

Effect of oxyethylene groups on the behaviour of thermodynamic properties of pyrrolidin-2-one and poly(ethylene glycols)

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Abstract

Dilatometric measurements of excess volume V^E and ultrasonic speed u have been carried out for mixtures of mono-, di-, tri- and tetra(ethylene glycol)s in pyrrolidin-2-one (PY) over the whole mole fraction range at 303.15 K. In the mixture of PY and monoethylene glycol, the V^E is positive except for slight negative variation at the high mole fraction of PY. The other three mixtures PY + di-, + tri- and + tetra(ethylene glycol)s show negative V^E over the entire composition range in the order di- < tri- < tetra-. There is a decrease in the values of ultrasonic speed u with increase in the mole fraction of PY in the case of monoethylene glycol while for other three systems u rises. From these measurements, partial molar quantities V_i^E and $K_{S,i}^E$ have been calculated and analysed. Estimates of isentropic molar quantity K_S equal to $-(\partial V/\partial p)_S$ and its excess counterpart K_S^E have also been computed. The K_S^E is positive for mono-, and negative for all the other mixtures over the whole composition range.

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Keywords: Ultrasonic speed; Excess volume; Pyrrolidin-2-one; Poly(ethylene glycol)s

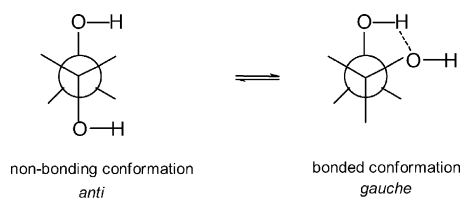
1. Introduction

Ethylene glycol is an important class of biological [1] solvents. When alone, or mixed with water, stabilises proteins against denaturation in solution. Diethylene glycol and triethylene glycol are very effective [2] dehydrating agents for natural gas. It has been shown that ethylene glycol exists as an associated form in the pure state (Scheme 1) characterised by a hydrogen bond which stabilises the gauche rotamer forming a pseudocyclic monomer, and by an extended hydrogen bonding network responsible for the highly structured total homopolymer [3,4]. A knowledge of thermodynamic properties of these glycols is very useful for industrial designing of processes. However, there are limited investigations on the study of excess thermodynamic functions of mixtures involving glycols. Most of the reports are in aqueous media. Huot et al. [1] have obtained negative excess volume of water + ethylene glycol mixture at 298.15 K due to the interaction involving the ethylene

glycol hydroxyl groups. The same mixture was analysed by Reddy et al. [5] at 308.15 K in which resultant V^E over the entire range have been attributed to the dominance of molecular association between unlike molecules over the dissociation in the like molecules. Sakuri [6] determined the partial molar volume of ethylene glycol and water at several temperatures. It was concluded that the partial molar volume is governed by the solvent compressibility and there exists only a weak hydrophobic interaction in the aqueous ethylene glycol solution. Tsierkezos and Molinou [7] also studied thermodynamic properties viz. excess volume, viscosity deviation, excess refraction and surface excess of water + ethylene glycol at various temperatures. Other than aqueous media, there are only few studies: two reports have appeared in which Marchetti et al. [8] measured V^E of ethylene glycol with DMF at various temperatures and showed that the observations were very useful to verify the possibility of a solvent–cosolvent complex formation. Iloukhani and Ghorbani [9] have also investigated the DMF + ethylene glycol mixture. The V^E results were explained in terms of dissociation of the self-associated ethylene glycol and the formation of aggregates between unlike molecules through C=O...H–O hydrogen bonding.

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Scheme 1. Limiting rotameric conformations of ethylene glycol molecule.

The V^E of water + poly(ethylene glycol)s viz. mono-, di-, tri-, and tetra(ethylene glycol)s have been reported by Müller and Rasmussen [10] and Pal et al. [11]. The results were explained qualitatively in terms of an increase in the order of the system, partially due to the formation of hydrogen bonds or structured liquid. More recently, Douhéret et al. [12] carried out detailed analysis of these systems by measuring the ultrasonic velocities and volumetric properties of mixtures at 298.15 K. The results were compared with the volumetric properties of aqueous mixtures of the family of poly(ethylene glycol) mono-alkyl ethers $H(CH_2)_mO(C_2H_4O)_nH(C_mE_n)$. Results in these investigations were mainly concerned with several type of structural modifications: the sensitivity to the alkyl chain length, the changes in the polar head and the branching in the alkyl group for isomeric species. In a recent study, Cocchi et al. [13] have reported measurements of excess molar volumes and partial molar quantities of the binary mixture containing ethylene glycol and diethylene glycol at various temperatures.

Replacing water with analogous solvent in glycols could bring significant changes in hydrogen equilibria and electrostatic interactions. The thermodynamic quantities obtained from systematic composition variations in water-analogue mixtures should provide information of central importance for understanding the unique aqueous fluctuation behaviour.

In our previous papers, [14–17] cyclic amide (lactam) e.g. pyrrolidin-2-one has been used as one of the solvent. The amide structure is of great interest since it is related to numerous structural problems of molecular biology. The basic structural element of this class of compound is the peptide bond $-NH-CO$ which, due to its donor-acceptor properties, can interact with other amide molecules through hydrogen bonds $N-H \cdots O=C$. These amides [18–21] constitute an important tool in the interpretation of complex molecules of biology as they constitute a simple model system for pep-

tides, polypeptides and proteins. Pyrrolidin-2-one is a polar, non-aqueous solvent with high dipole moment, the basic (CO) and acidic (NH) group of very common, naturally occurring peptide bond linked by a ring composed of methylene groups.

In the present paper, we have chosen to investigate glycols in pyrrolidin-2-one to analyse and to illustrate how the progressive addition of oxyethylene groups (OCH_2CH_2) in ethylene glycol affect the behaviour of thermodynamic properties, and to understand the nature and extent of the patterns on molecular aggregation that may exist in binary mixtures. The excess volume V^E and the ultrasonic speed u of poly(ethylene glycol)s ($HOCH_2(OCH_2CH_2)_nCH_2OH$) ($n = 0, 1, 2, 3$) in pyrrolidin-2-one at 303.15 K have been determined across the entire composition ranges. From these measurements, estimates were obtained for the molar isentropic compressibility and partial excess molar quantities.

2. Experimental

2.1. Materials

Pyrrolidin-2-one, monoethylene glycol, diethylene glycol, and tetraethylene glycol were purchased from Fluka whereas triethylene glycol was from Merck. The claimed purities for all the chemicals were >99%. Prior to use, pyrrolidin-2-one was dried with CaO and fractionally distilled as described elsewhere [22]. Mono-, di-, tri-, and tetraethylene glycols were used as-received. All the chemicals were stored for several days in the absence of light over A4 molecular sieves. To check the purity of all the chemical used, their densities were measured using Anton Paar digital precision densimeter. Table 1 lists the density values of PY and glycols at 303.15 K.

2.2. Methods

A continuous dilution dilatometer immersed in a water bath controlled to better than ± 0.01 K was used to measure the excess volumes. Using a proportional temperature controller in a circulating bath, regulated to ± 0.01 K, the temperature was calibrated to 303.15 ± 0.01 K with a precision platinum resistance thermometer. Details of the experimental set-up and the measuring procedure have been described elsewhere [24]. The results for V^E are estimated to be accurate to $\pm 0.002 \text{ cm}^3 \text{ mol}^{-1}$.

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_{expt}^* (kg m^{-3})	$\rho_{\text{lit.}}^*$ (kg m^{-3})	u^* (m s^{-1})	α_p^* (10^{-4} K^{-1})	C_p^* ($\text{J K}^{-1} \text{ mol}^{-1}$)
PY	1103.0	1103.0 [22]	1617.64	6.346	166.10 [12,22] ^a
Mono-	1106.4	1106.3 [22], 1110.2 [12] ^a	1639.92	6.463	151.0 [23]
Di-	1114.1	1112.8 [12] ^a	1565.81	2.055	244.8 [23]
Tri-	1123.2	1119.7 [12] ^a	1595.32	3.294	327.6 [23]
Tetra-	1125.9	1120.0 [12] ^a	1579.20	1.632	428.8 [23]

^a At 298.15 K.

Speed of sound u of the samples was determined by measuring the time interval τ between the pair of echoes of an ultrasonic wave, which is converted to electric pulse by transducer, by means of a ultrasonic time intervalometer (UTI-101) from Innovative instruments. The ultrasonic speed in the liquid sample is related to the time interval as

$$u = \frac{d}{\tau} \quad (1)$$

The value of d was obtained by calibration of the cell by using pure water as a reference [25]. The frequency of sound was 2.0 MHz and the maximum error in the measurement of speed of the sound is believed to be less than 0.01 m s^{-1} with a reproducibility of about 0.02 m s^{-1} .

Laplace equation has been used to determine the isentropic compressibility κ_S that is related to ultrasonic velocity as

$$\kappa_S = -V^{-1} \left(\frac{\partial V}{\partial P} \right)_S = (\rho u^2)^{-1} = \frac{\sum x_i V_i + V^E}{u^2 \sum x_i M_i} = \frac{V}{Mu^2} \quad (2)$$

Since the u and V^E measurements have not been made on the same samples, the V^E data were extrapolated to the mole fractions of the ultrasonic velocity using least square method. To make κ_S comparable with other thermodynamic quantities, it is necessary to shift the intensive quantity κ_S to molar quantity [26] as

$$K_S = - \left(\frac{\partial V}{\partial P} \right)_S = V \kappa_S = \frac{V^2}{Mu^2} \quad (3)$$

which assumes that dissipative effects are negligible and that the hydrodynamic equation of motion can be linearized. The above equations are valid only if there is no absorption of energy associated with ultrasonic wave.

3. Results and discussion

Volumetric study of aqueous mixtures of poly(ethylene glycol)s by various authors reveals that the excess molar volume V^E is negative over the whole composition range and decreases in the order mono- < di- < tri- < tetra-. Müller and Rasmussen [10] have attributed the variation in V^E in these systems to an increase in hydrophobicity resulting from the extension of polar head group.

In comparison to aqueous mixtures of glycols, in the present report the excess volume and ultrasonic velocity have been determined for PY + glycols. The excess volumes V^E of the binary mixtures of PY with poly(ethylene glycol)s ($\text{HOCH}_2(\text{OCH}_2\text{CH}_2)_n\text{CH}_2\text{OH}$) ($n = 0, 1, 2, 3$) at 303.15 K (listed in Table 2) are presented graphically in Fig. 1. It shows that for the mixture of PY and monoethylene glycol, the V^E is positive through out the composition range with very small negative deviation at large mole fraction of PY. Negative V^E is obtained over the entire range of mole

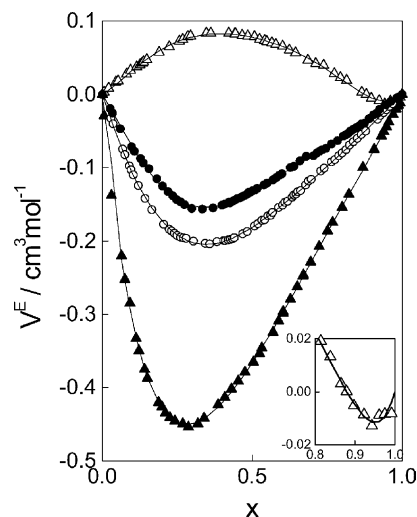


Fig. 1. Excess volumes V^E for x pyrrolidin-2-one + $(1-x)$ poly(ethylene glycol)s: (Δ) mono-; (\blacktriangle) di-; (\circ) tri-; (\bullet) tetra-; solid lines from Redlich-Kister fitting (inset shows negative V^E for mono-).

fraction for the other three mixtures PY + di-, + tri-, and + tetraethylene glycol.

The resultant variation of excess volume may be due to contribution from several factors. Chemical contribution resulting from the disruption of self-associated PY and poly(ethylene glycol)s through the breaking of H-bonds. This makes the positive contribution since the multimers tend to have smaller volumes than the sum of their counter parts. Non-specific physical interactions between real species present in the mixtures also contribute positively. Structural effects arise from several factors especially from interstitial accommodation, changes in the free volume and other packing effects.

In PY + glycol mixtures, the hydrogen bonding of the type $\text{C=O} \cdots \text{H-O}$ exists. The chemical and physical contributions seem to dominate in PY-monoethylene glycol system through out the composition range except at very high mole fractions of PY. The existence of strong hydrogen bonding may be due to the presence of two hydroxyl groups on mono-, both of which are taking part in the hydrogen bonding resulting in stronger interaction. For the other three mixtures, the excess volume decreases in the order tetra- < tri- < di-. As the oxyethylene groups are added to the glycol, the hydrocarbon character increases resulting in the less availability of $-\text{OH}$ to form hydrogen bond. This explains the less negative values of excess functions in PY-tetraethylene glycol than the mixtures of tri- and di- in PY. Moreover with longer chain of glycols, the attraction between unlike species decreases and repulsive interactions predominate, leading to less negative excess molar volume.

Ultrasonic velocities (summarised in Table 3) measured for the PY + glycols show that there is decrease in the value of ultrasonic speed with increase in x in case of monoethylene glycol while for other systems i.e. di-, tri- and tetra(ethylene glycol)s u rises (Fig. 2). A denser packing of the molecules

Table 2

Experimental V^E (in $\text{cm}^3 \text{mol}^{-1}$) values for x PY + $(1-x)$ monoethylene glycol, x PY + $(1-x)$ diethylene glycol, x PY + $(1-x)$ triethylene glycol, x PY + $(1-x)$ tetraethylene glycol at 303.15 K

PY + monoethylene glycol		PY + diethylene glycol		PY + triethylene glycol		PY + tetraethylene glycol	
x	V^E	x	V^E	x	V^E	x	V^E
0.0050	0.003	0.0052	-0.029	0.0276	-0.032	0.0265	-0.019
0.0215	0.008	0.0293	-0.138	0.0355	-0.040	0.0328	-0.025
0.0451	0.017	0.0637	-0.220	0.0671	-0.074	0.0600	-0.047
0.0516	0.018	0.0747	-0.253	0.0744	-0.082	0.0966	-0.071
0.0803	0.027	0.0914	-0.285	0.0894	-0.098	0.1068	-0.077
0.0944	0.032	0.1125	-0.333	0.0964	-0.103	0.1269	-0.088
0.1135	0.038	0.1211	-0.350	0.1039	-0.110	0.1365	-0.094
0.1254	0.040	0.1409	-0.375	0.1206	-0.124	0.1547	-0.101
0.1326	0.043	0.1505	-0.388	0.1414	-0.142	0.1825	-0.115
0.1368	0.044	0.1871	-0.420	0.1653	-0.158	0.2003	-0.125
0.1475	0.047	0.1986	-0.427	0.2039	-0.177	0.2198	-0.133
0.1886	0.058	0.2090	-0.435	0.2225	-0.184	0.2338	-0.138
0.2220	0.065	0.2251	-0.441	0.2311	-0.186	0.2474	-0.143
0.2574	0.073	0.2423	-0.446	0.2397	-0.189	0.2605	-0.147
0.2671	0.075	0.2678	-0.450	0.2499	-0.192	0.2729	-0.150
0.2838	0.079	0.2866	-0.454	0.2598	-0.194	0.2984	-0.155
0.2936	0.080	0.3181	-0.450	0.2694	-0.195	0.3333	-0.156
0.3466	0.083	0.3389	-0.442	0.2787	-0.196	0.3686	-0.155
0.3614	0.083	0.3855	-0.423	0.3028	-0.200	0.3985	-0.151
0.4220	0.083	0.4080	-0.414	0.3433	-0.203	0.4080	-0.150
0.4411	0.083	0.4301	-0.402	0.3569	-0.204	0.4209	-0.147
0.4432	0.083	0.4532	-0.391	0.3824	-0.201	0.4257	-0.148
0.4667	0.080	0.4758	-0.379	0.4042	-0.200	0.4344	-0.146
0.4842	0.079	0.5042	-0.365	0.4108	-0.200	0.4427	-0.144
0.5066	0.078	0.5247	-0.354	0.4186	-0.199	0.4507	-0.142
0.5250	0.075	0.5326	-0.347	0.4262	-0.198	0.4585	-0.141
0.5405	0.073	0.5684	-0.325	0.4337	-0.197	0.4661	-0.140
0.5481	0.072	0.5882	-0.309	0.4409	-0.196	0.4734	-0.138
0.5662	0.070	0.6025	-0.299	0.4689	-0.190	0.4807	-0.137
0.5786	0.068	0.6034	-0.297	0.4823	-0.187	0.4876	-0.135
0.6019	0.065	0.6269	-0.280	0.5072	-0.179	0.4894	-0.134
0.6227	0.060	0.649	-0.263	0.5188	-0.176	0.4946	-0.133
0.6450	0.057	0.6709	-0.247	0.5326	-0.171	0.5009	-0.132
0.6860	0.047	0.6691	-0.248	0.5418	-0.171	0.5016	-0.131
0.7119	0.042	0.6946	-0.229	0.5524	-0.166	0.5086	-0.130
0.7372	0.039	0.7227	-0.208	0.5626	-0.165	0.5160	-0.128
0.7742	0.028	0.7517	-0.187	0.5681	-0.161	0.5389	-0.124
0.7944	0.023	0.7679	-0.175	0.5877	-0.154	0.5488	-0.121
0.8138	0.019	0.8001	-0.154	0.6007	-0.151	0.5696	-0.116
0.8651	0.003	0.8222	-0.137	0.6087	-0.147	0.5807	-0.114
0.8793	0.000	0.8681	-0.100	0.6174	-0.146	0.5894	-0.111
0.8973	-0.006	0.9062	-0.075	0.6327	-0.140	0.5985	-0.108
0.9228	-0.009	0.9299	-0.057	0.6382	-0.137	0.6273	-0.100
0.9427	-0.013	0.9378	-0.051	0.6469	-0.136	0.6394	-0.098
0.9612	-0.009	0.9482	-0.045	0.6515	-0.132	0.6586	-0.091
0.9746	-0.009	0.9558	-0.038	0.6606	-0.131	0.6805	-0.085
0.9918	-0.004	0.9698	-0.028	0.6773	-0.123	0.7035	-0.084
		0.9794	-0.020	0.6870	-0.118	0.7156	-0.080
		0.9839	-0.016	0.6969	-0.116	0.7251	-0.078
		0.9875	-0.015	0.7287	-0.105	0.7348	-0.075
		0.9931	-0.012	0.7399	-0.101	0.7448	-0.074
				0.7634	-0.092	0.7648	-0.068
				0.7758	-0.089	0.7853	-0.063
				0.7883	-0.084	0.8034	-0.057
				0.7999	-0.080	0.8116	-0.055
				0.8120	-0.075	0.8198	-0.053
				0.8244	-0.069	0.8282	-0.050
				0.8372	-0.065	0.8370	-0.048
				0.8504	-0.060	0.8460	-0.045

Table 2 (Continued)

PY + monoethylene glycol		PY + diethylene glycol		PY + triethylene glycol		PY + tetraethylene glycol	
x	v^E	x	v^E	x	v^E	x	v^E
				0.8640	-0.055	0.8551	-0.043
				0.8781	-0.050	0.8646	-0.040
				0.9184	-0.034	0.8741	-0.039
				0.9279	-0.029	0.8900	-0.033
				0.9376	-0.025	0.9039	-0.028
				0.9471	-0.021	0.9156	-0.025
				0.9576	-0.017	0.9247	-0.020
				0.9679	-0.012	0.9435	-0.014
				0.9954	-0.002	0.9630	-0.009
						0.9859	-0.004

results in an increase [27] in the ultrasonic velocity and a decrease in the compressibility in the solution. This process continues until a concentration is reached at which all cavities are filled.

The excess molar isentropic compressibility K_S^E has been calculated by using the relation

$$K_S^E = K_S - K_S^{\text{id}} \quad (4)$$

It can be shown [26] that

$$K_S^{\text{id}} = \sum_i x_i \left[K_{S,i}^* + \frac{T(A_{P,i}^*)^2}{C_{p,i}^*} \right] - T \left\{ \frac{\sum_i x_i (A_{P,i}^*)^2}{\left(\sum_i x_i C_{p,i}^* \right)} \right\} \quad (5)$$

where $C_{p,i}^*$ is the isobaric molar heat capacity, $K_{S,i}^*$ the isentropic compressibility, x_i the mole fraction, T the temperature and $A_{P,i}^*$ the product of molar volume V_i^* and thermal expansivity $\alpha_{p,i}^*$ for the pure component i .

The deviation in ultrasonic velocity from their values in an ideal mixture can be calculated [28] as

$$u^D = u - u^{\text{id}} \quad (6)$$

Table 3

Ultrasonic velocity values u (in m s^{-1}) for x PY + $(1-x)$ monoethylene glycols; x PY + $(1-x)$ diethylene glycol, x PY + $(1-x)$ triethylene glycol, x PY + $(1-x)$ tetraethylene glycol binary mixtures at 303.15 K

Monoethylene glycol		Diethylene glycol		Triethylene glycol		Tetraethylene glycol	
x	u	x	u	x	u	x	u
0.0303	1637.82	0.0321	1569.74	0.0301	1597.44	0.0355	1580.74
0.0509	1636.44	0.0508	1571.08	0.0505	1598.56	0.0511	1581.65
0.0700	1635.27	0.0978	1573.87	0.0702	1599.67	0.0909	1583.92
0.0992	1633.68	0.2115	1579.74	0.1001	1600.38	0.1061	1584.75
0.2011	1629.62	0.3170	1586.30	0.2002	1603.31	0.2064	1589.32
0.3078	1625.19	0.4088	1591.90	0.3009	1605.65	0.3117	1593.56
0.4022	1621.24	0.4570	1594.67	0.4004	1608.75	0.4125	1597.54
0.4538	1620.02	0.5097	1597.44	0.4504	1610.16	0.5128	1601.72
0.4991	1619.08	0.5632	1600.14	0.5005	1611.39	0.5816	1604.24
0.5484	1618.65	0.6056	1602.10	0.5501	1612.33	0.6083	1605.27
0.5978	1618.41	0.7115	1606.59	0.6001	1613.09	0.7010	1608.47
0.7030	1617.73	0.7981	1610.25	0.7009	1614.70	0.8023	1611.29
0.7994	1616.50	0.9037	1615.08	0.8008	1616.88	0.9029	1614.79
0.9008	1614.98	0.9371	1616.50	0.9001	1618.40	0.9487	1616.50
0.9318	1614.97	0.9421	1616.79	0.9305	1618.12	0.9695	1617.16
0.9475	1615.16	0.9668	1617.35	0.9507	1617.64		
0.9688	1615.74						

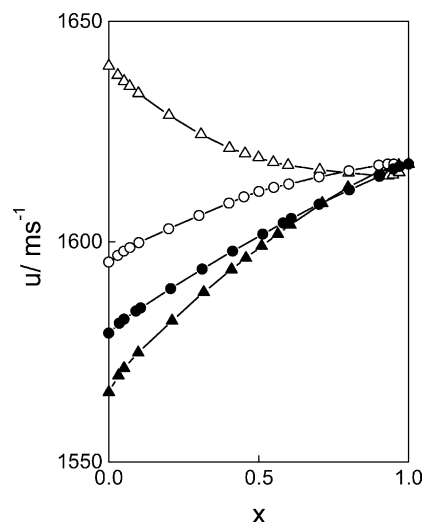


Fig. 2. Ultrasonic velocities, u for x pyrrolidin-2-one + $(1-x)$ poly(ethylene glycol)s: (Δ) mono-; (\blacktriangle) di-; (\circ) tri-; (\bullet) tetra-.

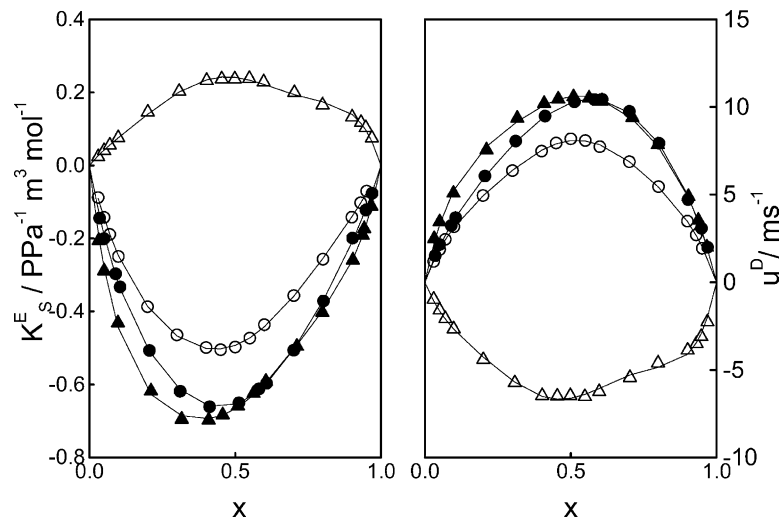


Fig. 3. Excess isentropic compressibilities K_S^E and deviations in ultrasonic velocities u^D for x pyrrolidin-2-one + $(1-x)$ poly(ethylene glycol)s: (Δ) mono-; (\blacktriangle) di-; (\circ) tri-; (\bullet) tetra-; solid lines from Redlich–Kister fitting.

where

$$u^{\text{id}} = \frac{V^{\text{id}}}{(K_S^{\text{id}} \sum_i x_i M_i)^{1/2}} \quad (7)$$

Fig. 3 depicts variation of K_S^E and u^D with x at 303.15 K. The values of u^D are negative for PY+mono- and positive for rest of the mixtures and vary in the order di- > tetra- > tri- > mono-. A reverse trend is being observed in K_S^E positive for mono- and negative for the other three mixtures. There is a parallel in the qualitative behaviour of K_S^E and V^E curves (Figs. 3 and 1).

The conventional approach to analyse the excess molar thermodynamic properties viz. excess molar volumes, deviation in ultrasonic velocities and excess molar isentropic com-

pressibilities of binary mixtures involves the Redlich–Kister equation of the form

$$Y^E = x(1-x) \sum_i A_i (2x-1)^i \quad (8)$$

Standard deviations along with the values for the coefficient A_i for each system are listed in Table 4.

Partial molar excess quantities of the components of a binary liquid mixture provide a more sensitive basis for judging the composition dependence. For non-Gibbsian properties such as isentropic and isochoric properties, there are several complicating issues which have only recently come to light and been successfully addressed recently by Blandamer [29] and Reis et al. [30].

Table 4

Least-square coefficients of Eq. (8) and standard deviation values for x PY + $(1-x)$ monoethylene glycol, x PY + $(1-x)$ diethylene glycol, x PY + $(1-x)$ triethylene glycol, x PY + $(1-x)$ tetraethylene glycol at 303.15 K

PY	A_0	A_1	A_2	A_3	A_4	σ	$Y^E (x=0.5)$
+ Mono-							
V^E	0.311	-0.171	-0.029	-0.144	-0.336	0.002	0.078
K_S^E	0.96	-0.17	-0.37	0.96	1.17	0.006	0.24
u^D	-26.48	5.72	10.13	-24.45	-43.47	0.179	-6.53
+ Di-							
V^E	-1.465	1.245	-0.828	0.536	-0.403	0.003	-0.367
K_S^E	-2.67	0.97	-0.58	0.48	-2.23	0.008	-0.67
u^D	42.45	4.81	4.76	-11.05	28.12	0.149	10.57
+ Tri-							
V^E	-0.725	0.527	-0.215	-0.102	0.109	0.001	-0.181
K_S^E	-1.97	0.61	0.16	0.20	-0.69	0.003	-0.49
u^D	32.35	3.22	-8.70	-1.39	24.30	0.061	8.12
+ Tetra-							
V^E	-0.529	0.451	-0.242	-0.254	0.305	0.002	-0.132
K_S^E	-2.63	0.55	0.06	0.36	-0.94	0.006	-0.65
u^D	41.13	11.39	1.01	-1.74	14.57	0.106	10.15

Table 5

Excess partial molar volumes $V_i^{E,\infty}$ (in $\text{cm}^3 \text{mol}^{-1}$) and excess partial molar isentropic compressibilities $K_{S,i}^{E,\infty}$ (in $\text{PPa}^{-1} \text{m}^3 \text{mol}^{-1}$) of x pyrrolidin-2-one + $(1-x)$ poly(ethylene glycol)s at infinite dilution at 303.15 K

	$V_1^{E,\infty}$	$V_2^{E,\infty}$	$K_{S,1}^{E,\infty}$	$K_{S,2}^{E,\infty}$
Mono-	0.27	-0.35	0.82	2.54
Di-	-4.56	-0.93	-6.42	-3.45
Tri-	-1.47	-0.18	-3.04	-1.59
Tetra-	-0.18	-0.04	-3.82	-2.51

PPa: penta Pascal, TPa: tera pascal.

In the present work, the partial molar quantities have been calculated from the following equations:

$$V_i^E = V^E + (1 - x_i) \left(\frac{\partial V^E}{\partial x_i} \right) \quad (9)$$

and

$$K_{S,i}^E = K_S^E + (1 - x_i) \left(\frac{\partial K_S^E}{\partial x_i} \right) \quad (10)$$

where V_i^E and $K_{S,i}^E$ represent the partial molar volume and compressibility of the components 1 and 2. Table 5 lists the partial excess molar quantities at infinite dilution viz. $V_i^{E,\infty}$ and $K_{S,i}^{E,\infty}$.

Figs. 4 and 5 show the variations of excess partial molar quantities, V_i^E and $K_{S,i}^E$ of PY and poly(ethylene glycol)s. The partial excess molar volume curves show a distinct maxima in the dilute region for PY + mono-system. The partial excess molar compressibilities are also positive for this system. This is an indication of positive contribution due to the breaking of self-associated pure components. For the other three mixtures, the partial excess mo-

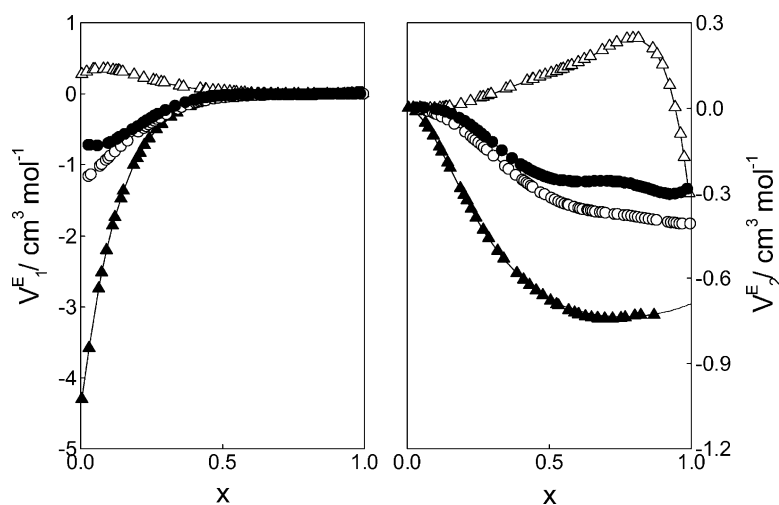


Fig. 4. Partial molar excess volumes V_1^E and V_2^E for x pyrrolidin-2-one + $(1-x)$ poly(ethylene glycol)s: (Δ) mono-; (\blacktriangle) di-; (\circ) tri-; (\bullet) tetra-.

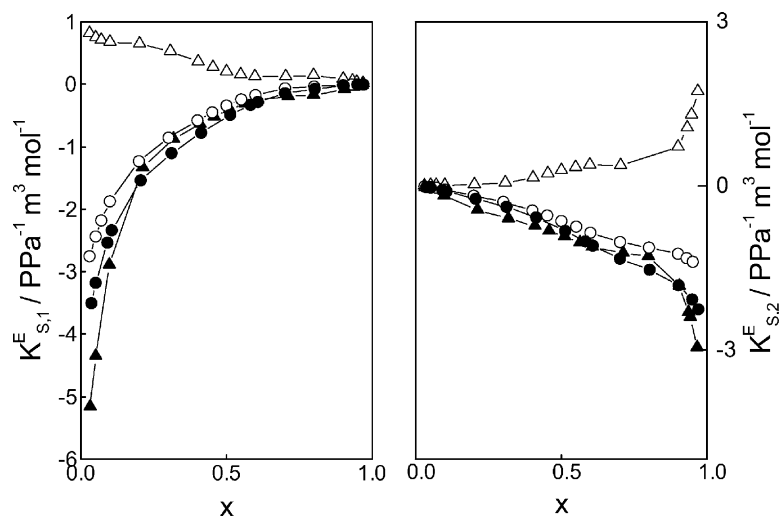


Fig. 5. Partial molar excess compressibilities $K_{S,1}^E$ and $K_{S,2}^E$ for x pyrrolidin-2-one + $(1-x)$ poly(ethylene glycol)s: (Δ) mono-; (\blacktriangle) di-; (\circ) tri-; (\bullet) tetra-.

lar quantities are mostly negative with a minima in V_i^E in dilute regions for PY + tetra-. Negative values are indicative of dominance of structural effects over the non-specific interactions.

4. Conclusion

A comparison of the present results of PY + poly(ethylene glycols) with those of aqueous mixtures of glycols reveals some useful information. Whereas the V^E is large negative for all the four systems in aqueous media, increasing in the order mono- > di- > tri- > tetra-, the PY + glycols show positive V^E for PY + ethylene glycol and comparatively less negative for rest of the mixtures in the order tetra- > tri- > di-. Thus on replacing water with PY, it seems that there are less interactions between PY and glycols as compared to PY and aqueous mixtures due to the non-availability of lone pair of electron as in water. The size of PY may also play an important role, it being bigger as compared to water. This results in less structural contribution for PY + glycols. These factors may be responsible for the reduction in V^E in the studied systems.

The K_S^E values become more negative as the number of oxyethylene group increase in the case of glycols in aqueous media whereas the same is not true for studied systems. It indicates that on replacing water with PY, a denser packing of the molecules results in an increase in the ultrasonic velocity and a decrease in the compressibility in the solution.

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