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Liquid−Liquid Equilibrium of Ternary Mixtures Formed by Some Oligooxaethylenes with Ethanol and Hexadecane[†]

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Liquid−liquid equilibria data including the tie-lines for ternary systems formed by oligooxaethylenes with ethanol and hexadecane are measured at two temperatures. The liquid−liquid measurements were made for the 2,5,8,11-tetraoxadodecane + ethanol + hexadecane system at (293.15 and 298.15) K and for the 2,5,8,11,14-pentaoxapentadecane + ethanol + hexadecane system at (298.15 and 303.15) K. These systems are characterized by the band type miscibility gap for two measured isotherms, where two binaries are partially miscible. Experimental data are smoothed by means of the correlation equation proposed by these authors similar to the Redlich and Kister equation.

Introduction

A great number of the separation processes in chemical industries require a knowledge of the liquid−liquid equilibrium data. The paper is an extension of our previous investigations of the binary liquid−liquid equilibria (LLE) for oligooxaethylene + alkane systems (Treszczanowicz et al.[1,2]). The aim of the paper is to investigate the liquid−liquid equilibrium of the ternary systems formed by oligooxaethylene with an active solvent (alkanol) and an inert alkane, where two binaries are partially miscible. Thermodynamic properties of both mixtures, alkanol + alkane and oligooxaethylene + alkane, were extensively investigated by us experimentally and analyzed by the theory. The investigated ternary systems show complex intermolecular interactions. The ethanol is self-associated via hydrogen bonds, while oligooxaethylenes are characterized by a highly ordered structure (Andreoli-Ball et al.[3]). There is some evidence that the pure oligooxaethylenes are weakly self-associated (Treszczanowicz et al.[4]). In the mixture with alkane, the pure liquid structures of the polar components are disrupted. In the miscible oligooxaethylene + ethanol system, besides the disruption of the structure of pure components, also order formation in the mixture[5] (see also Andreoli-Ball et al.[3]) is observed due to solvation of oligooxaethylene by ethanol molecules. In the literature by Sorensen et al.[6] as well as in chemical abstracts, there are no experimental LLE data for ternary systems formed by oligooxaethylene + alkanol + alkane.

Experimental Section

Materials. The 2,5,8,11-tetraoxadodecane (TODD) and 2,5,8,11,14-pentaoxapentadecane (POPD) analytical grade were supplied by Fluka Chemical Co. with mole fraction purities of 0.99. They were further purified and ampouled by Chemical Laboratory UNIPAN. In all cases, the purity of the final products estimated by GLC, using a flame ionization detector, exceeded 0.999 in mole fraction. Prior to their use, both ethers were stored over molecular sieves beads, type 3A. Hexadecane analytical pure grade Reachim Chemical Co. (Russia) was purified by distillation over sodium on a packed column at a reflux ratio of 1:40 and stored over type 4A molecular sieves beads. Ethanol, anhydrous analytical pure grade POCH SA Gliwice (Poland), mole fraction purity of 0.998 with a declared water mole fraction of 0.0005, was stored over molecular sieves type 3A. Densities of the liquids at $T = 298.15$ K were determined with an Anton Paar oscillator-type densimeter (model DMA 602) with an uncertainty of $\pm\ 2 \cdot 10^{-5}$ $g \cdot cm^{-3}$. These results are listed in Table 1 with values from the literature.

Table 1. Physicochemical Properties of the Pure Components[a]

solvent	M_i^c	$d/g \cdot cm^{-3}$ exptl	$d/g \cdot cm^{-3}$ lit.
TODD[b]	178.23	0.98042	0.97981[d]
POPD[b]	222.283	1.00620	1.00662[e]
ethanol	46.070	0.78504	0.78506[c]
hexadecane	226.448	0.77001	0.76994[f]

[a] *M*, Molecular Weight; and *d*, Density at 298.15 K. [b] TODD, 2,5,8,11,14-tetraoxadodecane; POPD, 2,5,8,11,14-pentaoxapentadecane. [c] Riddick et al.[7] [d] Benson et al.[8] [e] Treszczanowicz et al.[9] [f] Selected values of properties, API (1977).[10]

Measuring Procedure. The liquid−liquid coexistence curve was determined in the apparatus described by Treszczanowicz et al.[1] by means of a titration technique adapted from Letcher et al.[11] One of the pure components or homogeneous binary mixture (respectively, to the character of the miscibility gape) was added to a known amount of a two-phase mixture to obtain a homogeneous phase. From the quantities of the added mass of components, the composition of the equilibrium mixture was determined. Constant temperature was maintained by pumping thermostatted water through the jacket of the measuring cell, and the obtained uncertainty of the temperature is within ± 0.02 K. During the measurements, the mixtures were vigorously mixed. Uncertainties in the mole fractions are estimated to be within $5 \cdot 10^{-3}$ for measured binodal curve points.

The tie lines were determined using GLC chromatography for the starting solutions prepared by mass, whose compositions remain within the immiscible region of the phase diagram. The prepared mixtures were vigorously mixed for 1 h and left to

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Table 2. Compositions of Points on the Coexistence Curve for the Ternary Mixtures Oligooxaethylene (1) + Ethanol (2) + Hexadecane (3)

polar-rich phase		alkane-rich phase		polar-rich phase		alkane-rich phase	
x_1	x_3	x_1	x_3	x_1	x_3	x_1	x_3
2,5,8,11-Tetraoxadodecane (1) + Ethanol (2) + Hexadecane (3)							
293.15 K				298.15 K			
0	0.036	0	0.776	0	0.044	0	0.697
0.096	0.045	0.040	0.743	0.025	0.038	0.037	0.631
0.158	0.044	0.041	0.741	0.052	0.044	0.079	0.581
0.211	0.059	0.051	0.735	0.069	0.048	0.080	0.570
0.225	0.055	0.079	0.710	0.141	0.066	0.136	0.540
0.281	0.067	0.101	0.698	0.215	0.081	0.151	0.534
0.292	0.072	0.108	0.704	0.308	0.107	0.165	0.532
0.319	0.085	0.129	0.676	0.327	0.109	0.192	0.527
0.381	0.093	0.202	0.652	0.424	0.132	0.278	0.530
0.519	0.105	0.204	0.649	0.461	0.142	0.289	0.521
0.547	0.109	0.221	0.644	0.538	0.167	0.297	0.534
0.636	0.114	0.247	0.658	0.588	0.174	0.310	0.539
0.691	0.131	0.248	0.662	0.660	0.221	0.322	0.530
0.695	0.127	0.251	0.658	0.682	0.224	0.429	0.501
0.754	0.120	0.253	0.651	0.745	0.255	0.513	0.487
0.851	0.149	0.335	0.665				
2,5,8,11,15-Pentaoxapentadecane (1) + Ethanol (2) + Hexadecane (3)							
298.15 K				308.15 K			
0	0.044	0	0.697	0	0.054	0	0.636
0.027	0.047	0.008	0.707	0.061	0.072	0.025	0.623
0.107	0.050	0.036	0.697	0.087	0.068	0.027	0.610
0.136	0.043	0.044	0.718	0.092	0.079	0.040	0.605
0.147	0.060	0.048	0.702	0.155	0.090	0.048	0.616
0.163	0.058	0.077	0.729	0.189	0.096	0.070	0.603
0.230	0.056	0.116	0.799	0.213	0.098	0.091	0.616
0.269	0.053	0.129	0.817	0.249	0.100	0.106	0.618
0.452	0.058	0.133	0.803	0.364	0.096	0.124	0.643
0.456	0.057	0.133	0.812	0.384	0.102	0.145	0.661
0.482	0.060	0.134	0.820	0.457	0.113	0.154	0.705
0.598	0.065	0.137	0.828	0.464	0.106	0.187	0.746
0.663	0.055	0.148	0.836	0.480	0.117	0.190	0.740
0.721	0.062	0.152	0.848	0.568	0.132	0.216	0.784
0.727	0.071			0.642	0.128		
0.821	0.081			0.644	0.117		
0.843	0.075			0.718	0.121		
0.929	0.071			0.787	0.136		
				0.833	0.126		
				0.873	0.127		

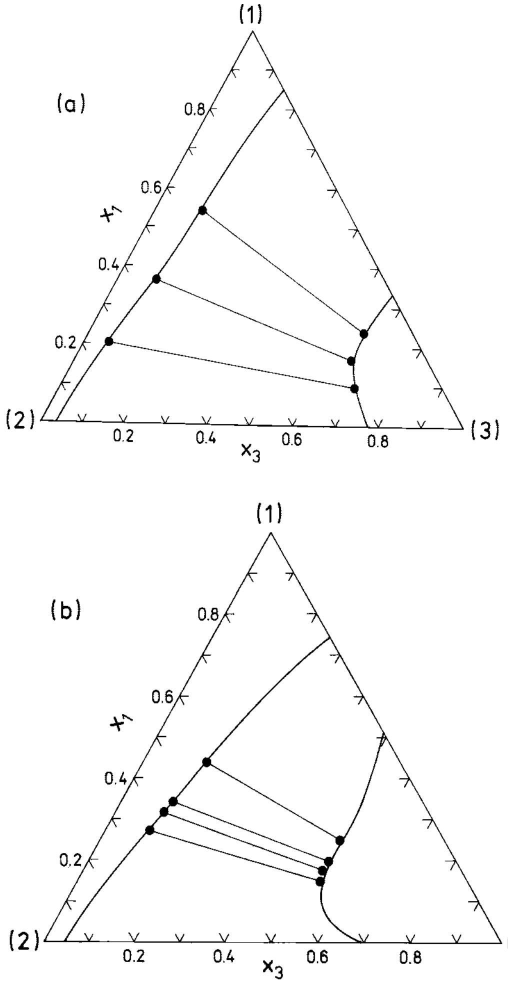

Figure 1. Liquid−liquid equilibrium in ternary system I: TODD (1) + ethanol (2) + hexadecane (3): (a) at $T = 293.15$ K and (b) at $T = 298.15$ K. The continuous lines correspond to the experimental data smoothed with eq 1 and parameters given in Table 3. The straight lines denote tie-lines, and points represent experimental data of the tie-line end point data given in Table 4.

separate into two phases, while equilibrium temperature was maintained within ± 0.02 K. After about 1 h, the samples of each of the separated phases were carefully withdrawn with a hypodermic injection syringe. The composition of each phase was determined by GLC, using a Hewlett-Packard chromatograph 5750 G equipped with an electronic integrator 3370 A. A good separation of the three components studied was obtained on a 1.40 m × 0.32 mm column, packed with chromosorb 80/100 QDMCS coated with carbowax 20 M, using a 20 cm^3 flow rate of helium as the carrier gas. A temperature programming from (60 to 150) °C was necessary, and the detection was carried out by thermal conductivity. Quantitative results were obtained by using two internal standards: ethanol and hexadecane. The reference samples were analyzed using the same chromatographic condition as the equilibrium samples. The relative uncertainty of mole fraction measurements is about 0.5 % for hydrocarbon and ethanol but 1 % for oligooxaethylene.

Results and Discussion

The two ternary systems were measured: (I) TODD with ethanol + hexadecane at (293.15 and 298.15) K and (II) POPD with ethanol + hexadecane at (298.15 and 308.15) K. The compositions of the coexistence curve over a temperature range are given in Table 2 and presented in Figures 1 and 2. Both systems show a band-type miscibility gap distinguished as type 2 in the classification given by Sorensen et al.[12] System I at 298.15 K forms a rare case of the transition between "parabolic" type 1 and "band" type 2 (cf. Treybal, ref 13), which show a disappearance of the binary miscibility gaps at $T_c = 298.60$ K (Treszczanowicz et al.[1,2]), higher by about 0.5 K than the temperature of measured isotherm. For system II, such a tendency is not observed because critical temperatures observed for the POPD + hexadecane system, $T_c = 324.35$ K,[1,2] and the ethanol + hexadecane system, $T_c = 326.98$ K,[14] are much higher than temperatures of the isotherms presented here. The results for binary immiscible systems given in Table 2 agree well with the literature data: ethanol + hexadecane,[14] TODD + hexadecane,[1,2] and POPD + hexadecane system.[1,2] The tie-line compositions for both investigated systems are given in Table 4 and are plotted in Figures 1 and 2. The tie-lines show deviation from radial spread from the hexadecane corner.

The coexistence (binodal) curves, taking into account their complex shape, were correlated by means of an empirical relation which was proposed by these authors. This relation expresses the hexadecane mole fraction x_3 as a function of the oligooxaethylene mole fraction x_1

$$x_3 = x_3^{(1,3)} + \left(\frac{x_3^{(2,3)} - x_3^{(1,3)}}{x_1^{(2,3)} - x_1^{(1,3)}}\right)\left(x_1 - x_1^{(1,3)}\right) + \left(x_1 - x_1^{(2,3)}\right)\left(x_1 - x_1^{(1,3)}\right)\sum_{i=1}^{k} a_i\left[x_1 - \frac{1}{2}\left(x_1^{(1,3)} + x_1^{(2,3)}\right)\right]^{i-1} \quad (1)$$

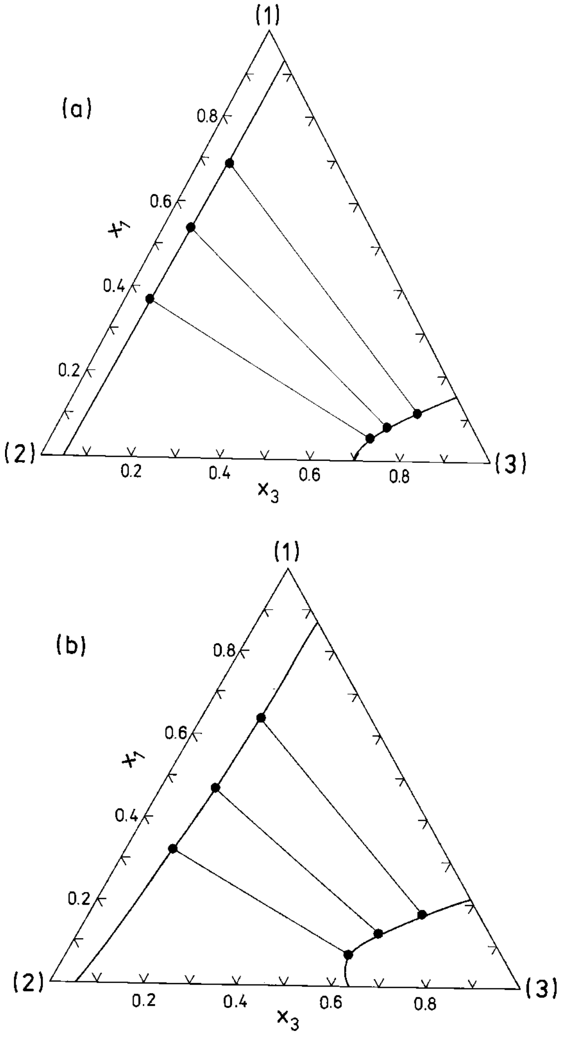

Figure 2. Liquid−liquid equilibrium in ternary system II: POPD (1) + ethanol (2) + hexadecane (3): (a) at $T = 298.15$ K and (b) at $T = 308.15$ K. Remaining denotations are the same as in Figure 1.

Table 4. Compositions of the Conjugate Solutions for the Investigated Systems[a]

polar-rich phase		alkane-rich phase		polar-rich phase		alkane-rich phase	
x''_1	x''_3	x'_1	x'_3	x''_1	x''_3	x'_1	x'_3
2,5,8,11-Tetraoxadodecane (1) + Ethanol (2) + Hexadecane (3)							
293.15 K				298.15 K			
0.203	0.062	0.098	0.695	0.272	0.096	0.152	0.533
0.364	0.093	0.171	0.654	0.318	0.104	0.179	0.523
0.544	0.112	0.243	0.645	0.339	0.115	0.198	0.524
				0.441	0.138	0.248	0.525
2,5,8,11,15-Pentaoxapentadecane (1) + Ethanol (2) + Hexadecane (3)							
298.15 K				308.15 K			
0.368	0.057	0.052	0.706	0.324	0.102	0.076	0.598
0.533	0.065	0.079	0.734	0.469	0.118	0.127	0.634
0.689	0.071	0.114	0.783	0.638	0.125	0.176	0.703

[a] The superscript ″ denotes the lower (polar component-rich) phase, and superscript ′ denotes the upper (alkane-rich) phase.

where $x_1^{(1,3)}$ and $x_3^{(1,3)} = 1 - x_1^{(1,3)}$ are mole fractions of oligooxaethylene and hexadecane in the binary system oligooxaethylene (1) + hexadecane (3) and $x_1^{(2,3)} = 0$ and $x_3^{(2,3)}$ in the binary system ethanol (2) + hexadecane (3). These limiting points are assumed as constraints for the function $x_3 = f(x_1)$ proposed above. The last term represents deviation of the binodal curve from the straight line. This deviation is described by the function similar to the Redlich and Kister correlation function (see Treszczanowicz et al., ref 15). The upper (alkaneous) and the lower (nonalkaneous) binodal curves presented in Figures 1 and 2 were smoothed separately. The parameters in eq 1 were calculated by the Levenberg−Marquardt nonlinear least-squares method[16] and are reported in Table 3 along with the standard deviation σ and maximum deviation $\max|x_{3,i}^{(\mathrm{calcd})} - x_{3,i}^{(\mathrm{exptl})}|$ values. No more than three parameters of eq 1 are sufficient for the smoothing of the experimental data. The standard deviation σ is defined by the formula

$$\sigma = \left[\sum_{i=1}^{n}\left(x_{3,i}^{(\mathrm{calcd})} - x_{3,i}^{(\mathrm{exptl})}\right)^2/(n-k-2)\right]^{1/2} \quad (2)$$

where n is the number of data points of the ternary system and k is the number of parameters.

The empirical function given by eq 1 is used for smoothing experimental data of each of the binodal curves. Such empirical smoothing LLE data are sometimes used for ternary systems with one immiscible binary system.[17−19]

Conclusion

Liquid−liquid equilibrium data for the two ternary mixtures 2,5,8,11-tetraoxdodecane + ethanol + hexadecane and 2,5,8,11,14-pentaoxapentadecane + ethanol + hexadecane were determined at two temperatures. These systems represent the band-type miscibility gap. The binodal curves were smoothed by empirical relation proposed by the authors. This relation is

Table 3. Coefficients of Equation 1, Standard Deviation σ_x, and Maximum Deviation *m.dv.* for the Correlation of the Binodal Curves of an Oligooxaethylene (1) + Ethanol (2) + Hexadecane (3) System at Various Temperatures *T*/K together with Coordinates of the Respective Binary Systems Used in Calculations

T/K	phase[a]	$x_3^{(2,3)}$	$x_1^{(1,3)}$	$x_3^{(1,3)}$	a_1	a_2	a_3	σ_x	*m.dv.*
2,5,8,11-Tetraoxadodecane (1) + Ethanol (2) + Hexadecane (3)									
293.15	u	0.776	0.335	0.665	1.9195			0.006_5	0.011
	l	0.036	0.851	0.149	−0.021972	−0.065553	1.2670	0.005_7	0.009
298.15	u	0.697	0.513	0.487	0.94158	−6.2943	18.163	0.005_9	0.010
	l	0.044	0.745	0.255	0.21047	0.13775	1.2858	0.005_4	0.010
2,5,8,11,15-Pentaoxapentadecane (1) + Ethanol (2) + Hexadecane (3)									
298.15	u	0.697	0.152	0.848	6.4520	−24.208		0.008_9	0.013
	l	0.044	0.929	0.071	−0.013986			0.006_1	0.012
308.15	u	0.636	0.216	0.784	7.2607	−22.698	−265.09	0.009_1	0.017
	l	0.054	0.873	0.127	−0.12238			0.007_7	0.011

[a] The letter u denotes the upper (alkane-rich) phase, and letter l denotes the lower (polar component-rich) phase.

especially recommended for the band-type miscibility gap for the ternary systems if the temperature of the isotherm is close to the temperature at which the band gaps separate or one of binary gaps disappears (see Figure 1). Prediction of the liquid−liquid equilibria for these systems using quasichemical models like UNIQUAC and models taking into account association and complex formation will be described in a separate paper.

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