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Densities, Viscosities, and Speeds of Sound of the Nitromethane + 1-Pentanol System near the Critical Demixing Temperature: Effect of Deuterium Substitution

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Densities, viscosities, and speeds of sound were measured for the binary mixtures of nitromethane and 1-pentanol and their deuterated forms in the vicinity of the upper critical solution temperature. The excess molar volumes and excess isentropic compressibilities as well as the deviations of viscosity were determined. The influence of the deuterium substitution was analyzed and discussed.

Introduction

Over the past few decades, thermodynamic properties of nonelectolyte mixtures have been extensively studied. Among others, binary solutions of nitromethane with alcohols have attracted considerable attention.[1−5] Nitromethane is an aprotic solvent with high polarity that is used in a variety of applications. Mixtures with alcohols of varying chain lengths reveal interesting properties due to specific interactions such as hydrogen bonding and others. Moreover, mixtures of nitromethane with higher alcohols exhibit limited miscibility characterized by the upper critical solution temperature (UCST).[3−5] Recently, we have studied the miscibility of nitromethane with 1-pentanol as well as the isotope effect.[5] The results obtained clearly show that isotope substitution both in the methyl group of nitromethane and the OH group of pentanol provokes the upward shift of the UCST, which means that the miscibility decreases. It should be noted that the critical concentration is not affected by the isotope substitution. Continuing the study on this system, we present here densities, viscosities, and speeds of sound of mixtures of nitromethane with pentanol and their deuterated derivatives CD_3NO_2 and $C_5H_{11}OD$. From these experimental results, the volumetric properties, isentropic compressibilities, isobaric expansivities, excess volumes, and excess isentropic compressibilities have been calculated. To the best of our knowledge, there exist some thermodynamic data for nitromethane + butanols and lower alcohols mixtures.[1,2] Recently, Cerderiña et al.[3] measured densities, speeds of sound, and isobaric heat capacities for nitromethane + butanol isomers mixtures, and Iwanowski et al.[4] reported on ultrasonic attenuation spectra for the nitromethane + 1-pentanol system near the UCST.

Experimental Section

Nitromethane, nitromethane-d_3 (99.9 at. % D), and pentanol (all from Aldrich) were the same chemicals as those used in the miscibility study.[5] Deuterated pentanol was synthesized in a triple-exchange reaction with D_2O (99.96 at. % D). Water was removed by distillation. The main fraction was dried over $CaCl_2$ and then over 5 Å molecular sieves and was redistilled to remove any trace of moisture. All chemicals after purification were stored over molecular sieves to dry them further. The molecular sieves used for drying the deuterated compounds were previously treated with D_2O and dried. Solutions of different composition were prepared gravimetrically. The accuracy of weighing was ±0.0001 g, hence the uncertainty of the mole fraction was estimated to be better than ±0.001. 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 ±0.01 K. The uncertainty of the density measurements was less than $\pm 0.0001\ g\cdot cm^{-3}$. The kinematic viscosity was determined by using an optoelectronic capillary viscometer[6] with a precision $\pm 0.001\ m^2\cdot s^{-1}$. The speed of sound was measured using an acoustic time-of-flight gauge (Ecolab) with an uncertainty of $\pm 1\ cm\cdot s^{-1}$. The temperature was stable to within ±0.01 K.

Table 1. Experimental Kinematic Viscosities, Densities, and Speeds of Sound for Nitromethane (NME-h_3) and Deuterated Nitromethane (NME-d_3)

	$10^{-6}\ \nu/m^2\cdot s^{-1}$		$\rho/g\cdot cm^{-3}$		$u/m\cdot s^{-1}$	
T/K	NME-h_3	NME-d_3	NME-h_3	NME-d_3	NME-h_3	NME-d_3
293.15	0.601	0.605	1.13721	1.19474	1337.6	1291.1
295.15	0.577	0.581	1.13314	1.19043	1329.5	1283.2
298.15	0.562	0.570	1.13042	1.18771	1317.4	1271.3
300.15	0.547	0.549	1.12755	1.18473	1309.4	1263.3
303.15	0.525	0.526	1.12349	1.18186	1297.3	1251.4
305.15	0.510	0.513	1.12082	1.17830	1289.2	1243.5
308.15	0.489	0.492	1.11654	1.17328	1277.1	1231.6

The densities, viscosities, and speeds of sound of pure liquids and their deuterated forms were measured in the temperature range of 293 K to 308 K and at $T - T_c = 0.04$ K and 5.04 K for binary mixtures of nitromethane and pentanol. For comparison purposes, additional measurements were performed at 303.15 K and $x = 0.5$ for all systems studied.

Results and Discussion

Pure Liquids. The measured densities, kinematic viscosities, and speeds of sound of pure liquids for selected temperatures are collected in Tables 1 and 2. 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),

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Table 2. Experimental Kinematic Viscosities, Densities, and Speeds of Sound for 1-Pentanol (PENT-*h*) and 1-Pentanol-d_1 (PENT-*d*)

	$10^{-6}\ \nu$/m^2·s^{-1}		ρ/g·cm^{-3}		u/m·s^{-1}	
T/K	PENT-*h*	PENT-*d*	PENT-*h*	PENT-*d*	PENT-*h*	PENT-*d*
293.15	4.964	4.992	0.81509	0.82169	1290.7	1282.3
295.15	4.444	4.458	0.81274	0.81950	1282.1	1273.7
298.15	4.223	4.238	0.81140	0.81804	1273.6	1265.1
300.15	3.942	3.969	0.80972	0.81642	1266.7	1258.3
303.15	3.635	3.685	0.80741	0.81424	1256.4	1248.5
305.15	3.450	3.456	0.80578	0.81310	1249.4	1241.1
308.15	3.129	3.148	0.80371	0.81047	1239.3	1230.8

Table 3. Comparison of the Measured Properties of Pure Liquids with the Literature Data

	nitromethane, $T = 298.15$ K		1-pentanol, $T = 303.15$ K	
properties	this work	literature	this work	literature
ρ/g·cm^{-3}	1.13042	1.12958[a] 1.13128[b]	0.80741	0.8072[f] 0.8076[g]
η/mPa·s	0.590	0.615[c] 0.591[d]	2.933	3.056[g]
$10^{-3}\alpha_p$/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/m·s^{-1}	1297.29 ($T = 303.15$ K)	1302[e] ($T = 303.15$ K)	1256.45	1256[f] 1258[j]

[a] Reference 3. [b] Reference 13. [c] Reference 2. [d] Reference 7. [e] Reference 14. [f] Reference 15. [g] Reference 16. [h] Reference 17. [i] Reference 18. [j] Reference 19.

Table 4. Deuterium Isotope Effect $\Delta X = [(X_D - X_H)/X_H]$ on Selected Thermodynamic Property X at 303.15 K

	$10^2\Delta X$	
property (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 expansivity, 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

[a] Reference 7. [b] Reference 8.

Table 5. Experimental Densities, Dynamic Viscosities, and Speeds of Sound for Nitromethane-h_3(1) + 1-Pentanol-*h*(2)

x_1	$T - T_c =$ 5.04 K	$T - T_c =$ 0.04 K	x_1	$T - T_c =$ 5.04 K	$T - T_c =$ 0.04 K
		ρ/g·cm^{-3}			
0.000	0.80517	0.80896	0.540	0.91583	0.92098
0.065	0.81514	0.81889	0.616	0.93900	0.94427
0.127	0.82447	0.82849	0.699	0.96799	0.97370
0.186	0.83467	0.83883	0.753	0.98794	0.99405
0.260	0.84861	0.85295	0.802	1.01021	1.01676
0.310	0.85874	0.86338	0.911	1.06452	1.07091
0.398	0.87850	0.88330	1.000	1.11936	1.12624
0.503	0.90513	0.91030			
		η/mPa·s			
0.000	2.6863	3.1133	0.620	0.7854	0.9425
0.113	2.0093	2.3790	0.752	0.6945	0.7812
0.203	1.7439	2.1194	0.801	0.6634	0.7348
0.314	1.4731	1.7431	0.824	0.6288	0.6790
0.398	1.2818	1.4874	0.849	0.6161	0.6730
0.469	1.0929	1.2312	0.934	0.5661	0.6149
0.516	0.9447	1.1112	1.000	0.5636	0.6091
		u/m·s^{-1}			
0.000	1246.17	1263.31	0.619	1226.62	1243.90
0.099	1240.61	1258.09	0.701	1230.23	1247.05
0.202	1234.60	1252.12	0.802	1241.71	1258.87
0.302	1230.61	1248.35	0.902	1262.13	1281.18
0.401	1227.73	1245.43	1.000	1285.19	1305.35
0.502	1225.51	1242.71			

Table 6. Experimental Densities and Dynamic Viscosities for Nitromethane-d_3(1) + 1-Pentanol-*h*(2)

x_1	$T - T_c =$ 5.04 K	$T - T_c =$ 0.04 K	x_1	$T - T_c =$ 5.04 K	$T - T_c =$ 0.04 K
		ρ/g·cm^{-3}			
0.000	0.80376	0.80733	0.615	0.96050	0.96620
0.080	0.81905	0.82307	0.669	0.98216	0.98830
0.178	0.83892	0.84308	0.749	1.01846	1.02462
0.245	0.85380	0.85821	0.860	1.07790	1.08442
0.351	0.87840	0.88303	0.959	1.14239	1.14988
0.401	0.89153	0.89626	1.000	1.17208	1.18003
0.490	0.91760	0.92260			
		η/mPa·s			
0.000	2.5703	2.9969	0.615	0.8939	1.0330
0.103	2.1580	2.4598	0.644	0.8578	1.0264
0.206	1.8198	2.1598	0.758	0.7064	0.7821
0.302	1.5169	1.7957	0.801	0.6878	0.7859
0.418	1.2512	1.4471	0.904	0.5971	0.6496
0.502	1.0770	1.2404	1.000	0.5819	0.6274
0.598	0.9159	1.0691			

the isobaric thermal expansivity (α_p), the isentropic compressibility (κ_S), and dynamic viscosity (η). The calculated values are related to the density, speed of sound, and kinematic viscosity by

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

$$\kappa_S = \frac{1}{u^2\rho} \tag{2}$$

$$\eta = \nu\rho \tag{3}$$

The results obtained presently agree satisfactorily well with previously reported data (Table 3). Table 4 summarizes the isotope effects on several thermodynamic properties studied for selected temperature 303 K. Whenever possible, we include for comparison the results obtained by Rabinovich[7] and Holz et al.[8] As can be seen in those few possible cases, the results presently obtained agree well with those reported in the literature except for the values of the isotope effect on the isobaric thermal expansivity. 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. The isotope effects on the molar volume are very close to the literature values. From a qualitative perspective, the observed sign of the isotope effect on the molar volume is as predicted.[7] A simple core-size analysis tells us that the molecular volume of nitromethane-h_3 is expected to be slightly greater than that of nitromethane-d_3 because anharmonicity, combined with higher internal vibrational frequencies for the lighter molecule, leads to greater vibrational amplitudes of the C−H stretching modes compared to those of the C−D modes. However, the isotope effect on the mass density is basically a consequence of the molar mass difference between isotopomers (nitromethane-h_3, 61.04×10^{-3} kg·mol^{-1}; nitromethane-d_3, 64.06×10^{-3} kg·mol^{-1}). In the case of substances that are able to form hydrogen bonds, the opposite effect is expected, and indeed for water and alcohols, molar volumes for deuterated species are slightly higher. The same trend is observed for pentanol. Viscosity isotope effects agree well with those reported by Rabinovich[7] and Holz et al.[8] The isotope substitution does not affect the kinematic viscosity of nitromethane significantly, and the resulting isotope effect on the dynamic viscosity is primarily due to the isotope effect on density. Thus, the

Table 7. Experimental Densities and Dynamic Viscosities for Nitromethane-h_3(1) + 1-Pentanol-d_1(2)

x_1	$T - T_c =$ 5.04 K	$T - T_c =$ 0.04 K	x_1	$T - T_c =$ 5.04 K	$T - T_c =$ 0.04 K
		ρ/g·cm^{-3}			
0.000	0.81188	0.81563	0.551	0.91749	0.92064
0.070	0.82185	0.82573	0.651	0.95015	0.95406
0.154	0.83521	0.83937	0.740	0.98356	0.98943
0.231	0.84781	0.85209	0.847	1.03112	1.03727
0.298	0.85810	0.86250	0.946	1.08388	1.09050
0.385	0.87380	0.87949	1.000	1.11915	1.12604
0.503	0.90401	0.90693			
		η/mPa·s			
0.000	2.6851	3.1177	0.623	0.8782	1.0036
0.106	2.1864	2.4654	0.679	0.7937	0.9207
0.245	1.6784	1.9365	0.718	0.7290	0.8419
0.386	1.3186	1.4966	0.749	0.6974	0.7878
0.508	1.0663	1.1606	0.774	0.6734	0.7451
0.555	0.9975	1.0973	1.000	0.5623	0.6074

viscous flow is almost independent of deuterium substitution. The speed of sound and isentropic compressibility are strongly dependent on isotope substitution, and it is again the density that makes the major contribution.

Binary Mixtures. All measurements have been carried out at temperatures above the UCST.[5] The experimental densities and dynamic viscosities for binary solutions of nitromethane + 1-pentanol (T_c = 301.11 K), nitromethane-d_3 + 1-pentanol (T_c = 302.46 K), and nitromethane + 1-pentanol-d_1 (T_c = 301.26 K) are given in Tables 5 to 7. The speed of sound was measured for nondeuterated mixtures (nitromethane + 1-pentanol system) only, and the results are listed in Table 5. Figure 1 shows that the speed of sound as a function of composition exhibits a pronounced minimum, whereas the isentropic compressibility shows only a positive deviation from linearity at two selected temperatures (Figure 2). No anomaly was detected even for temperatures in the immediate vicinity of the critical point ($T_c - T$ = 0.04 K). However, a closer examination of the behavior of the speed of sound at the critical concentration (x_1 = 0.617) reveals a sharp change in the speed of sound while entering the two-phase region (Figure 3). It occurs at temperature T = 301.15 K, which is very close to the critical temperature determined previously[5] by the precise light-scattering experiments. Recently, Cerderiña et al.[3] reported a small anomaly in the density of nitromethane + 1-butanol mixtures approaching the critical region. We were unable to detect any anomaly in the immediate vicinity of the critical demixing. It is possible that the precision of our measurements is too low to detect such a subtle effect.

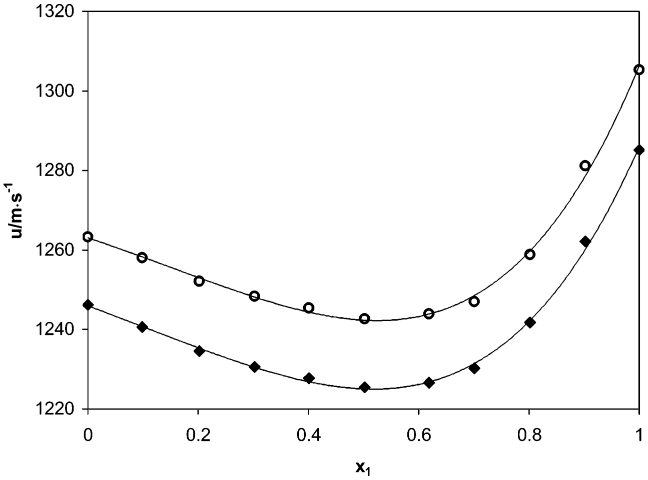

Figure 1. Concentration dependence of the speed of sound for the nitromethane(1) + 1-pentanol(2) system: ○, at $T - T_c$ = 0.04 K; ◆, at $T - T_c$ = 5.04 K.

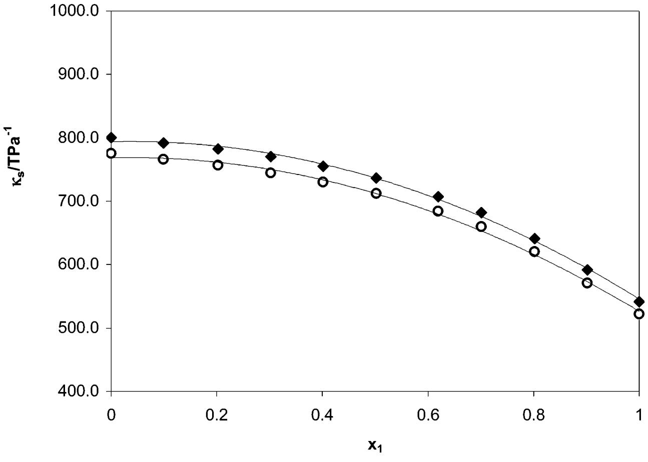

Figure 2. Concentration dependence of the isentropic compressibility for the nitromethane(1) + 1-pentanol(2) system: ○, at $T - T_c$ = 0.04 K; ◆, at $T - T_c$ = 5.04 K.

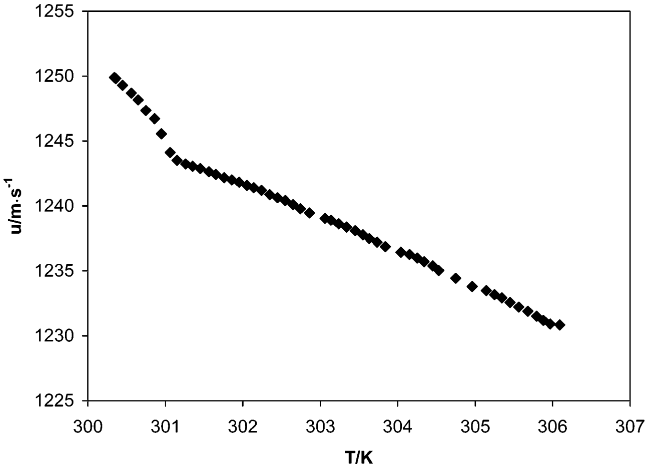

Figure 3. Temperature dependence of the speed of sound (u) for the nitromethane(1) + 1-pentanol(2) system at the critical concentration x = 0.617.

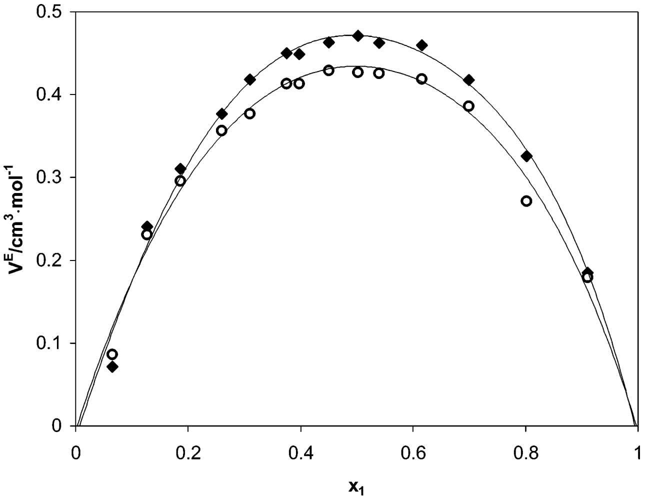

Figure 4. Excess volumes of the nitromethane(1) + 1-pentanol(2) system: ○, at $T - T_c$ = 0.04 K; ◆, at $T - T_c$ = 5.04 K.

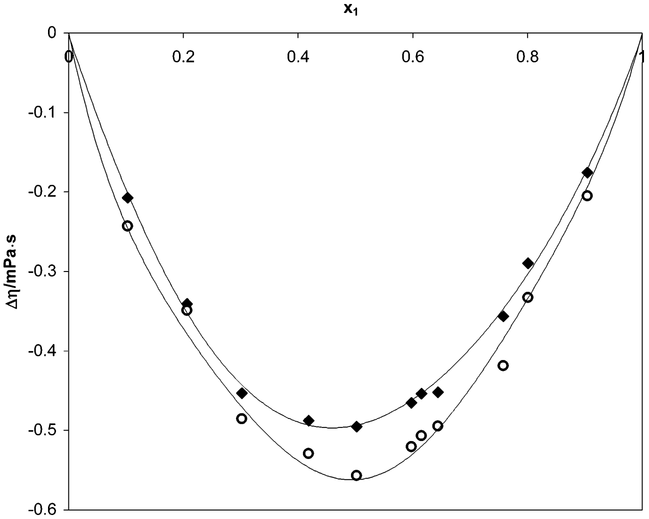

Figure 5. Viscosity deviations of the nitromethane(1) + 1-pentanol(2) system: ○, at $T - T_c = 0.04$ K; ◆, at $T - T_c = 5.04$ K.

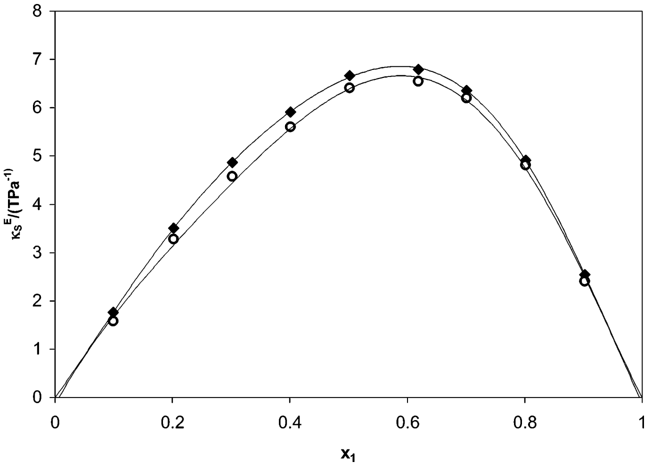

Figure 6. Excess isentropic compressibility of the nitromethane(1) + 1-pentanol(2) system: ○, at $T - T_c = 0.04$ K; ◆, at $T - T_c = 5.04$ K.

The excess molar volumes V^E and viscosity deviations $\Delta\eta$ were calculated from the experimental data according to the following equations

$$V^E = V_m - \sum x_i V^*_i \tag{4}$$

$$\Delta\eta = \eta_m - \sum x_i \eta^*_i \tag{5}$$

where x_i, V^*_i, and η^*_i are the mole fraction, molar volume, and viscosity of the ith pure component, respectively. V_m and η_m are the molar volume and the viscosity of the mixture, respectively. The molar volume of the mixture was calculated from the equation

$$V_m = \sum \frac{x_i M_i}{\rho_m} \tag{6}$$

where ρ_m is the mixture density and M_i is the molecular weight of component i in the mixture.

The excess isentropic compressibility was calculated using the ideality criterion of Benson and Kiyohara:[9]

$$\kappa_S^{id} = \kappa_T^{id} - \frac{T V_m^{id} (\alpha_p^{id})^2}{c_p^{id}} \tag{7}$$

where

$$\kappa_T^{id} = \sum \phi_i \kappa^*_{T,i} \tag{8}$$

$$\kappa_T = \kappa_S + \frac{T V_m \alpha_p^2}{c_p} \tag{9}$$

$$\alpha_p^{id} = \sum \phi_i \alpha^*_i \tag{10}$$

$$c_p^{id} = \sum x_i c^*_{p,i} \tag{11}$$

ϕ_i, κ_T, α_p, and c_p represent the volume fraction, isothermal compressibility, isobaric thermal expansion coefficient, and isobaric heat capacity, respectively, and the superscript * indicates the respective properties of pure component i. c_p^* and α_p^* of pure components needed to calculate κ_T values are taken from the literature.[3,10]

The results thus obtained for the different excess quantities and viscosity deviations for nitromethane + 1-pentanol mixtures at temperatures $T - T_c = 0.04$ K and 5.04 K are shown in Figures 4 to 6, where solid lines correspond to fitting polynomials of the Redlich−Kister type:

$$Y^E = x_1(1 - x_1) \sum A_i (2x_1 - 1)^i \tag{12}$$

The fitting parameters are listed in Table 8.

As can be seen in Figure 4, the V^E values are positive over the whole concentration range. No anomalies are seen in the neighborhood of the UCST, and this behavior is compatible with the existing literature data.[3] The visible difference between V^E for $T - T_c = 5.04$ K and 0.04 K is related rather to the changing temperature itself than to the influence of the criticality. Comparing the presently

Table 8. Redlich−Kister Parameters for the Nitromethane(1) + 1-Pentanol(2) System

	NME-h_3 + PENT-h			NME-d_3 + PENT-h		NME-h_3 + PENT-d_1	
	V^E/cm^3·mol^{-1}	$\Delta\eta$/mPa·s	κ^E/TPa^{-1}	V^E/cm^3·mol^{-1}	$\Delta\eta$/mPa·s	V^E/cm^3·mol^{-1}	$\Delta\eta$/mPa·s
				$T - T_c = 5.04$ K			
A_4	−0.8811	−3.8975	−9.695	0.6619	−0.2843	0.6018	1.384
A_3	−0.2859	−2.7677	6.8104	0.4633	0.2651	0.0963	−4.3193
A_2	0.8488	1.0678	2.8326	−2.4832	−0.0013	−1.2467	−5.4835
A_1	0.0192	0.1723	−10.0869	−1.1471	−0.3073	−0.8894	−1.6197
A_0	1.8092	−2.4505	26.4974	2.0593	−1.9816	1.85152	−2.1855
σ	0.016	0.012	0.02	0.017	0.009	0.023	0.004
				$T - T_c = 0.04$ K			
A_4	−0.4344	−3.891	−12.8666	0.6678	−3.0186	0.4564	−1.3489
A_3	−0.0587	−2.3355	7.5058	−0.2758	−0.1255	0.2272	0.2134
A_2	0.6044	1.0113	4.0848	−2.5262	1.1781	−1.8432	2.4919
A_1	0.0092	0.1091	−10.923	−1.0088	−0.2261	−1.4564	−0.8047
A_0	1.7266	−2.6651	25.3542	1.9242	−2.2423	1.8198	−2.3544
σ	0.019	0.006	0.04	0.021	0.028	0.034	0.003

Table 9. Isotope Effects on Excess Volumes and Deviations of Viscosity and Isentropic Compressibilities at $X = 0.5$ and $T = 303.15$ K

	V^E/cm^3·mol^{-1}	$\Delta\eta$/mPa·s	$\Delta\kappa_S$/TPa^{-1}
NME-h_3 + PENT-h	0.453	−0.582	6.64
NME-d_3 + PENT-h	0.459	−0.567	6.53
NME-h_3 + PENT-d	0.458	−0.572	6.50

obtained values with the previously published data,[2] we can observe a visible trend in V^E with the length of the chain in alcohols (i.e., at $T = 303.15$ K and $x = 0.5$, V^E changes from 0.28 cm^3·mol^{-1} for 1-propanol through 0.35 for 1-butanol to 0.45 for 1-pentanol). It is worth mentioning that for methanol solutions the excess molar volume is negative.[2] The behavior of the excess volume for the nitromethane + 1-pentanol mixture may be attributed to the disruption of the hydrogen-bonded alcohol by aprotic nitromethane. In comparison to methanol, 1-pentanol forms much weaker hydrogen bonds.

The results for $\Delta\eta$ are represented graphically in Figure 5. As can be seen, $\Delta\eta$ values are negative. Similar behavior was observed for mixtures of nitromethane with lower alcohols.[2] A clear trend in $\Delta\eta$ is seen, namely, the values decrease with increasing size of the alcohol molecule. At 303.15 K and $x = 0.5$, $\Delta\eta$ is equal to −0.12 mPa·s, −0.23 mPa·s, −0.45 mPa·s, and −0.58 mPa·s for methanol, ethanol, 1-propanol, and 1-pentanol, respectively.

Concentration dependences of κ_S^E are shown in Figure 6. As can be seen, κ_S^E is always positive, thus it has the same sign as V^E, and it is the most frequently observed case. The positive values of κ_S^E and V^E are easily explainable; namely, an expansion in volume (which is due to the breaking of hydrogen bonds during the mixing process) makes the mixture more compressible than the ideal mixture, which ultimately culminates in positive values of both κ_S^E and V^E.

As can be seen in Table 4, the effect of isotope substitution on various properties of pure liquids is visible in most cases. In the case of solutions, these changes are less visible; only the miscibility changes markedly.[5] Table 9 summarizes the values of the excess quantities or deviations from linearity at $x = 0.5$ and at 303.15 K. In all cases listed here, the isotope effects are of the order of 1 %; however, the directions of change are different. V^E becomes more positive on deuteration. Its direction and magnitude are compatible with those for the cyclohexane + benzene/benzene-d_6 system reported by Dutta-Choudhury et al.[11] They found that V^E for the deuterated system is about 1% more positive than that for the protiated one. However, Marczak[12] reported a negative excess molar volume for the 3-methylpyridine + H_2O system and found that it became even more negative for 3-methylpyridine + D_2O. The isotope shift of V^E at $x = 0.5$ reaches almost 5 %. The deviations in viscosity are less negative and the compressibility deviations (calculated as $\Delta\kappa_S = \kappa_S - \Sigma\phi_i\kappa^*_{S,i}$) are more positive upon deuteration. In both cases, the isotope shifts are relatively small. Unfortunately, no data are available for comparison.

Conclusions

It was shown that isotope substitution visibly affects the physicochemical properties of pure liquids and to a lesser extent their solutions. In particular, multiple deuterium substitution in nitromethane generates large isotope effects on density, speed of sound, and dynamic viscosity. A much smaller isotope effect is observed for 1-pentanol. The excess quantities correlate well with those reported earlier for nitromethane−lower alcohols mixtures. No detectable influence of the critical conditions on the thermodynamic properties has been observed.

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