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Excess molar volumes and excess viscosities for mixtures of *N*,*N*-dimethylformamide with methanol, ethanol and 2-propanol at different temperatures

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Abstract

Densities and viscosities for mixtures of *N*,*N*-dimethylformamide (DMF) with methanol, ethanol, and 2-propanol were measured as a function of mole fraction at (303.15, 308.15, 313.15, 318.15, 323.15) K and atmospheric pressure. From the measurements, excess molar volumes (V_m^E), excess viscosities (η^E), and Grunberg and Nissan interaction parameters (ε) were calculated. The excess parameters were fitted to the Redlich–Kister equation. Excess molar volumes (V_m^E) were found to be negative throughout the whole range of composition for all the three systems. The excess viscosities and interaction parameters of the DMF + methanol system were found to be positive whereas the values were negative for the other systems over the entire concentration range.

Keywords: Excess molar volume; Viscosity; *N*,*N*-dimethylformamide (DMF); Interaction parameter

1. Introduction

Liquid mixtures frequently appear in chemical research. Most of the mixtures are nonideal and show peculiar behavior. The interpretation of nonideality is a fascinating area and a large number of contributions was made over the last decade. Solution theory is still far from adequate to account for solution nonidealities in terms of the properties of the constituent molecules. The experimental data on macroscopic properties such as excess molar volumes, excess viscosities, surface tension, and refractive index often provide valuable information for the understanding of the nature of homo- and hetero-molecular interactions. The knowledge of the main factors involved in the nonideality of liquid mixtures is fundamental for a better understanding of excess molar volumes and excess viscosities. Alcohol-amide solutions are of practical importance.

DMF to some extent is associated by means of dipole–dipole interactions. Significant structural effects are absent due to the lack of hydrogen bonds. Therefore it acts as an aprotic protophilic solvent of moderately high dielectric constant ($\epsilon = 36.71$) of molecules with a large dipole moment ($\mu = 3.8$ D) at 298.15 K [1]. Because of its miscibility with almost all common polar and nonpolar solvents [2–5] it is classified as so-called supersolvent. A DMF molecule can interact with an alkanol molecule by virtue of better hydrogen bond acceptor ability of its oxygen atom, resulting in structural and packing effects. Volumetric, viscometric and related thermodynamic properties for the mixtures containing DMF were recently reported in the literature [6–22].

We have undertaken a program for studying the volumetric and viscometric properties of binary liquid mixtures on alcoholic solutions of water, amides and oxo-sulfur compounds. As part of our ongoing research [23–26] the present paper presents the excess molar volumes and excess viscosities data of DMF + methanol,+ethanol,+2-propanol over the whole range of compositions at five temperatures from 303.15 K to 323.15 K.

2. Experimental

Methanol, ethanol, and 2-propanol used in the present investigation were the same as in our earlier works [26–28].

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Table 1
Comparison of densities, (ρ/g·cm^{-3}), and viscosities, (η^{E}/mP), of pure liquids with literature data at different temperatures

Component	Property	Temperature/K				
		303.15	308.15	313.15	318.15	323.15
DMF	ρ	0.9394 0.9398[8] 0.93793[29]	0.9342 0.935717[30] 0.9351[8]	0.9301 0.9302[8] 0.92653[29] 0.93098[32]	0.9253 0.925986[30]	0.9201 0.921141[30]
	η	7.753 7.6000[5]	7.329 7.217[23]	6.900 6.955[5] 6.73[8]	6.530 6.461[23]	6.140 6.128[23]
Methanol	ρ	0.7813 0.7816[31] 0.78165[32]	0.7764 0.7769[31] 0.77710[32]	0.7729 0.7726[33]	0.7668 0.7676[34]	0.7627 0.7627[26]
	η	5.178 5.26[31] 5.03[32]	4.843 4.80[31] 4.6940[32]	4.515 4.48[33]	4.233 4.13[34]	3.950 3.950[26]
Ethanol	ρ	0.7834 0.7812[33] 0.78069[35]	0.7790 0.7762[31] 0.77655[36]	0.7746 0.7726[33]	0.7698 0.7678[34]	0.7661 0.7661[26]
	η	10.858 9.94[33] 9.985[16]	9.732 9.06[34] 9.069[16]	8.596 8.29[35] 8.248[16]	8.284 7.61[34]	7.493 7.493[26]
2-Propanol	ρ	0.7765 0.7769[37] 0.77662[39]	0.7726 0.772559[38] 0.77227[39]	0.7688 0.76813[23]	0.7635 0.7636[23]	0.7588 0.7589[23]
	η	17.919 17.92[38]	15.529 15.50[38]	13.554 13.52[38]	11.822 11.895[24]	10.469 10.468[24]

DMF was purchased from Merck. All chemicals were kept in sealed dark bottles dried over molecular sieves 4A 1/16 (Wako pure chemical) for 2 to 3 weeks prior to their use. The chemicals were manipulated under a nitrogen atmosphere and degassed using an ultrasonic technique. Binary mixtures were prepared by mass in air-tight, stoppered glass bottles using an analytical balance (LIBROR EX-180, Shimadzu) with a readability of 0.0001 g. Care was taken to avoid evaporation and solvent contamination during mixing. The mole fraction was accurate up to the fourth place of decimal. The densities of degassed pure liquids and binary mixtures were measured with a 5 mL bicapillary pycnometer. The pycnometer was calibrated using conductivity water having a conductivity $<1\times10^{-6}\ \Omega^{-1}\mathrm{cm}^{-1}$. An Ostwald U-tube viscometer with sufficiently long efflux time was used for viscosity measurements. An electronic digital stopwatch with a readability of ±0.01 s was used for flow time measurements. At least three repetitions of each data point obtained were reproducible to ±0.05 s and the results were averaged. All measurements were carried out in a thermostatic water bath (Techne, TE-8A) controlled to ±0.01 K. The purity of the solvents was assessed by comparing their measured density and viscosity data, which were in good agreement with the literature value [5,8,16,23,24,26,29–39] as can be seen in Table 1. The purities of the compounds were further confirmed by gas–liquid chromatography (GLC) single sharp peaks.

3. Results and discussion

Excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}}$, were calculated using the equation

$$V_{\mathrm{m}}^{\mathrm{E}} = [(x_1M_1 + x_2M_2)/\rho_{12} - (x_1M_1/\rho_1 + x_2M_2/\rho_2)] \tag{1}$$

where x_1, M_1 and ρ_1 are the mole fraction, molar mass and density of pure DMF, and x_2, M_2, ρ_2 are the corresponding quantities for alkanol in each system. ρ_{12} is the density of the corresponding binary solution. The densities and excess molar volumes at 303.15, 308.15, 313.15, 318.15 and 323.15 K are presented in Tables 2 to 4 for the three binary mixtures along with the mole fraction of DMF (x_1). The variation of $V_{\mathrm{m}}^{\mathrm{E}}$ with mole fraction of DMF at different temperatures are shown graphically in Figs. 1, 2, and 3 for the DMF + methanol, + ethanol, and + 2-propanol systems respectively. The excess properties were fitted to the Redlich–Kister polynomial equation [40] of the form,

$$Y^{E} = x_1x_2\sum_{n=1}^{P} a_n(x_2 - x_1)^{n-1} \tag{2}$$

where Y^{E} stands for $V_{\mathrm{m}}^{\mathrm{E}}$ or η^{E} and x_1 and x_2 are the mole fractions of DMF and alkanol, respectively. The coefficients a_n were obtained by fitting Eq. (2) to the experimental results using a least-squares regression method. In each case the optimum number of coefficients, p was ascertained from an examination of the variation of the standard deviation, σ, with the number of parameters, n,

$$\sigma = \left\{\sum_{i=1}^{m}\left(Y_{\mathrm{expt}}^{\mathrm{E}} - Y_{\mathrm{cal}}^{\mathrm{E}}\right)^{2}/(m-p)\right\}^{1/2} \tag{3}$$

where m is the number of experimental data points. The calculated values of a_{n} along with the standard deviations, σ, are given in Table 5.