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Isobaric vapor–liquid equilibria in the mixtures of 1-heptyne + butanal, 1-octyne + 3-octyne, +ethylbenzene and +dibutyl ether, 2-octyne + dibutyl ether and +1-butanol, and 3-octyne + 1-octene

H. Kirss, E. Siimer * and L. Kudryavtseva
Institute of Chemistry, Estonian Academy of Sciences, Tallinn (Estonia)

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Abstract

For seven binary systems containing isomeric alkynes, the isobaric variations of the boiling temperature with liquid-phase composition were determined using a semi-micro ebulliometer over the entire composition range. The experimental data were used to fit the adjustable parameters in the Redlich–Kister and Wilson equations. The new UNIFAC interaction parameters were determined separately for the terminal and internal triple-bond groups.

INTRODUCTION

In recent papers [1, 2], the vapor–liquid equilibria (VLE) and enthalpies of mixing H^E were investigated for several binary systems containing isomeric alkynes. Analysis of the results in terms of the UNIFAC group contribution [3] indicated a clear differentiation between the terminal and internal triple–bond groups for both VLE and H^E calculations.

The present paper continues the investigation initiated earlier by reporting the VLE data for 1-octene–3-octyne, 1-octyne–3-octyne, 1-octyne–ethylbenzene and 1-butanol–2-octyne at the pressures 760, 600, 400 and 200 torr, and for butanal–1-heptyne, 1-octyne–dibutyl ether and 2-octyne–dibutyl ether at 600, 400 and 200 torr.

EXPERIMENTAL

The isomeric alkynes were synthesized [4] and fractionally distilled in a 50-plate Teflon bristle-rotor column [5] to a purity of more than 99.5 mass%, as detected by gas chromatography (GC) on Carbowax-20M and squalane capillary columns using a hydrogen flame ionization detector. All

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* Corresponding author.

measurements were made with the alkynes recently purified. Two different samples of 1-octyne were used. Pure-grade butanal was distilled and had a purity of 99.9 mass%, according to GC analysis. The dibutyl ether and 1-butanol obtained from Reakhim (Kharkov, USSR) in high purity forms (Puriss Grade) were used without further purification. For both compounds, the GC analysis failed to show any significant impurities. The 1-octene and ethylbenzene used in the present measurements were the same as those employed in ref. 1.

Details of the experimental determinations of the boiling temperature have been given elsewhere [6]. The accuracy of these determinations is ±0.05 K. All the mixtures were prepared by weight. The liquid mole fraction X_i after correction for evaporation, was evaluated with an accuracy of better than 1×10^{-3}. The composition of the equilibrium vapor phase was obtained by calculation using the Redlich–Kister, Wilson and UNIFAC equations for the activity coefficients. Economy of experimental effort was achieved by an avoidance of sampling and analysis of samples. The vapor composition was thus calculated and the liquid mixtures were made up by mixing measured quantities of pure liquids.

RESULTS AND DISCUSSION

Table 1 gives the T–X_1 data for the seven binary systems. In order to avoid a restriction to certain compositions, all the experimental values for each system were fitted by the three-parameter Redlich–Kister and Wilson equations using the least-squares method, which is non-linear for the Wilson equation. The advantage of the latter equation is that it may be applied to multi-component systems by using the binary data alone, while the Redlich–Kister equation is known as one of the best means of describing binary VLE data. The results obtained in a binary data fit, together with the values of mean deviations δP, are given in Table 2.

The mean relative deviation is determined by

$$\delta P\% = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}}\right|_i \times 100 \tag{1}$$

where n is the number of experimental points.

The information on the boiling temperatures of pure liquids at different pressures was obtained in the same semi-micro ebulliometer. The experimental results given in Table 1, together with the data on the mixtures, were correlated with pressure by means of the Antoine equation in the form

$$T/\text{K} = \frac{B}{A - \ln P/\text{torr}} - C \tag{2}$$

The results of the determination of the constants A, B and C, and the mean deviations δP, are shown in Table 3.

TABLE 1

Experimental T–X_1 data for binary systems at different pressures

X_1	Boiling point in K for pressures in torr			
	200	400	600	760
1-Octene(1)–3-octyne(2)				
0.000	364.49	384.77	398.01	406.34
0.199	361.44	381.80	395.08	403.37
0.318	359.93	380.29	393.53	401.81
0.333	359.77	380.13	393.41	401.73
0.414	358.76	379.11	392.39	400.66
0.502	357.69	378.05	391.31	399.58
0.680	355.81	376.12	389.36	397.65
0.818	354.35	374.70	387.94	396.22
1.000	352.70	372.99	386.20	394.45
1-Octyne(1)–3-octyne(2)				
0.000	364.49	384.77	398.01	406.34
0.189	363.17	383.45	396.71	404.95
0.289	362.45	382.72	–	404.27
0.298	–	382.76	395.99	404.27
0.331	362.19	382.45	–	–
0.473	361.19	381.41	394.60	402.84
0.592	360.41	380.62	393.79	402.00
0.711	359.64	379.84	392.99	401.19
0.804	359.04	379.21	392.38	400.58
1.000	357.85	378.01	391.13	399.34
Butanal(1)–1-heptyne(2)				
0.000	333.87	352.81	365.23	
0.148	330.00	349.10	361.70	
0.295	326.23	345.36	357.95	
0.501	321.43	339.92	352.36	
0.701	317.77	336.07	348.18	
0.887	313.89	332.00	343.95	
1.000	311.84	329.81	341.69	
1-Octyne(1)–ethylbenzene(2)				
0.000	365.92	387.01	400.75	409.32
0.166	364.39	385.29	398.95	407.46
0.234	363.76	384.58	398.21	406.70
0.318	362.98	383.70	397.27	405.74
0.444	362.05	382.58	396.12	404.51
0.551	361.08	381.63	395.03	403.35
0.697	359.97	380.38	393.69	402.00
0.812	359.17	379.46	392.69	400.93
0.842	358.91	379.15	392.40	400.65
1.000	357.74	377.98	391.09	399.26

TABLE 1 (continued)

X_1	Boiling point in K for pressures in torr			
	200	400	600	760
1-Octyne(1)–dibutyl ether(2)				
0.000	372.16	393.07	406.71	
0.162	369.47	390.28	403.90	
0.345	366.67	387.32	400.85	
0.526	364.09	384.64	398.02	
0.693	361.84	382.20	395.53	
0.832	359.83	380.11	393.36	
1.000	357.74	377.98	391.09	
2-Octyne(1)–dibutyl ether(2)				
0.000	372.16	393.07	406.71	
0.174	371.60	392.45	406.08	
0.323	371.05	391.82	405.34	
0.511	370.49	391.17	404.68	
0.681	370.03	390.66	404.08	
0.854	369.42	390.01	403.39	
1.000	369.02	389.50	402.84	
1-Butanol(1)–2-octyne(2)				
0.000	369.02	389.50	402.84	411.18
0.144	359.65	379.20	382.38	400.91
0.260	356.71	375.42	387.83	395.39
0.347	355.51	373.65	385.47	392.90
0.430	354.76	372.70	384.30	–
0.565	354.36	371.85	383.19	390.24
0.696	354.27	371.46	382.56	389.46
0.799	354.61	371.60	382.55	389.34
0.888	355.54	372.22	382.98	389.66
1.000	357.51	373.82	384.32	390.82

The new UNIFAC group interaction parameters determined as described by Fredenslund et al. [3] are given in Table 4. The other interaction parameters used have been reported by us [2] and by Gmehling et al. [7].

Table 5 gives the values of the mean deviation of experimental pressures and those calculated by UNIFAC for five of the systems studied. The δP values obtained are generally higher than those shown in Table 2, particularly for the system containing 1-butanol. The best description of the latter is provided by the Redlich–Kister equation.

The ΔT values presented in Table 6 for the two remaining systems, 1-octene–3-octyne and 1-octyne–ethylbenzene, indicate that the UNIFAC model gave a fairly satisfactory prediction of the boiling temperatures.

To verify the applicability of the correlations used, the composition of the azeotropic mixture was calculated. An azeotrope was only found for

TABLE 2

Parameters of the Redlich–Kister (b, c, d) and Wilson (Λ_{12}, Λ_{21}) equations and the deviation of experimental pressures from the calculated values (δP in %)

P/torr	b	c	d	δP	Λ_{12}	Λ_{21}	δP
1-Octene(1)–3-octyne(2)							
200	0.0517	−0.0091	0.0320	0.066	0.8308	1.1268	0.098
400	0.0410	−0.0029	0.0168	0.048	0.9739	0.9840	0.059
600	0.0397	−0.0030	0.0167	0.053	0.9666	0.9926	0.066
760	0.0383	−0.0052	0.0089	0.061	0.8081	1.1694	0.062
1-Octyne(1)–3-octyne(2)							
200	−0.0023	0.0080	−0.0007	0.032	1.4963	0.6047	0.030
400	−0.0070	0.0157	−0.0081	0.072	0.8797	1.1368	0.112
600	−0.0044	0.0199	−0.0156	0.060	1.7094	0.4811	0.080
760	−0.0037	0.0192	−0.0062	0.079	0.9234	1.0829	0.140
Butanal(1)–1-heptyne(2)							
200	−0.1246	−0.0608	−0.1568	0.277	1.7195	0.5816	0.526
400	−0.1276	0.0007	−0.1200	0.408	1.5201	0.7015	0.473
600	−0.1507	0.0131	−0.1062	0.319	1.0380	1.1289	0.392
1-Octyne(1)–ethylbenzene(2)							
200	−0.0009	−0.0070	−0.0131	0.088	1.0803	0.9257	0.105
400	0.0086	0.0012	−0.0059	0.063	1.0965	0.9006	0.066
600	0.0018	0.0034	−0.0003	0.057	1.3550	0.6971	0.059
760	−0.0008	0.0043	−0.0082	0.046	0.9398	1.0640	0.055
1-Octyne(1)–dibutyl ether(2)							
200	−0.0463	−0.0297	0.0059	0.093	1.3749	0.7273	0.168
400	−0.0392	−0.0148	0.0236	0.108	1.3152	0.7604	0.136
600	−0.0432	−0.0104	0.0078	0.077	1.3397	0.7464	0.088
2-Octyne(1)–dibutyl ether(2)							
200	0.0013	−0.0040	−0.0025	0.084	0.6800	1.3799	0.085
400	0.0019	−0.0068	−0.0216	0.063	1.0534	0.9493	0.084
600	0.0013	−0.0024	−0.0252	0.084	1.0717	0.9331	0.086
1-Butanol(1)–2-octyne(2)							
200	1.2649	0.0822	−0.1328	0.276	0.5219	0.4045	0.538
400	1.1144	0.1573	−0.0867	0.175	0.6811	0.3684	0.440
600	1.0107	0.2401	−0.1123	0.185	0.8445	0.3144	0.561
760	0.9474	0.3050	−0.1835	0.113	0.9641	0.2817	0.770

1-butanol with 2-octyne. This azeotrope has a minimum in boiling temperature and exists at all four pressures used. The azeotropic minimum boiling temperature and the corresponding compositions were evaluated from T–X plots. The values obtained are listed in Table 7 together with the compositions estimated graphically by plotting the relative volatility

TABLE 3

Parameters of eqn. (2) and the corresponding relative mean errors δP (in %)

Compound	A	B	C	δP
1-Heptyne	15.73103	2778.86	−67.507	0.026
1-Octene	15.96357	3111.75	−60.937	0.006
1-Octyne[a]	15.89072	3046.91	−70.205	0.027
1-Octyne[b]	16.40954	3378.20	−53.706	0.018
2-Octyne	15.88663	3093.87	−76.825	0.018
3-Octyne	15.47861	2822.18	−87.276	0.039
Ethylbenzene	15.99272	3253.90	−61.657	0.006
Dibutyl ether	15.93818	3192.61	−72.099	0.000
Butanal	15.56869	2557.20	−62.841	0.084
1-Butanol	17.19557	3135.66	−93.948	0.010

[a] Parameters used for 1-octyne mixtures with 3-octyne. [b] Parameters used for 1-octyne mixtures with ethylbenzene and dibutyl ether.

TABLE 4

UNIFAC interaction parameters a_{mn} in K

Groups		a_{mn}	a_{nm}
m	n		
CH≡C	C≡C	17.73	24.07
	CHO	−65.26	−5.96
	CH_2O	192.92	−191.66
C≡C	OH	−11.82	858.51
	CH_2O	−119.28	181.77

TABLE 5

Pressure reproduction by the UNIFAC model

System	δP in % for pressures P in torr			
	200	400	600	760
1-Octyne–3-octyne	0.09	0.12	0.13	0.14
Butanal–1-heptyne	0.59	0.45	0.57	–
1-Octyne–dibutyl ether	0.15	0.14	0.10	–
2-Octyne–dibutyl ether	0.10	0.08	0.10	–
1-Butanol–2-octyne	2.79	0.84	0.66	1.64

TABLE 6

Boiling temperature prediction by the UNIFAC model $\overline{\Delta T} = (\sum_{i=1}^{n} |T_{\mathrm{exp}} - T_{\mathrm{calc}}|_i)/n$

System	$\overline{\Delta T}$ at pressures P in torr			
	200	400	600	760
1-Octene–3-octyne[a]	0.36	0.35	0.33	0.31
1-Octene–3-octyne[b]	0.43	0.40	0.41	0.41
1-Octyne–ethylbenzene[a]	0.08	0.11	0.07	0.05

[a] P values calculated by using the group interaction parameters taken from refs. 1 and 7. [b] P values calculated by using the group interaction parameters taken from refs. 1 and 8.

TABLE 7

Azeotropic parameters of the binary system 1-butanol(1)–2-octyne(2) at different pressures

Source of data	Pressure/torr							
	200		400		600		760	
	T/K	X_1	T/K	X_1	T/K	X_1	T/K	X_1
Ebulliometric experiment	354.2	0.685	371.4	0.720	382.5	0.759	389.3	0.791
Redlich–Kister		0.66		0.73		0.77		0.79
Wilson		0.68		0.75		0.79		0.82
UNIFAC		0.71		0.75		0.78		0.79

calculated by means of the Redlich–Kister, Wilson and UNIFAC equations. The agreement with the ebulliometric composition data can be considered satisfactory. In accordance with Wrewski's rule [9], the mole fraction of butanol in the azeotrope increases with increasing pressure.

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