Speed of Sound, Isentropic Compressibility, Viscosity, and Excess Volume of Binary Mixtures. 1. Alkanenitriles with Alkyl Acetates

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The density ϱ, speed of sound u, and viscosity η of eight binary mixtures of ethanenitrile and propanenitrile with methyl acetate, ethyl acetate, and butyl acetate and of adiponitrile with ethyl acetate and butyl acetate 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 therefrom. The values of V^E and K_S^E are explainable by considering the varying extent of interactions and the difference in free volumes between unlike components.

Introduction

The properties of liquid mixtures are very important as some of the polymers which are insoluble in pure solvent can be dissolved in a solvent mixture (Aminabhavi and Balundgi, 1987). Therefore, in addition to the studies of polymer solutions in a single solvent (Aminabhavi et al., 1988; Deshpande and Prabhu, 1977; Flory, 1970, Patterson et al., 1967), considerable attention has recently been paid to the study of polymer solutions in mixed solvents (Munk and Halbrook, 1976; Chu and Munk, 1978; Aminabhavi and Munk, 1979).

Alkanenitriles and alkyl acetates are very good solvents for polymers. Their mixtures can still be better and selective solvents for polymeric materials. Accordingly, the studies of thermodynamic, acoustic, and transport properties of mixtures of ethanenitrile, propanenitrile, and adiponitrile with methyl acetate, ethyl acetate, and butyl acetate will be very useful in providing information regarding their utility in the chemical industry. Such studies are also useful in investigating solvation behavior of copper(I) cation in mixed solvents containing nitriles (McLeod et al., 1977; Gill et al., 1988, and references therein). This cation interacts uniquely by dπ–pπ interactionn with the –C≡N group which gives it remarkable stability. The studies of mixtures containing industrially important adiponitrile are also very interesting as it has two nitrile groups separated by four methylene groups with symmetrical structure. As a part of our systematic studies on thermodynamic, acoustic, and transport properties of mixtures containing alkyl acetates (Oswal, 1988; Oswal and Palsanawala, 1989; Oswal and Patel, 1990; Oswal et al., 1994a,b), this study is undertaken and presented here.

Experimental Section

Ethanenitrile (E. Merck, Bombay, >99 mol %), propanenitrile (Ferak Berlin, >99 mol %), adiponitrile (Merck, Schuchardt, >98 mol %), methyl acetate (SISCO, Bombay, Extrapure), ethyl acetate (BDH, AR, >99.5 mol %), and butyl acetate (E. Merck, Bombay, >99.5 mol %) were used after further purification and drying by standard procedures (Riddick et al., 1986). Ethanenitrile was dried over anhydrous $CaCO_3$, refluxed repeatedly over P_2O_5 until no color appeared on the oxide, and fractionally distilled before use. Propanenitrile and adiponitrile were dried over molecular sieves, type 4A (Fluka, AG). Methyl acetate, ethyl acetate, and butyl acetate were dried over anhydrous K_2CO_3 for more than 72 h and were fractionally distilled twice before use.

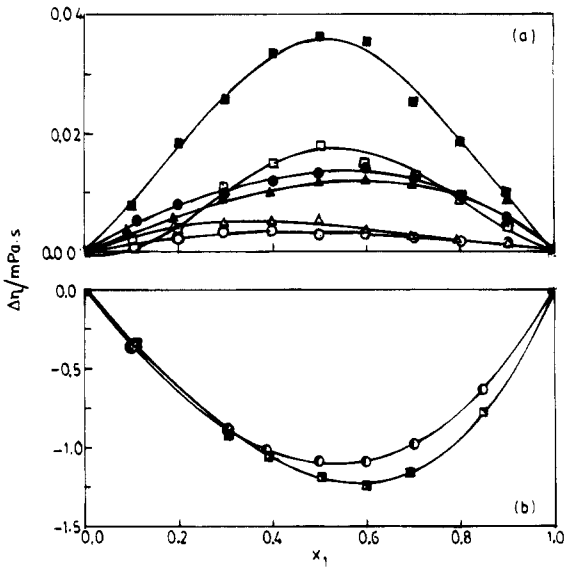

Figure 1. Deviation of viscosity from linear dependence on mole fraction. Experimental points: (a) ●, ethanenitrile + methyl acetate; ▲, ethanenitrile + ethyl acetate; ■, ethanenitrile + butyl acetate; ○, propanenitrile + methyl acetate; △, propanenitrile + methyl acetate; □, propanenitrile + butyl acetate; (b) ◐, adiponitrile + ethyl acetate; ◪, adiponitrile + ethyl acetate; (—) calculated with eq 7.

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 reliable literature values in Table 1.

Mixtures were prepared by mixing known masses of the pure liquids in air tight, narrow-mouth ground glass stoppered bottles taking due precaution to minimize the evaporation losses. All masses were determined with 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 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. The viscometer was designed to reduce surface tension effects to negligible values (Con-

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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	1264[b]	0.3244	0.3240[a]	1.397[a]	91.5[a]
propanenitrile	771.82	771.96[a]	1242		0.3886	0.3890[a]	1.335[a]	119.7[a]
adiponitrile	954.58		1560		4.9049		0.859[f]	226.6[g]
methylacetate	919.67	920.4[b]	1134	1136[c]	0.3442	0.3440[a]	1.513[f]	143.9[a]
ethylacetate	888.64	888.51[d]	1119	1119[c]	0.4026	0.4000[a]	1.394[f]	167.9[a]
butylacetate	871.36	871.29[d]	1176	1170[c] 1172[e] 1178[b]	0.6438	0.6444[a]	1.242[f]	228.4[a]

[a] Riddick et al. (1986). [b] TRC Database (1994). [c] Lagemann et al. (1951). [d] Timmermans (1965). [e] Palsanawala (1986). [f] Derived from measured densities at different temperatures. [g] Estimated by Missenard's group contribution method (Reid et al., 1987).

calves et al., 1991). The viscometer was calibrated, and two constants, C and B ($\eta = \varrho(Ct - B/t)$), of the viscometer were obtained by measuring the flow time t with pure water, benzene, and cyclohexane at (303.15 ± 0.02) K. The arithmetic mean of four or five sets of flow time for each fluid was taken for the purpose of the calculation of viscosity. The efflux time was measured with an accurate stopwatch with a resolution of 0.1 s. 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 a water thermostat. The details of the apparatus and procedure have been described previously (Oswal and Palsanawala, 1989; Oswal and Dave, 1992; Patel and Oswal, 1992). 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

Speed of sound u, isentropic compressibility K_S, and viscosity η for eight binary mixtures of ethanenitrile + methyl acetate, + ethyl acetate, and + butyl acetate, propanenitrile + methyl acetate, + ethyl acetate, and + butyl acetate, and adiponitrile + ethyl acetate and + butyl acetate for a number of mole fractions at 303.15 K are presented in Table 2.

K_S^E and V^E in each mixture were calculated from

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

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), Tamura et al. (1983), and Douheret et al. (1985)

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

Here

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

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

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 ϕ_i $x_iV_i^\circ/\sum x_jV_j^\circ$ 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 3 along with their sources (Riddick et al., 1986; Palsanawala, 1986; Reid et al., 1987). The calculated values of V^E and K_S^E are also included in Table 2.

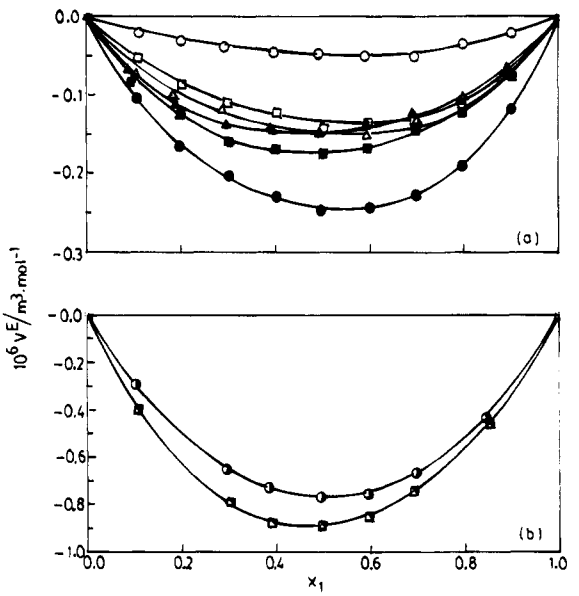

Figure 2. Dependence of excess volume on mole fraction at 303.15 K for alkanenitrile + alkyl acetate. Symbols same as in Figure 1, except ◑ for adiponitrile + ethyl acetate; (—) calculated with eq 8.

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

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

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) + Methyl Acetate (2)													
0.0000	1134	846	0.3442	919.67			0.5996	1208	808	0.3461	849.01	−0.2327	−24
0.1087	1147	835	0.3472	909.85	−0.1054	−8	0.7019	1223	803	0.3429	832.49	−0.2265	−25
0.1994	1158	829	0.3482	900.72	−0.1668	−13	0.7979	1236	803	0.3376	815.12	−0.1895	−21
0.3009	1169	823	0.3485	889.34	−0.2031	−17	0.9006	1249	806	0.3322	794.45	−0.1286	−14
0.4037	1182	816	0.3481	876.68	−0.2246	−20	1.0000	1260	816	0.3244	771.40		
0.4994	1194	812	0.3474	863.96	−0.2472	−24							
(ii) Ethanenitrile (1) + Ethyl Acetate (2)													
0.0000	1119	899	0.4026	888.64			0.5974	1189	844	0.3676	838.32	−0.1419	−19
0.0931	1127	891	0.3988	883.21	−0.0744	−8	0.6982	1205	835	0.3591	825.21	−0.1229	−18
0.1928	1139	880	0.3934	876.40	−0.1115	−13	0.8001	1221	829	0.3486	809.97	−0.1026	−14
0.2980	1151	869	0.3881	868.30	−0.1394	−15	0.8988	1239	822	0.3402	792.76	−0.0653	−9
0.3925	1163	860	0.3819	860.02	−0.1480	−18	1.0000	1260	817	0.3244	771.40		
0.4985	1177	850	0.3753	849.54	−0.1516	−21							
(iii) Ethanenitrile (1) + Butyl Acetate (2)													
0.0000	1176	830	0.6438	871.36			0.5972	1205	825	0.4884	835.84	−0.1683	−1
0.0981	1179	829	0.6208	867.73	−0.0764	0	0.6977	1215	821	0.4463	825.00	−0.1477	−4
0.2003	1182	829	0.5981	863.18	−0.1231	0	0.7987	1226	820	0.4071	811.51	−0.1217	−3
0.3003	1186	829	0.5737	858.00	−0.1606	1	0.8985	1241	818	0.3669	794.40	−0.0736	−2
0.4030	1191	828	0.5485	851.57	−0.1697	−0	1.0000	1260	817	0.3244	771.40		
0.5026	1197	826	0.5195	844.24	−0.1777	−1							
(iv) Propanenitrile (1) + Methyl Acetate (2)													
0.0000	1134	846	0.3442	919.67			0.5946	1196	836	0.3732	836.70	−0.0521	−7
0.1119	1144	844	0.3500	905.10	−0.0243	−1	0.6967	1207	836	0.3773	821.10	−0.0511	−6
0.2022	1154	841	0.3551	892.90	−0.0300	−4	0.7985	1219	836	0.3811	805.00	−0.0367	−5
0.2958	1164	839	0.3608	880.00	−0.0379	−6	0.9022	1232	836	0.3857	788.19	−0.0231	−4
0.4008	1176	836	0.3657	865.15	−0.0439	−7	1.0000	1243	839	0.3886	771.82		
0.4952	1186	836	0.3692	851.45	−0.0471	−8							
(v) Propanenitrile (1) + Ethyl Acetate (2)													
0.0000	1119	899	0.4026	888.64			0.5954	1183	860	0.3976	830.08	−0.1521	−8
0.1019	1130	890	0.4034	880.44	−0.0678	−4	0.6959	1197	854	0.3954	817.43	−0.1444	−8
0.1916	1139	884	0.4041	872.52	−0.0973	−7	0.7981	1211	848	0.3935	803.54	−0.1283	−7
0.2921	1149	878	0.4038	863.04	−0.1213	−7	0.9006	1227	843	0.3915	788.36	−0.0948	−4
0.3979	1161	871	0.4025	852.36	−0.1421	−8	1.0000	1243	839	0.3886	771.82		
0.4953	1172	865	0.4012	841.76	−0.1501	−9							
(vi) Propanenitrile (1) + Butyl Acetate (2)													
0.0000	1176	830	0.6438	871.36			0.5940	1202	835	0.5076	828.81	−0.1361	1
0.1100	1178	832	0.6161	865.54	−0.0522	1	0.7008	1210	835	0.4785	817.18	−0.1315	0
0.2014	1182	832	0.5958	860.15	−0.0885	0	0.7980	1219	836	0.4496	804.88	−0.1149	0
0.2942	1186	833	0.5799	854.01	−0.1090	1	0.8966	1228	839	0.4190	790.18	−0.0705	1
0.4034	1192	832	0.5557	845.78	−0.1212	−0	1.0000	1243	839	0.3886	771.82		
0.5034	1197	833	0.5332	837.50	−0.1408	−1							
(vii) Adiponitrile (1) + Ethyl Acetate (2)													
0.0000	1119	899	0.4026	888.64			0.5975	1401	543	1.8612	937.26	−0.8363	−81
0.1075	1171	810	0.5353	900.13	−0.3958	−41	0.6944	1442	510	2.3662	942.43	−0.7348	−67
0.3039	1266	680	0.8893	917.53	−0.7916	−82	0.8500	1504	466	3.4416	949.39	−0.4493	−37
0.3934	1307	633	1.1156	924.32	−0.8738	−88	1.0000	1560	431	4.9049	954.34		
0.4973	1355	585	1.4511	931.27	−0.8856	−87							
(viii) Adiponitrile (1) + Butyl Acetate (2)													
0.0000	1176	830	0.6438	871.36			0.5929	1391	560	2.0819	922.97	−0.7507	−61
0.0984	1207	779	0.7145	880.32	−0.2856	−20	0.6974	1433	523	2.6307	931.51	−0.6676	−53
0.3003	1277	683	1.0524	898.16	−0.6543	−51	0.8455	1495	474	3.6102	943.11	−0.4259	−34
0.3857	1310	644	1.2806	905.49	−0.7283	−58	1.0000	1560	431	4.9049	954.34		
0.4963	1353	597	1.6628	914.85	−0.7640	−63							

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

Discussion

The K_S varies almost linearly with x_1 within the experimental uncertainty for mixtures of ethanenitrile + butyl acetate, propanenitrile + ethyl acetate, and propanenitrile + butyl acetate while negative deviations in K_S are observed for ethanenitrile + methyl acetate, ethanenitrile + ethyl acetate, propanenitrile + methyl acetate, adiponitrile + ethyl acetate, and adiponitrile + butyl acetate.

It can be seen from the fourth column in Table 2 that the values of viscosities η decreases with an increase of x_1 for ethanenitrile + ethyl acetate, ethanenitrile + butyl acetate, and propanenitrile + butyl acetate binary mixtures while for propanenitrile + methyl acetate, adiponitrile + ethyl acetate, and adiponitrile + butyl acetate they increase with x_1. In the case of two mixtures, ethanenitrile + methyl acetate and propanenitrile + ethyl acetate, maxima around 0.3 and 0.2 mole fraction x_1, respectively, are observed. Figure 1a shows small but positive deviations from linear dependence on mole fractions ($\Delta\eta = \eta - x_1\eta_1 - x_2\eta_2$) over the entire range of composition for all six mixtures involving ethanenitrile and propanenitrile while both the mixtures containing adiponitrile (Figure 1b) exhibit large and negative deviations.

The values for V^E for all eight binary mixtures are negative. As shown in Figure 2, in general the dependence

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

property	A_1	A_2	A_3	A_4	A_5	σ
(i) Ethanenitrile (1) + Methyl Acetate (2)						
u/m·s^{-1})	1134.8	99.7	58.4	−32.0		0.9
K_S/TPa^{-1}	844.7	−74.6	−18.7	64.3		0.9
η/(mPa·s)	0.3446	0.0217	−0.0199	−0.0218		0.0005
K_S^E/TPa^{-1}	−90.3	46.2	−48.3			0.4
10^6V^E/(m^3·mol^{-1})	−0.9466	0.1678	−0.4894			0.0066
(ii) Ethanenitrile (1) + Ethyl Acetate (2)						
u(m·s^{-1})	1118.1	111.1	−10.0	40.3		0.8
K_S/TPa^{-1}	899.9	−113.4	30.0			0.9
η(mPa·s)	0.4019	−0.0314	−0.0441			0.0012
K_S^E/TPa^{-1}	−75.7	4.8	−28.5			1.0
10^6V^E/(m^3·mol^{-1})	−0.5853	−0.0846	−0.3081			0.0037
(iii) Ethanenitrile (1) + Butyl Acetate (2)						
u(m·s^{-1})	1176.0	29.2	−2.4	56.7		0.6
K_S/TPa^{-1}	830.1	−2.8	−11.8			0.9
η(mPa·s)	0.6415	−0.1776	−0.1412			0.0026
10^6V^E/(m^3·mol^{-1})	−0.6983	−0.0319	−0.2059			0.0031
(iv) Propanenitrile (1) + Methyl Acetate (2)						
u/m·s^{-1})	1134.2	97.7	10.8	10.8		0.6
K_S/TPa^{-1}	846.5	34.1	26.6			0.7
η/(mPa·s)	0.3442	0.0570	−0.0128			0.0005
K_S^E/TPa^{-1}	−29.1	14.5	−3.0			1.0
10^6V^E/(m^3·mol^{-1})	−0.1927	0.0283	−0.0836			0.0035
(v) Propanenitrile (1) + Ethyl Acetate (2)						
u/(m·s^{-1})	1119.2	100.0	0.5	23.9		0.3
K_S/TPa^{-1}	897.8	−72.5	13.6			0.6
η(mPa·s)	0.4034	0.0036	−0.0191			0.0009
K_S^E/TPa^{-1}	−33.3	−1.1	−20.4			0.4
10^6V^E(m^3·mol^{-1})	−0.5775	0.1703	−0.4681			0.0063
(vi) Propanenitrile (1) + Butyl Acetate (2)						
u(m·s^{-1})	1175.4	34.0	−1.3	33.7		0.8
K_S/TPa^{-1}	829.7	8.6				0.8
η(mPa·s)	0.6415	0.2079	0.0041	0.0428		0.0025
10^6V^E/(m^3·mol^{-1})	−0.5464	0.1389	−0.1794			0.0038
(vii) Adiponitrile (1) + Ethyl Acetate (2)						
u(m·s^{-1})	1118.8	483.4	13.8	−55.6		0.6
K_S/TPa^{-1}	898.3	−869.6	552.0	−150.2		0.6
η(mPa·s)	0.4033	1.0301	1.6620	0.2200	1.5888	0.0024
K_S^E/TPa^{-1}	−352.8	−93.7				0.9
10^6V^E/(m^3·mol^{-1})	−3.5387	−0.3669	−0.4841			0.0034
(viii) Adiponitrile (1) + Butyl Acetate (2)						
u(m·s^{-1})	1175.8	303.4	128.6	−47.9		0.5
K_S/TPa^{-1}	830.5	−535.5	135.1			0.8
η(mPa·s)	0.6415	0.5221	2.4376	1.3022		0.0029
K_S^E/TPa^{-1}	−251.5	31.5				0.5
10^6V^E/(m^3·mol^{-1})	−3.0783	0.0644	−0.3011			0.0036

of V^E on x_1 is unsymmetrical. The magnitude of V^E varies with the type of solvent. The negative values of V^E at x_1 = 0.5 for ethanenitrile as a common component decrease in the order methyl acetate > butyl acetate > ethyl acetate, while they decrease in the reverse order for propanenitrile and adiponitrile.

Figure 3 shows that the values of K_S^E are negative for all the binary mixtures except ethanenitrile + butyl acetate and propanenitrile + butyl acetate, for which values of K_S^E are almost zero. The negative values of K_S^E are much larger for adiponitrile mixtures than those for either ethanenitrile or propanenitrile mixtures. The asymmetry of the curves (Figures 2 and 3) may originate from two factors: first, the self-association of nitrile and, second, the

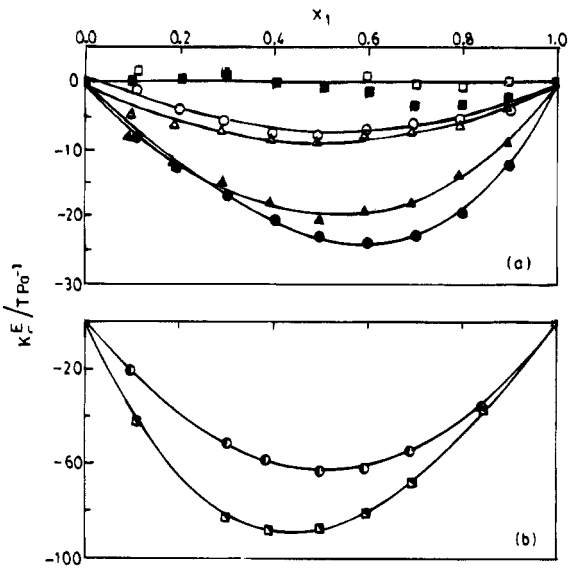

Figure 3. Dependence of excess isentropic compressibility on mole fraction at 303.15 K for alkanenitrile + alkyl acetate. Symbols same as in Figure 1; (—) calculated with eq 8.

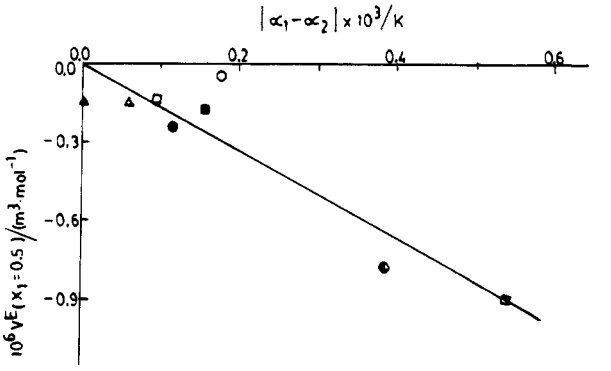

Figure 4. Equimolar excess volume against the difference of thermal expansion coefficients of component liquids. Symbols same as in Figure 1.

unlike interaction (dipole−dipole and dipole−induced dipole) between alkanenitrile and alkyl acetate.

The negative V^E and K_S^E values may result from two effects: (i) an interactional contribution and (ii) a free volume contribution (Van and Patterson, 1982). As far as the interactional part, the interactions may be dipole−dipole and dipole−induced dipole types which enhance the solvent structure in the mixture, in turn making negative contributions to V^E and K_S^E (Fort and Moore, 1965, 1966; Karvo, 1986; Gill et al., 1993; Haijum et al., 1993).

The dipole moments μ of all three esters methyl acetate (μ = 1.71 D), ethyl acetate (μ = 1.82 D), and butyl acetate (μ = 1.87 D) are essentially similar, so one would expect the dipole−dipole interaction between ethanenitrile (μ = 3.53 D) and ester to be of the same strength and its corresponding contribution to the excess functions to also be almost similar, but Figures 2 and 3 reveal that the magnitudes of V^E and K_S^E for ethanenitrile + ester mixture series differ considerably. They are similar for the mixtures involving propanenitrile and adiponitrile.

The variation in the values of V^E in each series may be attributed to the difference in free volume between unlike components when the mixture is formed. The free volume contribution is proportional to $|\alpha_1 - \alpha_2|$ and always has a negative sign (Van and Patterson, 1982). Figure 4 shows a correlation of V^E at x_i = 0.5 with the difference in the thermal expansion coefficient of unlike components $|\alpha_1 -$

$\alpha_2|$. The plot is almost linear with some scatter at low values of V^E. Thus, apart from dipole−dipole and/or dipole−induced dipole interaction contributions, the contraction of the solution is also due to free volume differences between the unlike components. However, at present it is difficult to estimate the extent of each contribution unless excess enthalpy measurements and spectroscopic investigations are carried out.

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