

Isotope effects on selected physicochemical properties of nitromethane and 1-pentanol

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Abstract Densities, kinematic viscosities, speed of sound and refractive indices of nitromethane and 1-pentanol and their deuterated derivatives CD_3NO_2 and $\text{C}_5\text{H}_{11}\text{OD}$ were measured. The data obtained allowed to calculate molar volumes, dynamic viscosities, isentropic compressibilities and isobaric thermal expansion. Deuterium isotope effect on the selected physicochemical properties of both nitromethane and 1-pentanol has been determined. Large isotope effects characterizing density, viscosity and speed of sound are observed for nitromethane and much smaller for 1-pentanol. Isotope effects on molar volume are small both for nitromethane and 1-pentanol, but of the opposite sign. These observations are in agreement with the expectations.

Key words deuterium • isotope effects • density • viscosity • speed of sound • nitromethane • 1-pentanol

Introduction

Recently, we have studied miscibility of nitromethane with 1-pentanol as well as the isotope effect thereon [7]. The system is characterized by the upper critical solution temperature which is very sensitive to the isotope substitution. The results obtained clearly show that deuterium substitution both in the methyl group of nitromethane and the OH group of pentanol provoke the upward shift of the upper critical solution temperature (UCST) what means that the miscibility decreases. Continuing the study on this system, we present here densities, viscosities, speed of sound and refractive indices of nitromethane and 1-pentanol and their deuterated derivatives: CD_3NO_2 and $\text{C}_5\text{H}_{11}\text{OD}$. From these experimental results, the molar volumes, isobaric thermal expansion and isentropic compressibilities have been calculated and isotope effect on these properties has been determined. It should be mentioned that the influence of the isotope substitution on some physicochemical properties of nitromethane was studied by Rabinovich [8] more than 40 years ago, however his data were of relatively low precision. No data are available on deuterated pentanol. This study gives good quality data on both substances.

Experimental

Nitromethane, nitromethane- d_3 (99.9 at.% D) and pentanol were purchased from Aldrich. Deuterated pentanol was synthesized in a triple exchange reaction with D_2O (99.96 at.% D from Aldrich). Water was

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removed by distillation. The main fraction was dried over CaCl_2 and then over molecular sieves 5 \AA and redistilled to remove any trace of moisture. All chemicals after purification were stored over molecular sieves for further drying. The molecular sieves used for drying the deuterated compounds were previously treated with D_2O and dried. A special care was taken to avoid moisture in the alcohol. Densities were measured using a vibrating-tube densimeter (Ecolab, Poland). The temperature in the measuring cell was regulated to $\pm 0.01 \text{ K}$. The uncertainty of the density measurements was less than $\pm 0.0001 \text{ g}\cdot\text{cm}^{-3}$. The kinematic viscosity was determined by using an optoelectronic capillary viscometer [6] with a precision of $\pm 0.001 \text{ m}^2\cdot\text{s}^{-1}$. The speed of sound was measured using an acoustic time-of-flight gauge (Ecolab) with an uncertainty of $\pm 1 \text{ cm}\cdot\text{s}^{-1}$. The temperature was stable within $\pm 0.01 \text{ K}$. The refractive index was measured in an Abbe refractometer.

The densities, viscosities, speed of sound and refractive index of pure liquids and their deuterated forms were measured in the temperature range from 293 K to 308 K .

Results and discussion

The temperature dependences of the measured densities, kinematic viscosities, speed of sound and refractive index are shown in Figs. 1–4. Several thermodynamic quantities can be calculated from the experimental density (ρ), kinematic viscosity (ν), and speed of sound (u) data. Among them are molar volumes, V_m , isobaric thermal expansion, α_p , isentropic compressibility, κ_s , and dynamic viscosities, η . The calculated values are related to density, speed of sound and kinematic viscosity by:

$$(1) \quad \alpha_p = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p$$

$$(2) \quad \kappa_s = \frac{1}{u^2 \rho}$$

$$(3) \quad \eta = \nu \cdot \rho$$

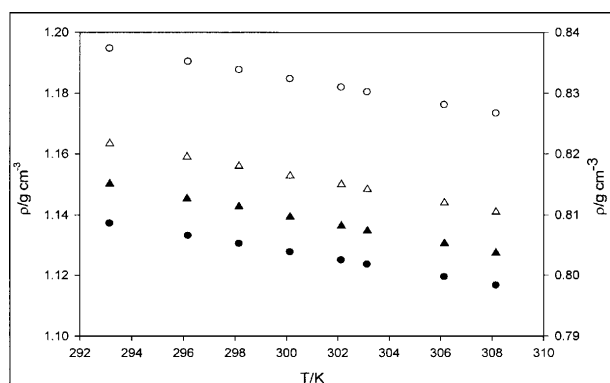


Fig. 1. Temperature dependence of density (the left axis refers to nitromethane): ● – nitromethane, ○ – nitromethane- d_3 ; ▲ – 1-pentanol, △ – 1-pentanol- d_1 .

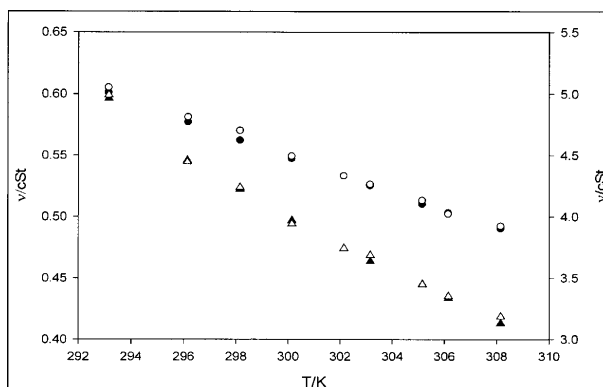


Fig. 2. Temperature dependence of kinematic viscosity (the left axis refers to nitromethane): ● – nitromethane, ○ – nitromethane- d_3 ; ▲ – 1-pentanol, △ – 1-pentanol- d_1 .

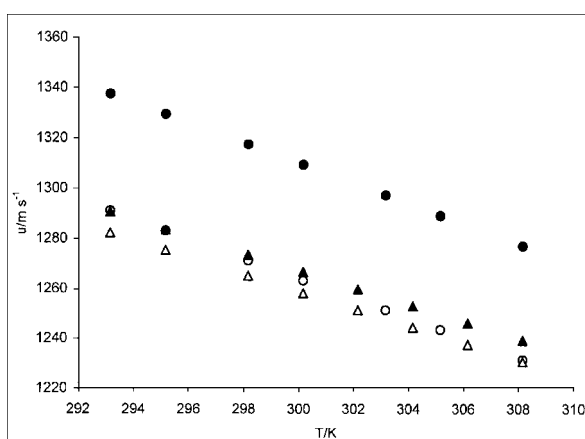


Fig. 3. Temperature dependence of speed of sound: ● – nitromethane, ○ – nitromethane- d_3 ; ▲ – 1-pentanol, △ – 1-pentanol- d_1 .

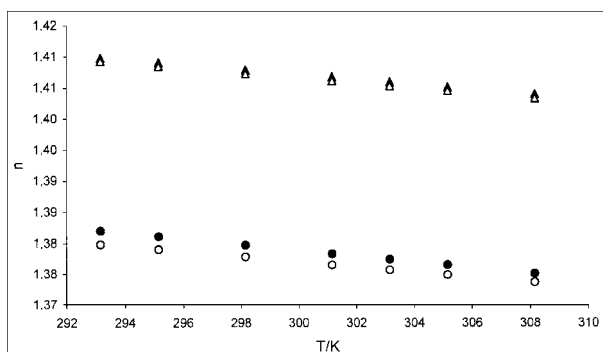


Fig. 4. Temperature dependence of refractive index: ● – nitromethane, ○ – nitromethane- d_3 ; ▲ – 1-pentanol, △ – 1-pentanol- d_1 .

The calculated values are shown in Figs. 5–8. The results obtained at present for nondeuterated species agree satisfactorily well with previously reported data (Table 1). Table 2 summarizes the isotope effects on several thermodynamic properties measured at a temperature of 298 K . Whenever possible we include for comparison the results obtained by Rabinovich [8] and Holz *et al.* [5]. As can be seen in those few possible cases, the results now obtained agree well with those reported in the literature except for the values of the

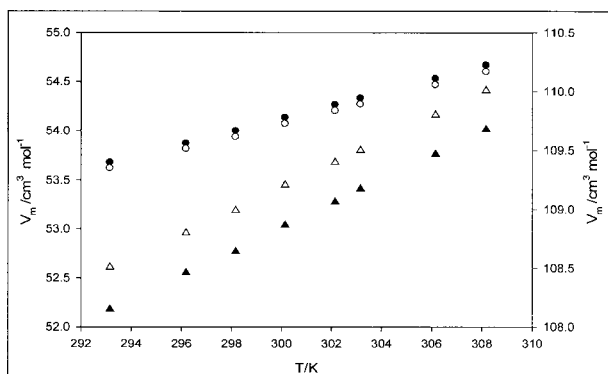


Fig. 5. Temperature dependence of molar volumes (the left axis refers to nitromethane): ● – nitromethane, ○ – nitromethane-d₃; ▲ – 1-pentanol, △ – 1-pentanol-d₁.

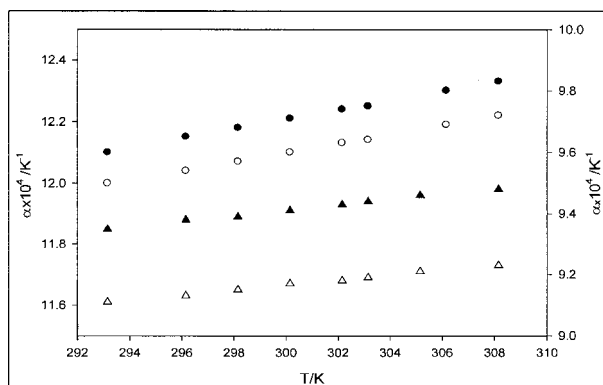


Fig. 7. Temperature dependence of isobaric thermal expansion (the left axis refers to nitromethane): ● – nitromethane, ○ – nitromethane-d₃; ▲ – 1-pentanol, △ – 1-pentanol-d₁.

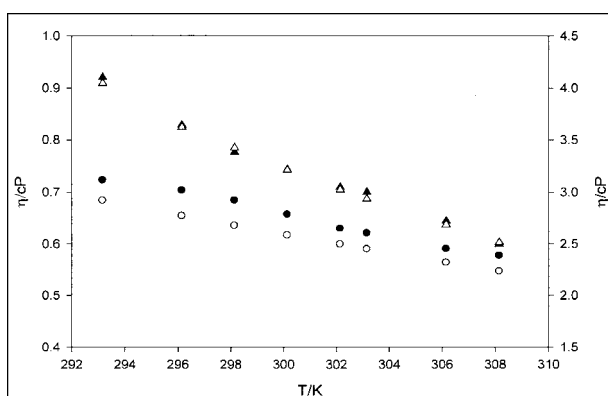


Fig. 6. Temperature dependence of dynamic viscosity (the left axis refers to nitromethane): ● – nitromethane, ○ – nitromethane-d₃; ▲ – 1-pentanol, △ – 1-pentanol-d₁.

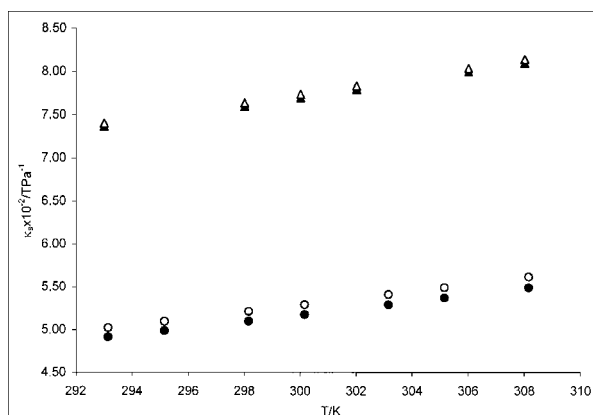


Fig. 8. Temperature dependence of isentropic compressibility (the left axis refers to nitromethane): ● – nitromethane, ○ – nitromethane-d₃; ▲ – 1-pentanol, △ – 1-pentanol-d₁.

isotope effect on the isobaric thermal expansion. Here, a significant disagreement should be mentioned. Nonetheless, one should keep in mind that isotope effects are very small and that this property is obtained from a derivative. Therefore, a proper choice of the fitting equation and careful evaluation procedure is of primary importance. In our opinion Rabinovich used oversimplified procedure to determine α values and hence his results must be considered as less reliable than ours. The isotope effects on the molar volume (Fig. 5)

are very close to the literature values. From a qualitative perspective, the observed sign for the isotope effect on the molar volume of both nitromethane and pentanol is as predicted [2]. A simple core-size analysis tells us that the molecular volume of nitromethane-h₃ is expected to be slightly greater than that of nitromethane-d₃ as unharmonic, combined with higher internal vibrational frequencies for the lighter molecule, lead to greater vibrational amplitudes of the C-H stretching modes compared to the C-D ones. On the

Table 1. Comparison of the measured properties of pure liquids with the literature data

Properties	Nitromethane, $T = 298.15$ K		1-pentanol, $T = 303.15$ K	
	this work	literature	this work	literature
$\rho/\text{g}\cdot\text{cm}^{-3}$	1.13042	1.12958 ^a 1.13128 ^b	0.80741	0.8072 ^f 0.8076 ^g
η/cP	0.590	0.615 ^c 0.591 ^d	2.933	3.056 ^g
$10^{-3}\alpha_p/\text{K}^{-1}$	1.208	1.208 ^a 1.217 ^b	0.919	0.893 ^h
κ_s/TPa^{-1}	509.7	508.55 ^a	740.1	736 ⁱ
$u/\text{m}\cdot\text{s}^{-1}$	1297.29 ($T = 303.15$ K)	1302 ^e ($T = 303.15$ K)	1256.45	1256 ^f 1258 ^j

^a Ref. [2]. ^b Ref. [11]. ^c Ref. [14]. ^d Ref. [8]. ^e Ref. [6]. ^f Ref. [9]. ^g Ref. [15]. ^h Ref. [4]. ⁱ Ref. [12]. ^j Ref. [10].

Table 2. Deuterium isotope effect $\Delta X = [(X_D - X_H)/X_H]$ on selected thermodynamic property X at 298.15 K

Property (X)	$10^2 \Delta X$	
	Nitromethane-d ₃	1-pentanol-d ₁
Mass density, ρ	4.8 (5.4) ^a	0.8
Molar volume, V_m	-0.1 (-0.15) ^a	0.3
Speed of sound, u	-3.5 (-4.4) ^a	-0.7
Isobaric thermal expansiveness, α_p	-0.1 (0.4) ^a	-0.3
Isentropic compressibility, κ_S	2.3 (2.1) ^a	0.5
Viscosity, η	4.8 (4.0 ^a , 4.6 ^b)	1.5
Refractive index, n	-0.5 (-0.6 ^a)	-0.1

^a Ref. [8]. ^b Ref. [5].

other hand, the isotope effect on the mass density is basically a consequence of the molar mass difference between isotopomers (nitromethane-h₃, 61.04×10^{-3} kg·mol⁻¹; nitromethane-d₃, 64.06×10^{-3} kg·mol⁻¹). In the case of substances, which are able to form hydrogen bonding, the opposite effect is expected, and indeed for water and alcohols molar volumes for deuterated species is slightly higher [1, 3, 8, 13]. The same trend is observed for pentanol. The inverse isotope effect on the molar volume of water has been discussed by Dutta-Choudhury and Van Hook [3] and that interpretation carries over in to the present case. It means that although the positive steric effect must be present in hydrogen bonded systems it is more than compensated for by an inverse effect involving librational motion in the hydrogen bonded network.

Viscosity isotope effect for nitromethane is relatively large and agrees well with those reported by Rabinovich [8] and Holz *et al.* [5]. It is substantially bigger than that for 1-pentanol. It is worth of mentioning that in each case isotope effects on viscosity do not depend on temperature and they do not follow the simple mass dependence, i.e. $\eta_D/\eta_H \neq (M_D/M_H)^{1/2}$ (compare observed isotope effects with $(M_D/M_H)^{1/2} = 1.024$ for nitromethane and 1.005 for pentanol). It means that apart from the square-root mass law other factors like intermolecular interaction contribution should be taken into account. Temperature dependence of the dynamic viscosity gives the activation energy equal to 11.1 kJ/mol for nitromethane and 12.1 kJ/mol for nitromethane-d₃, while for 1-pentanol it is equal to 23.4 kJ/mol and is practically the same for deuterated species. It is very likely that multiple isotope substitution in nitromethane generates a bigger isotope effect on viscosity and changes the condition of the flow more drastically (let us compare the ratio of molar masses of the isotopomers in both cases: 1.049 and 1.011 for nitromethane and pentanol, respectively). It is worthy of mention that the isotope substitution very weakly affects the kinematic viscosity of both nitromethane and pentanol, and the resulting isotope effect on the dynamic viscosity (Fig. 6) is primarily due to the isotope effect on density. Thus the viscous flow is almost independent of deuterium substitution. The speed of sound (Fig. 3) and isentropic compressibility (Fig. 7) show typical temperature dependence and are strongly dependent on isotope

substitution, in particular it is well seen for nitromethane. It seems that it is again the density which makes the major contribution. According to Rabinovich [8], the sign of the isotope effect on isentropic compressibility is related with the decrease of dispersion energy upon the isotope substitution and the relation $\kappa_D > \kappa_H$ holds in all cases independently of the property of the substance or functional groups. As expected, deuterium substitution changes visibly the refractive index of nitromethane and only slightly that of pentanol.

Conclusion

The thrust of this paper has been mainly experimental. Deuterium substitution in nitromethane and in the OH group of 1-pentanol generates visible changes in physicochemical properties of these liquids. Our values of observed and calculated properties are generally in good agreement with the very limited data found in the literature. In particular, a substantial isotope effects are observed on densities, viscosities and speed of sound in nitromethane in comparison to 1-pentanol. It is mainly due to the multiple isotope substitution in the relatively small molecule. Isotope effects on several volumetric properties are very small (typically less than 1%) and according to expectations deuterium substitution in the OH group actively participating in the hydrogen bonding brings about a change of the sign of the isotope effect on molar volume.

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