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Speed of Sound, Isentropic Compressibility, Viscosity, and Excess Volume of Binary Mixtures. 2. Alkanenitriles + Dimethylformamide, + Dimethylacetamide, and + Dimethyl Sulfoxide

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The speed of sound u, density ϱ, and viscosity η of nine binary mixtures of ethanenitrile, propanenitrile, and adiponitrile with dimethylformamide, dimethylacetamide, and dimethyl sulfoxide have been measured at 303.15 K. The isentropic compressibility K_S, excess volume V^E, and excess isentropic compressibility K_S^E have been calculated from the results. The values of V^E and K_S^E are examined as a function of composition, size, and polarity of the participating molecules.

Introduction

As a part of our systematic studies on thermodynamic, acoustic, and transport properties of binary liquid mixtures (Oswal and Patel, 1990; Oswal and Dave, 1992; Oswal et al., 1994), the speed of sound u, isentropic compressibility K_S, viscosity η, excess volume V^E, and excess isentropic compressibility K_S^E of eight binary mixtures of ethanenitrile, propanenitrile, and adiponitrile with methyl, ethyl and butyl acetates were reported in part 1 (preceding paper in this issue). To obtain more information about molecular interactions and molecular orientations in dipolar mixtures, in this paper we studied the same properties of nine pairs of mixtures of ethanenitrile, propanenitrile, and adiponitrile with dimethylformamide, dimethylacetamide, and dimethyl sulfoxide. The dipole moments of the latter three molecules differ by less than 1%, and they are more polar than the esters investigated in part 1.

Experimental Section

Ethanenitrile (E. Merck, Bombay, >99 mol %) was dried over anhydrous calcium chloride, refluxed repeatedly over P_2O_5 until no color appeared on the oxide, and was fractionally distilled before use (Riddick et al., 1986). Propanenitrile (Ferak Berlin, >99 mol %) and adiponitrile (Merck, Schuchardt, >98 mol %) were dried over molecular sieves, type 4A (Fluka, AG). Dimethylformamide (Sisco Research Laboratory, Bombay, 99.5 mol %) was dried over sodium carbonate and then distilled. Dimethylacetamide (Sisco Research Laboratory, Bombay, 99.5 mol %) and dimethyl sulfoxide (E. Merck, Bombay, >99 mol %) were dried over anhydrous K_2CO_3 and fractionally distilled. The middle fraction of the distilate was used.

Estimated purities determined by gas–liquid chromatography were better than 99.8 mol % for all the liquid samples. The densities, speeds of sound, and viscosities of purified liquids are compared with the literature values in Table 1.

Mixtures were prepared by mixing known masses of pure liquids in air tight, narrow-mouth ground glass stoppered bottles taking due precaution to minimize the evaporation losses. All the mass measurements were performed on an electronic balance (Mettler AE 163, Switzerland) accurate to 0.01 mg. The possible error in the mole fraction is estimated to be less than $\pm 1 \times 10^{-4}$.

The speeds of sound u in the pure liquids and the binary mixtures were measured with a single crystal multi-frequency ultrasonic interferometer (supplied by Mittal Enterprise, New Delhi). In the present work, a steel cell fitted with a quartz crystal of 2 MHz frequency was employed. The measurements of viscosity η were made with a modified suspended level Ubbelohde viscometer (Concalves et al., 1991). The viscometer was calibrated, and two constants, C and B, of the viscometer in the equation $\eta/\varrho = Ct - B/t$ were obtained by measuring the flow time t with pure water, benzene, and cyclohexane at (303.15 ± 0.02) K. The densities ϱ were measured with a high-precision vibrating tube digital densimeter DMA 60/602 (Anton-Paar, K.G., Austria). The temperature was maintained at (303.15 ± 0.02) K, by employing appropriate water thermostats. The details of the apparatus and procedure have been described previously (Oswal and Palsanawala, 1989; Oswal and Dave, 1992; Patel and Oswal, 1992). The values of the speed of sound u, viscosity η, and density ϱ were reproducible to within ±1.0 m·s^{-1}, ±0.002 mPa·s, and ±0.02 kg·m^{-3}, respectively. The isentropic compressibilities K_S determined from the relation $K_S = 1/(u^2\varrho)$ are believed to be reliable to within 2.0 TPa^{-1}.

Results

K_S^E and V^E in each mixture were calculated from K_S ($=1/u^2\varrho$) and ϱ of pure liquids and binary mixtures with the following expression:

$$Y^E = Y - Y^{id} \tag{1}$$

where Y is either K_S or V. The V^{id} for an ideal mixture was calculated from the usual relation

$$V^{id} = \sum x_i V_i^\circ = \sum x_i M_i/\varrho_i \tag{2}$$

while K_S^{id} for an ideal mixture was calculated from the relation recommended by Benson and Kiyohara (1979) and Douheret et al. (1985):

$$K_S^{id} = K_T^{id} - TV^{id}(\alpha^{id})^2/C_P^{id} \tag{3}$$

Here

$$K_T^{id} = \sum \phi_i[K_{S,i}^\circ + TV_i^\circ(\alpha_i^\circ)^2/C_{P,i}^\circ] \tag{4}$$

$$\alpha^{id} = \sum \phi_i \alpha_i^\circ \tag{5}$$

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Table 1. Properties of Pure Liquids at 303.15 K

liquid	ρ/(kg·m^{-3}) exptl	ρ/(kg·m^{-3}) lit.	u/(m·s^{-1}) exptl	u/(m·s^{-1}) lit.	η/(mPa·s) exptl	η/(mPa·s) lit.	$10^3\,\alpha$/K	C_P/(J·mol^{-1}·K^{-1})
ethanenitrile	771.40	771.25[a]	1260.0	1264[b]	0.3244	0.324[a]	1.397[a]	92[a]
propanenitrile	771.82	771.96[a]	1242.5		0.3886	0.389[a]	1.335[a]	120[a]
adiponitrile	954.34		1560.0		4.9049		0.859[f]	227[g]
dimethylformamide	939.59	939.67[c]	1444.0	1445[c]	0.7675		0.945[c]	151[c]
		941.20[a]						
dimethylacetamide	932.46	931.69[a]	1441.0		0.8769	0.871[a]	0.955[a]	178[a]
		931.70[d]				0.873[d]		
dimethyl sulfoxide	1090.54	1090.42[e]	1477.0		1.8034	1.810[e]	0.928[a]	153[a]

[a] Riddick et al. (1986). [b] Lagemann et al. (1949). [c] Rajasekhar and Reddy (1987). [d] Pikkarainen (1980). [e] Bicknell et al. (1982). [f] Derived from measured densities at different temperatures. [g] Estimated by Missenard's group contribution method (Reid et al., 1987).

and

$$C_P^{id} = \sum x_i C_{P,i}^{\circ} \tag{6}$$

in which the V_i°, α_i°, and $C_{P,i}^{\circ}$ are, respectively, the molar volume, isobaric thermal expansion coefficient, and molar isobaric heat capacity for pure component i and $\phi_i = x_i V_i^{\circ}/\sum x_j V_j^{\circ}$ is the volume fraction of i in the mixture, stated in terms of the unmixed components. The values of α_i° and $C_{P,i}^{\circ}$ used for these calculations are listed in Table 1. The results of u, K_S, η, V^E, and K_S^E for nine binary mixtures are presented in Table 2.

The values of Y (u, K_S, and η) are expressed by

$$Y = \sum_{i=0}^{m} A_i x_1^i \tag{7}$$

The values of excess properties Y^E (V^E and K_S^E) were fitted to the Redlich–Kister polynomial equation

$$Y^E = x_1(1 - x_1)\sum_{i=0}^{m} A_i(1 - 2x_1)^i \tag{8}$$

The coefficients A_i of the eqs 7 and 8 obtained by the least-squares method and the standard deviations σ as per eq 9 are listed in Table 3.

$$\sigma = \left[\frac{\sum(Y_{obsd} - Y_{calcd})^2}{n - m}\right]^{1/2} \tag{9}$$

where n and m represent the number of experimental points and number of coefficients used in eqs 7 and 8.

Discussion

The values of viscosities η decrease with an increase of the mole fraction x_1 of alkanenitrile for six binary mixtures involving ethanenitrile and propanenitrile while the trend is the opposite in the case of three mixtures containing adiponitrile. Figure 1 shows that deviations from linear dependence ($\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2)$) on mole fraction for all mixtures except ethanenitrile + dimethylformamide and ethanenitrile + dimethylacetamide mixtures are negative over the entire range of composition. For the mixture ethanenitrile + dimethylacetamide deviations are small but positive while in the case of ethanenitrile + dimethylformamide, the deviation changes sign from small positive to small negative as the composition of ethanenitrile in the mixture is increased. The mixture ethanenitrile + dimethyl sulfoxide was investigated by Fort and Moore (1966) at 298.15 K. The negative deviations $\Delta\eta$ at 298.15 K are slightly larger than those observed at 303.15 K in the present work.

As shown in Figure 2 the V^E are negative for six mixtures involving ethanenitrile and propanenitrile and positive for three adiponitrile mixtures. In general the dependence of V^E on x_1 is unsymmetrical and the magnitude varies with the type of solvent used. The negative values of V^E at $x_1 = 0.5$ for ethanenitrile and propanenitrile as a common component decrease in the order dimethylacetamide > dimethylformamide > dimethyl sulfoxide, while the order of V^E for adiponitrile mixtures is dimethyl sulfoxide > dimethylacetamide > dimethylformamide.

The results for K_S^E are plotted in Figure 3; like V^E, the values of K_S^E are negative for six binary mixtures involving ethanenitrile and propanenitrile and positive for the other three mixtures containing adiponitrile. However, the trend differs from that observed in the case of ethanenitrile and propanenitrile mixtures. The negative values of K_S^E for ethanenitrile and propanenitrile mixtures decrease in the order dimethyl sulfoxide > dimethylformamide > dimethylacetamide.

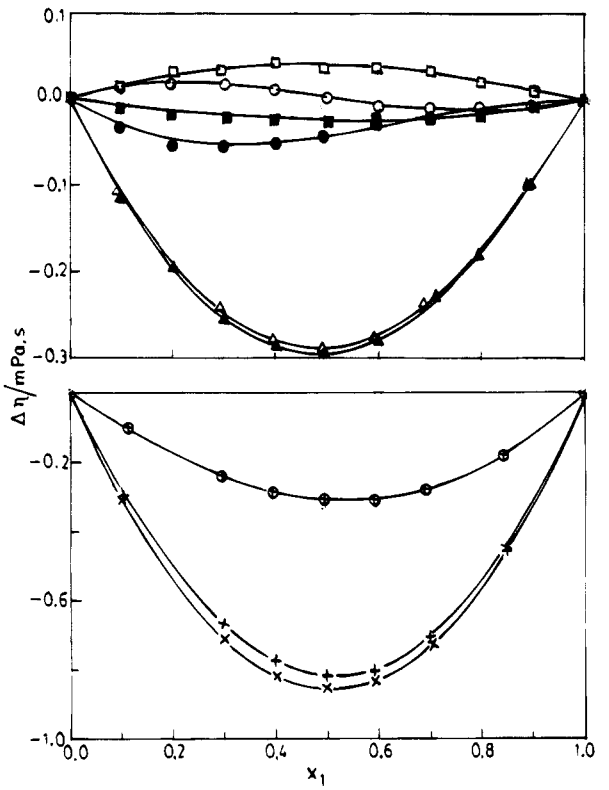

Figure 1. Deviations ($\Delta\eta$) of viscosity from linear additivity on mole fraction for binary mixtures at 303.15 K. Experimental points: ○, ethanenitrile + dimethylformamide; □, ethanenitrile + dimethylacetamide; △, ethanenitrile + dimethyl sulfoxide; ●, propanenitrile + dimethylformamide; ■, propanenitrile + dimethylacetamide; ▲, propanenitrile + dimethyl sulfoxide; +, adiponitrile + dimethylformamide; ×, adiponitrile + dimethylacetamide; ⊕, adiponitrile + dimethyl sulfoxide.

Table 2. Speed of Sound, Isentropic Compressibility, Viscosity, Density, Excess Volume, and Excess Isentropic Compressibility at 303.15 K

x_1	u/ (m·s^{-1})	K_S/ TPa^{-1}	η/ (mPa·s)	ϱ/ (kg·m^{-3})	10^6V^E/ (m^3·mol^{-1})	K_S^E/ TPa^{-1}	x_1	u/ (m·s^{-1})	K_S/ TPa^{-1}	η/ (mPa·s)	ϱ/ (kg·m^{-3})	10^6V^E/ (m^3·mol^{-1})	K_S^E/ TPa^{-1}
(i) Ethanenitrile (1) + Dimethylformamide (2)													
0.0000	1444.0	510.4	0.7675	939.59			0.6013	1339.4	649.6	0.4940	858.14	−0.2906	−39.5
0.0953	1430.0	526.1	0.7392	929.51	−0.0995	−11.5	0.6983	1321.0	682.6	0.4471	839.83	−0.2399	−38.7
0.1981	1413.0	545.8	0.6991	917.60	−0.1847	−20.9	0.8009	1301.0	721.4	0.4023	818.84	−0.1852	−32.1
0.3038	1395.2	568.2	0.6537	904.14	−0.2501	−28.6	0.8992	1282.0	764.5	0.3607	796.44	−0.0953	−21.0
0.3988	1378.3	591.0	0.6046	890.84	−0.2862	−35.4	1.0000	1260.0	816.5	0.3244	771.40		
0.5000	1359.0	618.6	0.5476	875.35	−0.3053	−38.4							
(ii) Ethanenitrile (1) + Dimethylacetamide (2)													
0.0000	1441.0	516.5	0.8769	932.46			0.5983	1350.0	634.7	0.5843	864.56	−0.4829	−34.1
0.0996	1431.3	528.4	0.8371	924.52	−0.1558	−9.0	0.7013	1327.9	670.3	0.5199	845.96	−0.4358	−32.5
0.2019	1417.0	544.1	0.7966	915.31	−0.2922	−16.4	0.7983	1307.0	708.9	0.4568	825.73	−0.3594	−28.3
0.2938	1403.6	560.3	0.7487	905.95	−0.3914	−22.6	0.9001	1282.3	759.4	0.3878	800.59	−0.2090	−16.6
0.3974	1387.0	581.4	0.7001	893.79	−0.4599	−28.5	1.0000	1260.0	816.5	0.3244	771.40		
0.4970	1368.6	606.5	0.6422	880.30	−0.4873	−31.6							
(iii) Ethanenitrile (1) + Dimethyl Sulfoxide (2)													
0.0000	1477.0	420.3	1.8034	1090.54			0.5977	1347.2	594.6	0.6451	926.52	−0.2229	−55.0
0.0948	1458.0	440.3	1.5539	1068.45	−0.0618	−13.9	0.6957	1325.0	637.8	0.5361	892.96	−0.2162	−52.4
0.2036	1434.0	467.0	1.3083	1041.31	−0.1110	−27.2	0.7957	1304.0	686.9	0.4469	855.99	−0.1740	−45.1
0.2949	1415.0	491.0	1.1244	1017.27	−0.1550	−37.8	0.8967	1281.1	746.5	0.3757	815.87	−0.1098	−27.6
0.4000	1391.0	523.2	0.9332	987.86	−0.1964	−46.6	1.0000	1260.0	816.5	0.3244	771.40		
0.4976	1369.0	556.7	0.7778	958.52	−0.2121	−52.1							
(iv) Propanenitrile (1) + Dimethylformamide (2)													
0.0000	1444.0	510.4	0.7675	939.59			0.5976	1320.8	678.6	0.5113	844.71	−0.1653	−42.1
0.1013	1425.6	532.0	0.6977	924.95	−0.0902	−16.1	0.6964	1301.6	713.2	0.4839	827.61	−0.1545	−38.9
0.1952	1405.6	555.8	0.6428	910.65	−0.1340	−26.5	0.7945	1281.6	750.4	0.4533	810.21	−0.1336	−30.4
0.3003	1382.6	585.1	0.5983	894.09	−0.1606	−34.8	0.9000	1260.8	795.4	0.4186	790.87	−0.0842	−16.8
0.4007	1360.8	615.2	0.5648	877.75	−0.1689	−39.8	1.0000	1242.5	839.2	0.3886	771.82		
0.4949	1340.8	645.2	0.5385	862.12	−0.1683	−41.8							
(v) Propanenitrile (1) + Dimethylacetamide (2)													
0.0000	1441.0	516.5	0.8769	932.46			0.5950	1325.2	669.9	0.5621	850.00	−0.2345	−30.4
0.0953	1424.0	534.9	0.8264	921.75	−0.1239	−9.1	0.6990	1304.6	706.2	0.5131	831.94	−0.2068	−29.1
0.2000	1404.0	558.2	0.7648	908.74	−0.1994	−16.8	0.7950	1284.0	744.9	0.4684	814.32	−0.1822	−23.2
0.3021	1383.0	584.2	0.7092	894.95	−0.2331	−22.0	0.9013	1263.0	790.3	0.4250	793.21	−0.1156	−14.5
0.3926	1366.0	607.7	0.6613	881.92	−0.2455	−26.9	1.0000	1242.5	839.2	0.3886	771.82		
0.4985	1344.9	638.6	0.6082	865.71	−0.2456	−30.0							
(vi) Propanenitrile (1) + Dimethyl Sulfoxide (2)													
0.0000	1477.0	420.3	1.8034	1090.54			0.6002	1323.2	633.6	0.6745	901.37	−0.1448	−56.7
0.1009	1447.2	450.8	1.5473	1059.17	−0.0457	−18.0	0.7153	1299.2	685.2	0.5619	864.62	−0.1492	−51.0
0.2020	1418.4	483.7	1.3222	1027.59	−0.0857	−32.5	0.7980	1280.8	727.5	0.4937	837.82	−0.1208	−40.2
0.3031	1394.4	516.5	1.1205	995.83	−0.1172	−46.0	0.8994	1261.6	780.6	0.4328	804.90	−0.0801	−24.1
0.4043	1367.2	555.0	0.9436	963.85	−0.1386	−52.4	1.0000	1242.5	839.2	0.3886	771.82		
0.4990	1347.8	590.2	0.8012	933.66	−0.1416	−58.0							
(vii) Adiponitrile (1) + Dimethylformamide (2)													
0.0000	1444.0	510.4	0.7675	939.59			0.5919	1516.8	458.1	2.4132	948.84	0.0793	1.8
0.1051	1458.2	499.5	0.9087	941.57	0.0151	1.1	0.6983	1528.6	450.2	2.9567	950.56	0.0442	1.3
0.2983	1483.7	481.1	1.3347	944.24	0.0927	1.1	0.8486	1543.4	440.7	3.8208	952.60	0.0148	1.4
0.3971	1494.4	473.5	1.6365	945.74	0.1042	2.0	1.0000	1560.0	430.6	4.9049	954.34		
0.4957	1504.8	466.2	2.0014	947.29	0.0991	2.7							
(viii) Adiponitrile (1) + Dimethylacetamide (2)													
0.0000	1441.0	516.5	0.8769	932.46			0.5898	1498.2	471.3	2.4202	945.26	0.1230	9.0
0.0999	1448.0	510.3	0.9801	934.57	0.0496	3.9	0.6990	1512.2	461.3	2.9648	947.95	0.0742	7.9
0.2976	1464.8	496.6	1.3630	938.65	0.1310	8.9	0.8491	1532.5	447.5	3.8501	951.36	0.0219	5.7
0.3998	1476.0	487.9	1.6663	940.88	0.1460	9.4	1.0000	1560.0	430.6	4.9049	954.34		
0.4988	1487.2	479.4	2.0294	943.17	0.1376	9.5							
(ix) Adiponitrile (1) + Dimethyl Sulfoxide (2)													
0.0000	1477.0	420.3	1.8034	1090.54			0.5947	1517.6	440.4	3.3426	987.04	0.8116	12.9
0.1031	1480.4	427.8	2.0270	1067.11	0.1762	5.9	0.6945	1526.5	440.1	3.6819	976.32	0.7886	11.6
0.2999	1492.6	435.8	2.4887	1029.40	0.5002	11.3	0.8441	1542.4	436.7	4.2431	963.52	0.5604	7.2
0.4015	1500.4	438.5	2.7598	1013.00	0.6467	12.9	1.0000	1560.0	430.6	4.9049	954.34		
0.5024	1506.4	441.5	3.0605	998.51	0.7673	14.8							

In pure ethanenitrile or propanenitrile, there are dipole–dipole as well as the usual dispersive interactions. The effect of adding a nonpolar second component is primarily to disrupt the dipolar interactions of the first component, but when the second component is also polar, then the dipole–dipole interaction in unlike molecules is most likely which results in a contraction in volume and the mixture becoming less compressible (Rowlinson and Swinton, 1982; Ohomuro, 1987; Venkatesu and Rao, 1994). Both the components involved in the present six binary mixtures of ethanenitrile and propanenitrile with dimethylformamide, dimethylacetamide, and dimethyl sulfoxide are highly polar, and there is evidence suggesting specific interactions leading to 1:1 complex formation between alkanenitriles and dimethyl sulfoxide (Ritchie and Pratt, 1964; Fort and Moore 1965, 1966). Therefore, it may be presumed that the positive contributions to V^E and to K_S^E due to the disruption of local dipolar order in both polar components

Table 3. Smoothing Coefficients A_i and Standard Deviations σ for Eqs 7 and 8 for Binary Mixtures at 303.15 K

property	A_1	A_2	A_3	A_4	σ
Ethanenitrile (1) + Dimethylformamide (2)					
u/(m·s^{-1})	1444.2	−147.9	−52.2	16.4	0.6
K_S/TPa^{-1}	509.9	169.2	52.5	84.1	0.8
η/(mPa·s)	0.7679	−0.2525	−0.5625	0.3533	0.0024
K_S^E/TPa^{-1}	−152.0	64.8	−36.7		0.7
10^6V^E/(m^3·mol^{-1})	−1.2058	−0.0406	−0.1550		0.0047
Ethanenitrile (1) + Dimethylacetamide (2)					
u/(m·s^{-1})	1441.2	−95.8	−114.3	28.6	0.7
K_S/TPa^{-1}	515.8	130.1	33.1	137.0	0.9
η/(mPa·s)	0.8760	−0.3453	−0.2908	−0.0830	0.0020
K_S^E/TPa^{-1}	−128.9	56.2	−22.5		0.6
10^6V^E/(m^3·mol^{-1})	−1.9649	−0.2361	−0.1187	0.2176	0.0042
Ethanenitrile (1) + Dimethyl Sulfoxide (2)					
u/(m·s^{-1})	1477.2	−203.2	−39.8	25.8	0.5
K_S/TPa^{-1}	419.6	222.8	31.1	142.4	0.9
η/(mPa·s)	1.8013	−2.6908	1.3471	−0.1331	0.0023
K_S^E/TPa^{-1}	−210.1	87.2	−33.0		0.4
10^6V^E/(m^3·mol^{-1})	−0.8570	0.3087	−0.1344		0.0039
Propanenitrile (1) + Dimethylformamide (2)					
u/(m·s^{-1})	1445.0	−202.1	−24.3	24.1	1.0
K_S/TPa^{-1}	509.4	224.8	85.3	19.4	1.0
η/(mPa·s)	0.7660	−0.7507	0.7803	−0.4106	0.0033
K_S^E/TPa^{-1}	−170.1	11.5	−19.3		0.8
10^6V^E/(m^3·mol^{-1})	−0.6761	−0.0314	−0.4486		0.0009
Propanenitrile (1) + Dimethylacetamide (2)					
u/(m·s^{-1})	1441.6	−189.2	−10.2		0.5
K_S/TPa^{-1}	515.9	199.5	62.5	60.8	0.6
η/(mPa·s)	0.8780	−0.5712	0.0384	0.0429	0.0015
K_S^E/TPa^{-1}	−118.3	35.4	−22.6		0.5
10^6V^E/(m^3·mol^{-1})	−0.9662	−0.0955	−0.6188		0.0044
Propanenitrile (1) + Dimethyl Sulfoxide (2)					
u/(m·s^{-1})	1476.6	−299.6	86.6	−20.8	0.9
K_S/TPa^{-1}	420.2	298.4	55.4	65.1	0.9
η/(mPa·s)	1.8039	−2.6775	1.4323	−0.15888	0.0018
K_S^E/TPa^{-1}	−229.1	41.6	−3.5		0.8
10^6V^E/(m^3·mol^{-1})	−0.5972	0.2148	−0.1536		0.0046
Adiponitrile (1) + Dimethylformamide (2)					
u/(m·s^{-1})	1444.0	142.1	−43.5	17.3	0.7
K_S/TPa^{-1}	510.0	−100.2	21.2		0.5
η/(mPa·s)	0.7676	1.0584	2.6931	0.386	0.0027
K_S^E/TPa^{-1}	9.1				0.6
10^6V^E/(m^3·mol^{-1})	0.3935	0.2113	−0.2876		0.0028
Adiponitrile (1) + Dimethylacetamide (2)					
u/(m·s^{-1})	1440.6	73.7	29.7	15.4	0.9
K_S/TPa^{-1}	516.7	−62.7	−23.2		0.5
η/(mPa·s)	0.8784	0.6637	3.2207	0.1419	0.0020
K_S^E/TPa^{-1}	40.2				0.6
10^6V^E/(m^3·mol^{-1})	0.5414	0.3860	−0.3285	−0.1638	0.0025
Adiponitrile (1) + Dimethyl Sulfoxide (2)					
u/(m·s^{-1})	1476.9	26.0	106.7	−19.1	0.5
K_S/TPa^{-1}	420.7	68.3	−58.4		0.6
η/(mPa·s)	1.8052	2.0419	0.7028	0.3552	0.0021
K_S^E/TPa^{-1}	55.6	4.6			0.5
10^6V^E/(m^3·mol^{-1})	3.0351	−1.7399	−0.2085	0.2362	0.0044

have been compensated to a varying extent by a negative contribution resulting from the new dipole−dipole specific interaction between the unlike components. The observed negative values of V^E and K_S^E for these mixtures indicate that the specific interactions dominate over the dispersive interaction. This is consistent with excess enthalpies and excess isochoric heat capacities for mixtures of ethanenitrile with dimethylformamide and dimethyl sulfoxide (Miyanaga et al., 1992; Nakamura et al., 1993).

For a given second component (dimethylformamide, dimethylacetamide, or dimethyl sulfoxide), the value of $|V_{min}^E|$ for the binary mixtures containing propanenitrile is lower than that for those containing ethanenitrile. The

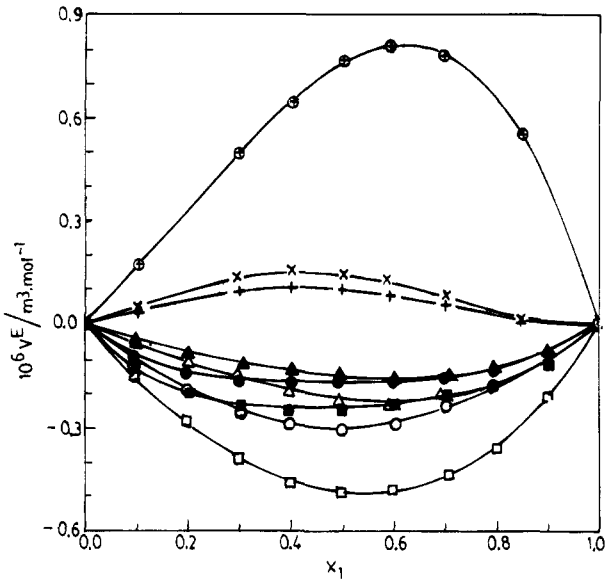

Figure 2. Excess volume for binary mixtures at 303.15 K. Symbols same as in Figure 1; (—) calculated with eq 8.

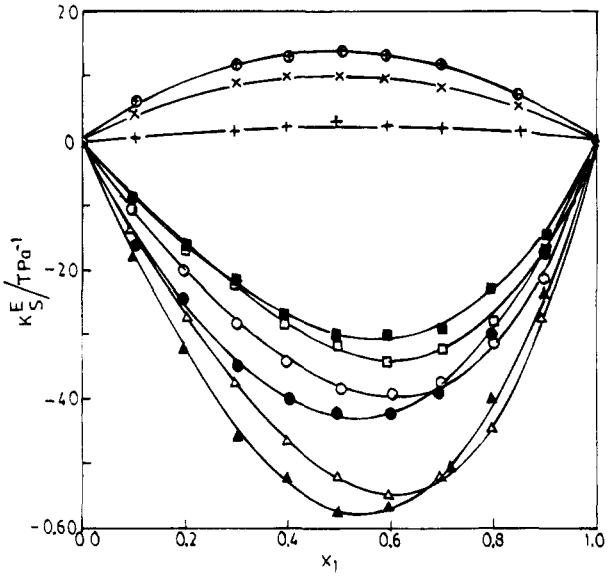

Figure 3. Excess isentropic compressibility for binary mixtures at 303.15 K. Symbols same as in Figure 1; (—) calculated with eq 8.

average ratio of the latter to the former is about 1.7. It seems that for a given second polar component, the interaction with ethanenitrile is stronger than that with propanenitrile.

The three binary mixtures involving adiponitrile have positive values of V^E and K_S^E. The positive values of V^E suggest that the expansion caused by the breaking of dipolar order in pure liquid molecules is larger than the contraction caused by the specific interactions between unlike molecules.

The cause of asymmetry in the curves (Figures 2 and 3) must presumably be related to the molecular correlation of orientation restricted by dipole−dipole interaction and the dipole−induced dipole interaction (Ohomuro et al., 1987; Haijum et al., 1993).

From this study it may be concluded that the polarity and size of molecules involved in the mixture formation have a dominating effect on the V^E and K_S^E as well as on the type and extent of intermolecular interactions.

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