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Liquid−Liquid Equilibria for Monoethylene Glycol + Water + Alkane Systems in the Range (273 to 313) K and Atmospheric Pressure

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Liquid−liquid equilibria of ternary mixtures of monoethylene glycol (MEG) with alkanes (hexane, heptane, octane, nonane, decane, 3-methylpentane, 2,4-dimethylpentane, and 2,2,4-trimethylpentane) and water were experimentally determined under atmospheric pressure at 293 K and for two of these systems (MEG + water + hexane and MEG + water + 3-methylpentane) at several temperatures (from 273 K to 313 K). The data were correlated using the Othmer−Tobias method. Two multicomponent systems containing MEG, water, *n*-alkanes, and branched alkanes were measured at 293 K.

Introduction

In the oil and petroleum industry, gas hydrates cause a serious problem in production, distribution, and storage plants. To prevent hydrate formation, methanol and glycols are commonly and extensively used as thermodynamic inhibitors. Some factors such as price, ease of handling, and regeneration capability are well known. However, because of their toxicity, the effects of these hazardous materials on the environment must be taken into account. So, knowledge of the partitioning behavior of inhibitors between the aqueous and hydrocarbon phases is essential and has been studied scarcely. Developments of methods for calculating the inhibition effects require experimental data. If few measurements of equilibrium hydrate formation in aqueous solutions containing methanol, monoethylene glycol, and diethylene glycol are reported in the literature[1,2] and are available, liquid−liquid equilibria (LLE) data for systems including glycols, water, and hydrocarbons are excessively scarce.

In this work, the LLE for ternary systems of monoethylene glycol (MEG) + water + alkanes (hexane, heptane, octane, nonane, decane, 3-methylpentane, 2,4-dimethylpentane, and 2,2,4-trimethylpentane) are measured under atmospheric pressure at 293.1 K. Two among these systems are determined at several temperatures (from 273.1 K to 313.1 K). Experimental data are evaluated using the Othmer−Tobias correlation. The variation of the distribution coefficient of MEG between the aqueous and organic phases is also studied. To verify the solubility of MEG in *n*-alkanes + water and branched alkanes + water mixtures, we have measured two multicomponent systems at 293.1 K

All the data reported here contribute new information to the literature.

Experimental Section

Chemicals. The chemicals studied in this work are given in Table 1. They were used without further purification. Water was distilled twice.

Table 1. Purity of Chemicals Used in This Work

chemical	specified purity	supplier
ethylene glycol	>99%	Aldrich
hexane	>98%	Fluka
heptane	>99.9%	Flucka
octane	>99.5%	Fluka
nonane	>99%	Fluka
decane	>99%	Elf
2-methylpentane	>98%	Merck
3-methylpentane	>99%	Fluka
2,4-dimethylpentane	>99%	Fluka
2,2,4-trimethylpentane	>99.9%	Elf

Table 2. Experimental LLE Data for the Monoethylene Glycol (1) + Water (2) + Hexane (3) System at (283.1, 293.1, 303.1, and 313.1) K

aqueous phase			organic phase			
x_1	x_2	x_3	x_1	x_2	x_3	x_1^a/x_1^o
			$T = 283.1$ K			
0.9699	0.0150	0.0151	0.1718	0.0056	0.8226	5.65
0.8014	0.1471	0.0515	0.0321	0.0064	0.9615	24.97
0.7512	0.2370	0.0118	0.0193	0.0056	0.9749	38.92
0.6608	0.3286	0.0104	0.0124	0.0077	0.9799	53.29
0.5602	0.4290	0.0108	0.0089	0.0077	0.9834	62.94
0.2966	0.7002	0.0032	0.0029	0.0176	0.9795	102.28
0.2347	0.7646	0.0007	0.0022	0.0089	0.9889	106.68
			$T = 293.1$ K			
0.9487	0.0504	0.0009	0.1502	0.0101	0.8397	6.32
0.8250	0.1713	0.0037	0.0387	0.0096	0.9517	21.32
0.7195	0.2781	0.0024	0.0192	0.0094	0.9714	37.47
0.6080	0.3915	0.0005	0.0131	0.0104	0.9765	46.41
0.4983	0.5008	0.0009	0.0083	0.0063	0.9854	60.04
0.4025	0.5919	0.0056	0.0052	0.0069	0.9879	77.40
0.3382	0.6614	0.0004	0.0041	0.0055	0.9904	82.49
			$T = 303.1$ K			
0.9133	0.0821	0.0046	0.1233	0.0329	0.8438	7.41
0.7907	0.2033	0.0060	0.0416	0.0216	0.9368	19.01
0.6590	0.3301	0.0109	0.0243	0.0167	0.9590	27.12
0.5025	0.4926	0.0049	0.0129	0.0107	0.9764	38.95
0.3486	0.6500	0.0140	0.0066	0.0169	0.9765	52.82
0.2814	0.7165	0.0021	0.0048	0.0131	0.9821	58.63
0.1937	0.8032	0.0031	0.0029	0.0108	0.9863	66.79
0.1684	0.8314	0.0002	0.0026	0.0022	0.9952	64.77
			$T = 313.1$ K			
0.7689	0.2245	0.0066	0.0702	0.0090	0.9208	10.95
0.6530	0.3415	0.0055	0.0512	0.0104	0.9384	12.75
0.5838	0.4108	0.0054	0.0298	0.0116	0.9586	19.59
0.4434	0.5539	0.0027	0.0173	0.0198	0.9629	25.63
0.2777	0.7205	0.0018	0.0089	0.0174	0.9737	31.20
0.1986	0.7888	0.0126	0.0062	0.0068	0.9870	32.03

Apparatus and Procedure. The equilibrium data were obtained using a jacketed glass cell whose volume was 100

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Table 3. Experimental LLE Data for the Monoethylene Glycol (1) + Water (2) + Linear Alkanes (3) (from Heptane to Decane) System at 293.1 K

aqueous phase			organic phase			
x_1	x_2	x_3	x_1	x_2	x_3	x_1^a/x_1^o
Ethylene Glycol (1) + Water (2) + Heptane (3)						
0.9233	0.0760	0.0008	0.0776	0.0064	0.9160	11.90
0.8553	0.1431	0.0015	0.0420	0.0084	0.9496	20.36
0.7623	0.2369	0.0008	0.0242	0.0201	0.9557	31.50
0.7339	0.2650	0.0010	0.0193	0.0061	0.9746	38.02
0.6766	0.3219	0.0015	0.0159	0.0039	0.9802	42.55
Ethylene Glycol (1) + Water (2) + Octane (3)						
0.9481	0.0515	0.0004	0.1537	0.0989	0.7474	6.17
0.8977	0.1021	0.0001	0.0743	0.0771	0.8486	12.08
0.8498	0.1486	0.0016	0.0464	0.0318	0.9218	18.31
0.8002	0.1989	0.0009	0.0345	0.0213	0.9442	23.19
0.7389	0.2605	0.0008	0.0236	0.0172	0.9592	31.31
0.6847	0.3147	0.0006	0.0171	0.0123	0.9706	40.04
0.6151	0.3816	0.0033	0.0127	0.0023	0.9850	48.43
0.5747	0.4170	0.0042	0.0111	0.0022	0.9867	51.77
0.4215	0.5615	0.0165	0.0060	0.0016	0.9924	70.25
Ethylene Glycol (1) + Water (2) + Nonane (3)						
0.9419	0.0565	0.0015	0.1180	0.0164	0.8656	7.98
0.8639	0.1349	0.0013	0.0447	0.0117	0.9437	19.33
0.7998	0.1980	0.0022	0.0270	0.0121	0.9609	29.62
0.6630	0.3335	0.0035	0.0150	0.0192	0.9658	44.20
0.5617	0.4371	0.0012	0.0105	0.0179	0.9716	53.50
0.5174	0.4794	0.0032	0.0082	0.0126	0.9792	63.10
Ethylene Glycol (1) + Water (2) + Decane (3)						
0.9682	0.0223	0.0095	0.1796	0.0745	0.7459	5.39
0.8884	0.1015	0.0101	0.0620	0.0333	0.9047	14.33
0.7979	0.1944	0.0077	0.0290	0.0215	0.9495	27.51
0.7235	0.2730	0.0035	0.0191	0.0218	0.9591	37.88
0.5979	0.3957	0.0064	0.0109	0.0197	0.9694	54.85
0.5509	0.4411	0.0080	0.0092	0.0237	0.9671	59.88
0.4316	0.5621	0.0063	0.0056	0.0122	0.9822	77.07

Table 4. Experimental LLE Data for the Monoethylene Glycol (1) + Water (2) + 3-Methylpentane (3) System at (273.1, 283.1, and 293.1) K

aqueous phase			organic phase			
x_1	x_2	x_3	x_1	x_2	x_3	x_1^a/x_1^o
$T = 273.1$ K						
0.9365	0.0624	0.0011	0.0694	0.0009	0.9297	13.49
0.8552	0.1412	0.0036	0.0285	0.0033	0.9682	30.01
0.7522	0.2459	0.0019	0.0150	0.0015	0.9835	50.15
0.6359	0.3619	0.0022	0.0088	0.0018	0.9894	72.26
0.4956	0.5040	0.0004	0.0056	0.0004	0.9940	88.50
$T = 283.1$ K						
0.9429	0.0514	0.0057	0.0934	0.0097	0.8969	10.09
0.8512	0.1439	0.0049	0.0318	0.0038	0.9644	26.77
0.7360	0.2609	0.0031	0.0171	0.0039	0.9790	43.04
0.6152	0.3839	0.0009	0.0100	0.0051	0.9849	61.52
0.5223	0.4767	0.0010	0.0069	0.0011	0.9920	75.70
$T = 293.1$ K						
0.9403	0.0572	0.0026	0.1025	0.0022	0.8953	9.17
0.8574	0.1419	0.0006	0.0428	0.0030	0.9542	20.03
0.7843	0.2153	0.0004	0.0260	0.0011	0.9729	30.17
0.7099	0.2897	0.0004	0.0172	0.0010	0.9818	41.27
0.6455	0.3537	0.0008	0.0129	0.0009	0.9862	50.04
0.5976	0.4019	0.0005	0.0107	0.0013	0.9880	55.85

Table 5. Experimental LLE Data for the Monoethylene Glycol (1) + Water (2) + 2,4-Dimethylpentane (3) and Monoethylene Glycol (1) + Water (2) + 2,2,4-Trimethylpentane (3) Systems at 293.1 K

aqueous phase			organic phase			
x_1	x_2	x_3	x_1	x_2	x_3	x_1^a/x_1^o
Ethylene Glycol (1) + Water (2) + 2,4-Dimethylpentane (3)						
0.8967	0.0673	0.0360	0.0944	0.0881	0.8175	9.50
0.8339	0.1488	0.0173	0.0418	0.0210	0.9372	19.95
0.6953	0.2994	0.0053	0.0176	0.0066	0.9758	39.51
0.6255	0.3698	0.0047	0.0130	0.0101	0.9769	48.12
0.5776	0.4171	0.0053	0.0108	0.0084	0.9808	53.48
0.5057	0.4921	0.0022	0.0085	0.0082	0.9833	59.49
Ethylene Glycol (1) + Water (2) + 2,2,4-Trimethylpentane (3)						
0.9370	0.0627	0.0003	0.1105	0.0007	0.8888	8.48
0.8156	0.1830	0.0015	0.0410	0.0009	0.9581	19.89
0.7587	0.2402	0.0011	0.0271	0.0021	0.9708	28.00
0.6344	0.3585	0.0071	0.0168	0.0012	0.9820	37.76
0.5040	0.4936	0.0024	0.0100	0.0018	0.9882	50.40

Table 6. Values of Parameters of Equation 1

T/K	points	a	$-\ln b$	R^2
Ethylene Glycol + Water + n-Hexane				
283.1	8	0.678	5.698	0.982
293.1	7	0.952	6.080	0.996
303.1	8	0.875	5.464	0.983
313.1	6	0.866	4.958	0.982
Ethylene Glycol + Water + Heptane				
293.1	5	0.902	6.269	0.979
Ethylene Glycol + Water + Octane				
293.1	9	1.176	6.865	0.998
Ethylene Glycol + Water + Nonane				
293.1	6	0.849	6.243	0.983
Ethylene Glycol + Water + n-Decane				
293.1	7	0.826	6.269	0.997
Ethylene Glycol + Water + 3-Methylpentane				
273.1	5	0.945	6.679	0.999
283.1	5	0.927	6.439	0.997
293.1	6	0.982	6.436	0.999
Ethylene Glycol + Water + 2,4-Dimethylpentane				
293.1	6	0.991	6.376	0.984
Ethylene Glycol + Water + 2,2,4-Trimethylpentane				
293.1	5	0.926	6.337	0.999

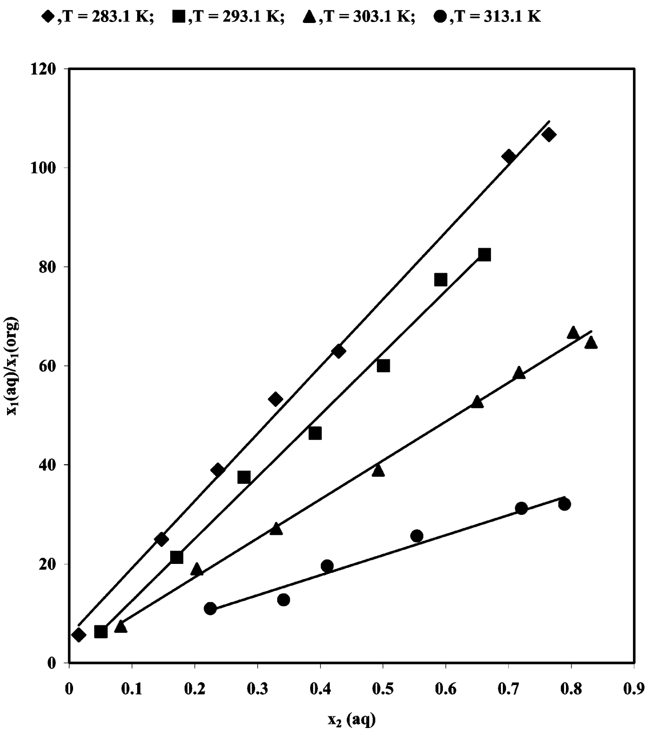

Figure 1. Distribution coefficient of monoethylene glycol between the aqueous (aq) and organic (org) phases in the ternary system monoethylene glycol (1) + water (2) + hexane (3) at four temperatures: ◆, T = 283.1 K; ■, T = 293.1 K; ▲, T = 303.1 K; ●, T = 313.1 K.

mL. The temperature inside the cell was kept constant by circulating water from a thermostatic bath and was measured with a PT-100 thermometer within ±0.1 K. Mixtures of known masses of monoethylene glycol, water, and hydrocarbons were introduced into the cell, were stirred for 1 h, and were kept for 4 h to separate into two phases. Generally the equilibrium state was reached when two phases became transparent after about 2 h. Samples were taken from both layers by a microsyringe (0.5μL ± 0.01μL) and introduced very quickly into a gas chromatograph (Shimadzu GC-14A) equipped with a fused silica megabore capillary column and a thermal conductivity detector. The carrier gas was helium. The injection temperature was 523 K, and the detector temperature was 573 K. The oven temperature was programmed as follows: an initial temperature of 373 K was set up for 6 min followed by a temperature gradient of 20 K/min up to 513 K. This latter temperature was held for 8 min.

The gas chromatograph was calibrated on pure components and mixtures of known masses of different chemicals

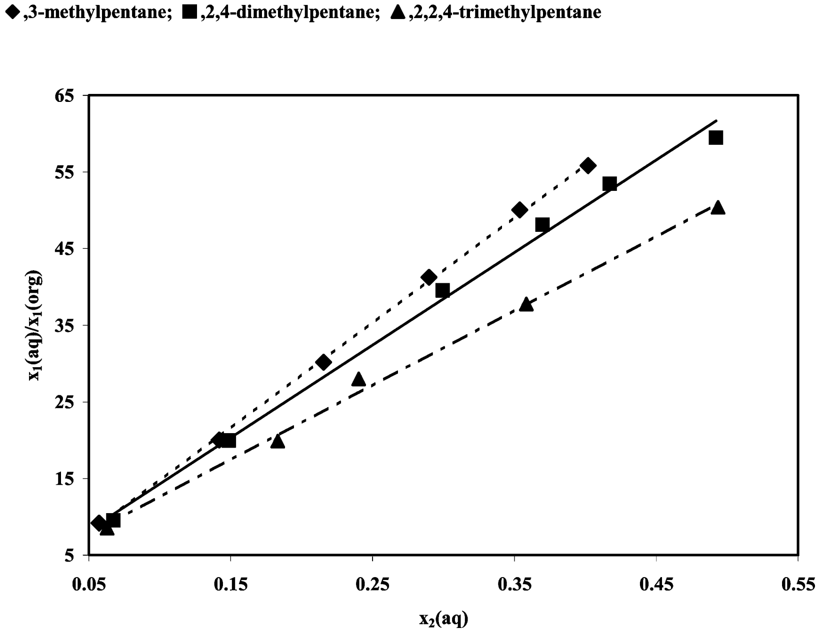

Figure 2. Distribution coefficient of monoethylene glycol between the aqueous (aq) and organic (org) phases in the ternary system monoethylene glycol (1) + water (2) + branched alkanes: ◆, 3-methylpentane; ■, 2,4-dimethylpentane; ▲, 2,2,4-trimethylpentane.

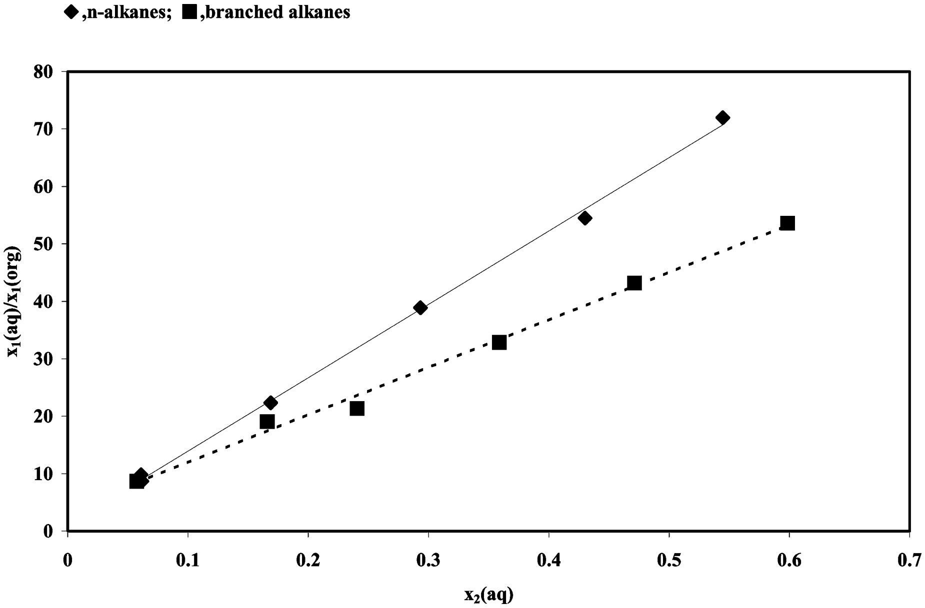

Figure 3. Distribution coefficient of monoethylene glycol between the aqueous (aq) and organic (org) phases in the systems monoethylene glycol (1) + water (2) + *n*-alkanes and monoethylene glycol (1) + water (2) + branched alkanes: ◆, *n*-alkanes; ■, branched alkanes.

covering a wide range of compositions. We have prepared the solutions using an electronic balance with a precision of $\pm 10^{-4}$ g, which corresponds to an uncertainty of $\pm 3 \times 10^{-5}$ mole fraction. The standard samples were analyzed using the same chromatographic conditions as those for the equilibrium samples. In all cases, the calibration curve was linear. For all systems investigated, the uncertainties of mole fraction measurements were estimated between ±0.002 and ±0.003 according as the phase was aqueous or organic.

Results and Discussion

The experimental LLE data for the system monoethylene glycol + water + hexane at four temperatures (between 283.1 K and 313.1 K) are given in Table 2. To show the effects of glycols in water + alkanes mixtures, we indicate in the last column of this table the distribution coefficient defined as the ratio of the molar fraction of monoethylene glycol between the aqueous and organic phases. After several trials, we found that it varies linearly as a function of the molar fraction of water in aqueous phase, as shown in Figure 1. The solubility of monoethylene glycol in the organic phase increases with temperature about two to three times greater at 313 K than at 283 K according to the water composition in the aqueous phase that varies from 0.2 to 0.8.

On the other hand, the comparison of LLE data of the monoethylene glycol + water + hexane and methanol + water + hexane[3] systems shows that monoethylene glycol about one a half to two times more soluble than methanol in the organic phase. For example, when the water composition in aqueous phase is equal to 0.5, the mole fraction of methanol in the organic phase[3] is 0.0073 at 298.15 K and that of monoethylene glycol is 0.0083 at 293.1

Table 7. Equilibrium Phase Compositions in Mole Fraction *x* for the Monoethylene Glycol (1) + Water (2) + Hexane (3) + Heptane (4) + Octane (5) + Nonane (6) + Decane (7) System at 293.1 K

aqueous phase							organic phase							
x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_1^a/x_1^o
0.9310	0.0615	0.0038	0.0010	0.0015	0.0007	0.0006	0.1074	0.0047	0.2200	0.1891	0.1799	0.1533	0.1456	8.67
0.9296	0.0609	0.0022	0.0007	0.0028	0.0032	0.0007	0.0946	0.1245	0.3050	0.2629	0.1380	0.0325	0.0425	9.83
0.8267	0.1687	0.0013	0.0007	0.0005	0.0019	0.0002	0.0370	0.0561	0.3553	0.3046	0.1612	0.0371	0.0487	22.34
0.7036	0.2933	0.0016	0.0003	0.0005	0.0003	0.0004	0.0181	0.0926	0.3472	0.2981	0.1580	0.0365	0.0495	38.87
0.5663	0.4301	0.0017	0.0007	0.0005	0.0005	0.0002	0.0104	0.0994	0.3492	0.2977	0.1621	0.0352	0.0460	54.45
0.4534	0.5447	0.0009	0.0003	0.0004	0.0001	0.0001	0.0063	0.0530	0.3666	0.3146	0.1674	0.0385	0.0536	71.97

Table 8. Equilibrium Phase Compositions in Mole Fraction *x* for the Monoethylene Glycol (1) + Water (2) + 2-Methylpentane (3) + 3-Methylpentane (4) + 2,4-Dimethylpentane (5) + 2,2,4-Trimethylpentane (6) System at 293.1 K

aqueous phase						organic phase						
x_1	x_2	x_3	x_4	x_5	x_6	x_1	x_2	x_3	x_4	x_5	x_6	x_1^a/x_1^o
0.9126	0.0574	0.0075	0.0158	0.0028	0.0039	0.1054	0.0301	0.2219	0.3303	0.1857	0.1266	8.66
0.8019	0.1660	0.0068	0.0132	0.0077	0.0044	0.0421	0.0240	0.2433	0.3414	0.2019	0.1473	19.05
0.7298	0.2407	0.0027	0.0153	0.0054	0.0061	0.0342	0.0184	0.2501	0.3451	0.2112	0.1410	21.34
0.6110	0.3589	0.0066	0.0107	0.0077	0.0051	0.0186	0.0170	0.2534	0.3499	0.2007	0.1604	32.85
0.5011	0.4713	0.0063	0.0128	0.0042	0.0043	0.0116	0.0142	0.2586	0.3511	0.2057	0.1588	43.20
0.3700	0.5987	0.0059	0.0152	0.0060	0.0042	0.0069	0.0105	0.2500	0.3482	0.2134	0.1710	53.62

K and 0.0129 at 303.1K. This result is nearly realized for all compositions.

The LLE data for the ternary systems monoethylene glycol + water + *n*-alkanes (from C7 to C10), monoethylene glycol + water + 3-methylpentane at three temperatures, monoethylene glycol + water + 2,4-dimethylpentane, and 2,2,4-trimethylpentane are reported in Tables 3−5. The distribution coefficient of monoethylene glycol increases with the number of carbon atoms. Therefore as can be seen in Figure 2, it decreases in branched alkanes when the degree of branching increases.

To evaluate our work, LLE experimental data are analyzed using the two-parameter correlation given by Othmer−Tobias[4,5]

$$\ln\left(\frac{1 - w_3^o}{w_3^o}\right) = a \ln\left(\frac{1 - w_1^a}{w_1^a}\right) + \ln b \qquad (1)$$

where w_3^o is the mass fraction of alkane in the organic phase, w_1^a the mass fraction of monoethylene glycol in the aqueous phase, and a and b are the fit parameters. The linearity of the plot $\ln(1 - w_3^o)/w_3^o$ against $\ln(1 - w_1^a)/w_1^a$ indicates the degree of consistency of the data. The values of parameters of eq 1 together with the correlation coefficient values R^2 are given in Table 6. As can be seen, linear regression yields for all data sets R^2 values better than 0.98.

To study the solubility of *n*-alkanes and branched alkanes in monoethylene glycol + water mixtures, we have measured the LLE of two multicomponent systems: monoethylene glycol + water + hexane + heptane + octane + nonane + decane and monoethylene glycol + water + 2-methylpentane + 3-methylpentane + 2,4-dimethylpentane + 2,2,4-trimethylpentane. Results are presented in Tables 7 and 8. As shown in Figure 3 for the two systems considered, the distribution coefficient of monoethylene glycol is the same when the mole fraction of water does not exceed 0.1. After this composition, it increases rapidly and the solubility of monoethylene glycol in organic phase is nearly twice greater for branched alkanes when water content exceeds 0.5.

Conclusion

LLE data for eight ternary systems including monoethylene glycol have been measured under atmospheric pressure at 293.1 K and for two of these systems over the temperature range (283.1 K to 313.1 K). All data sets are satisfactorily represented by the Othmer−Tobias correlation. Two multicomponent systems having six and seven species have been also studied in order to know the behavior of distribution coefficient of monoethylene glycol in *n*-alkanes and branched alkanes. The experimental results reveal that organic solubility of monoethylene glycol in water + alkanes mixtures increases significantly with temperature and with the size of alkane.

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