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Thermophysical properties of binary mixtures of *N,N*-dimethylformamide with three cyclic ethers

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Abstract: Densities and viscosities of binary mixtures consisting of tetrahydrofuran (THF), 1,3-dioxolane (1,3-DO) and 1,4-dioxane (1,4-DO) with *N,N*-dimethylformamide (DMF) over the entire range of composition were measured at the temperatures 298.15, 308.15 and 318.15 K and at atmospheric pressure. The ultrasonic speeds of sound of these binary mixtures were measured at ambient temperature and atmospheric pressure ($T = 298.15$ K and $p = 1.01 \times 10^5$ Pa). The various experimental data were utilized to derive the excess molar volumes (V_m^E), excess viscosities (η^E) and excess isentropic compressibilities (κ_s^E). Using the excess molar volumes (V_m^E), the excess partial molar volumes ($\bar{V}_{m,1}^E$ and $\bar{V}_{m,2}^E$) and excess partial molar volumes at infinite dilution ($\bar{V}_{m,1}^{0,E}$ and $\bar{V}_{m,2}^{0,E}$) of each liquid component in the mixtures were derived and are discussed. The excess molar volumes (V_m^E) as a function of composition at ambient temperature and atmospheric pressure were used to test further the applicability of the Prigogine–Flory–Patterson (PFP) theory to the experimental binaries. The excess properties were found to be either negative or positive depending on the nature of molecular interactions and structural effects of the liquid mixtures.

Keywords: *N,N*-dimethylformamide; cyclic ethers; excess molar volumes; excess viscosities; excess isentropic compressibilities; Prigogine–Flory–Patterson theory.

INTRODUCTION

The volumetric, viscometric and acoustic properties of mixed solvent systems and their dependence on composition find applications in many important chemical, industrial and biological processes. The study of functions, such as excess molar volume and excess viscosity, *etc.*, of binary mixtures are useful for

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the understanding of the nature and strength of molecular interactions between the component molecules.^{1,2} This is primarily because of the close connection between the liquid state³ and macroscopic properties. Excess molar volumes (V_m^E) and excess viscosities (η^E), *etc.* are often used to describe the intermolecular forces in mixtures, leading to an understanding of their behavior and enabling the development of theoretical models for their description and the simulation of processes. Hence, in recent years, there has been renewed interest in theoretical and experimental investigations of the excess thermodynamic properties of binary mixtures.^{4–6,8–14}

DMF is a polar, non-associative aprotic solvent with a dipole moment, μ , of 3.86 Debye¹⁵ and dielectric constant, ϵ , of 36.71^{15,16} at 298.15 K. In the liquid state, it is self-associated due to dipole–dipole interactions;¹⁷ while THF, 1,3-DO and 1,4-DO are non-polar, aprotic cyclic ethers differing in the number and position of the oxygen atom and carbon atoms; thus, these liquids differ in quadrupolar and dipolar order.⁷ It is well known that DMF, THF, 1,3-DO and 1,4-DO are versatile solvents used in the separation of saturated and unsaturated hydrocarbons and in pharmaceutical synthesis and serve as solvents for many polymers. Therefore, the increasing employment of the liquids under investigation in many industries has greatly stimulated the need for extensive information on the acoustic, transport and thermodynamic properties of these liquids and their mixtures.

Therefore, in continuation of systematic studies^{8–14} of the physicochemical properties of non-aqueous liquid mixtures, the present study attempts to unravel the nature of the molecular interactions in the binary mixtures of DMF with the cyclic ethers THF, 1,3-DO and 1,4-DO by measuring the densities, viscosities and ultrasonic speeds of sound of the mixtures over the entire composition range at different temperatures and at ambient pressure.

The calculated excess functions, such as excess molar volumes (V_m^E), excess viscosities (η^E) and excess isentropic compressibilities (κ_m^E) from the experimental data, were interpreted in terms of molecular interactions and structural effects. The partial molar volumes ($\bar{V}_{m,1}^0$ and $\bar{V}_{m,2}^0$) and excess partial molar volumes ($\bar{V}_{m,1}^{0,E}$ and $\bar{V}_{m,2}^{0,E}$) of each component at infinite dilution were also derived using the excess molar volumes (V_m^E) and interpreted in terms of the molecular interactions and the nature of the liquid mixtures. To the best of our knowledge, no comparable literature data for the systems studied in this work are available and treated in terms of the PFP theory; hence, a quantitative estimation of different contributions to the excess molar volumes (V_m^E) of the experimental binary systems at ambient temperature and pressure was attempted in terms of the PFP theory. Moreover, ultrasonic speeds of sound in all the binary mixtures were theoretically predicted based on some theories and empirical relations, such as the collision factor theory, the Nomoto relation, the impedance dependence relation and the ideal mixture relation, and the Flory theory.

EXPERIMENTAL

Materials

DMF (S. D. Fine Chemicals, India, AR, purity > 99 %) was purified by the method described by Y. Zhao *et al.*¹⁸ 1, 4-DO and THF (Merck, India, purity > 99 %) were purified as described earlier.¹⁹ 1,3-DO (S. D. Fine Chemicals, India, AR, purity > 99 %) was refluxed with PbO₂ and fractionally distilled after the addition of xylene.¹⁶ After purification, all the purified chemicals were found to be better than 99.5 % pure as ascertained by GLC and also by comparing their experimental densities and viscosities at the experimental temperatures with their literature values²⁰⁻³¹ (given in Table I).

TABLE I. Physical properties of pure liquids at 298.15, 308.15 and 318.15 K

Pure liquid	T / K	$\rho \times 10^{-3} / \text{kg m}^{-3}$		$\eta / \text{mPa s}$		$u / \text{m s}^{-1}$	
		Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
DMF	298.15	0.9442	0.9442 ¹⁸	0.803	0.802 ²⁰	1464.8	1465.0 ²⁰
			0.9445 ¹⁹		0.803 ²¹		1462.0 ²⁰
	308.15	0.9350	0.9344 ²⁰ 0.9347 ²¹	0.709	0.706 ²²	–	–
	318.15	0.9258	0.9251 ²⁰ 0.9252 ²¹	0.617	0.633 ²²	–	–
THF	298.15	0.8807	0.8807 ²²	0.463	0.4630 ²⁴	1277.8	1292.2 ²⁴ 1277.8 ²⁵
			0.8712		0.428		0.4277 ²⁴
	318.15	0.8614	0.8614 ²²	0.390	0.3902 ²⁴	–	–
1,3-DO	298.15	1.0571	1.0577 ²²	0.588	0.5878 ²⁴	1338.2	1338.2 ²⁶
			1.0572 ²⁴		0.588 ²⁶		1340.2 ²⁷
	308.15	1.0459	1.0463 ²² 1.0462 ²⁶	0.513	0.5128 ²⁴	–	–
	318.15	1.0334	1.03364 ²⁶	0.458	0.4580 ²⁴	–	–
1,4-DO	298.15	1.0265	1.0278 ²⁷	1.196	1.196 ²⁹	1343.4	1344.4 ²⁴
			1.0282 ²⁸		1.178 ³⁰		1344.8 ²⁷
	308.15	1.0166	1.0168 ²²	1.013	0.9985 ²⁴ 0.999 ³⁰	–	–
	318.15	1.0052	1.00526 ²⁶	0.887	0.901 ³¹	–	–

Methods

The binary mixtures were prepared by mass in a dry box and each thus prepared solution was distributed into three recipients (in airtight bottles) to perform all the measurements in triplicate with the aim of determining possible dispersions in the obtained results. The mass measurements, made on a digital electronic analytical balance (Mettler, AG 285, Switzerland), accurate to ± 0.01 mg. The reproducibility in mole fraction was within ± 0.0002 . The densities were measured with a vibrating-tube density meter (Anton Paar, DMA 4500M), maintained at ± 0.01 K of the desired temperatures and calibrated at the experimental temperatures with doubly distilled water and dry air. The uncertainty in the density was estimated to be ± 0.0001 g cm⁻³ and that of the temperature was ± 0.01 K. The viscosity was measured by means of a suspended Ubbelohde type viscometer, thoroughly cleaned, dried and calibrated at the experimental temperatures with triply distilled water and purified methanol.^{15,32,33} It was

filled with experimental liquid and placed vertically in a glass sided thermostatted maintained constant to ± 0.01 K. After attainment of thermal equilibrium, the efflux times of flow of the liquids were recorded with a digital stopwatch correct to ± 0.01 s. In all determinations, an average of three measurements was taken into account and adequate precautions were taken to minimize evaporation losses during the actual measurements. The uncertainty in viscosity measurements was within ± 0.003 mPa s. The ultrasonic speeds of sound (u) were measured with an accuracy of 0.3 % using a single crystal variable-path ultrasonic interferometer (Mittal Enterprise, New Delhi, M-81) working at 2 MHz. It was calibrated with doubly distilled water, purified methanol and benzene at 298.15 K. During the measurements, the temperature was maintained within ± 0.01 K of 298.15 K by circulating thermostatted water around the jacketed cell (of 2 MHz) containing the experimental solutions with the aid of a circulating pump. The uncertainty of the ultrasonic speed measurements was around ± 0.2 m s⁻¹. Adequate precautions were taken to minimize evaporation losses during all the measurements. The details of the methods and measurement techniques had been described elsewhere.^{14,34,35}

RESULTS AND DISCUSSION

The experimental densities (ρ), viscosities (η), excess molar volumes (V_m^E) and excess viscosities (η^E) for the binary mixtures studied at different temperatures are listed in Table S-I of the Supplementary material. The excess molar volumes (V_m^E) were calculated using the following equation:

$$V_m^E = \sum_{i=1}^2 x_i M_i (1/\rho - 1/\rho_i) \quad (1)$$

where ρ is the density of the mixture and x_i , M_i and ρ_i are the mole fraction, molar mass and density of the i^{th} component in the mixture, respectively. The estimated uncertainty in the excess molar volumes, V_m^E , was ± 0.005 cm³ mol⁻¹. Excess molar volumes (V_m^E) of the binary mixtures as a function of mole fraction (x_i) of DMF at the experimental temperatures are shown graphically in Fig 1. The excess molar volumes (V_m^E) for all the binary systems, except for the DMF + 1,4-DO system at 298.15 and 308.15 K, were negative over the entire range of compositions at all the experimental temperatures. The values of excess molar volumes (V_m^E) for the three systems were observed to follow the order: DMF + 1,4-DO > DMF + 1,3-DO > DMF + THF. According to Treszczanowicz *et al.*³⁶ V_m^E is a function of several opposing effects generally categorized into three types *viz.*, physical, chemical, and structural. While physical effects offer a positive contribution to V_m^E , the chemical or specific intermolecular interactions (such as hydrogen bond interaction, dipole–dipole/dipole-induced–dipole interaction, formation of charge transfer complexes, *etc.*) result in a net volume decrease, and thus offer negative contributions to V_m^E . The structural effects such as interstitial accommodation (due to differences in size and shape of the components) and changes in the free volume also offer negative contributions to V_m^E . Therefore, the actual volume change would depend on the relative strength of these effects.

The molar volumes of DMF are 77.42, 78.18 and 78.96 cm³ mol⁻¹, and those of THF, 1,3-DO and 1,4-DO are 81.87, 82.77 and 83.71 cm³ mol⁻¹; (70.07, 70.83 and 71.68) cm³ mol⁻¹; and 85.83, 86.67, and 87.65 cm³ mol⁻¹ at 298.15, 308.15 and 318.15 K, respectively. Evidently, the molar volumes of the components in the studied mixtures differ appreciably and, depending on the differences in the molar volumes of the components, it is to be expected that the mutual or geometrical fitting of the component liquids may follow the order: DMF + 1,4-DO > DMF + 1,3-DO > DMF + THF; but a reversed trend in the V_m^E values was observed for the studied binary mixtures. A perusal of Fig. 1 shows that the V_m^E values increase in the order: DMF + THF < DMF + 1,3-DO < DMF + 1,4-DO. It is satisfying to observe that the values of the dielectric constant of the cyclic ethers follow the reverse order: THF ($\epsilon = 7.58^{37}$) > 1,3-DO ($\epsilon = 7.13^{38}$) > 1,4-DO ($\epsilon = 2.21^{37}$). This indicates that a cyclic ether with a larger value of dielectric constant than another has greater specific interactions with DMF and that the negative V_m^E values for all the studied systems can primarily be attributed to dipole-dipole or dipole-induced-dipole interactions between the component liquids in the mixtures. Moreover, the V_m^E values decrease with increasing temperatures of the mixtures, indicating an increase in intermolecular interactions between the component molecules with increasing temperature, which is probably due the greater thermal agitation that ultimately increases the mutual fitting of the mixing components to some extent at higher temperatures.

The partial molar volumes, $\bar{V}_{m,i}$ of the i^{th} component in the binaries over the entire composition range at the experimental temperatures were calculated using the relation:

$$\bar{V}_{m,i} = V_{m,i}^E + V_{m,i}^* + (1 - x_i)(dV_{m,i}^E/dx_i)_{T,p} \quad (2)$$

where $V_{m,i}^*$ is the molar volume of the i^{th} component in the binaries. The derivatives, $(dV_{m,i}^E/dx_i)_{T,p}$, used in Eq. (2) were obtained by following the procedure¹² of fitting the excess molar volumes (V_m^E) of the binary mixtures to the Redlich-Kister polynomial,³⁹ with standard deviations (SD) in the range 0.000–0.002. Redlich-Kister polynomial is expressed as follows:

$$V_{m,i}^E = x_1 x_2 \sum_{i=1}^2 a_i (1 - 2x_2)^i \quad (3)$$

where x_1 and x_2 are the mole fractions of the liquid 1 and 2, respectively, and a_i represent the multiple-regression coefficients. The standard deviations (SD) were calculated using the relation:

$$SD = \left[\sum_{i=1}^n (V_{m,Calc}^E - V_{m,Expt}^E)^2 / (n - j) \right]^{1/2} \quad (4)$$

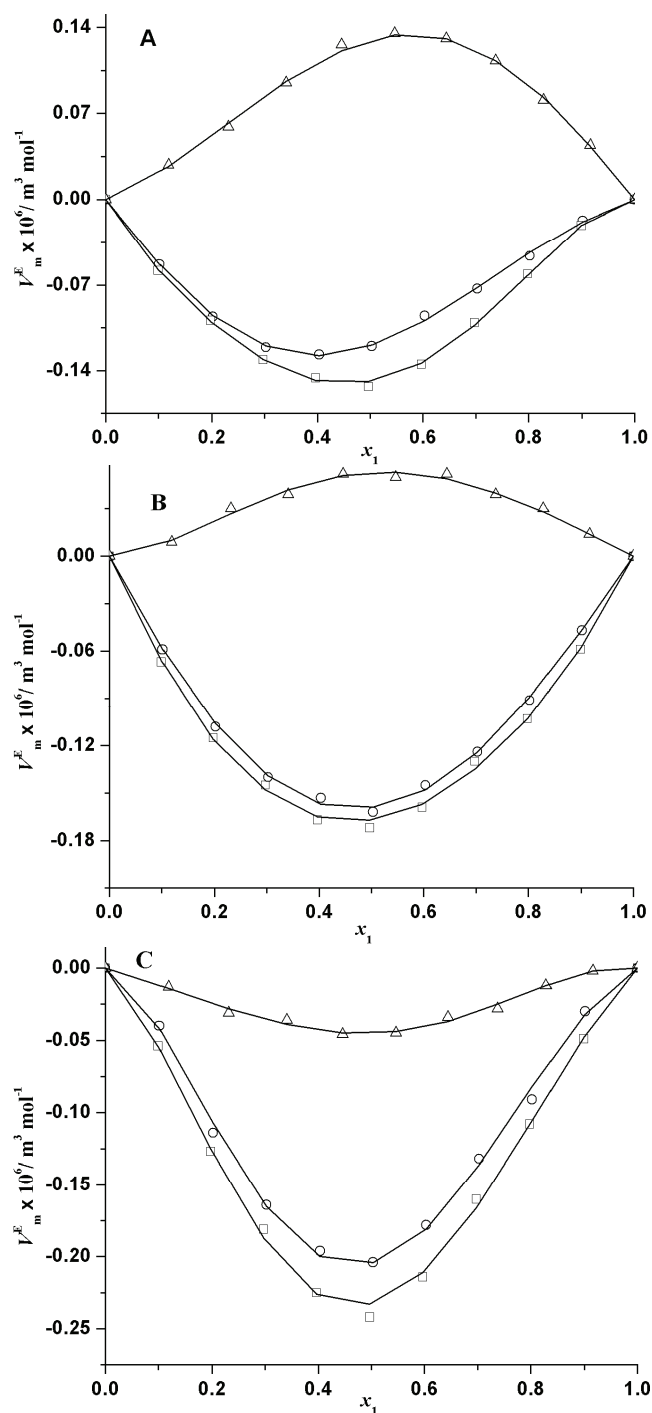


Fig. 1. Excess molar volume (V_m^E) vs. mole fraction of DMF (x_1) for binary mixtures of DMF + cyclic ethers: A, at $T = 298.15$ K; B, at $T = 308.15$ K; C, at $T = 318.15$ K. The graphical points represent the excess molar volumes (V_m^E): \square , THF; \circ , 1,3-DO; Δ , 1,4-DO. Lines represent the V_m^E values obtained from the Redlich–Kister polynomial.

where n is the number of experimental data points and j is the number of a_i coefficients. For the excess molar volumes (V_m^E) fitted to the Redlich–Kister polynomial, the standard deviations (SD) were in the range 0.002–0.006. The values of the partial molar volumes, $\bar{V}_{m,i}$ allow the calculation of the excess partial molar volumes ($\bar{V}_{m,1}^E$) by using the following relation:

$$\bar{V}_{m,i}^E = \bar{V}_{m,i} - V_{m,i}^* \quad (5)$$

The excess partial molar volume at infinite dilution ($\bar{V}_{m,i}^{0,E}$) can be determined from the following relation:

$$\bar{V}_{m,i}^{0,E} = (dV_{m,i}^E/dx_i)_{x_i=0, T, p} \quad (6)$$

The excess partial molar volumes ($\bar{V}_{m,1}^E$ and $\bar{V}_{m,2}^E$) at infinite dilution for the three binaries at the experimental temperatures are listed in Table S-II of the Supplementary material.

The excess partial molar volumes ($\bar{V}_{m,1}^E$ and $\bar{V}_{m,2}^E$) of each component in the studied binaries are graphically shown in Fig. 2 as a function of x_1 . The $\bar{V}_{m,1}^E$ and $\bar{V}_{m,2}^E$ values were found to be negative for all the studied binary systems, except that containing 1,4-DO over the entire composition range at the experimental temperatures. Moreover, the excess partial molar volumes at infinite dilution ($\bar{V}_{m,1}^{0,E}$ and $\bar{V}_{m,2}^{0,E}$) were negative for both components in all the binary systems except for that containing 1,4-DO (however, $\bar{V}_{m,1}^{0,E}$ and $\bar{V}_{m,2}^{0,E}$ values were negative at 318.15 K for this system). These results suggest that while the 1,4-DO system is characterized by volume expansion on mixing with DMF at 298.15 and 308.15 K, the other systems are characterized by volume contraction on mixing with DMF.

In recent years, Flory's statistical theory^{40–43} and its modified version known as the Prigogine–Flory–Patterson theory,^{44,45} have been successfully used to estimate and analyze theoretically the excess thermodynamic functions of binary liquid mixtures; the PFP theory is applicable to both non-polar and polar molecules present in a binary mixture. The reduced equation of state in Flory's notation⁴² is given by:

$$\frac{\tilde{p}\tilde{V}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{v}\tilde{T}} \quad (7)$$

$$\tilde{v} = \frac{V}{V^*} \quad (8)$$

$$\tilde{T} = \frac{T}{T^*} \quad (9)$$

$$\tilde{p} = \frac{p}{p^*} \quad (10)$$

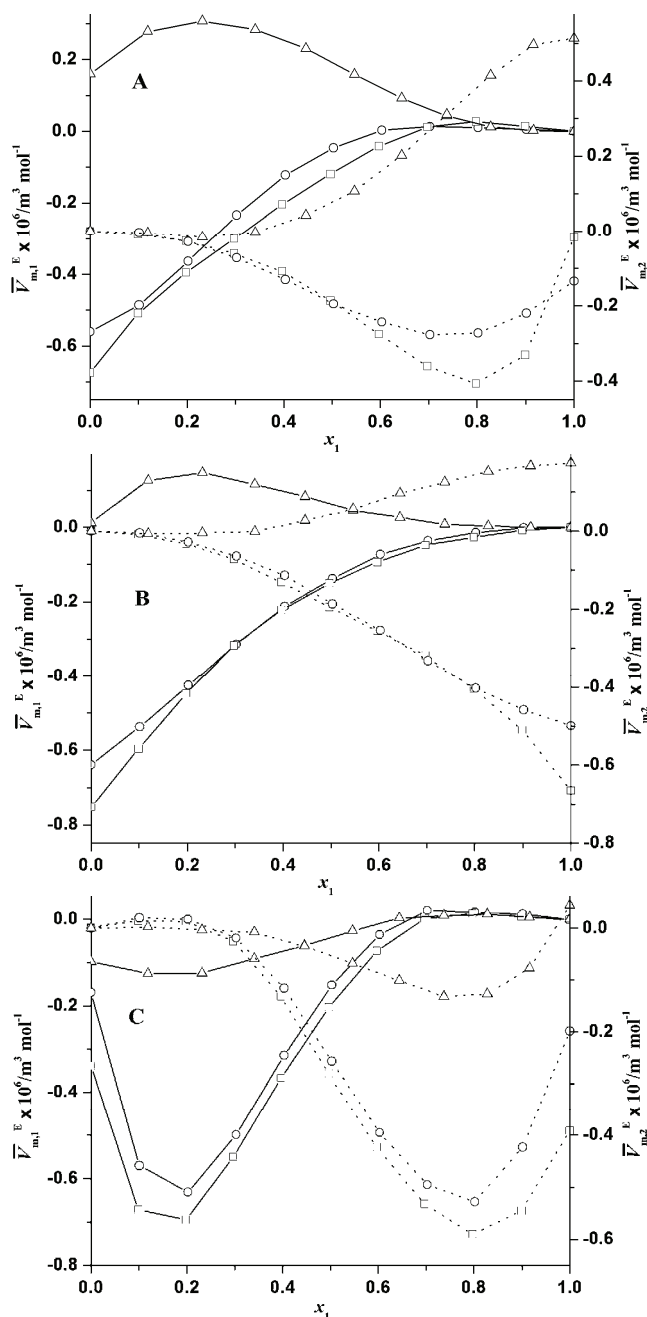


Fig. 2. Excess partial molar volume ($\bar{V}_{m,i}^E$) for the i^{th} component against mole fraction of DMF (x_1) for binary mixtures of DMF + cyclic ethers: A, at $T = 298.15$ K; B, at $T = 308.15$ K; C, at $T = 318.15$ K. The graphical points represent the $\bar{V}_{m,i}^E$ values for the mixtures of DMF with THF, \square ; 1,3-DO, \circ ; 1,4-DO, Δ . Lines represent the $\bar{V}_{m,i}^E$ values for DMF and the dotted curves represent the $\bar{V}_{m,i}^E$ values for cyclic ethers.

where are \tilde{v} , \tilde{T} and \tilde{p} are the reduced volume, reduced temperature and reduced pressure, respectively, and V^* , T^* and p^* are the characteristic volume, charac-

teristic temperature and characteristic pressure, respectively, of each pure liquid component. In the Flory treatment, the reduced equation of state in the limit of zero pressure (or without appreciable error at 1 atmospheric pressure⁴³) takes the following forms:

$$\tilde{T} = \frac{\tilde{v}^{1/3} - 1}{\tilde{v}^{4/3}} \quad (11)$$

$$\tilde{v} = \left[\frac{1 + (4/3)\alpha T}{1 + \alpha T} \right]^3 \quad (12)$$

$$T^* = \frac{T}{\tilde{T}} = \frac{T\tilde{v}^{4/3}}{\tilde{v}^{1/3} - 1} \quad (13)$$

$$p^* = \gamma T \tilde{v}^2 \quad (14)$$

where the thermal expansion coefficient (α) and thermal pressure coefficient (γ) are given by the following relations:

$$\alpha = V^{-1}(dV/dT)_P = -\rho^{-1}(d\rho/dT)_P \quad (15)$$

$$\gamma = (dP/dV)_V = \alpha \kappa_T^{-1} \quad (16)$$

where κ_T is the isothermal compressibility, which can be determined using the relation:

$$\kappa_T = \kappa_S + \frac{T\alpha^2 V}{C_p} \quad (17)$$

The Flory parameters for each liquid component are given in Table II. Isobaric enthalpies (C_p) for the different component liquids required for the calculation of isothermal compressibilities (κ_T) were taken from literature.^{46,47}

Using the well-known Prigogine-Flory-Patterson theory,^{48,49} a quantitative estimation of the different contributions to V_m^E can be obtained. In terms of three contributions, the approximate expression for V_m^E is:

$$\begin{aligned} \frac{V_m^E}{x_1 V_1^* + x_2 V_2^*} = & \underbrace{\frac{(\tilde{v}^{1/3} - 1)\tilde{v}^{2/3}\psi_1\theta_2}{[(4/3)\tilde{v}^{-1/3} - 1]P_1^*}}_{\chi_{1,2} \text{ contribution}} - \underbrace{\frac{(\tilde{v}_1 - \tilde{v}_2)^2[(14/9)\tilde{v}^{-1/3} - 1]\psi_1\psi_2}{[(4/3)\tilde{v}^{-1/3} - 1]\tilde{v}}}_{\tilde{v} \text{ contribution}} + \\ & + \underbrace{\frac{(\tilde{v}_1 - \tilde{v}_2)(p_1^* - p_2^*)\psi_1\psi_2}{(p_1^*\psi_2 + p_2^*\psi_1)}}_{p^* \text{ contribution}} \end{aligned} \quad (18)$$

where p_i^* , V_i^* and ψ_i are characteristic pressure, volume and the molecular contact energy fraction of i^{th} pure component, respectively, and θ_2 is the molecular site fraction of the second component in a binary liquid mixture. The molecular

contact energy fraction and the molecular site fractions are defined by the relations:

$$\psi_1 = 1 - \psi_2 = \frac{\phi_1 P_1^*}{\phi_1 P_1^* + \phi_2 P_2^*} \quad (19)$$

$$\theta_1 = 1 - \theta_2 = \frac{\phi_1}{\phi_1 + (V_1^* / V_2^*)^{1/3}} \quad (20)$$

$$\phi_1 = 1 - \phi_2 = \frac{x_1 V_1^*}{x_1 V_1^* + x_2 V_2^*} \quad (21)$$

TABLE II. The Flory parameters for pure liquids at 298.15 K

Liquid	\tilde{v}	$\tilde{T} \times 10^2$	$V^* \times 10^6 / \text{m}^3 \text{mol}^{-1}$	p^* / Pa	T^* / K	$\alpha \times 10^4 / \text{K}^{-1}$	$K_T \times 10^{10} / \text{Pa}^{-1}$
DMF	1.2424	5.618	62.31	701.85	5307	9.744	6.389
THF	1.2670	5.987	64.62	562.13	4980	10.96	9.329
1,3-DO	1.2720	6.067	55.09	726.60	4921	11.21	7.442
1,4-DO	1.2553	5.815	68.37	674.51	5127	10.38	7.227

Actually, in deriving the interaction parameter ($\chi_{1,2}$), the V_m^E values of each composition (of each system) were fitted to Eq. (18) using Eqs. (11)–(17) using a computer program that finally provided an optimized value of the interaction parameter ($\chi_{1,2}$) with least error and values of different contributions to the V_m^E values embodied in Eq. (18). Table III contains the optimized $\chi_{1,2}$ values, the calculated and experimental V_m^E values, their deviation and values of different contributions to the V_m^E values for equimolar ($x_1 \approx 0.5$) composition at 298.15 K. It is clear from Table III that the calculated values of excess molar volumes $V_{m,\text{PFP}}^E$ reasonably agree with the experimental excess molar volumes $V_{m,\text{exp}}^E$ values for all the studied systems. A comparison between the $V_{m,\text{exp}}^E$ values and the $V_{m,\text{PFP}}^E$ values as a function of mole fraction (x_1) of DMF at 298.15 K is depicted in Fig. S-1 of the Supplementary material.

TABLE III. The values of the interaction parameter ($\chi_{1,2}$), the calculated and experimental values of the excess molar volumes ($V_{m,\text{PFP}}^E$ and $V_{m,\text{exp}}^E$), their deviations (ΔV_m^E) and the different PFP contributions at 298.15 K

DMF (1) +	$\chi_{1,2}$ J m^{-3}	$V_{m,\text{exp}}^E \times 10^6$ $\text{m}^3 \text{mol}^{-1}$	$V_{m,\text{PFP}}^E \times 10^6$ $\text{m}^3 \text{mol}^{-1}$	$\Delta V_m^E \times 10^6$ $\text{m}^3 \text{mol}^{-1}$	PFP contributions $\times 10^3$		
					int ^a	fv ^b	ip ^c
THF (2)	-4.588	-0.1531	-0.1427	-0.0104	-0.826	-0.224	-1.362
1,3-DO (2)	-15.08	-0.1204	-0.1204	0	-1.979	-0.326	0.255
1,4-DO (2)	18.01	0.1353	0.1243	0.0110	2.270	-0.063	-0.128

^ainteraction contribution; ^bfree volume contribution; ^cinternal pressure contribution

According to the PFP theory, the interaction contribution is proportional to the interaction parameter $\chi_{1,2}$, the free volume contribution arises from the

dependence of the reduced volume on the reduced temperature due to the differences between the degree of expansion of the two mixing components (always negative as dV^2/dT^2 is positive) and the internal pressure contribution depends on the product of the differences between the reduced volumes and characteristic pressures of the mixing components. Table III shows that the interaction contributions are negative for the systems with THF and 1,3-DO but positive for the system with 1,4-DO; the internal pressure contributions, except for 1,3-DO system, are negative for all the systems. From Table III, it is evident that while the interaction contribution ($\chi_{1,2}$) plays a dominant role in deciding the sign and magnitude of the $V_{m,\text{PFP}}^E$ values for the systems containing 1,3-DO and 1,4-DO, the internal pressure contribution (p^*) plays a major role in deciding the nature of $V_{m,\text{exp}}^E$ for the remaining system with THF.

The excess viscosity (η^E) can be defined as the difference between the measured viscosity (η) and the ideal viscosity (η_{id}) of a solution and is expressed by Eq. (20):⁵⁰

$$\eta^E = \eta - \eta_{\text{id}} \quad (22)$$

Using the Eyring approach of viscosity as a rate process,⁵¹ η_{id} can be defined by Eq. (23):

$$\eta_{\text{id}} = \exp\left(\sum_{i=1}^2 x_i \ln \eta_i\right) \quad (23)$$

where η_i is the viscosity of the i^{th} component in the mixture and the additivity law in a logarithm form is considered for ideal mixtures. The estimated uncertainty for the excess viscosities (η^E) was within ± 0.004 mPa s. Plots of the excess viscosity (η^E) versus the mole fraction (x_1) of DMF for the different binary mixtures at the experimental temperatures are depicted in Fig. 3. The η^E values of the binary mixtures were fitted to Redlich–Kister polynomial (shown as curves in Fig. 3) with standard deviations (SD) lying in the range 0.001–0.002.

Figure 3 shows that the η^E values, except for the system with THF at 318.15 K, are negative for all the mixtures over the entire composition range at all the experimental temperatures. The negative values indicate the presence of dispersion forces in these mixtures, while positive values may be attributed to the presence of specific interactions. As expected, the values of η^E become less negative or increase as the temperature increases but decrease as the dielectric constant of the ethers decrease from THF to 1,4-DO (Fig. 3). This suggests that the strength of molecular interactions in the mixture follows the order: DMF + THF > DMF + 1,3-DO > DMF + 1,4-DO and increase with increasing temperature. Thus, the functions V_m^E and η^E compliment each other in describing the behavior of the studied binary mixtures.

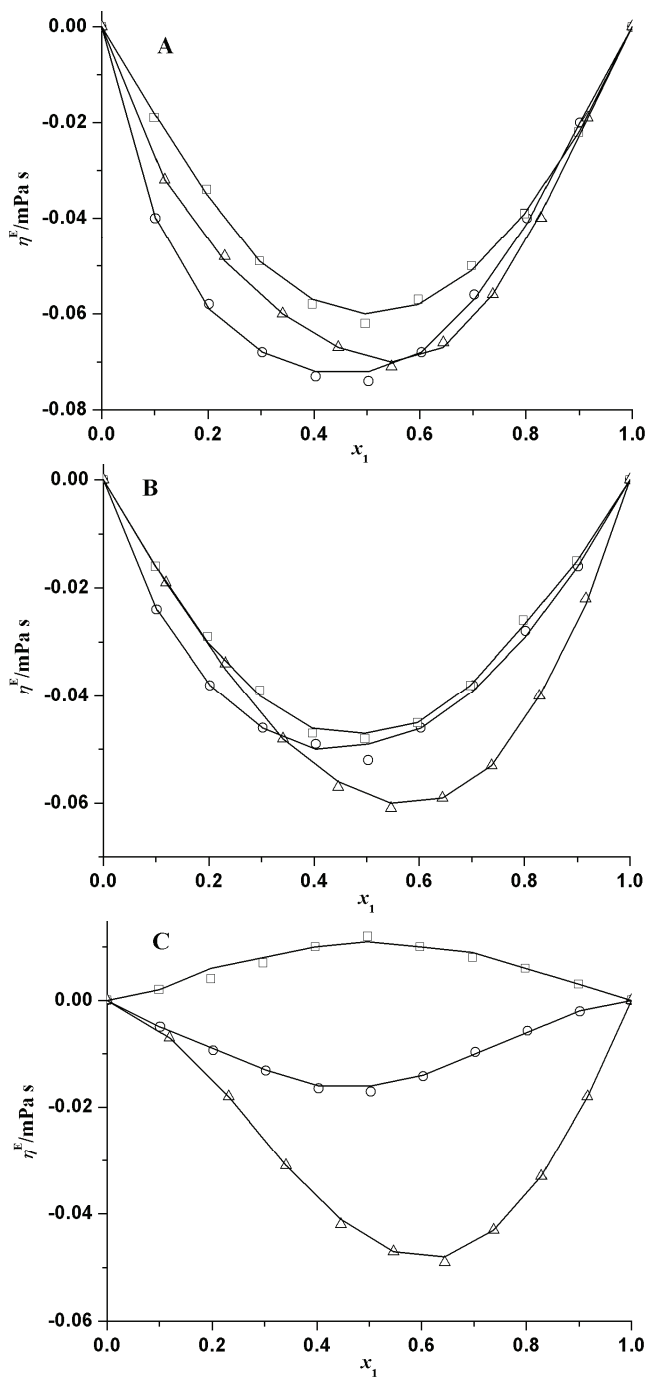


Fig. 3. Excess viscosities (η^E) vs. mole fraction of DMF (x_1) for binary mixtures of DMF with cyclic ethers: A, at $T = 298.15$ K; B, at $T = 308.15$ K; C, at $T = 318.15$ K. The graphical points represent the experimental η^E values: \square , THF; \circ , 1,3-DO; Δ , 1,4-DO and lines represent the η^E values obtained from the Redlich–Kister polynomial.

The Eyring viscosity relation⁵¹ yields the following equation for the free energy of viscous flow (ΔG^*):

$$\eta = (hN/V) \exp(\Delta G^* / RT) \quad (24)$$

where h is Planck's constant, N is Avogadro's number and the other symbols have their usual meanings. Rearranging Eq. (24) and putting $\Delta G^* = \Delta H^* - T\Delta S^*$, one obtains the relation:

$$R \ln(\eta V / hN) = \Delta H^* / T - \Delta S^* \quad (25)$$

Thus, the linear regressions of $R \ln(\eta V / hN)$ against $(1/T)$ could give the values of enthalpy (ΔH^*) and entropy (ΔS^*) of activation of viscous flow from the slope and negative intercept, respectively. The values of ΔH^* , ΔS^* and the linear regression coefficient (R^2) values as given in Table S-III of the Supplementary material show that while the ΔH^* values are positive, the ΔS^* values are negative for all the studied binary mixtures throughout the entire composition range. According to Corradini *et al.*⁵² the enthalpy of activation of viscous flow may be regarded as a measure of the degree of cooperation between the species participating in the viscous flow. In a highly structured liquid, there will be a considerable degree of order; hence, for cooperative movement of the entities, a large heat of activation is required for the flow process. Thus the ΔH^* values indicate that the ease of formation of activated species necessary for viscous flow follow the order: DMF + THF > DMF + 1,3-DO > DMF + 1,4 DO. This order is also supported by negative values of ΔS^* for the mixtures.

A combination of the ultrasonic speed (u) and density data enabled the determination of the isentropic compressibilities (κ_S) and the excess isentropic compressibility (κ_S^E)⁵³ of the binary mixtures using the following equations:

$$\kappa_S = 1 / u^2 \rho \quad (26)$$

$$\kappa_S^E = \kappa_S - \kappa_S^{\text{id}} \quad (27)$$

$$\kappa_S^{\text{id}} = \sum_{i=1}^2 \varphi_i \left[\kappa_{S,i} + \frac{TV_i \alpha_i^2}{C_{p,i}} \right] - \left\{ \frac{T \sum_{i=1}^2 (x_i V_i) \sum_{i=1}^2 (\varphi_i \alpha_i)^2}{\sum_{i=1}^2 (x_i C_{p,i})} \right\} \quad (28)$$

where φ_i , $\kappa_{S,i}$, V_i , α_i and $C_{p,i}$ are the volume fraction, isentropic compressibility, molar volume, thermal expansion coefficient and isobaric enthalpy of the i^{th} pure component in the binary mixtures, respectively, at 298.15 K. The experimental values of the speeds of sound, the isentropic compressibilities (κ_S) and the excess isentropic compressibilities (κ_S^E) at 298.15 K are given in Table S-IV of the

Supplementary material. The estimated uncertainty of the isentropic compressibility (κ_S) was within $\pm 1.0 \times 10^{10} \text{ Pa}^{-1}$.

For all the investigated binary mixtures, the excess isentropic compressibilities (κ_S^E) were negative, except for that containing 1,4-DO in the 1,4-DO-rich region, as shown in Table S-IV of the Supplementary material. The κ_S^E values of the binary mixtures were also fitted to the Redlich–Kister polynomial (shown as curves in Fig. 4) with standard deviations (*SD*) lying in the range 0.003–0.007.

Figure 4 depicts the composition dependence of the excess isentropic compressibilities κ_S^E for the investigated binary mixtures at 298.15 K are depicted in Fig. 4. It shows that the values of excess isentropic compressibility (κ_S^E) decrease in the order: DMF + 1,4-DO > DMF + 1,3-DO > DMF + THF, thereby supporting the observations obtained from the V_m^E and η^E values.

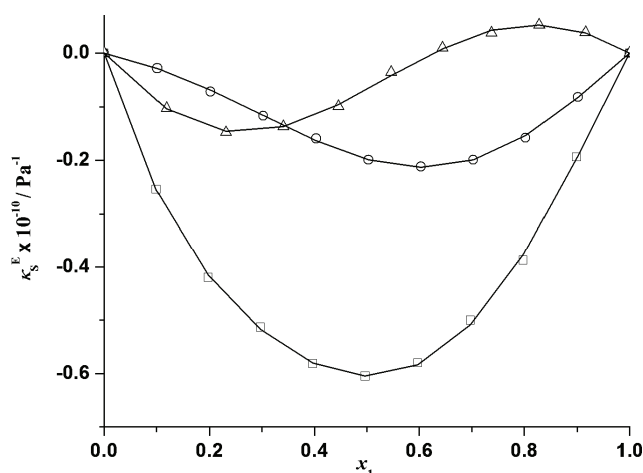


Fig. 4. The excess isentropic compressibility (κ_S^E) vs. mole fraction of DMF (x_1) for binary mixtures of DMF with cyclic ethers at $T = 298.15 \text{ K}$. The graphical points represent experimental κ_S^E values: \square , THF; \circ , 1,3-DO; Δ , 1,4-DO and lines represent κ_S^E values obtained from the Redlich–Kister polynomial.

Ultrasonic speeds of sound of all the three binary mixtures were theoretically predicted using the following theories and empirical relations:

The Flory theory⁴⁰ yields:

$$u_{\text{FLO}} = \left(\frac{10^4 \sigma}{6.3 \rho} \right) \quad (29)$$

where σ is the surface tension of a liquid or liquid mixture calculated following the Pandey approach⁵⁴ through an extension of the work of Patterson and Rastogi.⁵⁵

The collision factor theory (CFT)⁵⁶ yields:

$$u_{\text{CFT}} = u_{\infty} \frac{\sum_{i=1}^2 (x_i S_i) \sum_{i=1}^2 (x_i B_i)}{V_{\text{mix}}} \quad (30)$$

where $u_{\infty} = 1600 \text{ m s}^{-1}$, S_i and B_i represent the collision factor and actual volume of a molecule per mole for the i^{th} pure component in the mixtures, respectively.

The Nomoto relation (NOM)⁵⁷ yields:

$$u_{\text{NOM}} = \left(\frac{\sum_{i=1}^2 (x_i R_i)}{\sum_{i=1}^2 (x_i V_i)} \right)^3 \quad (31)$$

where R_i stands for the molar speed of sound for the i^{th} pure component in the mixtures.

The impedance dependence relation (IDR)⁵⁸ yields:

$$u_{\text{IDR}} = \frac{\sum_{i=1}^2 (x_i Z_i)}{\sum_{i=1}^2 (x_i \rho_i)} \quad (32)$$

where Z_i stands for specific acoustic impedance for the i^{th} pure component in the mixtures.

The ideal mixture relation (IMR)⁵⁹ yields:

$$u_{\text{IMR}} = \left[\frac{\sum_{i=1}^2 (x_i M_i) \sum_{i=1}^2 (x_i / M_i u_i^2)}{\sum_{i=1}^2 (x_i M_i)} \right]^{\frac{1}{2}} \quad (33)$$

where u_i is the ultrasonic speed of sound for the i^{th} pure component in the mixtures. It was observed that the values obtained from all the theories and empirical relations show some deviations from the experimental speeds of sound and based on the *MRS*D % values, listed in Table S-V and shown graphically in Fig S-2 of the supplementary material, the relative predictive capability for the different equations follows the orders: for the DMF + THF system: FLORY > IDR > CFT > NOM >> IMR; for the DMF + 1,3-DO system: CFT \approx NOM > IDR > IMR >> >> FLORY and for the DMF + 1,3-DO system: CFT > IDR > NOM \approx IMR >> >> FLORY.

CONCLUSIONS

Based on the nature and magnitude of various excess functions (V_m^E , η^E and κ_S^E) and other derived parameters ($\bar{V}_{m,1}^E$, $\bar{V}_{m,2}^E$, $\bar{V}_{m,1}^{0,E}$, $\bar{V}_{m,2}^{0,E}$, *etc.*), evidently the molecular interactions in the studied binary systems can primarily be attributed to dipole–dipole or dipole-induced–dipole interactions. The PFP theory provided satisfactory quantitative estimations of the different contributions to the excess molar volumes (V_m^E) of the systems at ambient temperature and pressure.

SUPPLEMENTARY MATERIAL

Comparisons of the experimental results with literature data, and some derived parameters (Tables S-I, S-II, S-III, S-IV and S-V, and Figs. S-1 and S-2) are available electronically from <http://www.shd.org.rs/JSCS/> or from the corresponding author on request.

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ИЗВОД

ТЕРМОФИЗИЧКА СВОЈСТВА БИНАРНИХ СМЕША *N,N*-ДИМЕТИЛФОРМАМИДА СА ТРИ ЦИКЛИЧНА ЕТРА

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Гуштине и вискозности бинарних система тетраhydroфурана (THF), 1,3-диоксолана (1,3-DO) и 1,4-диоксана (1,4-DO) са *N,N*-диметилформамидом (DMF) измерене су на температурама од 298,15, 308,15 и 318,15 К и атмосферском притиску у целом опсегу удела компоненти. Измерена је и брзина звука кроз ове системе на собној температури и атмосферском притиску ($T = 298,15$ К и $p = 1,01 \times 10^5$ Па). На бази измерених вредности израчуната је допунска моларна запремина (V_m^E), допунска вискозност (η^E) и допунска изентропска компресибилност (κ_S^E). Коришћењем допунских моларних запремина, израчунате су и анализиране допунске парцијалне моларне запремине ($\bar{V}_{m,1}^E$ и $\bar{V}_{m,2}^E$) и ове при бесконачном разблажењу ($\bar{V}_{m,1}^{0,E}$ и $\bar{V}_{m,2}^{0,E}$) свих течних компонената у смешама. Зависност V_m^E од састава смеше на атмосферским условима коришћена је за проверу применљивости Prigogine–Flory–Patterson (PFP) теорије. Утврђено је да су вредности допунских величина или негативне или позитивне у зависности од природе молекулских интеракција и структуре компонената у течним смешама.

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REFERENCES

1. B. Garcia, R. Alcalde, J. M. Leal, J. S. Mantos, *J. Chem. Soc., Faraday Trans.* **93** (1997) 1115
2. Y. Mahan, C. N. Liew, A. E. Mather, *J. Solution Chem.* **31** (2002) 743
3. C. R. Reid, B. E. Poling, *The properties of Gases and Liquids*, McGraw Hill, New York, 1998, Ch. 1

4. A. Villares, S. Rodriguez, C. Lafuente, F. M. Royo, M. C. Lopez, *J. Solution Chem.* **33** (2004) 1119
5. A. Ali, J. D. Pandey, N. K. Soni, A. K. Nain, B. Lal, D. Chand, *Chin. J. Chem.* **23** (2005) 377
6. A. K. Nain, *J. Solution Chem.* **35** (2006) 1417
7. P. Brocos, E. Calvo, A. Pineiro, R. Bravo, A. Amigo, *J. Chem. Eng. Data* **44** (1999) 1341
8. M. N. Roy, A. Sinha, B. Sinha, *J. Solution Chem.* **34** (2005) 1311
9. M. N. Roy, B. Sinha, *J. Mol. Liq.* **136** (2006) 128
10. M. N. Roy, B. Sinha, *J. Mol. Liq.* **133** (2007) 89
11. M. N. Roy, B. K. Sarkar, B. Sinha, *J. Chem. Eng. Data* **54** (2009) 1076
12. B. Sinha, *Phys. Chem. Liq.* **48** (2010) 183
13. R. S. Sah, B. Sinha, M. N. Roy, *J. Chem. Eng. Data* **55** (2010) 4536
14. B. K. Sarkar, A. Choudhury, B. Sinha, *J. Solution Chem.* **41** (2012) 53
15. J. A. Dean, *Lange's Handbook of Chemistry*, 11th ed., McGraw Hill, New York, 1973
16. J. A. Riddick, W. B. Bunger, T. K. Sakano, *Organic solvents. Techniques of Chemistry*, Vol. 2, 4th ed., Wiley Interscience, New York, 1986
17. R. Gopal, S. Agarwal, D. K. Agarwal, *J. Chem. Thermodyn.* **8** (1976) 1205
18. Y. Zhao, J. Wang, X. Xuan, J. Lu, *J. Chem. Eng. Data* **45** (2000) 440
19. M. N. Roy, R. Dey, A. Jha, *J. Chem. Eng. Data* **46** (2001) 1327
20. I. Johnson, M. Kalidoss, R. Srinivasamoorthy, *J. Chem. Eng. Data* **47** (2002) 1388
21. P. S. Nikam, S. J. Kharat, *J. Chem. Eng. Data* **50** (2005) 455
22. S. Akhtar, A. N. Qamar Faruk, M. A. Saleh, *Phys. Chem. Liq.* **39** (2001) 383
23. P. Pacak, *J. Solution Chem.* **16** (1987) 71
24. M. Das, M. N. Roy, *J. Chem. Eng. Data* **51** (2006) 2225
25. A. Valen, I. Gascon, C. Lafuente, J. S. Urieta, F. M. Royo, M. Postigo, *Int. J. Thermophys.* **23** (2002) 1587
26. L. Sarkar, M. N. Roy, *J. Chem. Eng. Data* **54** (2009) 3307
27. A. Villares, S. Martin, M. Haro, B. Giner, H. Artigas, *J. Chem. Thermodyn.* **36** (2004) 1027
28. A. Inglese, J.-P. E. Groller, E. Wilhelm, *J. Chem. Eng. Data* **28** (1983) 124
29. S. M. Contreras, *J. Chem. Eng. Data* **46** (2001) 1149
30. T. M. Aminabhavi, V. B. Patil, *J. Chem. Eng. Data* **43**, 497(1998)
31. K. P. Rao, K. S. Reddy, *J. Chem. Eng. Data* **33** (1988) 130
32. K. N. Marsh, *Recommended Reference Materials for the Realisation of Physicochemical Properties*, Blackwell Scientific Publications, Oxford, UK, 1987
33. A. Chatterjee, B. Das, *J. Chem. Eng. Data* **51** (2006) 1352
34. M. N. Roy, D. K. Hazra, *Indian J. Chem. Technol.* **1** (1994) 93
35. P. S. Nikam, M. Hosan, *J. Chem. Eng. Data* **33** (1988) 165
36. A. J. Treszczanowicz, O. Kiyohora, G. C. Benson, *J. Chem. Thermodyn.* **13** (1981) 253
37. J. F. Coetzee, T.-H. Chang, *Pure. Appl. Chem.* **57** (1985) 633.
38. A. Sinha, M. N. Roy, *J. Mol. Liq.* **140** (2008) 39
39. O. Redlich, A. T. Kister, *Ind. Eng. Chem.* **40** (1948) 345
40. P. J. Flory, R. A. Orwell, A. Vrijji, *J. Am. Chem. Soc.* **86**, (1964) 3507
41. P. J. Flory, R. A. Orwell, A. Vrijji, *J. Am. Chem. Soc.* **86** (1964) 3515
42. P. J. Flory, *J. Am. Chem. Soc.* **87** (1965) 1833
43. A. Abe, P. J. Flory, *J. Am. Chem. Soc.* **87** (1965) 1838
44. D. Patterson, G. Delmas, *J. Polym. Sci., C* **30** (1970) 1
45. D. Patterson, *Pure. Appl. Chem.* **47** (1976) 305

46. C. de Visser, G. Perron, J. E. Desnoyers, *J. Chem. Eng. Data* **22** (1977) 74
47. P. Brocos, E. Calvo, R. Bravo, M. Pintos, A. Amigo, *J. Chem. Eng. Data* **44** (1999) 67
48. I. Prigogine, R. Defay, *Chemical Thermodynamics*, 5th ed., Longman, London, 1994, p. 8
49. P. Tancrede, P. Bothorel, P. St. Romain, D. Patterson. *J. Chem. Soc., Faraday Trans. II* **73** (1977) 15
50. M. A. Saleh, S. Akhtar, M. S. Ahmed, *Phys. Chem. Liq.* **44** (2006) 551
51. S. Glasstone, K. J. Laidler, H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941
52. F. Corradini, L. Marcheselli, A. Marchetti, M. Tagliazucchi, L. Tassi, G. Tosi, *Bull. Chem. Soc. Jpn.* **65** (1992) 503
53. D. Kiyohora, G. C. Benson, *J. Chem. Thermodyn.* **11** (1979) 861
54. J. D. Pandey, *J. Chem. Soc., Faraday Trans. I* **75** (1979) 2160
55. D. Patterson, A. K. Rastogi, *J. Phys. Chem.* **74** (1970) 1067
56. B. Jacobson, *J. Chem. Phys.* **20** (1952) 927
57. O. Nomoto, *J. Phys. Soc. Jpn.* **13** (1958) 1528
58. M. Kalidoss, R. Srinivasamoorthy, *J. Pure. Appl. Ultrason.* **19** (1997) 9
59. W. Van Dael, E. Vangaël, in *Proceedings of 1st International Conference on Calorimetry and Thermodynamics*, Warsaw, Poland, 1969, p. 555.