Thermochimica Acta, 195 (1992) 85–94
Elsevier Science Publishers B.V., Amsterdam

Measurement, correlation and prediction of binary vapour–liquid equilibria and enthalpies of mixing for systems containing isomeric alkynes

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(Received 30 April 1991)

Abstract

The experimental isobaric vapour–liquid equilibria (VLE) in the five binary systems formed by 1-octyne with 1-octene, and by 1-octyne and 3-octyne with butyl acetate and acetonitrile, were measured at pressures of 200, 400, 600 and 760 Torr. Data on the binary enthalpies of mixing (H^E) were obtained at 298.15 K for the whole composition range of the six systems containing 1-octyne with 1-octene, 2-octyne and butyl acetate, 1-nonyne with 1-nonene, and 2-octyne with 1-octene and ethylbenzene. In addition, the equimolar H^E values of some binary systems were measured. The experimental results were examined on the basis of the UNIFAC group contribution model. The new UNIFAC parameters determined for terminal and internal triple-bond groups separately were used for calculation of VLE and H^E data.

INTRODUCTION

In this paper, several binary systems formed by isomeric alkynes are investigated using the UNIFAC group contribution model [1]. Thermodynamic data for these systems are not very common in the literature and therefore we present here the results of VLE and H^E measurements in order to describe the behaviour of such mixtures as well as to determine UNIFAC model parameters. An attempt to predict simultaneously VLE and H^E values by the UNIFAC model for systems containing unsaturated hydrocarbons as one of components was recently reported [2]. Some success was achieved for only a few systems formed by *n*-alkenes and cycloalkenes. For systems containing isomeric alkynes, the H^E prediction from VLE appeared unreliable. The present paper is focused on this consideration, thereby paying special attention to using the interaction parameters determined for terminal and internal triple bond groups separately.

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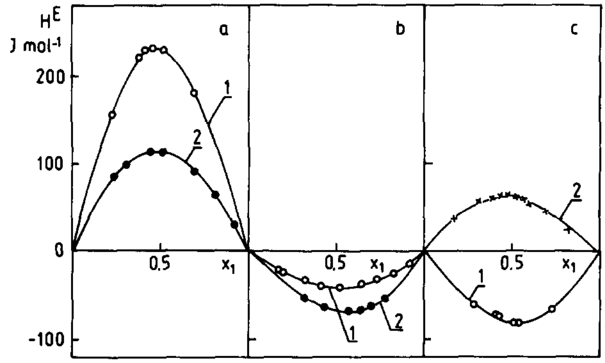

Fig. 1. Experimental and calculated H^E data for binary mixtures formed by 1-octene with 1-octyne and 2-octyne (a), ethylbenzene with 1-octyne and 2-octyne (b), and 2-octyne with 1-octyne and 4-octyne (c). Points are experimental values for 1-octyne (○), 2-octyne (●) and 4-octyne (×) mixtures; lines represent the calculations of eqn. (2) for mixtures containing terminal (curves 1) and internal (curves 2) isomers of octyne. The experimental data for the systems ethylbenzene–1-octyne and 2-octyne–4-octyne are taken from refs. 3 and 4, respectively.

Differences in the behaviour of isomeric alkynes with the triple bond in a terminal and an internal position in the molecule are readily shown in the excess properties of their mixtures, for example in Fig. 1 which represents the experimental and smoothed H^E concentration dependence for isomeric octyne mixtures with 1-octene and ethyl benzene, and those formed between the isomeric octynes themselves. In general, systems formed by different internal isomers of a given alkyne are similar in behaviour [5,6]. Therefore, the internal triple bond group C≡C could be considered as a new group.

EXPERIMENTAL

Materials and methods

Analytical grade 1-octene and 1-nonene were purified by distillation. Acetonitrile was purified according to ref. 7. The final purities of these compounds were shown by gas chromatography to be better than 99%. Butyl acetate and ethylbenzene obtained from Reakhim (Kharkov, USSR) in high purity (puriss, p.a. > 99%) were used without further purification. All these substances were stored under an argon atmosphere and protected from light and moisture.

The isomeric alkynes were synthesised [8] and fractionally distilled in a 50-plate Teflon bristle-rotor column [9] to more than 99.5% pure, as detected by gas chromatography on PEG-20 M and squalane capillary columns using a hydrogen flame ionization detector. All measurements were made with recently purified alkynes. The physical properties of the alkynes at 293.15 K were: density $\rho = 746.3$ kg m^{-3}, $n_D = 1.41606$ for 1-octyne; $\rho = 759.3$ kg m^{-3}, $n_D = 1.42785$ for 2-octyne; $\rho = 751.7$ kg m^{-3}, $n_D = 1.4253$ for 3-octyne and $\rho = 756.8$ kg m^{-3}, $n_D = 1.4220$ for 1-nonyne.

Details of the measurements of boiling temperatures at constant pressure, as well as excess enthalpies at 298.15 K over the entire composition range of the mixtures have been outlined in previous papers [10,11]. The errors in the boiling temperature determinations were estimated to be lower than 0.05 K, and those in the determination of H^E and the liquid phase mole fraction, X, to be lower than 2% and 1×10^{-3}, respectively.

The estimation of the UNIFAC interaction parameters on the basis of VLE and H^E experimental data was determined using the simplex method, the Nelder–Mead procedure, described in detail by Fredenslund et al. (ref. 1, pp. 79–85). The program for parameter estimation was written in turbobasic language and all calculations were performed on an IBM personal computer. The minimisation function

$$F = \sum_{i=1}^{n} \left(\frac{Y_{\text{calc}_i} - Y_{\text{exp}_i}}{Y_{\text{exp}_i}} \right)^2 = \min \tag{1}$$

was used where Y is the total pressure or enthalpy of mixing in VLE and H^E calculations, respectively.

RESULTS AND DISCUSSION

The experimental data obtained in this work are presented in Tables 1 and 5. The parameters of pure component Antoine equations used for VLE calculations are given in Table 2. Table 3 contains a complete summary of the results by the Redlich–Kister correlation for VLE of all the five binary systems. The system 1-octyne–butyl acetate shows a temperature minimum at the pressures considered. The azeotropic parameters (interpolated values) at different pressures are presented in Table 4.

The experimental H^E values of six binary systems were fitted to the smoothing equation

$$H^E(\text{J mol}^{-1}) = X_1 X_2 \sum_{i=0}^{n-1} A_i (X_1 - X_2)^i \tag{2}$$

Values for the standard deviations $\sigma(H^E)$ are given by

$$\sigma(H^E) = \left[\sum \left(H^E_{\text{calc}} - H^E_{\text{exp}} \right)^2 / (n - N) \right]^{1/2} \tag{3}$$

where n is the number of experimental points and N is the number of coefficients A_i. The values of the coefficients A_i determined by the least-squares method and the standard deviations are given in Table 6.

TABLE 1

Experimental $T-X$ data for binary systems at different pressures

X_1	Boiling point (K) at P (Torr)			
	200	400	600	760
1-Octene(1)–1-octyne(2)				
0.000	357.86	377.99	391.13	399.32
0.159	356.58	376.77	389.91	398.11
0.308	355.55	375.75	388.93	397.14
0.499	354.43	374.65	387.85	396.06
0.689	353.62	373.85	387.07	395.29
0.814	353.18	373.43	386.63	394.85
1.000	352.70	372.99	386.20	394.45
Butyl acetate(1)–1-octyne(2)				
0.000	357.86	377.99	391.13	399.32
0.190	357.91	377.93	390.95	399.07
0.313	357.96	377.90	390.86	398.95
0.392	358.01	377.91	390.84	398.90
0.491	358.10	377.95	390.84	398.90
0.645	358.28	378.05	390.92	398.94
0.793	358.49	378.19	391.02	399.02
1.000	358.85	378.50	391.28	399.24
Butyl acetate(1)–3-octyne(2)				
0.000	364.49	384.77	398.01	406.34
0.118	362.92	383.12	396.25	404.45
0.208	361.91	381.99	395.07	403.20
0.295	361.27	381.32	394.38	402.48
0.354	360.88	380.85	393.89	401.96
0.428	360.33	380.30	393.29	401.36
0.517	359.96	379.81	392.74	400.81
0.654	359.44	379.25	392.13	400.13
0.775	359.08	378.79	391.65	399.62
0.901	358.89	378.57	391.35	399.33
1.000	358.85	378.50	391.28	399.24
Acetonitrile(1)–1-octyne(2)				
0.000	357.86	377.99	391.13	399.32
0.223	327.71	347.70	360.79	368.89
0.355	323.39	342.62	355.14	362.96
0.521	320.55	339.15	351.32	358.89
0.654	319.10	337.59	349.59	357.05
0.798	317.90	336.26	348.12	355.48
1.000	317.12	335.48	347.37	354.75
Acetonitrile(1)–3-octyne(2)				
0.000	364.49	384.77	398.01	406.34
0.317	322.44	342.00	354.95	362.95
0.446	319.97	339.17	351.55	359.29
0.521	319.17	338.08	350.32	357.93
0.651	318.43	337.04	349.05	356.52
0.774	317.82	336.19	348.08	355.46
1.000	317.12	335.48	347.37	354.75

TABLE 2

Parameters of the Antoine equation, $\ln P$ (Torr) $= A - B/(C+T)$ and corresponding mean errors δP

Compound	A	B	C	δP (%)
1-Octene	15.96357	3111.75	−60.937	0.006
1-Octyne	15.91811	3061.89	−69.542	0.037
3-Octyne	15.47815	2822.04	−87.275	0.039
Butyl acetate	16.17362	3139.27	−70.187	0.074
Acetonitrile	16.61924	3186.66	−35.635	0.003

In Table 7, the experimental values of equimolar H^E obtained for a mixture of 2-octyne with butyl acetate and for 1- and 2-octyne with acetonitrile are compared with the calculated results.

TABLE 3

Parameters of the Redlich–Kister equation and the corresponding mean errors of total pressure δP

P (Torr)	b	c	d	δP (%)
1-Octene(1)–1-octyne(2)				
200	0.1095	0.0139	−0.0122	0.024
400	0.0967	0.0154	−0.0144	0.018
600	0.0873	0.0116	−0.0035	0.033
760	0.0837	0.0124	−0.0024	0.029
Butyl acetate(1)–1-octyne(2)				
200	0.0370	−0.0015	−0.0078	0.010
400	0.0389	0.0030	−0.0040	0.017
600	0.0436	−0.0012	−0.0065	0.020
760	0.0440	−0.0038	−0.0063	0.021
Butyl acetate(1)–3-octyne(2)				
200	0.2256	−0.0225	0.0089	0.096
400	0.2018	−0.0129	0.0086	0.098
600	0.1921	−0.0157	0.0235	0.098
760	0.1909	−0.0201	0.0277	0.077
Acetonitrile(1)–1-octyne(2)				
200	1.4094	0.1743	0.2222	0.226
400	1.3090	0.2103	0.1798	0.133
600	1.2428	0.2310	0.1602	0.159
760	1.2058	0.2346	0.1597	0.164
Acetonitrile(1)–3-octyne(2)				
200	1.7231	0.2718	0.2364	0.123
400	1.6222	0.2172	0.2451	0.119
600	1.5198	0.2540	0.2185	0.116
760	1.4716	0.2543	0.2185	0.107

TABLE 4

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

200		400		600		760	
T (K)	X_1	T (K)	X_1	T (K)	X_1	T (K)	X_1
357.8	0.96	377.9	0.69	390.8	0.56	398.8	0.51

The adjustable parameters in UNIFAC equations were fitted to the experimental data of Table 1, using some group parameters published earlier [12,13]. The values of the estimated parameters based on the

TABLE 5

Experimental values of excess enthalpies H^E for binary mixtures at 298.15 K

X_1 [a]	H^E (J mol^{-1})	X_1 [a]	H^E (J mol^{-1})
1-Octene–1-octyne		2-Octyne–1-octyne	
0.223	157	0.280	−60
0.377	221	0.416	−71
0.420	230	0.420	−74
0.461	232	0.512	−81
0.523	229	0.521	−80
0.698	181	0.715	−67
1-Octene–2-octyne		1-Octyne–butyl acetate	
0.240	84	0.115	−102
0.290	98	0.245	−162
0.449	113	0.361	−202
0.512	112	0.380	−204
0.700	90	0.529	−225
0.820	63	0.548	−222
0.930	35	0.622	−216
1-Nonene–1-nonyne		0.650	−214
0.172	117	0.727	−184
0.262	162	0.764	−167
0.342	195	0.880	−90
0.422	210		
0.487	213	2-Octyne–ethylbenzene	
0.545	215	0.227	−56
0.560	215	0.303	−63
0.591	204	0.365	−69
0.637	203	0.432	−68
0.760	162	0.566	−64
0.810	142	0.678	−56

[a] Mole fraction of the first component.

TABLE 6

Values of parameters A_i, eqn. (2), and the standard deviations $\sigma(H^E)$ (eqn. (3)) for binary systems at 298.15 K

System	A_0	A_1	A_2	A_3	$\sigma(H^E)$
1-Octene–1-octyne	925.109	−131.626	−178.735	219.050	0.74
1-Octene–2-octyne	450.594	−132.320	−36.003	349.247	2.42
1-Nonene–1-nonyne	860.811	−0.600	29.554	195.186	2.69
2-Octyne–1-octyne	−318.098	−130.492	30.228	501.366	1.50
1-Octyne–butyl acetate	−891.915	−147.565	−53.626	415.539	1.96
2-Octyne–ethylbenzene	−270.080	60.688	−53.380	–	1.20

experimental VLE data obtained in this work and in our previous studies [14,15] are given in Table 8. In addition, the estimated parameters obtained from H^E data for $CH_2/HC\equiv C$ and $CH_2/C\equiv C$ groups are presented in this table.

Parameters of the UNIFAC group volume R_m, and surface area Q_m, for $C\equiv C$ groups were calculated from the group parameters given by Bondi [16], being 1.0613 and 0.7840, respectively.

The correlation and prediction abilities of the UNIFAC model are tested by means of percent deviations δP and δH^E between the calculated and experimental values of the total pressure and enthalpy of mixing. The

TABLE 7

Experimental and calculated equimolar excess enthalpies H^E of binary systems at 298.15 K using different sets of UNIFAC group parameters

System	H^E (J mol^{-1})			
	Experimental	Calcd. with parameters		
		[12]	[13]	This work
1-Octene–1-octyne	231	176	69	62 [a], 74 [b]
1-Octene–2-octyne	113	86	23	−115 [a], −99 [b]
1-Nonene–1-nonyne	215	170	64	67 [b]
Ethylbenzene–1-octyne	−41 [3]	–	–	−106 [a]
Ethylbenzene–2-octyne	−68	–	–	−201 [a]
Butyl acetate–1-octyne	−223	–	–	−100 [a]
Butyl acetate–2-octyne	150	–	–	16 [a]
Acetonitrile–1-octyne	730	329	–	196 [a]
Acetonitrile–2-octyne	1049	508	–	301 [a]

[a] Value estimated by using the above-given $CH_2/HC\equiv C$ and $CH_2/C\equiv C$ group parameters and those taken from ref. 12.

[b] Value estimated by using the above-given $CH/HC\equiv C$ and $CH_2/C\equiv C$ group parameters and those taken from ref. 13.

TABLE 8

UNIFAC interaction parameters α_{mn} (K)

m	n	α_{mn}	α_{nm}
Calcd. from VLE data			
CH_2	$HC\equiv C$	243.8	17.9
CH_2	$C\equiv C$	530.8	−250.9
$C=C$	$HC\equiv C$	73.6 [a]	571.0 [a]
		(11.4) [b]	(115.3) [b]
$C=C$	$C\equiv C$	179.3 [a]	5287 [a]
		(−10.5) [b]	(114.2) [b]
AC	$HC\equiv C$	−36.9 [a]	101.5 [a]
AC	$C\equiv C$	329.4 [a]	−298.8 [a]
CCOO	$HC\equiv C$	80.3 [a]	−124.0 [a]
CCOO	$C\equiv C$	164.8 [a]	−135.0 [a]
CH_3CN	$HC\equiv C$	−164.1 [a]	90.4 [a]
CH_3CN	$C\equiv C$	22.8 [a]	−132.7 [a]
Calcd. from H^E data			
CH_2	$HC\equiv C$	456.6	181.5
CH_2	$C\equiv C$	501.2	167.0

[a] Value estimated by using the above-given $CH_2/HC\equiv C$ and $CH_2/C\equiv C$ group parameters and those taken from ref. 12.

[b] Value estimated by using the above-given $CH/HC\equiv C$ and $CH_2/C\equiv C$ group parameters and those taken from ref. 13.

deviation δ is defined by

$$\delta Y = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{Y_{\mathrm{calc}_i} - Y_{\mathrm{exp}_i}}{Y_{\mathrm{exp}_i}}\right| \times 100 \tag{4}$$

where Y may be P or H^E.

A comparison of the correlated total pressures in the five systems investigated is presented in Table 9 and indicates good agreement with the experimental values given in Table 1. In addition, the prediction by UNIFAC for three binary systems whose group interaction parameters are given in

TABLE 9

Calculation of the total vapor pressure δP (%) with the UNIFAC parameters presented here (correlation) and given in ref. 12 (prediction)

System	Correlation	Prediction
1-Octene–1-octyne	0.29	0.37
Butyl acetate–1-octyne	0.03	–
Butyl acetate–3-octyne	0.26	–
Acetonitrile–1-octyne	0.79	5.38
Acetonitrile–3-octyne	1.58	5.13

TABLE 10

Systems applied to the determination of UNIFAC parameters a_{mn} using the H^E data, and the corresponding mean errors δH^E

System	T (K)	Number of points	δH^E (%)	Ref.
Heptane–1-heptyne	298.15, 318.15	32	11	5
Octane–1-octyne	298.15, 308.15 318.15	44	6	5
Nonane–1-nonyne	298.15, 318.15	29	4	5
Octane–1-heptyne	298.15	9	8	18
Heptane–1-octyne	298.15	8	7	18
Decane–1-decyne	298.15	9	7	5
Octane–2-octyne	298.15, 318.15	27	8	5
Octane–3-octyne	298.15, 318.15	25	7	5
Octane–4-octyne	298.15, 318.15	28	7	5
Hexane–3-hexyne	298.15	23	8	19

ref. 12 is presented in Table 9. These predicted values are systematically lower for 1-octene mixtures and higher for those of acetonitrile than the experimental data.

The deviations between the experimental equimolar excess enthalpies of nine binary systems and those predicted by the UNIFAC method are given in Table 7. For comparison, the result for ethylbenzene–1-octyne [13] is also included. As is well known, the model considered, in general, cannot correctly predict H^E using VLE parameters.

For the systems investigated, this model also exhibits significant deviations, as seen in Table 7. The best prediction results in the systems formed by isomeric alkynes with 1-alkenes and acetonitrile are obtained when using the group parameters of Gmehling et al. [12]. The prediction with the parameters of this work gives only the correct signs of H^E in the other systems.

The failure of H^E prediction, as well as the experimental material accumulated and the attractiveness of the UNIFAC model suggested that we fit parameters with excess enthalpy data. The method developed by Pathanjali and Singh [17] was used. The matrix of interaction parameters they presented does not include the triple bond groups. Therefore, as a first step, the $CH_2/HC{\equiv}C$ and $CH_2/C{\equiv}C$ group interaction parameters were determined. Table 10 contains a summary of the results obtained by the UNIFAC correlation for the H^E values of all the binary systems used in the parameter determination. Further results will be presented separately.

REFERENCES

1 A. Fredenslund, J. Gmehling and P. Rasmussen, Vapor–Liquid Equilibria using UNIFAC, Elsevier, Amsterdam, 1977.

2 M. Kuus, H. Kirss, E. Siimer and L. Kudryavtseva, Thermochim. Acta, 182 (1991) 29.
3 L. Kudryavtseva, M. Kuus, H. Kirss and J. Vink, Eesti NSV Tead. Akad. Toim. Keem. (Proc. Estonian Acad. Sci. Chem.), 38 (1989) 84.
4 E. Otsa and L. Kudryavtseva, 5th Conf. Mixtures of Non-Electrolytes and Intermolecular Interaction, Halle (Germany), 1983.
5 E. Otsa, L.S. Kudryavtseva and O.G. Eisen, Monatsh. Chem., 111 (1980) 37.
6 E. Otsa and L.S. Kudryavtseva, Int. Data Ser., Sel. Data Mixtures, Ser. A, 1979 (1980) 117.
7 J.A. Riddick and W.B. Bunger, Organic Solvents, Wiley, New York, 1971.
8 V. Pällin and T. Ilomets, Transactions of Tartu University, 384 (1976) 98.
9 V. Mihkelson, A. Kõbu and O. Eisen, Eesti NSV Tead. Akad. Toim. Keem. (Proc. Estonian Acad. Sci. Chem.), 29 (1980) 109.
10 V. Mihkelson, H. Kirss, L. Kudryavzeva and O. Eisen, Fluid Phase Equil., 1 (1977–1978) 201.
11 E. Otsa, V. Mihkelson and L. Kudryavtseva, J. Fiz. Khim., 53 (1979) 899.
12 J. Gmehling, P. Rasmussen and A. Fredenslund, Ind. Eng. Chem. Proc. Des. Dev., 21 (1982) 118.
13 E.A. Macedo, U. Weidlich, J. Gmehling and P. Rasmussen, Ind. Eng. Chem. Proc. Des. Dev., 22 (1983) 678.
14 E. Otsa, L.S. Kudryavtseva, O.G. Eisen and E.M. Piotrovskaja, Monatsh. Chem., 111 (1980) 607.
15 E. Otsa, L. Kudryavtseva and O. Eisen, Eesti NSV Tead. Akad. Toim. Keem. (Proc. Estonian Acad. Sci. Chem.), 29 (1980) 272.
16 A. Bondi, Physical Properties of Molecular Crystals, Liquids and Gases, Wiley-Interscience, New York, 1968.
17 G.A. Pathanjali and R.P. Singh, Pol. J. Chem., 62 (1988) 187.
18 L.S. Kudryavtseva, E.K. Otsa and H.H. Kirss, Thermodynamics of Organic Compounds, Gorki State University, USSR, 1981, p. 79.
19 W. Woycicki and P. Rhensius, J. Chem. Thermodyn., 11 (1979) 153.