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Deuterium Isotope Effects on Miscibility Curves of Nitromethane + Pentanol and Nitromethane + Isobutanol

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The miscibility of nitromethane with pentanol and isobutanol and the influence of deuterium substitution over a broad concentration range have been reported. The miscibility results enable the construction of the phase diagrams for eight systems. It appears that deuteration both in the OH group of alcohol and/or the methyl group of nitromethane increases the domain of the limited miscibility, and the isotope shift of the upper critical solution temperature ranges from 0.15 K for deuterated alcohols to 1.38 K for deuterated nitromethane + regular isobutanol system. The phase diagrams can be described by using a scaling equation with a critical exponent β close to the predicted one and practically independent of the isotope substitution. The good description of the system was also obtained by using the classical equations based on the mean-field theory.

The recent experimental study of the influence of H/D isotope substitution on the miscibility of acetonitrile with water revealed interesting behavior (Hürth and Woermann, 1987; Szydlowski and Szykula, 1999). Contrary to the predicted decrease of the domain of immiscibility in the case of deuteration of the methyl group, an increase of this domain was observed. According to the Rabinovich theory (Rabinovich, 1970), the replacement of the hydrogen atom involved in the hydrogen bonding by deuterium should generate the upward shift of the upper critical solution temperature (UCST)—thus it should increase the immiscibility gap. On the other hand the substitution of the hydrogen atom not involved actively in the hydrogen bonding is supposed to decrease the UCST and reduce the domain of the limited miscibility. From this point of view, the results obtained recently are very intriguing and some doubts appear about whether the Rabinovich approach, which works in the case of deuterium substitution in water, can cope with more general cases. In a recent paper we explained the results obtained in terms of the inter- and intramolecular interactions not taken into account by Rabinovich. We emphasized there the very strong dipole−dipole interaction between acetonitrile molecules and the vibrational coupling between CH stretching modes and N···O···H hydrogen bridge. To gain additional evidence supporting our explanation, we decided to extend the miscibility study to nitromethane mixtures with some alcohols. Nitromethane and acetonitrile seem to have something in common: in both cases the small methyl group is bonded with a strongly polar group, −CN or $-NO_2$. Both molecules have very high dipole moments (4.40 D for acetonitrile (Sato et al., 1978) and 3.54 D for nitromethane (Groves and Sugden, 1937)), and consequently in both cases strong dipole−dipole interactions are predominant. In the present study nitromethane + pentanol and nitromethane + isobutanol were selected because of their convenient upper critical solution temperatures. There are some older data (Francis, 1961) in the literature placing the critical temperatures for nitromethane + pentanol and nitromethane + isobutanol systems at 294.15 K and 290.15 K, respectively. However no phase diagrams have been reported so far.

Experimental Section

Nitromethane (Aldrich) was carefully purified by column distillation. The purity of the collected fraction (bp, 374.2 K) was at least 99.95% as checked by GLC/MS analysis. Nitromethane-d_3 (from Aldrich) was twice distilled. Both nitromethanes were carefully dried over 5 Å molecular sieves. Isobutanol and pentanol (Aldrich) were distilled, and fractions collected at 381.1 K and 410.2 K, respectively, were dried over molecular sieves. Deuterated pentanol and isobutanol were synthesized in a triple exchange reaction with D_2O (99.96% D). Water was removed by distillation. The main fractions were dried over $CaCl_2$ and then over molecular sieves and redistilled to remove any trace of moisture. NMR analysis showed at least 98 ± 1% D. 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.

The samples for the miscibility measurements were prepared gravimetrically. The accuracy of weighing was ±0.0001 g; hence the accuracy of the mole fraction was estimated to be better than ±0.001. Special care was undertaken to avoid moisture in the alcohols. The apparatus and technique were essentially similar to those described earlier (Szydlowski et al., 1992; Szydlowski and Szykula, 1999) with minor modifications only. The samples were placed in a thermostated cell equipped with inlet and outlet fiber optic cables. The pressure was kept constant at 0.1 MPa as measured by a Heisse 710A digital indicator. The temperature was measured by using an RTD probe (100 Ω of Omega Engineering calibrated against IPTS-68 traceable to NBS) with a precision of ±2 mK. The phase transition was detected by the loss of the transmitted light intensity from a 5 mW Polythec HeNe laser shining through the fiber optic cables and the cell and detected by a photodiode. The temperature was changed slowly at the rate of <0.01 K/min. No detectable influence of the rate on the transition temperature was found up to 0.1 K/min.

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Table 1. Experimental Liquid−Liquid Miscibility Data for Nitromethane (1) + Pentanol (2) and Their Deuterated Forms[a]

NME + PENT		NME-*d* + PENT		NME + PENT-*d*		NME-d + PENT-*d*	
x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
0.365	297.28	0.357	298.11	0.412	298.92	0.398	300.03
0.395	298.41	0.398	299.83	0.463	300.32	0.437	301.05
0.431	299.39	0.431	300.83	0.502	300.84	0.473	301.81
0.458	300.00	0.468	301.55	0.541	301.14	0.498	302.25
0.490	300.47	0.500	302.02	0.583	301.27	0.526	302.45
0.511	300.70	0.526	302.31	0.625	301.26	0.564	302.58
0.524	300.84	0.584	302.46	0.649	301.25	0.601	302.61
0.540	300.91	0.616	302.49	0.680	301.20	0.632	302.62
0.570	301.04	0.632	302.48	0.705	301.11	0.656	302.56
0.604	301.11	0.650	302.43	0.726	300.92	0.668	302.52
0.630	301.11	0.675	302.37	0.740	300.62	0.671	302.51
0.644	301.12	0.693	302.25	0.786	299.47	0.701	302.36
0.647	301.09	0.716	302.09	0.821	298.04	0.717	302.22
0.652	301.09	0.750	301.81	0.730	302.14		
0.665	301.09	0.771	301.35	0.773	301.25		
0.675	301.06	0.790	300.86	0.807	299.27		
0.691	300.98	0.813	299.62				
0.716	300.92	0.835	297.93				
0.742	300.65						
0.760	300.26						
0.793	299.23						
0.823	297.51						

[a] x_1 is the mole fraction of nitromethane. NME and PENT denote nitromethane and pentanol, respectively; *d* refers to the deuterated form.

Table 2. Experimental Liquid−Liquid Miscibility Data for Nitromethane (1) + Isobutanol (2) and Their Deuterated Forms[a]

NME + ISOBU		NME-*d* + ISOBU		NME + ISOBU-*d*		NME-*d* + ISOBU-*d*	
x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
0.335	288.98	0.280	287.71	0.336	289.11	0.345	290.43
0.355	289.37	0.333	289.51	0.411	290.72	0.432	292.09
0.397	290.32	0.382	291.25	0.438	291.18	0.463	292.40
0.413	290.75	0.414	292.01	0.469	291.45	0.495	292.59
0.429	290.95	0.460	292.24	0.495	291.60	0.536	292.65
0.440	291.10	0.487	292.42	0.538	291.66	0.585	292.75
0.480	291.40	0.520	292.57	0.573	291.67	0.632	292.60
0.493	291.44	0.559	292.56	0.605	291.63	0.652	292.44
0.523	291.53	0.603	292.53	0.632	291.46	0.674	292.34
0.535	291.51	0.632	292.43	0.660	291.29	0.714	291.90
0.574	291.52	0.660	292.35	0.680	291.12	0.753	290.71
0.586	291.49	0.687	292.03	0.710	290.53	0.817	288.67
0.615	291.41	0.735	290.97	0.760	289.29		
0.654	291.19	0.755	290.43				
0.663	291.07	0.782	289.22				
0.677	290.91						
0.700	290.69						
0.726	290.28						
0.743	289.69						
0.781	288.21						

[a] x_1 is the mole fraction of nitromethane. NME and ISOBU denote nitromethane and isobutanol, respectively; *d* refers to the deuterated form.

The details of the procedure for the determination of the transition temperatures with accuracy better than 0.01 K were given previously (Szydlowski and Szykula, 1999).

Results and Discussion

The experimental values of the liquid−liquid miscibility temperatures as a function of composition x for the binary systems of nitromethane with isobutanol and pentanol are listed in Tables 1 and 2 and displayed graphically in Figures 1 and 2.

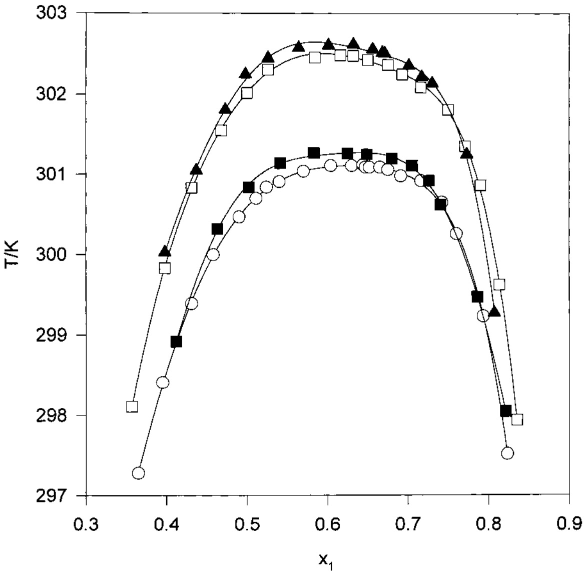

Figure 1. Phase diagrams for variously deuterated nitromethane + pentanol systems: ○, NME(h) + PENT(h); ■, NME(h) + PENT(d); □, NME(d) + PENT(h); ▲, NME(d) + PENT(d).

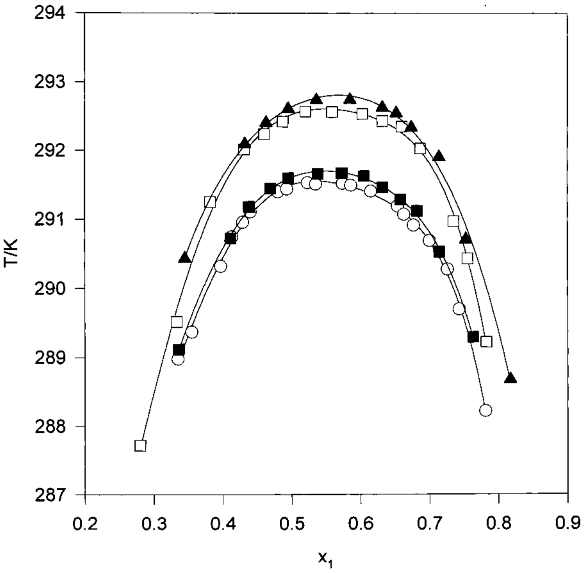

Figure 2. Phase diagrams for variously deuterated nitromethane + isobutanol systems: ○, NME(h) + ISOBU(h); ■, NME(h) + ISOBU(d); □, NME(d) + ISOBU(h); ▲, NME(d) + ISOBU(d).

The statistical analysis employed nonlinear least-squares fits based on the scaling equation with a skewing term (Wegner correction) to account for the asymmetry (Wilson, 1971; Greer, 1976; Singh and Van Hook, 1987)

$$x = x_c + A_1\left|1 - \frac{T}{T_c}\right|^{\beta}\left(1 + A_2\left|1 - \frac{T}{T_c}\right|^{0.5}\right) \qquad (1)$$

In the above equations x and T are mole fractions of nitromethane and temperature, x_c and T_c are the appropriate critical values, and A_1, A_2, and β are the critical amplitudes and critical exponent, respectively. The results of the analysis are listed in Table 3.

An alternative approach of the evaluation of the experimental data making use of the mean-field concept was proposed by Singh and Van Hook (1987). Adopting their procedure, the simplest representation for the excess free energy in a solution will be a one-term Redlich−Kister expansion, $G^E = B(x - x^2)$, defining the regular mixtures.

Table 3. Critical Parameters from Scaling Equation (Equation 1) for Nitromethane (1) + Pentanol(2) and Nitromethane (1) + Isobutanol (2) Systems[a]

	NME + PENT	NME + PENT-*d*	NME-d_3 + PENT	NME-d_3 + PENT-*d*	NME + ISOBU	NME + ISOBU-*d*	NME-d_3 + ISOBU	NME-d_3 + ISOBU-*d*
$x_{1,c}$	0.617 ± 0.002	0.614 ± 0.002	0.614 ± 0.003	0.606 ± 0.002	0.553 ± 0.001	0.555 ± 0.002	0.556 ± 0.003	0.563 ± 0.003
T_c/K	301.11 ± 0.002	301.26 ± 0.029	302.46 ± 0.004	302.60 ± 0.002	291.52 ± 0.001	291.67 ± 0.003	292.57 ± 0.001	292.70 ± 0.004
β	0.344 ± 0.011	0.312 ± 0.017	0.347 ± 0.017	0.325 ± 0.016	0.365 ± 0.008	0.378 ± 0.012	0.338 ± 0.012	0.368 ± 0.016
A_1	0.470 ± 0.016	0.427 ± 0.099	0.492 ± 0.024	0.438 ± 0.048	0.439 ± 0.011	0.458 ± 0.017	0.420 ± 0.013	0.486 ± 0.024
A_2	-0.278 ± 0.057	-0.647 ± 0.42	-0.169 ± 0.027	-0.269 ± 0.15	-0.063 ± 0.038	-0.3338 ± 0.06	-0.114 ± 0.050	-0.161 ± 0.07
$\sigma^2 \times 10^5$	4.21	9.94	7.65	2.5	3.04	1.69	3.27	3.24

[a] NME, PENT, and ISOBU denote nitromethane, pentanol, and isobutanol, respectively; *d* refers to the deuterated form.

Table 4. Fitting Parameters for Equation 3 for Nitromethane (1) + Pentanol (2) and Nitromethane (1) + Isobutanol (2) Systems[a]

	NME + PENT	NME + PENT-*d*	NME-d_3 + PENT	NME-d_3 + PENT-*d*	NME + ISOBU	NME + ISOBU-*d*	NME-d_3 + ISOBU	NME-d_3 + ISOBU-*d*
$a \times 10^3$	10.5 ± 0.6	19.2 ± 0.2	$13.8 \pm 0.\ 3$	12.0 ± 0.4	15.6 ± 0.6	14.0 ± 0.3	15.9 ± 0.6	13.7 ± 0.2
$B_1/(\mathrm{J \cdot mol^{-1}})$	5384.1 ± 15.4	5760.2 ± 42.6	5822.6 ± 10.4	5731.5 ± 5.7	5643.4 ± 6.7	5622.1 ± 9.1	5663.0 ± 8.9	5695.5 ± 25.5
$B_2/(\mathrm{J \cdot mol^{-1}})$	1523.8 ± 31.0	1989.4 ± 61.0	2046.7 ± 14.1	1928.1 ± 7.4	2085.4 ± 15.9	2040.3 ± 19.1	2105.1 ± 17.5	2151.7 ± 59.6
$B_3/(\mathrm{J \cdot mol^{-1}})$	386.3 ± 10.3	486.6 ± 2.36	477.4 ± 1.34	460.4 ± 1.6	645.1 ± 2.2	624.6 ± 3.2	630.8 ± 3.5	621.3 ± 5.7
$\sigma^2 \times 10^4$	6.31	11.4	3.76	1.82	8.33	2.54	7.85	2.78

[a] NME, PENT, and ISOBU denote nitromethane, pentanol, and isobutanol, respectively; *d* refers to the deuterated form.

Table 5. Fitting Coeficients of Equation 4 for Nitromethane (1) + Pentanol (2) and Nitromethane (1) + Isobutanol (2) Systems

	NME + PENT	NME + PENT-*d*	NME-d_3 + PENT	NME-d_3 + PENT-*d*	NME + ISOBU	NME + ISOBU-*d*	NME-d_3 + ISOBU	NME-d_3 + ISOBU-*d*
$\varphi = x_{1,C}$	0.625 ± 0.006	0.634 ± 0.006	0.625 ± 0.001	0.613 ± 0.001	0.562 ± 0.001	0.563 ± 0.001	0.566 ± 0.001	0.567 ± 0.002
$\tau_0 = T_c$/K	301.11 ± 0.02	301.22 ± 0.03	302.46 ± 0.03	302.59 ± 0.02	291.53 ± 0.04	291.67 ± 0.03	292.54 ± 0.04	292.67 ± 0.04
τ_1/K	-0.152 ± 0.1	-3.301 ± 1.17	-5.013 ± 1.56	-4.188 ± 1.42	-6.307 ± 1.97	-5.349 ± 2.38	-1.69 ± 1.7	-2.665 ± 1.82
τ_2/K	-159.7 ± 27.3	-67.38 ± 13.6	-36.35 ± 16.1	-107.9 ± 18.1	-45.29 ± 24.1	-70.97 ± 37.04	-95.18 ± 15.81	-81.9 ± 16.2
τ_3/K	53.01 ± 4.04	61.9 ± 6.2	54.09 ± 4.4	417.6 ± 112	29.79 ± 7.68	154.1 ± 13.7	151.4 ± 36.7	153.9 ± 36.7
$\sigma^2 \times 10^3$	2.14	14.2	3.33	0.68	4.92	1.90	4.08	2.72

[a] NME, PENT, and ISOBU denote nitromethane, pentanol, and isobutanol, respectively; *d* refers to the deuterated form.

This gives a coexistence curve that is parabolic and centered at $x_c = 0.5$ with $T_c = B/2R$. However, in the present case due to a slight asymmetry, a three-term expansion has to be used:

$$G^E = (x - x^2)[B_1 + B_2(1 - 2x) + B_3(1 - 2x)^2 + ...] \quad (2)$$

The application of the coexistence conditions $(\delta G/\delta x)_{x'} = (\delta G/\delta x)_{x''}$ gives an expression for the coexistence curve:

$$RT \ln\left(\frac{x'}{x''}\right)^2 = 2B_1(x' - x'') + 6B_2[(x' - x'') - ((x')^2 - (x'')^2)] + 2B_3[5(x' - x'') - ((x')^2 - (x'')^2) + 8((x')^3 - (x'')^3)] \quad (3)$$

where x' and x'' are the compositions of the coexisting phases.

The coexistence data for all systems studied have been fitted to eq 3 using the least-squares analysis. In this process $x' = 2x_c + a(T_c - T) - x''$ to account for the nonsymmetrical shape of the curve around x_c; a is a fitting parameter. To reduce the dimensionality T_c and x_c from Table 3 were taken as the fixed values. The parameters of this fitting to eq 3 are listed in Table 4. A somewhat similar approach was used by Cuevas et al. (1995) to analyze the miscibility data of some nitriles with selected hydrocarbons. In the present case we adopted the fitting equation in the form

$$T = \sum_{i=0}^{3} \tau_i \{[x/\varphi - (1 - x)/(1 - \varphi)]/[x/\varphi + (1 - x)/(1 - \varphi)]\}^{2i} \quad (4)$$

where T and x are experimental points, τ_i and φ are constants to be determined in the fitting procedure. It appears that τ_0 is analogous to the critical temperature, T_c, and φ corresponds to the critical concentration, x_c. Table 5 collects the appropriate fitting parameters. It is seen that the critical temperatures are close to those determined by the scaling equation; however, the critical concentrations show some disagreement.. To decide which equation is the better representation, the variances in T, $\sigma^2(T)$, were computed for all cases. Comparing these values given in Tables 3−5, it is seen that both representations based on the classical approach work comparably well; however, a preference of the scaling approach is apparent. This finding seems to correspond to the well-known fact that flat diagrams are better described by the scaling equations. Anyway, the results obtained show that the scaling approach works nicely even outside the Ginzburg limit, and, on the other hand, the classical approach can be reasonably adopted for the entire concentration range, including the points lying in the direct neighborhood of the critical concentration.

The data presented in Figures 1 and 2 show that the solubility curves represent the phase diagrams with the upper critical solution temperatures. From these results it is also seen that the deuteration noticeably influences the miscibility of nitromethane with both alcohols. Table 6 gives the appropriate isotopic shifts of the UCST. In all cases the replacement of hydrogen atoms by deuterium leads to the increase of the immiscibility domain. It is worth noting that the shape of the phase diagrams is almost the same in all cases. It means that H/D substitution does not influence the shape (width) of the coexistence curve. According to the expectation there is also no isotope

Table 6. Isotope Shifts of the UCST in Nitromethane (1) + Pentanol (2) and Nitromethane (1) + Isobutanol (2) Systems[a]

	ΔT_c/K = $T_{c,D} - T_{c,H}$	$\Delta T_c/T_c$/%
[NME + PENT-*d*]:[NME + PENT]	0.15	0.05
[NME-d_3 + PENT]:[NME + PENT]	1.05	0.36
[NME-d_3 + PENT-*d*]:[NME + PENT]	1.18	0.41
[NME-d_3 + PENT-*d*]:[NME + PENT-*d*]	1.03	0.35
[NME-d_3 + PENT-*d*]:[NME-d_3 + PENT]	0.13	0.04
[NME + ISOBU-*d*]:[NME + ISOBU]]	0.15	0.05
[NME-d_3 + ISOBU]:[NME + ISOBU]	1.38	0.46
[NME-d_3 + ISOBU-*d*]:[NME + ISOBU]	1.50	0.50
[NME-d_3 + ISOBU-*d*]:[NME + ISOBU-*d*]	1.35	0.45
[NME-d_3 + ISOBU-*d*]:[NME-d_3 + ISOBU]	0.12	0.04

[a] NME, PENT, and ISOBU denote nitromethane, pentanol, and isobutanol, respectively; *d* refers to the deuterated form.

effect on the critical concentration. The critical exponent does not depend on isotope substitution and is close to its limiting value predicted by the nonclassical theory ($\beta = 0.325 \pm 0.005$). A very small positive isotope shift of UCST, $\Delta T = T_{c,D} - T_{c,H} > 0$, for deuterated alcohols is compatible with Rabinovich theory and existing literature data (Rabinovich, 1970; Fenby et al., 1981; Schön et al., 1986). In fact it is much smaller than that reported for water or methanol mixtures; however, hydrogen bonding in alcohols being used presently is expected to be relatively weak, and this factor will predominantly determine the magnitude of the isotope effect. More interestingly, we note that deuteration of the methyl group in nitromethane brings about the appearance of the remarkable positive isotope shift of UCST. Hence, we meet here the situation similar to that observed for the acetonitrile + water system. It is then believed that in some special cases, i.e., for small molecules with a large permanent dipole moment, multiple deuterium replacement brings about the apparent changes of the dipole moment and consequently the increase of the dipole−dipole interactions. It becomes then clear that apart from the specific interactions, visualized by hydrogen bonding, and dispersion interactions considered by Rabinovich, for proper explanation of the miscibility isotope effects, another type of intermolecular interactions should be taken into account, too. Moreover in analogy to the previously discussed acetonitrile−water system (Szydlowski and Szykula, 1999), some intramolecular interaction, i.e., vibrational coupling, cannot be excluded; however, it is expected to be much smaller here because the hydrogen bonding between the NO_2 group of nitromethane and the OH group of the alcohols is expected to be significantly weaker than that between acetonitrile and water. Unfortunately no spectroscopic data on the systems studied are available.

Further studies on the miscibility isotope effects are in progress to clarify the role of various types of the intermolecular interactions.

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