8541	0.5858	-0.0742	0.07703	-0.7550	-115.90	1305.3	687.2	167.0
0.5478	0.2563	0.8690	0.6274	-0.0689	0.06644	-0.7070	-92.30	1312.8	667.7	162.0
0.6450	0.2012	0.8840	0.6700	-0.0612	0.05550	-0.6140	-72.20	1326.7	642.7	151.0
0.7386	0.1481	0.8993	0.7161	-0.0487	0.04100	-0.5050	-47.43	1351.0	609.2	131.0
0.8289	0.0970	0.9145	0.7608	-0.0364	0.02957	-0.3430	-33.58	1394.5	562.3	97.0
0.9160	0.0476	0.9302	0.8069	-0.0215	0.01747	-0.1810	-21.97	1450.8	510.8	58.0
1.0000	0.0000	0.9461	0.8586	0.0000	0.00000	0.0000	0.00	1465.2	440.7	0.0
<i>N,N</i> -Dimethylformamide (A) + benzene(B) + DEE (C)										
0.0000	0.4869	0.7902	0.3396	-0.0636	0.16770	-0.5930	-149.83	1231.1	835.0	232.0
0.1036	0.4364	0.8051	0.3936	-0.0568	0.13130	-0.7240	-6.68	1273.2	766.2	180.0
0.2064	0.3864	0.8201	0.4449	-0.0523	0.10686	-0.8030	76.39	1292.9	729.5	160.0
0.3084	0.3367	0.8353	0.4944	-0.0492	0.08974	-0.8420	118.97	1308.8	698.9	146.0
0.4096	0.2875	0.8508	0.5420	-0.0477	0.07860	-0.8510	128.90	1321.0	673.5	137.0
0.5099	0.2386	0.8662	0.5884	-0.0470	0.07088	-0.7940	117.13	1321.3	661.2	141.0
0.6095	0.1901	0.8819	0.6353	-0.0455	0.06354	-0.7110	92.89	1332.0	639.1	135.0
0.7083	0.1420	0.8978	0.6863	-0.0394	0.05125	-0.5970	71.94	1347.9	613.0	125.0
0.8063	0.0943	0.9137	0.7364	-0.0340	0.04178	-0.4260	35.94	1377.1	577.1	105.0
0.9035	0.0470	0.9298	0.7947	-0.0200	0.02321	-0.2290	15.69	1433.5	523.4	67.0
1.0000	0.0000	0.9461	0.8586	0.0000	0.00000	0.0000	0.00	1465.2	440.7	0.0
<i>N,N</i> -Dimethylformamide (A) + benzene (B) + 2-ME (C)										
0.0000	0.4932	0.9229	1.0157	-0.0583	0.04851	-0.7550	116.78	1228.2	718.3	172.6
0.1048	0.4415	0.9269	1.0006	-0.0508	0.04393	-0.8290	107.22	1267.4	671.7	137.0
0.2085	0.3903	0.9306	0.9806	-0.0485	0.04400	-0.8770	84.83	1305.2	630.8	107.0
0.3111	0.3397	0.9343	0.9593	-0.0477	0.04532	-0.9170	57.87	1325.7	609.0	96.0
0.4127	0.2896	0.9375	0.9336	-0.0515	0.05114	-0.9120	18.99	1340.8	593.4	91.0
0.5131	0.2401	0.9402	0.9105	-0.0530	0.05459	-0.8690	-14.16	1349.7	583.8	92.0
0.6125	0.1911	0.9427	0.8891	-0.0530	0.05636	-0.8030	-43.84	1360.2	573.4	92.0
0.7109	0.1426	0.9444	0.8743	-0.0466	0.05101	-0.6720	-54.50	1376.2	559.0	88.0
0.8083	0.0946	0.9457	0.8623	-0.0376	0.04229	-0.5090	-57.14	1403.5	536.8	76.0
0.9046	0.0470	0.9462	0.8597	-0.0194	0.02245	-0.2770	-31.15	1460.1	495.7	45.0

TABLE II. Continued

x_A	x_B	ρ g cm ⁻³	η mPa s	$\Delta\eta$ mPa s	I_A	V^E cm ³ mol ⁻¹	ΔG^{*E} J mol ⁻¹	u m s ⁻¹	K_s 10 ⁻¹² Pa ⁻¹	K_s^E 10 ⁻¹² Pa ⁻¹
<i>N,N</i> -Dimethylformamide (A) + benzene (B) + 2-ME (C)										
1.0000	0.0000	0.9461	0.8586	0.0000	0.00000	0.0000	0.00	1465.2	440.7	0.0
<i>N,N</i> -Dimethylformamide (A) + benzene (B) + 2-EE (C)										
0.0000	0.5354	0.9066	1.1640	-0.0022	0.03794	-0.8320	357.25	1280.9	672.3	123.1
0.1128	0.4750	0.9139	1.1302	-0.0013	0.03793	-1.0870	323.16	1315.6	632.2	95.2
0.2224	0.4163	0.9202	1.0944	-0.0033	0.03962	-1.2200	283.41	1342.6	602.9	77.8
0.3290	0.3592	0.9252	1.0574	-0.0076	0.04265	-1.2330	238.98	1362.6	582.1	68.6
0.4327	0.3037	0.9297	1.0205	-0.0126	0.04571	-1.1800	191.86	1371.6	571.8	69.5
0.5336	0.2497	0.9331	0.9855	-0.0165	0.04707	-1.0320	147.35	1383.5	559.9	68.6
0.6318	0.1971	0.9361	0.9526	-0.0192	0.04651	-0.8560	104.14	1394.6	549.2	68.6
0.7275	0.1459	0.9390	0.9222	-0.0202	0.04333	-0.6680	63.44	1415.4	531.6	61.3
0.8207	0.0960	0.9414	0.8968	-0.0170	0.03456	-0.4490	33.23	1441.3	511.4	51.2
0.9115	0.0474	0.9437	0.8744	-0.0114	0.02160	-0.2200	8.82	1483.6	481.4	31.1
1.0000	0.0000	0.9461	0.8586	0.0000	0.00000	0.0000	0.00	1465.2	440.7	0.0

In order to secure more comparable viscous antagonistic results, the so called antagonistic interaction index (I_A), introduced by Howell,³⁷ was taken into account:

$$I_A = (\eta_{cal} - \eta_{exp}) / \eta_{cal} \quad (2)$$

The antagonistic interaction index (I_A) values at 298.15 K for the ternary mixtures (A) + (B) + 1,3-DO, 1,4-DO, THF, 1,2-DME, DIE, DEE, 2-ME and 2-EE (C) are plotted against x_A in Fig. 3. It was found that each mixture had a maxi-

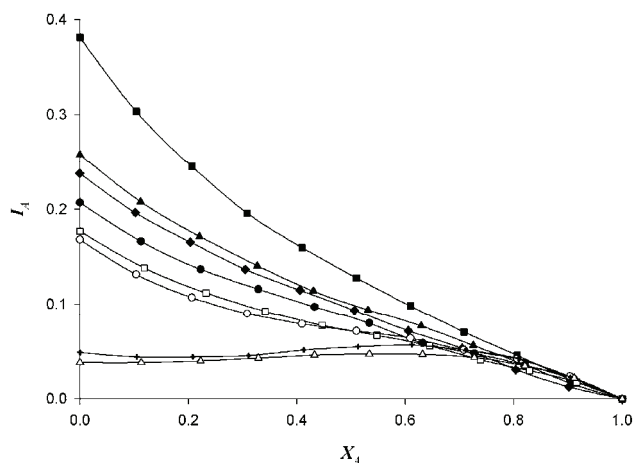


Fig. 3. Antagonistic Index (I_A) of: ■ DMF (A) + benzene (B) + 1,3-DO (C); ▲ DMF (A) + benzene (B) + 1,4-DO (C); ◆ DMF (A) + benzene (B) + THF (C); ● DMF (A) + benzene (B) + 1,2-DME (C); □ DMF (A) + benzene (B) + DIE (C); ○ DMF (A) + benzene (B) + DEE (C); + DMF (A) + benzene (B) + 2-ME (C); △ DMF (A) + benzene (B) + 2-EE (C) mixtures with mole fraction of DMF (x_A) at 298.15 K.

imum at $x_A = 0.0$, which then decreased with increasing x_A . A perusal of Table II shows that the experimentally determined viscosities, η_{exp} for all mixtures for various mole fractions at the experimental temperature are lower than those of their calculated values, η_{calcd} , which demonstrates viscous antagonism in the eight mixtures studied herein. The explanation of this behavior is based on the known phenomenon of molecular dissociation, as a consequence of the weakening of the non-covalent bonding formed between the molecules, causing a decrease in the size of the molecular package, which logically implies an increase in I_A .^{1,12} The maxima observed indicate strong specific interaction between the unlike molecules, which is predominated by non-covalent interaction. Thus, the molecular package increases gradually with the addition of DMF to the mixtures, which implies a decrease in I_A .

The excess molar volumes, V^E were calculated from the density data according to the following equation:³⁹

$$V^E = \sum_{i=1}^3 x_i M_i (1/\rho - 1/\rho_i) \quad (3)$$

where M_i , and ρ_i are the molar mass and density of the pure components, respectively, and ρ is the density of the mixture. For the ternary systems, in general, the V^E values were found to be negative over the whole composition range under study at 298.15 K, which is depicted as a representative plot in Fig. 4 as a function of the mole fraction of both DMF (x_A) and benzene (x_B). The V^E values for the eight ternary mixtures under examination are presented in Fig. 5. The values at first decreases to minima and then increase with increasing x_A . The eight ternary mixtures show minima at the same point, *i.e.*, at $x_A = 0.3$. The trend is:

(A)+(B)+1,3-DO > 1,4-DO > THF > 1,2-DME > DIE > DEE > 2-ME > 2-EE

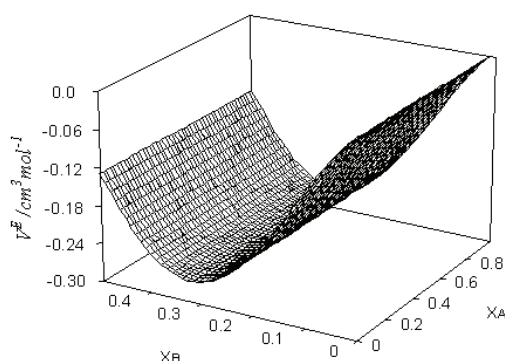


Fig. 4. 3D mesh plots of excess molar volumes (V^E) of: DMF (A) + benzene (B) + 1,3-DO (C) mixtures with mole fraction of DMF (x_A) and benzene (x_B) at 298.15 K.

The negative values of V^E indicate the presence of strong molecular interaction between the components of the mixture. Volume changes for a mixed system result from changes in the free volume of the liquids, since the bond

lengths and bond distances in the molecules themselves do not change. The optimum packing condition is directly related to differences in molecular sizes and intermolecular attractions, in particular when hydrogen bonding occurs between unlike molecules creating association complexes, as well as being effected by the breaking of interactions between like molecules.³² Several effects contribute to the value of V^E , such as: dipolar interaction, interstitial accommodation and possible hydrogen bonded interactions between unlike molecules.⁴⁰ The actual volume change would, therefore, depend on the relative strength of these three effects. Similar results have been reported earlier.^{41,42}

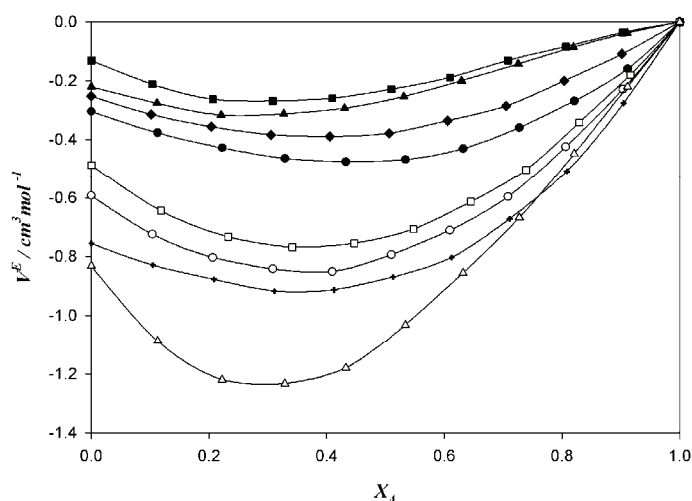


Fig. 5. Excess molar volumes (V^E) of: ■ DMF (A) + benzene (B) + 1,3-DO (C); ▲ DMF (A) + benzene (B) + 1,4-DO (C); ◆ DMF (A) + benzene (B) + THF (C); ● DMF (A) + benzene (B) + 1,2-DME (C); □ DMF (A) + benzene (B) + DIE (C); ○ DMF (A) + benzene (B) + DEE (C); (+), DMF (A) + benzene (B) + 2-ME (C); △ DMF (A) + benzene (B) + 2-EE (C) mixtures with mole fraction of DMF (x_A) at 298.15 K.

Based on the theory of absolute reaction rates,³⁸ the excess Gibbs energy, ΔG^{*E} , of viscous flow for a ternary system was calculated from:

$$\Delta G^{*E} = RT \ln(\eta M / \rho) - RT \sum_{i=1}^3 x_i \ln(\eta_i M_i / \rho_i) \quad (4)$$

where M and M_i are the molar mass of the mixture and of the pure components i . According to the literature, positive ΔG^{*E} values indicate specific interactions, while negative values indicate the dominance of dispersion forces.^{43,44} From the ΔG^{*E} values recorded in Table II, it can be seen that for all the ternary mixtures, these values are negative or positive keeping similarity with the $\Delta\eta$ values and thereby supports the conclusion drawn from the V^E and $\Delta\eta$ considerations.

Table II contains the sound velocity (u), the isentropic compressibility (K_s) and excess isentropic compressibility (K_s^E) data for the observed mixtures, which were calculated using the following equations:⁴⁵

$$K_s = (u^2 \rho_{\text{exp}})^{-1} \quad (5)$$

$$K_s^E = K_s - \sum_{i=1}^3 x_i K_{s,i} \quad (6)$$

where, $K_{s,i}$ gives the isentropic compressibility for the pure components of the mixture.

Figure 6 predicts the curves for the ternary mixtures of K_s^E . The values are positive in all the cases and decreases as the mole fraction of DMF increases. There is a parallel in the qualitative behavior of the K_s^E and V^E curves. The K_s^E values follow the sequence:

(A)+(B)+1,3-DO > 1,4-DO > THF > 1,2-DME > DIE > DEE > 2-ME > 2-EE

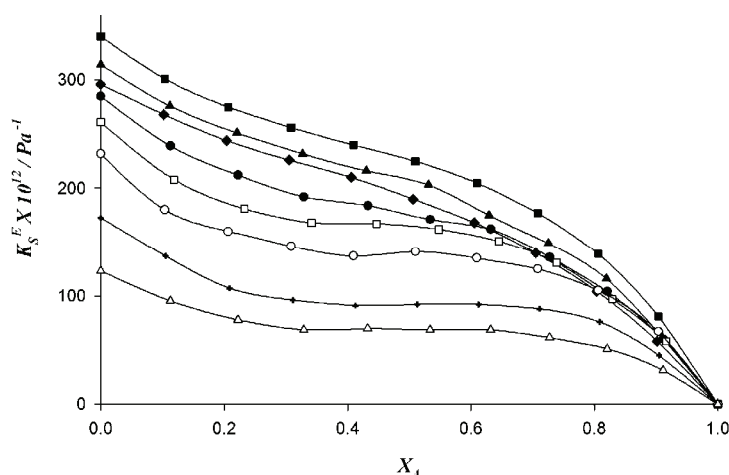


Fig. 6. Excess isentropic compressibility (K_s^E) of: ■ DMF (A) + benzene (B) + 1,3-DO (C); ▲ DMF (A) + benzene (B) + 1,4-DO (C); ◆ DMF (A) + benzene (B) + THF (C); ● DMF (A) + benzene (B) + 1,2-DME (C); □ DMF (A) + benzene (B) + DIE (C); ○ DMF (A) + benzene (B) + DEE (C); (+), DMF (A) + benzene (B) + 2-ME (C); △ DMF (A) + benzene (B) + 2-EE (C) mixtures with mole fraction of DMF (X_A) at 298.15 K.

The positive K_s^E values are due to the breaking of interactions and the corresponding disruption of molecular order in the pure components.²⁴ The donor–acceptor interaction between the component molecule plays an important part for the mixtures containing open chain ethers, especially those having a hydroxyl group, where there is strong specific interaction between the component molecules leading to lower value of K_s^E . Interactions between the molecules of DMF,

benzene or ethers are broken in the mixing process; the breaking leads to positive K_s^E values for the mixture containing cyclic ethers as compared to the open chain ethers. Similar results were reported earlier by some authors.^{24,32}

CONCLUSIONS

After a thorough study of the behavior of ethers in *N,N*-dimethylformamide + benzene mixtures, a clear idea about the type and amount of molecular interactions between them was obtained and an idea about antagonism was given. The similarity in the working formula of the antagonistic interaction index and viscosity deviation would probably indicate that the two properties are similar but a close comparison between these two parameters gave a clear distinction.

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ИЗВОД

ИСПИТИВАЊЕ ВИСКОЗНОСТИ, ДОПУНСКЕ МОЛАРНЕ ЗАПРЕМИНЕ, ПРОМЕНЕ ВИСКОЗНОСТИ И ИЗЕНТРОПСКЕ КОМПРЕСИБИЛНОСТИ ТЕРНЕРНИХ СИСТЕМА *N,N*-ДИМЕТИЛФОРМАМИДА, БЕНЗЕНА И ЕТАРА НА 298,15 К

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Извршена су мерења густина (ρ) и вискозности (η) тернерних смеша *N,N*-диметилформамид + бензен + етар, у функцији састава и на температури од 298,15 К. Из експерименталних података су израчунате вредности допунске моларне запремине (V^E), промене вискозности ($\Delta\eta$), интеракциони индекс (I_A) и Гибсову слободну енергију активације (ΔG^{*E}). Такође, на температури на којој су извршени експерименти, мерене су и брзине звука и израчунате допунске изентропске компресибилности (K_s^E). Добијени резултати су анализирани у функцији молекулског паковања и специфичних интеракција проузрокованих присуством водоничних веза.

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