

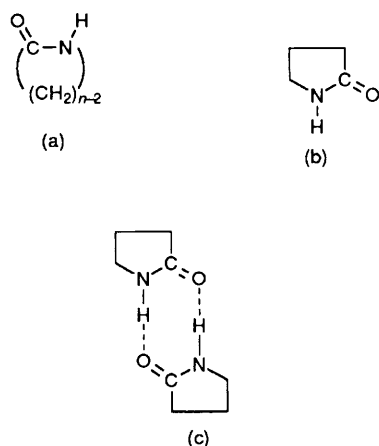
Excess volumes and isentropic compressibilities of pyrrolidin-2-one-alkanol (C_1 – C_5) binary mixtures

S. K. Mehta,* R. K. Chauhan and R. K. Dewan

Department of Chemistry, Panjab University, Chandigarh 160 014, India

The velocity of sound, u , and excess volume, V^E , have been determined at 303.15 K for binary mixtures of pyrrolidin-2-one + n -alkanol (C_1 – C_5) over the whole composition range. The isentropic compressibilities K_S and their excess values K_S^E have been estimated and shown to be negative for all systems over the entire composition range and to vary in the order methanol < ethanol < propanol < butanol < pentanol. The V^E results have been used to estimate the excess partial molar volumes of the components and have also been analysed in the light of Prigogine–Flory–Patterson theory. An analysis of each of the three contributions *viz.* interactional, free volume and P^* to V^E shows that the interactional contribution is positive for all systems except methanol which has a small negative interactional contribution. The free volume effect and P^* contribution are negative for all the mixtures. To explore the nature of the interactions, various thermodynamic parameters *i.e.* free volume, V_f , solvation number, S_n , Wada's constant W , and Rao's constant, R , have been derived from the u and ρ data. The behaviour of these parameters indicates the absence of any complex formation in the mixtures studied.

The structure of lactams is of great interest because they are related to many structural problems in molecular biology. The basic structural element of lactams is the peptide bond $-\text{NH}\cdot\text{CO}$. Owing to its donor–acceptor properties, it can interact with other amide molecules *via* hydrogen bonds. In this way, lactams provide small molecular models for the amide group in peptides, polypeptides and proteins. Self association of the (*Z*)-lactams also serves as a model for the hydrogen bonding of the bases in nucleic amides. The generalised formula for lactams (a) and the structure of pyrrolidin-2-one (b) and its cyclic dimer (c) are shown below.



IR spectroscopic investigations have shown^{1–6} that self-association of pyrrolidin-2-one is relatively strong. There have been relatively few studies of the volumetric properties of binary mixtures of pyrrolidin-2-one with other species. Excess volumes and dielectric properties have been reported by Ruostesuo and Pirita-Honkmenen.^{7,8} The results were discussed in terms of the possible interactions between like and unlike molecules.

Continuing our systematic studies,^{9–11} we report here the volumes of mixing and velocities of ultrasound propagation for binary mixtures of pyrrolidin-2-one-alkanol (C_1 – C_5) at 303.15 K over the whole range composition. The components have been chosen because of their characteristic properties. The experimental V^E results obtained for pyrrolidin-2-one

mixtures have been analysed in the light of Prigogine–Flory–Patterson theory.¹²

Ultrasonics has proved to be a useful tool for gaining information on the dynamics of liquid systems. The measurement of ultrasonic velocity enables the accurate determination of isentropic compressibility coefficients which can be used to provide qualitative information about the physical nature of the aggregates occurring in the liquid phase. To investigate the nature of the interactions, various thermodynamic parameters^{13–16} have been calculated which are sensitive to interactions between solute and solvent. Trends in these properties with changes in composition can offer some qualitative assessment of solution behaviour in the intermediate composition range. A comparison of these properties for the mixtures studied is presented and analysed.

Experimental

Pyrrolidin-2-one (Fluka) was dried with CaO and fractionally distilled. Alkanols (all pure grade) were dried and fractionally distilled as described elsewhere.¹⁷ Prior to use, all the chemicals were dried with IDPL A4 molecular sieves. The purity of the chemicals was checked by measuring their densities (Table 1). The agreement between experimental and literature^{8,18} density is good.

Excess volumes were measured in a continuous dilution dilatometer immersed in a water bath controlled to better than ± 0.01 K. Details of the experimental set-up and the measuring procedure have been described elsewhere.¹⁹ The dilatometer was calibrated with benzene–cyclohexane mix-

Table 1 Densities ρ , ultrasonic velocities u , isobaric thermal expansivities α_p and molar isobaric heat capacities C_p for the component liquids at 303.15 K

component	ρ /kg m ^{–3}	u /m s ^{–1}	α_p /10 ⁴ K ^{–1}	C_p /J K ^{–1} mol ^{–1}
pyrrolidin-2-one	1103.0	1615.79	7.253	166.10
methanol	781.6	1085.38	12.425	81.50
ethanol	780.7	1126.52	11.350	112.34
propanol	795.5	1188.67	10.559	143.80
butanol	801.8	1223.34	9.875	177.02
pentanol	807.4	1259.63	9.400	208.28

tures at 303.15 K. The results for V^E are estimated to be accurate to $\pm 0.002 \text{ cm}^3 \text{ mol}^{-1}$.

An ultrasonic time intervalometer (UTI-101) from Innovative instruments, based on a pulse-echo overlap technique (PET), coupled with an oscilloscope was used for the ultrasonic velocity measurements. The frequency of sound was 2.0 MHz. The cell was calibrated with water as a reference. The uncertainty in the measurement of u was $\pm 2 \times 10^{-2} \text{ ms}^{-1}$.

Results and Discussion

Excess volume

The V^E values determined experimentally at 303.15 K are presented in Table 2. The Redlich-Kister equation in the form

$$V^E/\text{cm}^3 \text{ mol}^{-1} = x(1-x) \sum_i A_i(2x-1)^i \quad (1)$$

where x is the mole fraction of pyrrolidin-2-one, was fitted to the experimental V^E values. The values of A_i are listed in Table 3.

The partial molar excess volumes \bar{V}_1^E and \bar{V}_2^E may be calculated from V^E using:

$$\bar{V}_1^E = V_1 - \bar{V}_1 = V^E/x + x(1-x)[\partial(V^E/x)/\partial x]_{P,T} \quad (2)$$

$$\bar{V}_2^E = V_2 - \bar{V}_2 = V^E/(1-x) + x(1-x)[\partial\{V^E/(1-x)\}/\partial(1-x)]_{P,T} \quad (3)$$

where \bar{V}_1 and \bar{V}_2 represent the partial molar volumes of the components 1 and 2, in this case pyrrolidin-2-one and alkanol. The results are presented graphically in Fig. 1 and 2. The V^E values are negative for all the mixtures studied over the complete range of composition and vary in the order methanol < ethanol < propanol < butanol < pentanol. The location of the V^E minimum shifts from $x = 0.38$ for methanol to $x = 0.60$ for pentanol.

It is well known that self association in pyrrolidin-2-one is relatively strong. Mixing alkanols, known to be self associated, with pyrrolidin-2-one can be expected to bring changes in the hydrogen-bonding equilibria and electrostatic interactions with different resultant contributions to the volume of mixing. The disruption of alkanol multimers through breaking of hydrogen bonds as well as weakening of the interactions between molecules will result in an increase in volume. A decrease in volume, on the other hand, might arise from interstitial accommodation.

The negative V^E values obtained suggest that the interactions between unlike molecules exceed the structure-breaking effect between like molecules. These interactions are

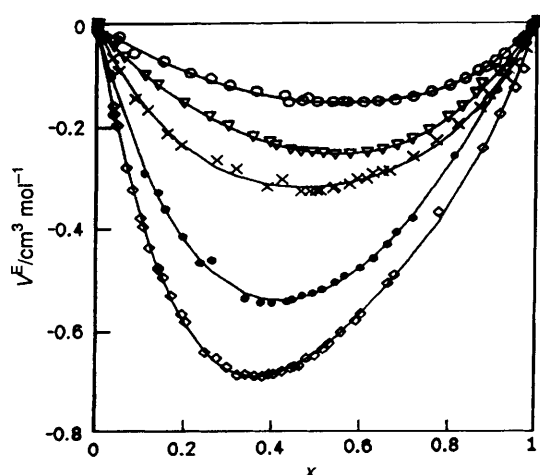


Fig. 1 V^E for $x\text{C}_4\text{H}_8\text{NO}-(1-x)\text{C}_n\text{H}_{2n+1}\text{OH}$: \diamond , methanol, \bullet , ethanol; \times , propanol; ∇ , butanol; \circ , pentanol

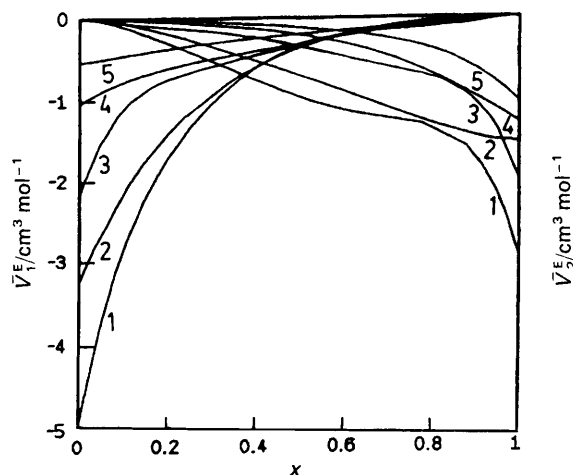


Fig. 2 \bar{V}_1^E and \bar{V}_2^E for $x\text{C}_4\text{H}_8\text{NO}-(1-x)\text{C}_n\text{H}_{2n+1}\text{OH}$

relatively strong between pyrrolidin-2-one and methanol. Increasing the chain length of the alkanol tends to dilute the interaction between pyrrolidin-2-one and alkanol. It is therefore expected that V^E should decrease in the sequence found.

The molar volumes of the alkanols increase with chain length but the free volumes follow the reverse order. The geometrical fitting, contributing negatively, and arising from interstitial accommodation due to difference in molar volume and free volume between pyrrolidin-2-one and alkanols does not, therefore, play any significant role in the magnitude of V^E . Hence, the negative contributions to V^E from the interaction between unlike molecules will be the most important factor in determining its magnitude.

The excess partial molar volumes increase systematically with increasing chain length of the alkanol. The increase in \bar{V}_1^E values at small x provides evidence for the breaking of the self association in the pyrrolidin-2-one structure. The increase in \bar{V}_2^E values for small mole fraction of alkanol is clear evidence of the breaking of the alkanol multimers in this concentration range.

Prigogine-Flory-Patterson theory

Patterson and Delmas¹² used the Prigogine-Flory theory^{20,21} to interpret the excess volume V^E for a number of binary systems. In this theory, V^E is divided into an interactional contribution, a free volume contribution and a P^* contribution. The expression for V^E which separates the three contributions is given as

$$\frac{V^E}{x_1 V_1^* + x_2 V_2^*} = \frac{(\bar{v}^{1/3} - 1)\bar{v}^{2/3}\psi_1\theta_2}{[(4/3)\bar{v}^{-1/3} - 1]P_1^*} X_{12} \text{ (interactional)} \\ - \frac{(\bar{v}_1 - \bar{v}_2)^2(14/9\bar{v}^{-1/3} - 1)\psi_1\psi_2}{[(4/3)\bar{v}^{-1/3} - 1]\bar{v}} (\bar{v} \text{ curvature}) \\ + \frac{(\bar{v}_1 - \bar{v}_2)(P_1^* + P_2^*)\psi_1\psi_2}{P_2^*\psi_1 + P_1^*\psi_2} (P^* \text{ effect}) \quad (4)$$

where ψ represents the contact energy fraction and is given by

$$\psi_1 = 1 - \psi_2 = \frac{\phi_1 P_1^*}{\phi_1 P_1^* + \phi_2 P_2^*} \quad (5)$$

and other parameters pertaining to the pure components and the mixture are obtained through the Flory theory.^{24,25} The parameters of the pure components computed using Flory's expression are given in Table 4.

Table 2 Experimental V^E values for pyrrolidin-2-one-alkanol binary mixture at 303.15 K

x	$V^E/\text{cm}^3 \text{ mol}^{-1}$	x	$V^E/\text{cm}^3 \text{ mol}^{-1}$	x	$V^E/\text{cm}^3 \text{ mol}^{-1}$
methanol		ethanol		propanol	
0.0014	−0.0069	0.0059	−0.0190	0.0101	−0.0211
0.0036	−0.0176	0.0284	−0.0870	0.0362	−0.0687
0.0373	−0.1660	0.0317	−0.0965	0.0497	−0.0898
0.0388	−0.1720	0.1091	−0.2820	0.0877	−0.1392
0.0473	−0.2048	0.1406	−0.3400	0.1163	−0.1688
0.0674	−0.2762	0.1563	−0.3655	0.1597	−0.2054
0.0826	−0.3248	0.1964	−0.4217	0.1917	−0.2277
0.1006	−0.3770	0.2359	−0.4652	0.2723	−0.2725
0.1074	−0.3953	0.3386	−0.5323	0.3166	−0.2917
0.1211	−0.4299	0.3744	−0.5423	0.4206	−0.3212
0.1416	−0.4764	0.3998	−0.5457	0.4638	−0.3262
0.1421	−0.4774	0.4337	−0.5459	0.4993	−0.3266
0.1525	−0.4987	0.4457	−0.5447	0.5408	−0.3231
0.1705	−0.5322	0.4684	−0.5410	0.5911	−0.3130
0.1948	−0.5713	0.4926	−0.5348	0.6266	−0.3023
0.2035	−0.5836	0.5135	−0.5276	0.6491	−0.2942
0.2479	−0.6349	0.5432	−0.5147	0.3873	−0.3143
0.2746	−0.6570	0.5643	−0.5036	0.4846	−0.3268
0.2981	−0.6716	0.6003	−0.4812	0.5085	−0.3262
0.3231	−0.6825	0.6308	−0.4589	0.5373	−0.3235
0.3413	−0.6876	0.6608	−0.4340	0.5741	−0.3171
0.3615	−0.6907	0.6811	−0.4156	0.6133	−0.3066
0.3802	−0.6912	0.7181	−0.3790	0.6645	−0.2881
0.3936	−0.6903	0.8122	−0.2692	0.7180	−0.2638
0.4046	−0.6887	0.9112	−0.1328	0.7715	−0.2349
0.4238	−0.6845	0.9449	−0.0831	0.8202	−0.2043
0.4439	−0.6779	0.9933	−0.0101	0.8719	−0.1653
0.4520	−0.6747			0.8926	−0.1468
0.4625	−0.6701			0.9297	−0.1078
0.4789	−0.6619			0.9504	−0.0816
0.4981	−0.6509			0.9970	−0.0059
0.5161	−0.6392				
0.5306	−0.6290				
0.5571	−0.6085				
0.5907	−0.5796				
0.6024	−0.5689				
0.6621	−0.5103				
0.6770	−0.4949				
0.7767	−0.3848				
0.8782	−0.2531				
0.9174	−0.1892				
0.9512	−0.1230				
0.9709	−0.0779				
butanol		pentanol			
0.0177	−0.0178	0.0433	−0.0222		
0.0379	−0.0368	0.0508	−0.0259		
0.0622	−0.0581	0.0842	−0.0417		
0.1085	−0.0946	0.1509	−0.0701		
0.1379	−0.1152	0.2107	−0.0920		
0.1972	−0.1517	0.2570	−0.1066		
0.2549	−0.1817	0.3007	−0.1186		
0.2977	−0.2007	0.3615	−0.1323		
0.3542	−0.2220	0.4259	−0.1435		
0.3928	−0.2339	0.4345	−0.1447		
0.4071	−0.2378	0.4662	−0.1486		
0.4396	−0.2455	0.4783	−0.1499		
0.4628	−0.2499	0.4996	−0.1518		
0.4883	−0.2538	0.5346	−0.1542		
0.5140	−0.2566	0.5592	−0.1551		
0.5409	−0.2582	0.5686	−0.1554		
0.5748	−0.2583	0.6044	−0.1554		
0.6141	−0.2553	0.6373	−0.1542		
0.6485	−0.2498	0.6762	−0.1510		
0.6817	−0.2418	0.7169	−0.1456		
0.7163	−0.2303	0.7587	−0.1371		
0.7535	−0.2144	0.8010	−0.1252		
0.7975	−0.1904	0.8362	−0.1122		
0.8303	−0.1686	0.8666	−0.0984		
0.8612	−0.1450	0.8850	−0.0887		
0.9138	−0.0976	0.9059	−0.0764		
0.9665	−0.0409	0.9262	−0.0630		
0.9735	−0.0327	0.9585	−0.0384		
0.9801	−0.0247	0.9659	−0.0321		
0.9913	−0.0110	0.9702	−0.0283		
		0.9878	−0.0121		

Table 3 Least-squares coefficients of eqn. (1) and the standard deviation of x pyrrolidin-2-one-(1-x)alkanol binary mixtures at 303.15 K

		A_0	A_1	A_2	A_3	A_4	s	$V^E (x = 0.5)/\text{cm}^3 \text{ mol}^{-1}$
methanol	V^E	-2.5989	1.2421	-0.6561	-0.2436	-0.6909	0.005	-0.6497
	Δu	372.10	-122.39	37.03	-19.15	10.94	0.33	93.02
	K_s^E	-547.06	466.39	-309.020	295.45	-200.23	0.697	-136.76
ethanol	V^E	-2.1298	0.6617	-0.2537	0.2078	—	0.005	-0.5325
	Δu	129.93	-20.01	13.70	-35.50	26.69	0.39	32.48
	K_s^E	-486.33	257.63	-112.65	114.18	-88.67	0.610	-121.58
propanol	V^E	-1.3065	0.0688	-0.0067	0.0320	-0.7647	0.005	-0.3266
	Δu	-20.34	-11.26	31.50	4.38	-16.93	0.472	-5.08
	K_s^E	-345.56	94.14	-49.86	13.51	6.41	0.471	-86.39
butanol	V^E	-1.0210	-0.2207	-0.1339	0.0989	—	0.003	-0.2553
	Δu	-125.55	-31.8869	13.2053	-0.2239	-2.002	0.306	-31.39
	K_s^E	-264.15	11.37	-19.75	8.75	-1.57	0.271	-66.03
pentanol	V^E	-0.6075	-0.1637	-0.1694	-0.0833	—	0.003	-0.1519
	Δu	-195.56	-61.06	8.79	17.04	-15.19	0.330	-48.89
	K_s^E	-192.49	-29.44	-29.07	-13.91	19.80	0.328	-48.12

The X_{12} parameter required for the calculation of V^E using Flory–Patterson theory was derived by fitting the V^E expression to the experimental equimolar value of V^E for each system investigated. The calculated equimolar values of the three contributions together with the X_{12} parameter for each system are listed in Table 5.

An analysis of each of the three contributions to V^E shows that the interactional contribution and free volume effects are positive for all systems except methanol which has a slightly negative interactional term. The P^* contribution is negative for all the mixtures.

The interactional contribution, which is proportional to the X_{12} parameter, when positive, shows the absence of hydrogen bonding or other specific interactions. However, it is slightly negative for the methanol system, suggesting that some weak interactions are operating between pyrrolidin-2-one and methanol.

The free volume effect is generally negative and is a measure of geometrical accommodation. For the present set of mixtures the negative free volume effect decreases with increase in the chain length of the alkanol implying that, as the chain length increases, the contribution of this factor to the resultant

V^E decreases. The third contribution *i.e.* the P^* effect is highly negative for all systems.

It appears that the dominant role is played by the difference in internal pressures and reduced volumes of the respective components *i.e.* the P^* effect and this is the main parameter for deciding the sign and magnitude of excess volumes for pyrrolidin-2-one–alkanol mixtures.

Ultrasonic velocity

The experimental values of the ultrasonic velocity in the mixtures are summarised in Table 6. In an attempt to explore the nature of the interactions, various thermodynamic parameters^{13–16} were derived from the ultrasonic velocity and density data. The densities were calculated from V^E data extrapolated to the mole fractions of the ultrasonic velocity experiments using the A_i from eqn. (1). Various parameters such as isentropic compressibility, K_s , free volume²⁶ V_f , specific acoustic impedance, Z , solvation number²⁷ S_n , relative association R_A , molecular association M_A , Rao's constant,²⁸ R , Wada's constant²⁹ W , intermolecular free length³⁰ L_f , van der Waal's constant,³¹ b , molecular radius,³¹ r , geometrical

Table 4 Characteristic parameters of components at 303.15 K

component	K_T/TPa^{-1}	\bar{v}	$V/\text{cm}^3 \text{ mol}^{-1}$	$V^*/\text{cm}^3 \text{ mol}^{-1}$	T^*/K	$P^*/\text{J cm}^{-3}$
pyrrolidin-2-one	421.34	1.1913	77.16	64.77	6371	740.58
methanol	1321.44	1.2993	40.99	31.55	4712	481.21
ethanol	1214.48	1.2785	59.01	46.16	4929	463.06
propanol	1067.26	1.2626	75.55	59.84	5118	478.13
butanol	987.74	1.2485	92.44	74.04	5306	472.45
pentanol	921.01	1.2386	109.18	88.15	5454	474.64

Table 5 Calculated values of the three contributions to the excess volume from the Prigogine–Flory–Patterson theory for pyrrolidin-2-one–alkanol at 303.15 K

	$X_{12}/\text{J cm}^{-3}$	calculated contributions		
		interaction	free volume	P^* effect
(1 - x) methanol	-7.3704	-0.0421	-0.1547	-0.4529
(1 - x) ethanol	17.2871	0.1239	-0.1353	-0.5210
(1 - x) propanol	31.8126	0.2581	-0.1116	-0.4732
(1 - x) butanol	30.7753	0.2719	-0.0836	-0.4435
(1 - x) pentanol	33.2125	0.3120	-0.0642	-0.3997

Table 6 u , K_s and K_s^E values for pyrrolidin-2-one-alkanol binary mixtures at 303.15 K

x	u/ms^{-1}	K_s/TPa^{-1}	K_s^E/TPa^{-1}
methanol			
0.0019	1088.51	1077.94	−5.59
0.0076	1093.87	1062.15	−14.22
0.0106	1097.53	1052.29	−20.21
0.0194	1106.21	1028.07	−33.29
0.0292	1116.56	1000.93	−48.23
0.0402	1127.25	973.37	−62.26
0.0594	1146.48	927.27	−85.40
0.0676	1154.41	909.02	−93.92
0.0760	1162.24	891.43	−101.78
0.0925	1177.04	859.26	−115.12
0.1003	1184.43	844.10	−121.44
0.1474	1224.21	767.22	−147.22
0.1911	1258.65	708.40	−161.45
0.2836	1324.22	612.61	−170.76
0.3971	1391.91	531.22	−158.64
0.4934	1440.14	481.82	−137.88
0.5939	1484.84	441.72	−112.40
0.7347	1537.88	399.62	−73.38
0.7948	1557.61	385.28	−56.41
0.8942	1587.22	365.05	−28.72
0.9549	1604.22	354.28	−12.26
0.9800	1610.69	350.31	−5.42
ethanol			
0.0142	1136.79	982.93	−14.97
0.0509	1161.56	922.08	−46.57
0.1017	1192.89	850.89	−77.91
0.1877	1242.48	752.22	−111.09
0.2901	1298.21	659.24	−129.07
0.3729	1341.11	598.28	−131.70
0.4790	1393.67	533.91	−124.17
0.5825	1441.97	482.90	−108.03
0.7184	1502.66	428.27	−78.77
0.8039	1538.74	399.82	−56.76
0.9015	1578.04	371.74	−29.35
0.9516	1597.15	359.00	−14.43
0.9819	1608.53	351.71	−5.30
propanol			
0.0308	1202.31	858.49	−15.07
0.0554	1212.41	835.83	−24.86
0.0708	1218.36	822.56	−30.00
0.1007	1231.82	795.23	−41.61
0.2005	1273.55	716.21	−67.76
0.3015	1314.93	647.70	−82.35
0.4012	1356.22	588.21	−88.19
0.5037	1398.14	535.05	−85.79
0.5900	1435.79	493.71	−80.08
0.6991	1483.48	447.48	−66.49
0.8023	1528.15	409.32	−47.75
0.8983	1571.20	377.07	−26.81
0.9486	1593.28	361.84	−14.07
0.9754	1605.11	354.08	−6.92
butanol			
0.0340	1234.14	809.88	−10.20
0.0723	1245.57	785.28	−19.57
0.0974	1253.44	769.19	−25.56
0.1942	1283.69	710.87	−43.94
0.2959	1316.57	654.08	−56.93
0.3924	1348.92	604.08	−63.55
0.4914	1385.41	554.80	−66.42
0.5954	1425.03	507.24	−63.00
0.6972	1468.31	462.53	−55.42
0.7960	1513.05	422.16	−42.71
0.8970	1562.12	383.66	−24.37
0.9482	1588.32	365.22	−12.97
0.9791	1604.50	354.46	−5.37
pentanol			
0.0264	1264.66	769.01	−3.74
0.0706	1274.67	748.07	−11.20
0.1111	1284.05	729.14	−17.46
0.2009	1304.84	688.77	−28.44
0.2965	1329.91	645.23	−38.63
0.4048	1359.50	598.06	−45.19
0.4977	1387.99	557.74	−48.01
0.6010	1423.92	512.97	−47.91
0.6951	1461.30	472.31	−44.36
0.8045	1510.15	426.18	−34.71
0.9011	1559.53	386.32	−20.86
0.9357	1578.67	372.37	−14.43
0.9754	1600.96	356.90	−5.72

volume, B , molar surface area, Y , and available volume³⁰ V_a of a binary mixture have been calculated using the following relations

$$K_s = (\rho u^2)^{-1} \tag{6}$$

$$V_f = V(u_g/u)^3 \tag{7}$$

$$Z = u\rho \tag{8}$$

$$S_n = (n_1/n_2)[1 - (K_s/K_{s,1})] \tag{9}$$

$$R_A = (L_f/L_f^*)^3 \tag{10}$$

$$M_A = [(u^2/u_{im}^2) - 1] \tag{11}$$

$$R = \bar{M}u^{1/3}/\rho \tag{12}$$

$$W = \bar{M}K_s^{-1/7}/\rho \tag{13}$$

$$L_f = K(K_s)^{1/2} \tag{14}$$

$$b = (M/\rho) - (RT/\rho^2u^2)\{[1 + (Mu^2/3RT)]^{1/2} - 1\} \tag{15}$$

$$r^3 = 3b/16\pi N \tag{16}$$

$$B = 4/3\pi Nr^3 \tag{17}$$

$$Y = (36\pi NB^2)^{1/3} \tag{18}$$

$$V_a = V - V_0 \tag{19}$$

where u_g and u_{im} are the ultrasonic velocity in the vapour phase and in an ideal mixture. n_1 , n_2 are the number of moles of the respective components, L_f , the free length of ideal mixing, \bar{M} the average molecular weight and V_0 the volume at absolute zero. K is a temperature dependence constant. These parameters are listed in Table 7 for the pure components and are graphically represented for mixtures as a function of x in Fig. 3 and 4. The value of the acoustic impedance, Z , increases with increasing x for all the mixtures while L_f and S_n behave in an opposite manner. The graphs do not exhibit any sudden variation in their behaviour, thereby implying the absence of any complex formation; this is further supported by the linear variation in the R , W and b parameters.

The R_A values decrease with increasing x for all the mixtures, which signifies that the AB interactions in these mixtures may be strongly dissociative. Similarly, Fig. 4 shows the maximum deviation from zero in molecular association. Large

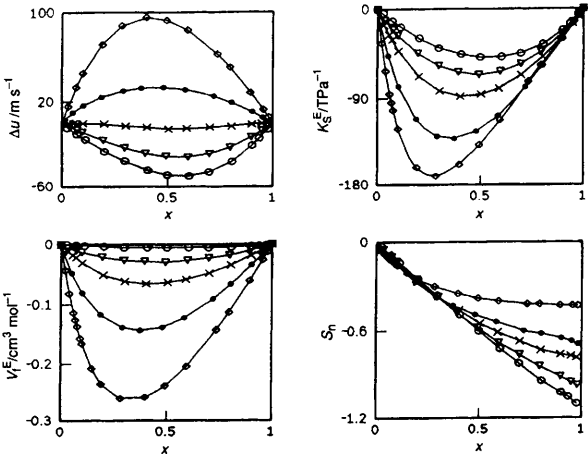


Fig. 3 Deviation in u , K_s^E , V_f^E , S_n for $xC_4H_4NO-(1-x)C_nH_{2n+1}OH$: \diamond , methanol; \bullet , ethanol; \times , propanol; ∇ , butanol; \circ , pentanol

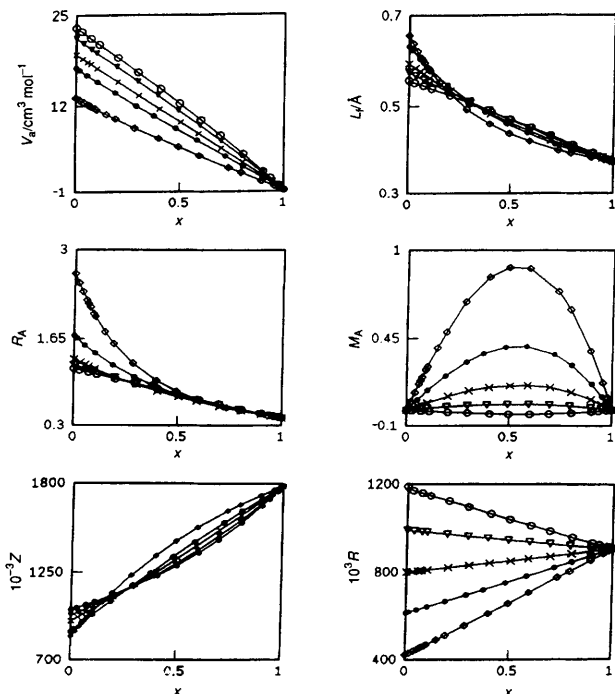


Fig. 4 V_g , L_f , R_A , M_A , Z and R for $x\text{C}_4\text{H}_9\text{NO}-(1-x)\text{C}_n\text{H}_{2n+1}\text{OH}$: \diamond , methanol; \bullet , ethanol; \times , propanol; ∇ , butanol; \circ , pentanol

deviations in M_A are obtained with methanol and these deviations decrease with increase in the chain length of the alkanol. It is thus concluded that the non-ideality of systems varies in the order methanol > ethanol > propanol > butanol > pentanol.

Deviations from linear dependence of the ultrasonic velocity, Δu , isentropic compressibility, K_S^E , and free volume, V_f^E ,

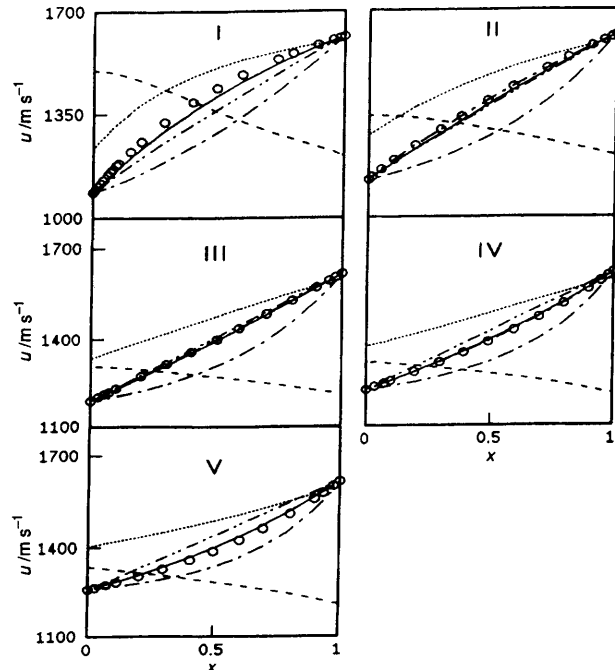


Fig. 5 Experimental and calculated ultrasonic velocities u ($\circ\circ\circ$), u_F (\cdots), u_{FLT} ($---$), u_{CFT} ($- \cdot - \cdot -$), u_J ($---$) and u_N ($---$) for $x\text{C}_4\text{H}_9\text{NO}-(1-x)\text{C}_n\text{H}_{2n+1}\text{OH}$: I, methanol; II, ethanol; III, propanol; IV, butanol; V, pentanol

Table 7 Values of isentropic compressibilities and the other derived parameters of the pure components

components	K_S/TPa^{-1}	Z	$V_f/\text{cm}^3 \text{mol}^{-1}$	$b/10^{-6} \text{m}^3$	r	$B/\text{cm}^3 \text{mol}^{-1}$	$Y/\text{\AA}^2$	S	$V_g/\text{cm}^3 \text{mol}^{-1}$	$L_f/\text{\AA}$	$L'_f/\text{\AA}$	R_A	$R \times 10^3$	$W \times 10^3$
pyrrolidin-2-one	347.26	1782.22	0.101	73.21	0.194	18.30	28.37	4.26	-0.76	0.371	0.496	0.419	905	646
methanol	1086.06	848.33	0.918	37.03	0.154	9.26	18.01	3.00	13.18	0.657	0.476	2.631	421	292
ethanol	1009.35	879.47	0.648	54.04	0.175	13.51	23.17	3.08	17.46	0.633	0.530	1.698	614	424
propanol	889.69	945.59	0.446	69.95	0.191	17.49	27.52	3.21	19.42	0.594	0.540	1.332	800	553
butanol	833.37	980.87	0.349	86.23	0.204	21.56	31.64	3.28	21.76	0.575	0.535	1.242	989	683
pentanol	780.59	1017.03	0.280	102.46	0.217	25.61	35.49	3.36	23.23	0.557	0.524	1.196	1179	814

with mole fraction are obtained from the relations

$$\Delta u = u - x_1 u_1 - x_2 u_2 \quad (16)$$

$$V_f^E = V_f - x_1 V_{f1} - x_2 V_{f2} \quad (17)$$

$$K_s^E = K_s - K_s^{\text{id}} \quad (18)$$

where K_s^{id} is defined³² as

$$K_s^{\text{id}} = \sum_i \phi_i^{\text{id}} [(K_{s,i}) + T V_{i,i} (\alpha_{p,i})^2 / C_{p,i}] - T [V^{\text{id}} (\alpha_p^{\text{id}})^2 / C_p^{\text{id}}] \quad (19)$$

where $C_{p,i}$ and $\alpha_{p,i}$ are the isobaric molar heat capacity and thermal expansivity for the pure component i . The volume fraction ϕ_i^{id} is defined as

$$\phi_i^{\text{id}} = x_i V_i / V^{\text{id}} \quad (20)$$

The values of Δu and K_s^E were fitted with a polynomial expression similar to eqn. (1). The coefficient and standard errors are listed in Table 3. Fig. 3 depicts the variation of Δu , V_f^E and K_s^E with x at 303.15 K. The values of Δu are positive for n -alkanol (C_1 , C_2) and negative for the rest of the systems. Negative deviations in K_s^E are observed for all the systems. There is a parallel in the qualitative behaviour of the K_s^E and V_f^E curves (Fig. 3 and 1). It is also interesting to compare the excess free volumes with the excess volume for these systems. The excess volume of a non-ideal mixture is attributed to the increase or decrease in free space in the liquids on mixing. However, one cannot conclude that excess free volume will be identical to the excess volume. A comparison of Fig. 3 and Fig. 1 indicates that the magnitude of the two is different although the sign is the same.

One may conclude that in the present set of mixtures the excess free volume contributes significantly to the resultant magnitude of the negative excess volumes. At equimolar composition, the excess properties for all the systems have the same sequence i.e. methanol < ethanol < propanol < butanol < pentanol.

For comparison, the theoretical values of ultrasonic velocities, u , are computed using five theories and empirical equations:

Flory's theory:^{33,34}

$$u_F = (\sigma / 6.3 \times 10^{-4} \rho)^{2/3}$$

collision factor theory:³¹

$$u_{\text{CFT}} = u_\infty (x_1 S_2 + x_2 S_2) [(x_1 B_1 + x_2 B_2) / V]$$

free length theory:³⁰

$$u_{\text{FLT}} = K / (L_f \rho^{1/2})$$

Junjie's equation:³⁵

$$u_j = [(x_1 M_1 / \rho_1) + (x_2 M_2 / \rho_2)] / \{(x_1 M_1 + x_2 M_2)^{1/2} \times [(x_1 M_1 / \rho_1 u_1^2) + (x_2 M_2 / \rho_2 u_2^2)]^{1/2}\}$$

Nomoto equation:³⁶

$$u_N = [(x_1 R_1 + x_2 R_2) / (x_1 V_1 + x_2 V_2)]^3$$

Reference should be made to our earlier papers^{13–16} for details of the derivations and symbols.

Fig. 5 summarises the computed u_F , u_{FLT} , u_{CFT} , u_j and u_N values in comparison with experimental values for all the mixtures. The results clearly indicate that the simple Nomoto expression predicts the experimental data extremely well, whereas the free length theory gives maximum deviation for the present set of binary mixtures.

References

- 1 J. A. Walmsley, E. J. Jacob and H. B. Thompson, *J. Phys. Chem.*, 1976, **80**, 2745.
- 2 J. A. Walmsley, *J. Phys. Chem.*, 1978, **82**, 2031.
- 3 J. Jazdyn, J. Malecki and C. Jazdyn, *J. Phys. Chem.*, 1978, **82**, 2128.
- 4 A. V. Hambly and R. H. Laby, *Aust. J. Chem.*, 1961, **14**, 318.
- 5 G. Malewski and R. Konig, *Spectrochim. Acta*, 1964, **20**, 565.
- 6 R. Konig and G. Malewski, *Spectrochim. Acta*, 1968, **24**, 219.
- 7 P. Pirita-Honkmenen and P. Ruostesus, *J. Chem. Eng. Data*, 1987, **32**, 303.
- 8 P. Ruostesus and P. Pirita-Honkmenen, *J. Solution Chem.*, 1990, **19**, 473.
- 9 R. K. Dewan, S. Madaan and S. K. Mehta, *J. Solution Chem.*, 1991, **20**, 233.
- 10 R. K. Dewan, S. K. Mehta, R. Parashar and K. Bala, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 1561.
- 11 R. K. Dewan, S. K. Mehta, R. Parashar and H. Kaur, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 227.
- 12 D. Patterson and G. Delmas, *Discuss. Faraday Soc.*, 1970, **49**, 98.
- 13 R. K. Dewan, C. M. Gupta and S. K. Mehta, *Acustica*, 1988, **65**, 245.
- 14 R. K. Dewan and S. K. Mehta, *Asian J. Chem.*, 1992, **4**, 152.
- 15 R. K. Dewan, S. K. Mehta and S. T. Ahmad, *Acoust. Lett.*, 1992, **15**, 193.
- 16 R. K. Dewan, S. K. Mehta and J. Singh, *Acustica*, 1991, **74**, 284.
- 17 J. A. Riddick and W. B. Bunger, in *Organic solvents: Physical Properties and Methods of Purification*, Wiley-Interscience, New York, 3rd edn., 1970.
- 18 J. Ortega, *J. Chem. Eng. Data*, 1982, **27**, 312.
- 19 E. Dickinson, D. C. Hunt and I. McLure, *J. Chem. Thermodyn.*, 1975, **7**, 731.
- 20 I. Prigogine and R. Defay, in *Chemical Thermodynamics*, Longman, London, 5th edn., 1969, p.8.
- 21 P. J. Flory, *Discuss. Faraday Soc.*, 1970, **49**, 7.
- 22 P. Tancrede, P. Bothorel, P. St. Romain and D. Patterson, *J. Chem. Soc., Faraday Trans. 2*, 1977, **73**, 15.
- 23 P. St. Romain, H. T. Van and D. Patterson, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 1770.
- 24 P. J. Flory, *J. Am. Chem. Soc.*, 1965, **87**, 1833.
- 25 P. J. Flory and A. Abe, *J. Am. Chem. Soc.*, 1964, **86**, 3563.
- 26 D. D. Desphande and L. G. Bhatgadde, *J. Phys. Chem.*, 1968, **72**, 261.
- 27 K. Tamura, S. Murakami and S. Doi, *J. Chem. Thermodyn.*, 1985, **17**, 325.
- 28 M. R. Rao, *Indian J. Phys.*, 1940, **14**, 109.
- 29 Y. Wada, *J. Phys. Soc. Jpn.*, 1949, **4**, 280.
- 30 B. Jacobson, *J. Chem. Phys.*, 1952, **20**, 927.
- 31 W. Schaaffs, *Acustica*, 1975, **33**, 272.
- 32 G. C. Benson and O. Kiyohara, *J. Chem. Thermodyn.*, 1979, **11**, 1061.
- 33 P. J. Flory, *J. Am. Chem. Soc.*, 1965, **87**, 1833.
- 34 J. R. Partington, *An Advanced Treatise on Physical Chemistry*, Longmans, London, 1951, vol. 2.
- 35 Z. Junjie, *J. China Univ. Sci. Techn.*, 1984, **14**, 298.
- 36 O. Nomoto, *J. Phys. Soc. Jpn.*, 1958, **13**, 298.

Paper 5/06170I; Received 19th September, 1995