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Miscibility Isotope Effect in Ethylene Glycol – Nitromethane System

by A. Milewska, A. Siporska and J. Szydłowski

Department of Chemistry, Warsaw University, Żwirki i Wigury 101, 02-089 Warsaw, Poland

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Recently an extensive study of the thermodynamic properties of ethylene glycol + nitromethane mixtures has been reported by Salvi and Van Hook [1]. Apart from the PVT properties of protio and deutrio ethylene glycols $(CH_2OH)_2$ and $(CH_2OD)_2$ they investigated H/D isotope effects on critical demixing in ethylene glycol/nitromethane solutions and found a moderate effect on the miscibility of ethylene glycol and nitromethane. This isotope shift in the upper critical solution temperature (UCST), equal to $\Delta T_c = T_c(D) - T_c(H) = 2.03$ K, means that deuteration of ethylene glycol in OH group makes the miscibility worse. This observation is compatible with the general Rabinovich approach [2], which states that deuteration in polar groups should worsen the miscibility, whereas the deuteration of nonpolar groups leads to an improvement of the miscibility. However, the recent results on binary mixtures involving deuterated nitromethane [3,4] revealed that in these cases the miscibility is worse as well. Therefore, we decided to extend the measurements on deuterated nitromethane/ethylene glycol system to verify this behaviour.

Nitromethane and glycol, both from (Aldrich) were carefully purified by column distillation at the reduced pressure. The purity of the collected fractions was at least 99.95%, as checked by GLC/MS analysis. Both nitromethane and glycol were carefully dried over 5A molecular sieves. Nitromethane-d_3 (99.92%D, Polatom, Poland) was used without further purification. The molecular sieves used for drying deuterated nitromethane were previously treated by D_2O. The samples for the miscibility measurements were prepared gravimetrically. The accuracy of weighing was ±0.0001g, hence the accuracy of the mole fraction was estimated to be better than ±0.001. Special care was undertaken to avoid moisture. The apparatus and technique were essentially similar to those described earlier [5]. The details of the procedure for the determination of the transition temperature with accuracy better than 0.01 K were given previously [6]. The experimental values of the liquid-liquid phase separation temperatures as a function of composition x for the binary system of nitromethane and deuterated nitromethane with ethylene glycol are given in Table 1. The statistical analysis employed non-linear least-squares fits based on the scaling equation:

$$|x - x_c| = A\, t^{\beta} \tag{1}$$

where $t = 1 - T/T_c$; x and T are mole fractions of nitromethane and temperature, x_c and T_c the corresponding critical values; A and β the critical amplitude and critical exponent, respectively. The results of the analysis are listed in Table 2. Analysis of Table 2 shows, that the critical temperature and critical concentration ($T_c = 313.04$ K and $x_c = 0.631$) are in excellent agreement with the results presented by Salvi and Van Hook ($T_c = 313.05$ and $x_c = 0.637$) [1]. The critical exponent obtained presently is close to the theoretically predicted value ($\beta = 0.325$). Let us note that β obtained by Salvi and Van Hook lies far away from this value (reported β is equal to 0.51) and the reason of this serious discrepancy may come from the relatively small set of experimental points, used by the previous authors to construct the phase diagram at 1 bar. The data, presented in Fig. 1, show that the solubility curves represent the phase diagrams with an upper critical solution temperature (UCST). From these results, it is also seen that deuteration of nitromethane influences the miscibility of nitromethane with ethylene glycol noticeably and the direction of the isotope shift of the UCST is the same as in the case of the deuteration of glycol. It is worth noting, that the shape of the phase diagrams is almost the same in both cases. This means, that H/D substitution does not influence the shape (width) of the coexistence curve. According to the expectation, there is also no isotope effect on the critical concentration. The critical exponent does not practically depend on isotope substitution either. The positive shift of UCST, $\Delta T = T_{c,D} - T_{c,H}$, means that deuteration of nitromethane makes the miscibility with glycol worse and this finding is not compatible with the Rabinovich theory [2], but it is consistent with the previous results from this laboratory [7,8]. Table 3 presents the comparison of the isotope shift of the critical temperature in several binary mixtures of nitromethane with different solvents. The influence of the solvent on the isotope effect is striking – the largest effect is seen for solution of nitromethane with non-polar tetrachlorethylene and consequently smaller one with the polar components. Moreover, for water the change of sign is even observed. The role of the solvent is not clear as yet. It cannot be explained in the frame of the Rabinovich's concept. Even the more quantitative approach based on the Singh – Van Hook formalism [9] fails to interpret correctly the recent results. In the frame of their model, the usually observed blue shift of the CH(CD) stretching frequencies upon transfer of a molecule from the neat liquid to the infinite dilution in solution should correspond to a downward shift of the UCST – instead we found the upward shift. The facts observed suggest the strong coupling of CH(D) stretching modes of the methyl group with the vibrations of the NO_2 group participating in the specific interactions (eventual NO...H hydrogen bridge). The stronger the interaction, the smaller the positive isotope shift of the UCST, however, no simple correlation of the isotope shift with the properties of the solvent has been found. It means that the origin of the isotope effects on miscibility is much more complex than that proposed by Rabinovich and even Singh – Van Hook model is too simplified. More deeper studies, combining the theory of the condensed phase isotope effects with the appropriate thermodynamic model of solutions, are necessary to explain the newly accumulated experimental results on the isotope effects on miscibility.

Table 1. Experimental miscibility data for nitromethane/ethylene glycol and nitromethane-d_3/ethylene glycol.

NME/GLY		NME-d_3/GLY	
x_{NME}	T(K)	x_{NME}	T(K)
0.341	302.98	0.419	310.29
0.388	306.41	0.458	311.75
0.425	309.46	0.504	312.99
0.470	311.15	0.548	313.35
0.515	312.38	0.588	313.80
0.556	312.76	0.628	314.02
0.599	313.05	0.662	313.89
0.634	313.04	0.687	313.77
0.674	313.05	0.727	313.65
0.713	312.95	0.760	313.23
0.769	311.75	0.800	312.05
0.832	310.06		
0.885	306.25		
0.916	302.67		

Table 2. Critical parameters from scaling Eq 1.

Critical parameters	NME + GLY	NME-d_3 + GLY
x_c	0.631±0.004	0.636±0.006
T_c/K	313.04±0.03	313.92±0.01
β	0.329±0.021	0.346±0.009
A_1	0.227±0.09	0.617±0.04
$\sigma^2 \times 10^4$	3.56	0.12

σ^2 – variance of the fitting.

Table 3. Comparison of the isotope effect on UCST upon deuteration of methyl group of nitromethane in solutions of various solvents.

System	ΔT/K
Nitromethane + water	–0.17[a]
Nitromethane + ethylene glycol	0.88
Nitromethane + isobutanol	1.05[b]
Nitromethane + n-pentanol	1.38[b]
Nitromethane + tetrachlorethylene	2.33[c]

[a] – ref. 7; [b] – ref. 3; [c] – ref. 4.

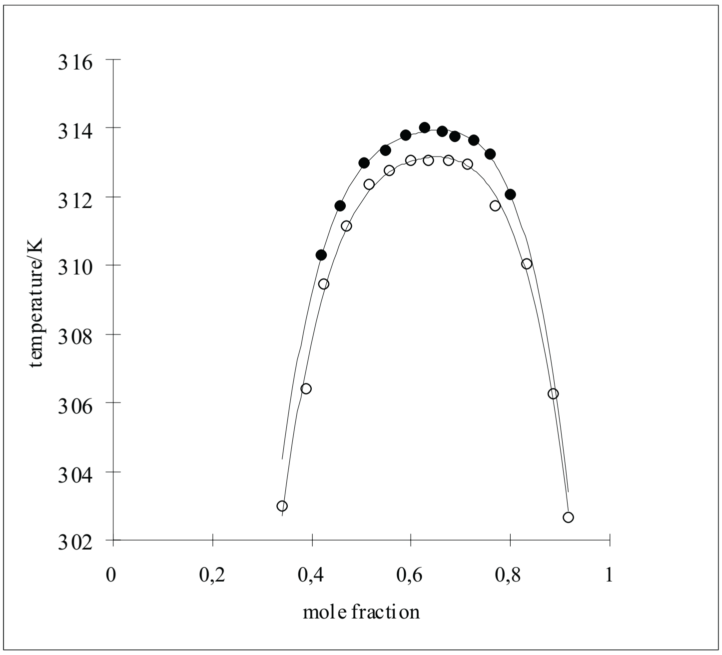

Figure 1. Phase diagrams for nitromethane + ethylene glycol (○) and nitromethane-d_3+ ethylene glycol (●).

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