

Speeds of Sound, Isentropic Compressibilities, and Excess Volumes of Binary Mixtures of Acrylonitrile with Organic Solvents

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The isentropic compressibilities K_S , excess isentropic compressibilities K_S^E , and excess molar volumes V^E have been determined from the measurements of speeds of sound u and densities ρ of seven binary mixtures of acrylonitrile with ethanenitrile, methyl acetate, ethyl acetate, *n*-butyl acetate, dimethylformamide, dimethylacetamide, and dimethyl sulfoxide at 303.15 K. Variable-degree polynomials were fitted to the results. The values of the excess functions indicate a varying extent of molecular interaction and interstitial accommodation between unlike components. The experimental speeds of sound have been analyzed in terms of the collision factor theory of Schaaffs (*Molekularakustik*; Springer-Verlag: Berlin, 1963) and the free length theory of Jacobson (*Acta Chem. Scand. A* **1952**, *6*, 1485–1498).

Introduction

In previous papers (Oswal and Patel, 1995a,b) we have reported the speed of sound u , the isentropic compressibility K_S , the viscosity η , and the excess molar volume V^E for binary mixtures of ethanenitrile (EN), propanenitrile (PN), and adiponitrile with methyl acetate (MA), ethyl acetate (EA), *n*-butyl acetate (BA), dimethylformamide (DMF), dimethylacetamide (DMA), and dimethyl sulfoxide (DMSO). It was observed that the polarity and size of the molecules involved in the mixture formation have a dominating effect on the results of the excess properties of V , K_S , and η as well as on the type and the extent of molecular interactions.

The study of mixtures of acrylonitrile in various solvents is of interest because of its wide use as an important industrial monomer for polyacrylonitrile, as well as for investigating the effect of the simultaneous presence of the C=C double bond and the polar nitrile C≡N group on the molecular interactions. Further, the properties of liquid mixtures are also very important from a polymer solution point of view, as some of the polymers which are insoluble in a single solvent can be dissolved in a solvent mixture (Chu and Munk, 1978; Fernandez-Pierola and Horta, 1981). The solution properties of a polymer in a mixed solvent depend not only on the interactions between the polymer and each one of the liquids but also on the interactions between the liquids themselves. In fact these interactions between liquids are decisive in determining the solubilization of the polymer and the expansion of the polymer coils in solution. Therefore, as an extension of our studies, in this paper we report the u , K_S , and V^E of binary mixtures of acrylonitrile (AN) with the same six solvents and ethanenitrile.

Experimental Section

The u values in pure liquids and in binary mixtures were measured with a multifrequency 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 densities were measured

with an Anton Paar vibrating tube digital densimeter (model DMA 60/602) with a thermostated bath controlled to ± 0.01 K. The isentropic compressibilities K_S were determined from the relation $K_S = 1/(u^2\rho)$. The details of the experimental procedure have already been described elsewhere (Oswal and Palsanawala, 1989; Oswal and Phalak, 1993; Patel and Oswal, 1992).

AN (Riedel) was dried over anhydrous CaCl_2 and distilled fractionally (Riddick et al., 1986). EN (E. Merck, Bombay) was dried over anhydrous CaCO_3 , refluxed repeatedly over P_2O_5 until no color appeared on the oxide, and fractionally distilled. MA (SRL, Bombay), EA (BDH, Bombay), and BA (E. Merck, Bombay) of analytical grade were kept over anhydrous K_2CO_3 for more than 72 h and distilled fractionally (Riddick et al., 1986). DMF (SRL, Bombay) was dried over Na_2CO_3 and then distilled. DMA (SRL, Bombay) and DMSO (E. Merck, Bombay) were dried over anhydrous K_2CO_3 and fractionally distilled before use (Riddick et al., 1986). The middle fraction of the distillates was used.

The purity of each liquid sample was checked by measuring the boiling point and via gas–liquid chromatography analysis at Gujarat Insecticide Ltd, Ankleswar. The estimated purity of each sample was >99.8 mol %. Furthermore, the experimental densities and speeds of sound are compared with the literature values in Table 1. The agreement between the two is good.

Mixtures were prepared by mixing known masses of pure liquids in narrow-mouthed, ground glass, stoppered bottles. 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 values of ρ , u , and K_S were reproducible within ± 0.01 kg m^{-3} , ± 1 m s^{-1} , and ± 2 T Pa^{-1} , respectively.

Results and Discussion

The results for the speed of sound u , the density ρ , the isentropic compressibility K_S , the excess molar volume V^E , and the excess isentropic compressibility K_S^E are given in Table 2.

K_S^E and V^E for each mixture were calculated from the K_S and ρ values of the pure liquids and the binary mix-

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Table 1. Pure Component Properties at 303.15 K

liquid	$\rho/(\text{kg}\cdot\text{m}^{-3})$		$u/(\text{m}\cdot\text{s}^{-1})$		α°/kK	$C_p/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$
	exptl	lit.	exptl	lit.		
AN	795.43	795.10, ^a 794.70 ^b	1172		1.390 ^c	108.8 ^c
MA	919.67	920.40 ^d	1134	1136 ^e	1.513 ^f	143.9 ^c
EA	888.64	888.60 ^e	1119	1119 ^e	1.394 ^f	167.9 ^e
BA	871.36	871.29 ^g	1176	1172, ^h 1178 ^d	1.242 ^f	228.4 ^g
DMF	939.59	939.67, ⁱ 941.20 ^c	1444	1445 ⁱ	0.766 ^j	148.4 ^e
DMA	932.46	931.69, ^c 931.70 ^j	1441		0.921 ^e	178 ^c
DMSO	1090.54	1090.42, ^k 1090.68 ^l	1477		0.916 ^k	153.2 ^e
EN	771.40	771.25 ^c	1260	1264 ^d	1.397 ^e	91.5 ^c

^a Jain, D. V. S.; Wadi, R. K.; Saini, S. B.; Singh, J. *Ind. J. Chem., Sect. A* **1978**, *16*, 561–563. ^b Jain, D. V. S.; Saini, S. B.; Chaudhry, V. *Ind. J. Chem., Sect. A* **1979**, *18*, 198–200. ^c Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents Physical Properties and Methods of Purification*; Wiley Interscience: New York, 1986. ^d TRC Source database for Chemistry and Engineering Thermodynamic Tables; Thermodynamic Research Center, The Texas A&M University System: College Station, TX, 1994. ^e Lagman, R. T.; McLeary, E. C.; Milner, O. *J. Am. Chem. Soc.* **1951**, *73*, 5891. ^f Derived from measured densities at different temperatures. ^g Timmermans, J. *Physico-Chemical Constants for Pure Organic Compounds*; Elsevier Publishing Co.: New York, 1965; Vol. 2. ^h Palsanawala, P. P. M. Phil. Dissertation, South Gujarat University, Surat, India, 1986. ⁱ Rajasekhar, P.; Reddy, K. S. *Thermochim. Acta* **1987**, *117*, 379–383. ^j Pikkarainen, L. *Finn. Chem. Lett.* **1980**, 185–188. ^k Bicknell, R. T. M.; Davies, D. B.; Lawrence, K. G. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 1595–1601. ^l Heinrich, J.; Survoy, J. *Sb. Pr. Chem. Fak SVST* **1966**, 207.

Table 2. Experimental Densities, Speeds of Sound, Isentropic Compressibilities, Excess Molar Volumes, and Excess Isentropic Compressibilities for Acrylonitrile Binary Mixtures at 303.15 K

x_1	$\rho/\text{kg m}^{-3}$	$u/\text{m s}^{-1}$	$K_S/T \text{ Pa}^{-1}$	$10^9 V^E/\text{m}^3 \text{ mol}^{-1}$	$K_S^E/T \text{ Pa}^{-1}$	x_1	$\rho/\text{kg m}^{-3}$	$u/\text{m s}^{-1}$	$K_S/T \text{ Pa}^{-1}$	$10^9 V^E/\text{m}^3 \text{ mol}^{-1}$	$K_S^E/T \text{ Pa}^{-1}$
1. AN + EN Mixture											
0.0000	771.40	1260	816			0.5983	787.41	1203	877	-28.1	-3
0.0965	774.50	1250	826	-18.5	-1	0.6941	789.50	1195	886	-25.4	-2
0.2002	777.43	1240	836	-20.9	-3	0.7977	791.63	1187	896	-19.7	-2
0.2977	780.10	1230	847	-26.6	-3	0.8997	793.70	1179	905	-19.2	-1
0.3966	782.63	1221	857	-28.1	-4	1.0000	795.43	1172	915		
0.4928	784.99	1212	867	-30.1	-3						
2. AN + MA Mixture											
0.0000	919.67	1134	845			0.6012	852.76	1158	874	-175.8	-9
0.1018	909.90	1139	847	-77.5	-4	0.6955	840.27	1162	881	-158.2	-9
0.1999	899.79	1144	849	-122.8	-8	0.8014	825.67	1166	890	-136.8	-8
0.3006	888.94	1147	855	-161.9	-8	0.8960	811.83	1169	901	-94.7	-5
0.4001	877.47	1151	860	-171.5	-10	1.0000	795.43	1172	915		
0.4946	866.12	1154	866	-175.9	-9						
3. AN + EA Mixture											
0.0000	888.64	1119	898			0.5946	844.54	1150	895	-207.7	-11
0.0974	883.06	1126	893	-79.3	-6	0.6974	833.99	1155	898	-185.1	-10
0.2010	876.51	1131	891	-144.1	-9	0.7978	822.60	1161	901	-148.4	-8
0.3020	869.44	1136	891	-186.7	-11	0.9018	809.41	1166	908	-86.0	-4
0.3997	861.86	1141	891	-205.8	-12	1.0000	795.43	1172	915		
0.4964	853.65	1145	893	-211.9	-11						
4. AN + BA Mixture											
0.0000	871.36	1176	829			0.5941	841.24	1173	863	-220.8	-4
0.0988	867.96	1176	833	-80.1	-1	0.6991	832.45	1172	874	-199.1	-3
0.2033	863.77	1176	837	-139.8	-3	0.7966	822.78	1171	886	-165.5	-1
0.3022	859.22	1175	842	-182.4	-3	0.8992	810.43	1171	899	-100.0	-1
0.4010	853.98	1175	848	-208.9	-4	1.0000	795.43	1172	915		
0.4962	848.18	1174	855	-223.2	-4						
5. AN + DMF Mixture											
0.0000	939.59	1444	510			0.5957	865.54	1284	700	-528.1	-62
0.0990	929.96	1419	534	-229.6	-19	0.6984	849.67	1256	746	-491.1	-58
0.2027	918.41	1392	561	-380.3	-36	0.7980	833.18	1228	795	-405.0	-46
0.2977	906.98	1367	590	-478.2	-48	0.8950	815.85	1202	848	-255.5	-30
0.4005	893.51	1339	624	-527.6	-58	1.0000	795.43	1172	915		
0.4970	880.04	1312	660	-539.8	-62						
6. AN + DMA Mixture											
0.0000	932.46	1441	516			0.5995	866.46	1290	693	-428.2	-47
0.0998	923.66	1419	537	-123.0	-12	0.6984	851.45	1262	737	-384.3	-44
0.1982	914.28	1397	560	-229.1	-24	0.7976	835.05	1232	788	-318.6	-36
0.2970	904.05	1372	587	-316.4	-33	0.9005	816.00	1201	849	-187.5	-21
0.3941	893.10	1347	617	-380.3	-41	1.0000	795.43	1172	915		
0.5009	879.81	1318	654	-414.2	-46						
7. AN + DMSO Mixture											
0.0000	1090.54	1477	420			0.6018	925.26	1285	654	-537.2	-80
0.1020	1064.49	1442	451	-145.5	-23	0.7045	893.45	1255	710	-486.0	-73
0.2051	1037.57	1409	485	-285.7	-45	0.8066	860.70	1226	772	-380.5	-58
0.3025	1011.50	1376	522	-405.9	-60	0.8999	829.73	1199	838	-227.5	-34
0.3994	984.56	1346	560	-486.5	-72	1.0000	795.43	1172	915		
0.5057	954.03	1313	608	-541.1	-78						

tures with the following expression:

$$Y^E = Y - Y^{\text{id}} \quad (1)$$

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

$$V^{\text{id}} = \sum x_i V_i^{\circ} = \sum x_i M_i / \rho_i \quad (2)$$

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

$$K_S^{\text{id}} = \sum \varphi_i \{ K_{S,i}^{\circ} + TV_i^{\circ} (\alpha_i^{\circ})^2 / C_{p,i}^{\circ} \} - T \left(\sum x_i V_i^{\circ} \right) \left(\sum \varphi_i \alpha_i^{\circ} \right)^2 / \left(\sum x_i C_{p,i}^{\circ} \right) \quad (3)$$

in which V_i° , α_i° , and $C_{p,i}^{\circ}$ are respectively the molar volume, the isobaric thermal expansion coefficient, and the molar isobaric heat capacity of pure component i and $\phi_i = x_i V_i / \sum x_j V_j$ is the volume fraction of i in the mixture, stated in terms of the unmixed components. The values of α° and C_p° used for these calculations are listed in Table 1.

The mixing quantity Δu has been calculated, as has been common in the literature (Kiyohara et al., 1978; Tamura et al., 1983; Aicart et al., 1990), by

$$\Delta u = u - \sum_i x_i u_i^{\circ} \quad (4)$$

The estimated accuracy in the values of V^E is $5 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$. For a compact and smooth representation, the values of ρ , u , and K_S were fitted to a polynomial equation of the form

$$Y = \sum_{i=1}^m A_i x_1^{i-1} \quad (5)$$

where $Y = \rho$, u , and K_S .

The values of V^E , K_S^E , and Δu were smoothed to a Redlich–Kister (1948) polynomial regression of the type

$$\Psi^E = x_1 x_2 \sum_{i=1}^m A_i (1 - 2x_1)^{i-1} \quad (6)$$

The values of the coefficients A_i of eqs 5 and 6 and the corresponding standard deviations σ obtained by the method of least squares, assigning equal weights to each point, are given in Tables 3 and 4.

The experimental results for V^E , K_S^E , and Δu and their corresponding curves fitted by eq 6 are plotted in Figures 1–3. No published work on the speed of sound and isentropic compressibility and excess molar volume measurements was found for the present systems with which to compare our results. Values of V^E and K_S^E for all the seven systems with AN are negative (Figures 1 and 2). In general the dependence of V^E and K_S^E on composition is unsymmetrical and the magnitude varies with the type of solvent used. However, the sequence $\text{EN} < \text{MA} < \text{EA} \approx \text{BA} < \text{DMA} < \text{DMF} \approx \text{DMSO}$ for the negative values of V^E is slightly different than $\text{EN} \approx \text{BA} < \text{MA} < \text{EA} < \text{DMA} < \text{DMF} < \text{DMSO}$ for K_S^E . The maximum in K_S^E is around $0.4x_1$ for AN + EA, $0.45x_1$ for AN + EN and AN + BA, around $0.5x_1$ for AN + MA, around $0.55x_1$ for AN + DMF and AN + DMSO, and around $0.6x_1$ for AN + DMA mixtures. Thus, the maxima are dependent on the type and

Table 3. Coefficients A_i of Eq 5 and Standard Deviations σ

property	A_1	A_2	A_3	A_4	A_5	σ
1. AN + EN Mixture						
$\rho/(\text{kg m}^{-3})$	771.41	32.92	-15.44	11.41	-4.85	0.04
$u/(\text{m s}^{-1})$	1260.0	-104.5	13.6	2.9		0.2
$K_S/(\text{T Pa}^{-1})$	815.8	106.1	-5.5	-1.7		0.4
2. AN + MA Mixture						
$\rho/(\text{kg m}^{-3})$	919.65	-91.41	-43.05	26.22	-15.96	0.06
$u/(\text{m s}^{-1})$	1134.5	43.4	-5.7			0.5
$K_S/(\text{T Pa}^{-1})$	845.0	14.7	54.2			0.9
3. AN + EA Mixture						
$\rho/(\text{kg m}^{-3})$	888.62	-53.41	-35.09	7.87	-12.55	0.03
$u/(\text{m s}^{-1})$	1119.4	63.2	-32.9	22.4		0.5
$K_S/(\text{T Pa}^{-1})$	897.9	-64.4	186.5	-205.2	100.5	0.5
4. AN + BA Mixture						
$\rho/(\text{kg m}^{-3})$	871.43	-31.44	-32.91	18.46	-29.97	0.05
$u/(\text{m s}^{-1})$	1175.8	7.3	-34.6	23.2		0.4
$K_S/(\text{T Pa}^{-1})$	829.2	31.3	28.7	25.8		0.3
5. AN + DMF Mixture						
$\rho/(\text{kg m}^{-3})$	939.58	-89.09	-86.24	67.58	-36.38	0.06
$u/(\text{m s}^{-1})$	1444.0	-247.6	-47.5	23.5		0.4
$K_S/(\text{T Pa}^{-1})$	510.3	211.6	216.0	-120.7	97.5	0.5
6. AN + DMA Mixture						
$\rho/(\text{kg m}^{-3})$	932.45	-84.31	-35.28	-6.69	-10.73	0.05
$u/(\text{m s}^{-1})$	1440.8	-204.5	-98.4	33.8		0.4
$K_S/(\text{T Pa}^{-1})$	515.6	207.0	80.1	112.1		0.5
7. AN + DMSO Mixture						
$\rho/(\text{kg m}^{-3})$	1090.52	-252.78	-18.32	-38.30	14.32	0.04
$u/(\text{m s}^{-1})$	1477.1	-347.1	51.6	-9.7		0.5
$K_S/(\text{T Pa}^{-1})$	419.3	309.4	54.4	131.6		0.9

Table 4. Coefficients A_i of Eq 6 and Standard Deviations σ

property	A_1	A_2	A_3	σ
1. AN + EN Mixture				
$10^9 V^E/(\text{m}^3 \text{ mol}^{-1})$	-103.9	-2.2	-143.1	3.5
$\Delta u/(\text{m s}^{-1})$	-16.1	-0.3	8.3	0.2
$K_S^E/(\text{T Pa}^{-1})$	-13.2	-2.9		0.5
2. AN + MA Mixture				
$10^9 V^E/(\text{m}^3 \text{ mol}^{-1})$	-703.5	78.1	-348.8	5.6
$\Delta u/(\text{m s}^{-1})$	4.6	4.9	4.8	0.5
$K_S^E/(\text{T Pa}^{-1})$	-38.5	3.8	-19.7	0.7
3. AN + EA Mixture				
$10^9 V^E/(\text{m}^3 \text{ mol}^{-1})$	-856.6	28.1	-130.1	2.4
$K_S^E/(\text{T Pa}^{-1})$	-46.5	-10.5	-16.4	0.5
4. AN + BA Mixture				
$10^9 V^E/(\text{m}^3 \text{ mol}^{-1})$	-884.3	125.9	-177.1	1.8
$K_S^E/(\text{T Pa}^{-1})$	-16.4	-3.2	8.5	0.5
5. AN + DMF Mixture				
$10^9 V^E/(\text{m}^3 \text{ mol}^{-1})$	-2171.6	101.1	-752.2	4.7
$\Delta u/(\text{m s}^{-1})$	10.9	5.3		0.5
$K_S^E/(\text{T Pa}^{-1})$	-247.9	60.5	-26.6	0.8
6. AN + DMA Mixture				
$10^9 V^E/(\text{m}^3 \text{ mol}^{-1})$	-1670.4	441.2	-94.9	4.3
$\Delta u/(\text{m s}^{-1})$	46.2	16.2	-17.3	0.6
$K_S^E/(\text{T Pa}^{-1})$	-184.3	62.0	-1.2	0.3
7. AN + DMSO Mixture				
$10^9 V^E/(\text{m}^3 \text{ mol}^{-1})$	-2146.4	571.6	146.0	3.5
$\Delta u/(\text{m s}^{-1})$	-35.3	-2.1	7.0	0.6
$K_S^E/(\text{T Pa}^{-1})$	-317.0	79.9		0.8

the size of the second component. Δu values (Figure 3) are positive for mixtures of AN with DMF, DMA, and MA but negative for EN and DMSO. For the other two mixtures, u varies almost linearly with mole fraction.

The values of the excess properties V^E and K_S^E are very slightly negative for the AN + EN mixture, which suggests

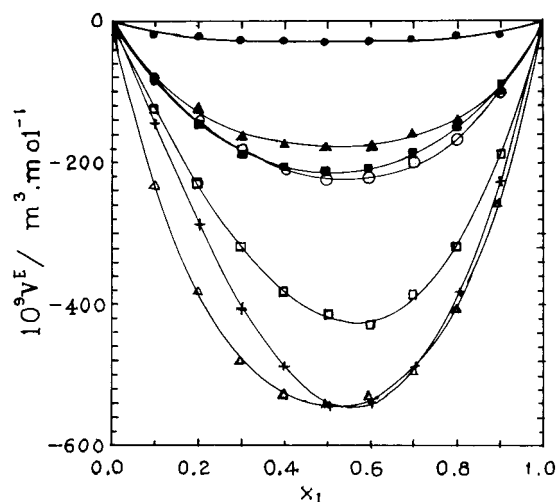


Figure 1. Excess molar volumes for acrylonitrile binary mixtures at 303.15 K. Experimental points: second component (●) ethanenitrile (EN); (▲) methyl acetate (MA); (■) ethyl acetate (EA); (○) *n*-butyl acetate (BA); (△) dimethylformamide (DMF); (□) dimethylacetamide (DMA); (+) dimethyl sulfoxide (DMSO); (—) calculated with eq 6.

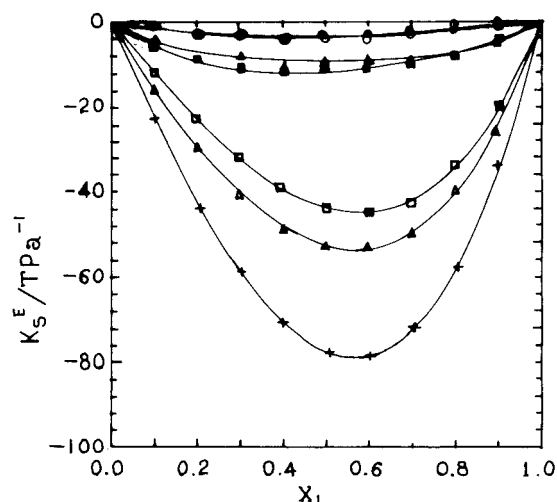


Figure 2. Excess isentropic compressibility for acrylonitrile binary mixtures at 303.15 K. Symbols same as in Figure 1. (—) Calculated with eq 6.

that the combined effect of specific interactions and free volume contributions is counterbalanced by the dispersion interactions. For the mixtures AN + MA, AN + EA, and AN + BA, the values of V^E and K_S^E are moderately negative, which indicates that the combined effect of specific interactions and free volume contributions is relatively large compared to the dispersion interactions between the participating molecules. On the other hand, the magnitudes of the negative V^E and K_S^E are very large for mixtures of AN with DMF, DMA, and DMSO; hence, the specific interactions between the two unlike components are very strong (Ohomuro, 1987; Venkatesu and Rao, 1994). The interactions in the present mixtures of acrylo-

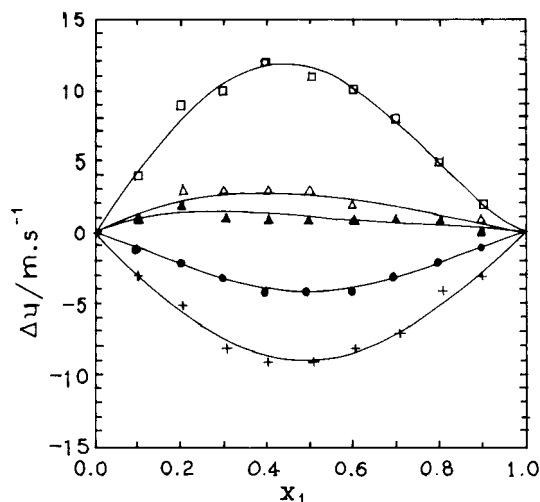


Figure 3. Deviations in speed of sound Δu for acrylonitrile binary mixtures at 303.15 K. Experimental points: second component (●) ethanenitrile (EN); (▲) methyl acetate (MA); (△) dimethylformamide (DMF); (□) dimethylacetamide (DMA); (+) dimethyl sulfoxide (DMSO); (—) calculated with eq 6.

nitrile with a second component may be considered as of dipole–dipole type and $n-\pi$ type. The dipole–dipole type is possible since each component in the mixtures possesses a permanent dipole moment (Fort and Moore, 1965; Rowlinson and Swinton, 1986). The $n-\pi$ type is possible since the π electrons of the C=C in acrylonitrile may interact with the lone pair of either O or N atoms in the second component, the former molecule acting as an acceptor while the latter acts as a donor (Bolinga et al., 1978).

The asymmetry in the V^E and K_S^E curves (Figures 1 and 2) may originate from the self-association of acrylonitrile and from the molecular correlation of the orientation restricted by the dipole–dipole interaction and the dipole–induced-dipole interaction (Ohomuro et al., 1987; Haijium et al., 1993).

The speeds of sound u in the present binary mixtures except for AN + DMSO were also evaluated theoretically from both the collision factor theory (CFT) of Schaaffs (1963) and the intermolecular free length theory (FLT) of Jacobson (1952). The pertinent relations in these calculations and their theoretical basis have been outlined several times by Jacobson (1952), Schaaffs (1963, 1975), Nutsch-Kuhnkies (1965), and Patel (1993) and will not be repeated here.

The collision factor S , the surface area Y , and the free length L_f for the pure components were estimated from the speed of sound, the molar volumes, the critical temperature, and the ratio of the principle heat capacities. The values of the molar volume V , the collision factor S , the ratio of the principle heat capacities γ , the critical temperature T_c , the available free volume V_a , the surface area Y , and the free length L_f for the pure components employed in and evaluated from the CFT and the FLT are listed in Table 5. The theoretical speeds of sound u in the binary mixtures over the entire range of composition at intervals

Table 5. Properties of Pure Components for the CFT and the FLT

liquid	$V/(\text{cm}^3 \text{mol}^{-1})$	S	γ	T_c/K	$V_a/(\text{cm}^3 \text{mol}^{-1})$	$Y/(\text{cm}^2 \text{mol}^{-1})$	$L_f/\text{\AA}$
EN	51.218	3.226	1.422	545.5	11.07	47.90	0.4621
MA	80.550	3.081	1.459	506.8	19.28	63.48	0.6073
EA	99.147	3.028	1.387	520.2	22.87	73.46	0.6226
BA	133.309	3.141	1.329	579.2	26.57	91.91	0.5783
DMF	77.794	3.857	1.183	596.6	14.92	64.59	0.4619
DMA	93.431	3.968	1.261	637.0	15.36	74.61	0.4117

Table 6. Comparison of Speeds of Sound u Estimated from the CFT and the FLT with Those Observed Experimentally along with the Values of the Free Length L_f for Acrylonitrile Mixtures at 303.15 K

x_1	$U_{CFT}/$ (m s ⁻¹)	dev%	$U_{FLT}/$ (m s ⁻¹)	dev%	$L_f/\text{Å}$
AN + EN Mixture					
0.1	1252	-0.18	1250	-0.02	0.4731
0.2	1243	-0.30	1239	0.01	0.4785
0.3	1235	-0.39	1229	0.06	0.4839
0.4	1226	-0.44	1219	0.08	0.4893
0.5	1217	-0.45	1210	0.09	0.4945
0.6	1208	-0.44	1202	0.07	0.4995
0.7	1199	-0.39	1194	0.03	0.5044
0.8	1190	-0.31	1187	-0.01	0.5092
0.9	1181	-0.18	1180	-0.03	0.5141
		$\sigma = 0.38$			$\sigma = 0.06$
AN + MA Mixture					
0.1	1139	-0.07	1139	-0.08	0.5969
0.2	1144	-0.12	1144	-0.12	0.5870
0.3	1148	-0.15	1148	-0.12	0.5776
0.4	1152	-0.17	1152	-0.10	0.5686
0.5	1156	-0.18	1155	-0.08	0.5598
0.6	1160	-0.18	1159	-0.09	0.5510
0.7	1164	-0.17	1163	-0.14	0.5423
0.8	1167	-0.16	1168	-0.20	0.5337
0.9	1170	-0.11	1171	-0.20	0.5257
		$\sigma = 0.16$			$\sigma = 0.14$
AN + EA Mixture					
0.1	1126	-0.14	1122	0.21	0.6122
0.2	1132	-0.25	1125	0.40	0.6020
0.3	1138	-0.33	1128	0.56	0.5917
0.4	1144	-0.39	1132	0.68	0.5815
0.5	1150	-0.42	1137	0.73	0.5711
0.6	1155	-0.42	1142	0.71	0.5606
0.7	1160	-0.39	1149	0.62	0.5501
0.8	1165	-0.32	1156	0.46	0.5395
0.9	1169	-0.19	1164	0.25	0.5292
		$\sigma = 0.35$			$\sigma = 0.58$
AN + BA Mixture					
0.1	1178	-0.23	1172	0.36	0.5731
0.2	1179	-0.27	1169	0.58	0.5673
0.3	1180	-0.40	1167	0.74	0.5613
0.4	1181	-0.50	1165	0.87	0.5553
0.5	1181	-0.56	1164	0.96	0.5494
0.6	1181	-0.59	1163	0.99	0.5435
0.7	1181	-0.56	1163	0.92	0.5374
0.8	1179	-0.48	1165	0.72	0.5311
0.9	1176	-0.31	1168	0.39	0.5248
		$\sigma = 0.48$			$\sigma = 0.81$
AN + DMF Mixture					
0.1	1421	-0.18	1433	-1.08	0.4603
0.2	1397	-0.33	1419	-1.94	0.4600
0.3	1371	-0.41	1398	-2.39	0.4623
0.4	1344	-0.41	1372	-2.46	0.4667
0.5	1317	-0.39	1342	-2.35	0.4724
0.6	1289	-0.39	1313	-2.25	0.4786
0.7	1261	-0.41	1285	-2.26	0.4846
0.8	1234	-0.45	1257	-2.26	0.4912
0.9	1205	-0.39	1222	-1.79	0.5010
		$\sigma = 0.40$			$\sigma = 2.25$
AN + DMA Mixture					
0.1	1447	0.09	1425	-0.48	0.4467
0.2	1392	0.18	1405	-0.70	0.4501
0.3	1367	0.26	1381	-0.81	0.4545
0.4	1341	0.30	1357	-0.90	0.4596
0.5	1314	0.29	1332	-1.01	0.4655
0.6	1288	0.23	1307	-1.14	0.4720
0.7	1261	0.13	1278	-1.25	0.4797
0.8	1233	0.03	1248	-1.21	0.4893
0.9	1204	-0.04	1213	-0.86	0.5020
		$\sigma = 0.21$			$\sigma = 1.02$

of 0.1 mole fraction were estimated and are compared in Table 6 together with the percentage deviations dev%. The standard percentage deviations $\sigma\%$ have also been calcu-

lated for each individual mixture, considering dev% for all the mole fractions from 0.1 to 0.9 using the relation

$$\sigma\% = \left[\sum (\text{dev}\%)^2 / (n - 1) \right]^{1/2} \quad (7)$$

where n represents the number of data points, that is, 9.

The study of Table 6 reveals that the values of $\sigma\%$ for the CFT are in the range from 0.16 to 0.48 for six AN mixtures. The corresponding values of $\sigma\%$ for the FLT are from 0.06 to 2.25. Thus, the estimation of speed of sound in the mixtures by both theories is satisfactory. However, the prediction by the CFT is somewhat better than that by the FLT formulations.

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