Influence of Temperature on the Liquid−Liquid Equilibria of the Ternary System Nitromethane + 1-Hexanol + Octanoic Acid

Valerii P. Sazonov,* Nikolai I. Lisov, and Nikolai V. Sazonov

Department of General and Inorganic Chemistry, Technical University, Samara 443100, Russia

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Liquid−liquid equilibria and mutual solubility for (nitromethane + 1-hexanol + octanoic acid) have been studied in the temperature range 16.5 °C to 35.6 °C with analysis by gas chromatography. Phase diagrams, including tie lines and plait points, are reported over this temperature range. The form of the binodal curves in the region near their point of contact is discussed.

Ternary systems with two pairs of partially miscible liquids belong to Type II in Treybal's classification[1] of extraction systems. These systems are interesting from a theoretical point of view because of the possibility of the two-phase regions coming into contact as the temperature is changed in an appropriate way. The first system of this type to be studied was water + succinonitrile + ethanol.[2] However, in this system coalescence of the two-phase regions does not occur because of crystallization of the nitrile and of water. In a review Sazonov[3] gives information about more than 50 ternary systems in which the coalescence of two two-phase regions occurs.

With regard to the mechanism of the coalescence of two-phase regions in these systems, Roozeboom and Schreinemakers[4] suggested that the contact is carried out by plait points, and through a point of contact two tangents are possible to lead to branching binodal curves.

The present paper reports results on mutual solubility and compositions of the equilibrium phases of the ternary system nitromethane (A) + 1-hexanol (B) + octanoic acid (C) and the two partially miscible binaries: nitromethane + 1-hexanol and nitromethane + octanoic acid between 16.5 °C and the highest critical solution temperature of these binary systems (35.6 °C). No data on this ternary system were found in the literature. However, solubility data for both binary systems were previously published.[5]

Experimental Section

Nitromethane (pure grade; Reakhim, Russia) was dried over molecular sieves Type 4A and distilled twice through a column of 20 theoretical plates packed with glass spirals 5 mm in diameter. The purity of the substance, according to chromatographic analysis, was 99.8 mass % and 0.2 mass % of water. The measured density and refractive index are $\rho(20\ °C) = 1138.1\ kg \cdot m^{-3}$ and $n(20\ °C, D) = 1.3819$ and the same values reported in the literature[6] for comparison are $\rho(20\ °C) = 1137.9\ kg \cdot m^{-3}$ and $n(20\ °C, D) = 1.38189$). 1-Hexanol (pure grade; Reakhim, Russia) was dried over CaO and distilled repeatedly through a column of 60 theoretical plates packed with steel rings 3 mm in diameter. The purity was 99.5 mass %; as impurities there was a small amount of water (0.1 mass %) as well as homologues and isomers of 1-hexanol. The measured properties are $\rho(20\ °C) = 819.7\ kg \cdot m^{-3}$ and $n(20\ °C, D) = 1.4182$ [values available in the literature[6,7] are $\rho(20\ °C) = 818.6\ kg \cdot m^{-3}$ and $n(20\ °C, D) = 1.41816$]. Octanoic acid (pure grade; Reakhim, Russia) was dried over molecular sieves Type 4A and repeatedly fractionally distilled at about 270 Pa. Chromatographic analysis carried out on the pure component showed that, in the case of octanoic acid, the impurity concentration was 0.8 mass %, a minor concentration of water being around 0.2 mass % and unstated impurity 0.6 mass %. The measured density and refractive index are $\rho(20\ °C) = 909\ kg \cdot m^{-3}$ and $n(20\ °C, D) = 1.4279$ and the same values reported in the literature[6] for comparison are $\rho(20\ °C) = 908.94\ kg \cdot m^{-3}$ and $n(20\ °C, D) = 1.4279$).

Heterogeneous binary and ternary mixtures were prepared gravimetrically in glass ampules with an internal diameter of 20 mm and height of 70 mm. The ternary mixtures had a constant mole relationship of B and C (x_B/x_C = constant) of 1:6.4, 1:2.8, 1:1.1, or 3.3:1. The total mass of the mixture was (8 to 11) g, depending on the overall composition. The solubility curves of the binary and ternary systems were determined by a synthetic (cloud-point) method. The sealed ampules were put into a 30-L water thermostat with transparent sides, were heated with vigorous stirring to a temperature somewhat higher than the homogenization temperature, and then slowly cooled at a rate of about 0.1 K min^{-1} until turbidity appeared. Heating and cooling cycles were repeated twice. Temperature values obtained for the appearance and disappearance turbidity were averaged. The temperature variations at a specified temperature were ±0.05 °C, measured in Hg mercury thermometers TR-2 (Russia) with 0.01 °C scale divisions. These points were recorded as the cloud-point temperature and plotted against the mole fraction of nitromethane.

The borders of the regions of immiscibility were determined by a titration method. The apparatus and procedure are described elsewhere.[8] Heterogeneous mixtures of the two substances were titrated by the third component until a single phase appeared. The addition of a component was made with a microsyringe, the needle of which was pushed through the hermetic rubber stopper. The relative error in determination of the solubility curves did not exceed 1%.

Composition analysis of each liquid phase was carried out by gas chromatography, employing a thermal conductivity detector as described previously.[6] The chromatograph used was "Tsvet-100", Russia. The thermostat temperature

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* To whom correspondence should be addressed. E-mail: sazonov@sstu.edu.ru.

10.1021/je010309d CCC: $22.00

Table 1. Mutual Solubility for the Binary Systems Nitromethane (A) + 1-Hexanol (B) and Nitromethane (A) + Octanoic Acid (C)[a]

	nitromethane + 1-hexanol		nitromethane + octanoic acid	
	x_A	t (°C)	x_A	t (°C)
	0.216	17.3	0.427	19.1
	0.275	24.1	0.480	24.1
	0.336	28.6	0.517	26.7
	0.392	31.1	0.574	30.6
	0.452	32.9	0.626	32.7
	0.513	34.3	0.666	33.6
	0.557	35.1	0.706	34.5
	0.612	35.4	0.735	34.8
	0.641	35.5	0.753	34.9
	0.691	35.6	0.774	35.0
	0.719	35.5	0.796	34.9
	0.765	35.3	0.836	34.6
	0.802	34.6	0.871	33.6
	0.851	31.9	0.898	31.4
	0.888	27.8	0.923	27.7
	0.901	25.5	0.946	21.2
	0.931	17.4	0.959	16.5
UCST	0.68	35.6	0.78	35.0
UCST[5]	0.657	35.3	0.77	34.9

[a] x_A is the mole fraction of nitromethane in the mixture.

was 175 °C and the carrier gas was helium, flowing at 32 cm^3·min^{-1}. The initial mixtures were kept for (3 to 3.5 h) in a water thermostat at a given temperature to attain equilibrium and complete phase separation. Analytical samples (three to five samples from each liquid phase) were taken by a microsyringe through a rubber stopper. The areas of the chromatographic peaks and the retention times of the components were measured with a digital integrator. Calibration measurements carried out on the pure component and on homogeneous solutions showed that nitromethane and 1-hexanol mole fractions could be determined with an uncertainty of better than 0.001 while, for octanoic acid, the uncertainty was found to be better than 0.002.

Results and Discussion

The experimental values for the solubility curves of the nitromethane + 1-hexanol and nitromethane + octanoic acid binary systems are given in Table 1 with their corresponding upper critical solution temperature (UCST) at 35.6 °C with $x_A = 0.68$ and 35.0 °C with $x_A = 0.78$, respectively. Both sets of critical parameters were obtained by graphic interpolation. These experimental results are generally in agreement with solubility data reported in ref 5.

The curves correlating the cloud-point temperatures for ternary mixtures with the mole fraction of nitromethane are shown in Figure 1. The form of these curves is similar to the solubility curves for the binary systems. The upper part of these curves in a range $(t_{max} - t) \leq 2$ (where t_{max} − maximal temperature of the solubility curve) is satisfactorily described by the equation of a parabola:

$$t = a_0 + a_1 x_A + a_2 (x_A)^2 \tag{1}$$

The best values of the parameters of eq 1 obtained for this system are given in Table 2 with the corresponding standard deviations. Since each curve corresponds to a known ratio of mole fractions of alcohol and acid and since the sum of the mole fraction of three components is equal to 1.0, the borders of the regions of immiscibility were determined at (20.0, 25.0, 29.5, 29.7, 30.0, 31.0, and 35.0) °C from these curves. These results together with the titration data are given in Table 3.

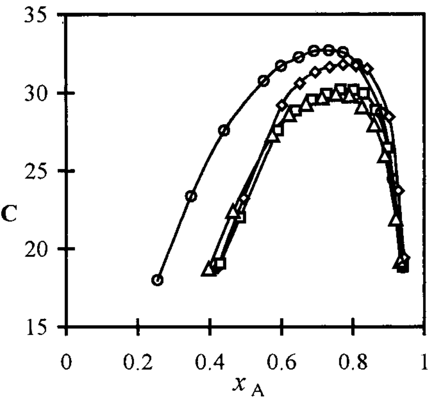

Figure 1. Experimental solubility curves for the nitromethane + 1-hexanol + octanoic acid ternary system. Constant mole fraction ratios of 1-hexanol to octanoic acid (x_B/x_C): ◇, 0.157; □, 0.353; △, 0.944; and ○, 3.288.

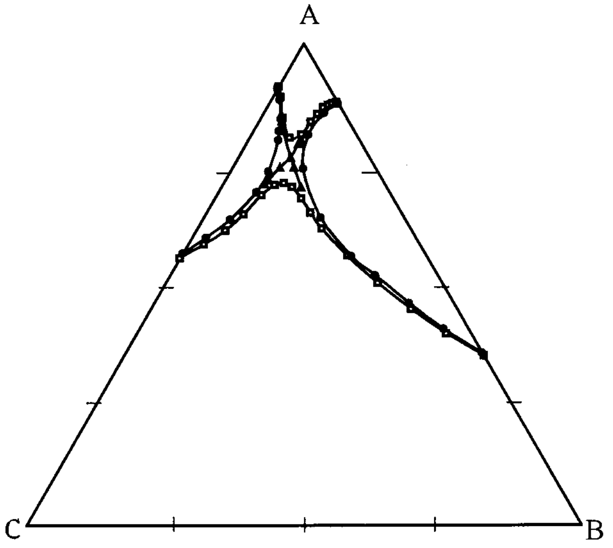

Figure 2. Isothermal solubility curves (mole fractions) for the nitromethane + 1-hexanol + octanoic acid ternary system at several temperatures: □, 29.5 °C; △, 29.7 °C; and ○, 30.0 °C.

Table 2. Parameters of Eq 1 and Standard Deviation for Solubility Curves of the Ternary System Nitromethane (A) + 1-Hexanol (B) + Octanoic Acid (C)

solubility curve	a_0	a_1	a_2	standard deviation
1	−0.0033	80.27	−50.77	0.990
2	−0.0072	79.61	−52.77	0.990
3	−0.0079	78.90	−52.41	0.983
4	−0.0049	91.26	−63.84	0.996

Liquid−liquid equilibrium data for the system nitromethane + 1-hexanol + octanoic acid at (20.0, 25.0, 30.0, 31.0, and 32.0) °C are shown in Table 4. Composition values in Table 4 corresponding to the plait points of the nitromethane-rich and alcohol-rich phase or the nitromethane-rich and acid-rich phase were determined by Hand's method[9] are also included. Compositions are always expressed in mole fractions x_{iA}, x_{iB}, or x_{iC} where the first index refers to the component and the second to the phase (A = nitromethane-rich phase; B = alcohol-rich phase; C = acid-rich phase).

As the binary boundary subsystems A + B and A + C have limited miscibility and close upper critical solution temperatures, the mutual solubility in the ternary system

Table 3. Mutual Solubility Data for the Ternary System Nitromethane (A) + 1-Hexanol (B) + Octanoic Acid (C) at Several Temperatures[a]

Band-Type Solubility Curves											
x_A	x_B	x_C	x_A	x_B	x_C	x_A	x_B	x_C	x_A	x_B	x_C
		t = 20.0 °C						t = 25.0 °C			
0.433*	0.000	0.567	0.950*	0.000	0.050	0.489*	0.000	0.511	0.936*	0.000	0.064
0.436	0.039	0.525	0.943*	0.008	0.049	0.506	0.035	0.459	0.923*	0.010	0.067
0.444*	0.075	0.481	0.937*	0.017	0.046	0.521*	0.065	0.414	0.917*	0.022	0.061
0.446	0.110	0.444	0.932	0.026	0.042	0.527	0.094	0.379	0.915	0.032	0.053
0.447*	0.144	0.409	0.929*	0.035	0.036	0.533*	0.121	0.346	0.913*	0.042	0.045
0.445	0.178	0.377	0.927	0.043	0.030	0.536	0.149	0.315	0.906	0.053	0.041
0.440	0.211	0.349	0.926	0.050	0.024	0.533	0.176	0.291	0.909	0.062	0.029
0.429	0.247	0.324	0.925*	0.058	0.017	0.526	0.205	0.269	0.907*	0.071	0.022
0.417*	0.283	0.300	0.924	0.065	0.011	0.515*	0.235	0.250	0.906	0.080	0.014
0.399	0.322	0.279	0.925	0.069	0.006	0.501	0.267	0.232	0.905	0.088	0.007
0.377	0.365	0.258	0.925*	0.075	0.000	0.483	0.303	0.214	0.905*	0.095	0.000
0.334	0.453	0.213	0.213			0.433	0.385	0.182			
0.295*	0.541	0.164	0.164			0.372*	0.482	0.146			
0.271	0.620	0.109	0.109			0.331	0.568	0.101			
0.251	0.694	0.055	0.055			0.304	0.645	0.051			
0.235*	0.765	0.000	0.000			0.281*	0.719	0.000			
		t = 29.5 °C						t = 29.7 °C			
0.555*	0.000	0.445	0.912*	0.000	0.088	0.711*	0.075	0.214	0.704*	0.143	0.153
0.584	0.029	0.387	0.890*	0.015	0.095	0.719	0.078	0.203	0.744	0.111	0.145
0.613*	0.053	0.334	0.846*	0.040	0.114	0.744	0.086	0.170	0.820	0.054	0.126
0.647	0.070	0.283	0.805	0.073	0.122	0.793	0.095	0.112	0.839*	0.042	0.119
0.686*	0.082	0.232	0.812*	0.091	0.097	0.798*	0.098	0.104			
0.707	0.094	0.199	0.837	0.095	0.068						
0.712	0.109	0.179	0.854	0.099	0.047						
0.703	0.128	0.169	0.867*	0.102	0.031						
0.679*	0.156	0.165	0.872	0.109	0.019						
0.650	0.188	0.162	0.876	0.115	0.009						
0.616	0.225	0.159	0.878*	0.122	0.000						
0.561	0.298	0.141									
0.502*	0.382	0.116									
0.449	0.469	0.082									
0.398	0.558	0.044									
0.352*	0.648	0.000									
Two Separate Solubility Curves											
		t = 30.0 °C						t = 31.0 °C			
0.565*	0.000	0.435	0.358*	0.642	0.000	0.581*	0.000	0.419	0.388*	0.612	0.000
0.598	0.026	0.376	0.408	0.547	0.045	0.639	0.031	0.330	0.427	0.531	0.042
0.636*	0.050	0.314	0.460	0.459	0.081	0.672*	0.045	0.283	0.496	0.428	0.076
0.692	0.069	0.239	0.519*	0.369	0.112	0.705	0.051	0.244	0.560*	0.337	0.103
0.735	0.069	0.196	0.559	0.306	0.135	0.741	0.050	0.209	0.718	0.181	0.101
0.800	0.055	0.145	0.640	0.211	0.149	0.819	0.033	0.148	0.773	0.145	0.082
0.819*	0.047	0.134	0.741	0.124	0.135	0.860*	0.019	0.121	0.812	0.127	0.061
0.843	0.038	0.119	0.810	0.104	0.086	0.902*	0.000	0.098	0.834*	0.127	0.039
0.884*	0.016	0.100	0.856*	0.110	0.034				0.862*	0.138	0.000
0.910*	0.000	0.090	0.874*	0.126	0.000						
Only One Solubility Curve											
		t = 35.0 °C									
0.553*	0.447	0.000	0.698	0.278	0.024						
0.587	0.374	0.039	0.785*	0.215	0.000						

[a] Values marked with asterisks correspond to the composition of ternary mixtures obtained by the synthetic (cloud-point) method. Other compositions of ternary mixtures are obtained by the titration method. x_i is the mole fraction of component i in the mixture.

decreases with cooling. Figure 2 shows that as two regions of immiscibility continuously approach one another and then come into contact at the special plait point, "a homogeneous plait point" in Schreinemakers's classification[4] or "col" in the terminology of Francis[10] occurs which is situated at (29.7 ± 0.1) °C with a ternary composition: $x_A = 0.765$, $x_B = 0.094$, and $x_C = 0.141$ for this system. The position of this point was determined as follows. The curve of plait points in Figure 3 is indicated by a smooth curve connecting from Table 4 all plait points and both binary UCST. The lowest point on this curve corresponds to temperature 29.7 °C. The coordinates of the "col" point were obtained from Figure 2 graphically from the intersection of the solubility curves at 29.7 °C. At the subsequent coalescence of two regions of immiscibility, one region of band-type immiscibility is formed. Thus, at a temperature

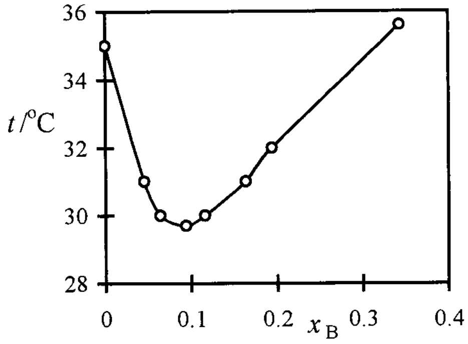

Figure 3. Curve connecting all plait points ternary systems (Table 4) and passing by the "col" and both binary UCSTs.

Table 4. Liquid−Liquid Equilibrium Data for the System Nitromethane (A) + 1-Hexanol (B) + Octanoic Acid (C)[a]

Band-Type Binodal Curve

x_{AA}	x_{BA}	x_{AC}	x_{BC}	x_{AA}	x_{BA}	x_{AC}	x_{BC}
$t = 20.0$ °C				$t = 25.0$ °C			
0.950	0.000	0.433	0.000	0.936	0.000	0.491	0.000
0.937	0.016	0.440	0.062	0.917	0.020	0.539	0.124
0.931	0.029	0.447	0.125	0.912	0.045	0.520	0.224
0.928	0.038	0.441	0.190	0.910	0.058	0.477	0.313
0.926	0.045	0.429	0.254	0.907	0.071	0.435	0.379
0.925	0.051	0.396	0.329				
		x_{AB}	x_{BB}			x_{AB}	x_{BB}
0.925	0.057	0.363	0.391	0.906	0.083	0.349	0.530
0.925	0.063	0.314	0.503	0.905	0.089	0.296	0.674
0.925	0.069	0.285	0.571	0.905	0.095	0.282	0.718
0.925	0.072	0.245	0.723				
0.925	0.075	0.207	0.793				
Two Separate Binodal Curves							
$t = 30.0$ °C				$t = 31.0$ °C			
0.910	0.000	0.565	0.000	0.902	0.000	0.581	0.000
0.900	0.006	0.588	0.019	0.888	0.005	0.618	0.018
0.895	0.011	0.612	0.034	0.875	0.010	0.639	0.032
0.875	0.021	0.641	0.055	0.854	0.021	0.679	0.045
0.859	0.029	0.667	0.065	0.772*	0.045*		
0.770*	0.064*						
		x_{AB}	x_{BB}			x_{AB}	x_{BB}
0.874	0.126	0.361	0.639	0.879	0.121	0.388	0.612
0.872	0.123	0.441	0.495	0.866	0.130	0.441	0.516
0.870	0.122	0.475	0.439	0.855	0.135	0.490	0.438
0.865	0.117	0.517	0.372	0.848	0.129	0.538	0.368
0.857	0.110	0.563	0.306	0.840	0.126	0.575	0.320
0.844	0.106	0.612	0.244	0.823	0.125	0.633	0.255
0.827	0.104	0.653	0.195	0.743*	0.163*		
0.759*	0.116*						
$t = 32.0$ °C							
		x_{AB}	x_{BB}				
0.852	0.148	0.418	0.582				
0.848	0.143	0.462	0.503				
0.840	0.143	0.520	0.416				
0.826	0.143	0.573	0.347				
0.810	0.148	0.614	0.301				
0.730*	0.194*						

[a] Values marked with asterisks correspond to plait points calculated by Hand's method.[9] x_{iA} is the mole fraction of component i in the nitromethane-rich phase; x_{iB} is the mole fraction of component i in the alcohol-rich phase; x_{iC} is the mole fraction of component i in the acid-rich phase.

near 29.7 °C the isothermal solubility curves represent two pairs of curves with opposite curvature. Earlier[11] similar pairs of curves for the system water + 1-butanol + 2-butanone were mathematically described by the equations of conjugate hyperbolas. However, the conjugate hyperbolas are formed by the crossing of a hyperbolic paraboloid by two parallel planes close to a saddle point. Probably the binodal surface of the system nitromethane + 1-hexanol + octanoic acid, investigated by us, and the binodal surface of other similar ternary systems[12] in coordinates T, x_1, and x_2 has the form of a deformed hyperbolic paraboloid.

Between both binary critical solution temperatures, this ternary system has only one partially miscible region. Therefore, between these temperatures, it is of type I in Treybal's classification.[1]

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Received for review November 26, 2001. Accepted February 26, 2002.

JE010309D