

Isothermal vapour-liquid equilibria for binary mixtures of *n*-octane with isomeric-butanols at 333·15 K

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Abstract. Isothermal vapour-liquid equilibrium (VLE) data were measured for the binary systems of *n*-octane with 1-butanol, 2-methyl-1-propanol, 2-butanol and 2-methyl-2-propanol at 333·15 K. The values of excess free energy, G_m^E , calculated are positive for all the systems. The results were correlated using Redlich-Kister and Wilson equations.

Keywords. Vapour-liquid equilibria; binary mixtures; excess free energy; alcohol-alkane interactions.

1. Introduction

Isothermal vapour-liquid equilibrium (VLE) studies for four binary systems of *n*-octane (1) and 1-butanol (2); *n*-octane (1) and 2-methyl-1-propanol (2); *n*-octane (1) and 2-butanol (2); and *n*-octane (1) and 2-methyl-2-propanol (2), at 333·15 K, were undertaken in the present work. The excess free energy of mixing, G_m^E , was calculated from these isothermal VLE data.

2. Experimental

2.1 Materials

Analytical reagent grade butanols were purified by fractional distillation over NaOH pellets, using a meter long column packed with glass helices. Reagent grade *n*-octane was purified over sodium. All the compounds were stored over 4A molecular sieves. The purity of the compounds as estimated by gas chromatography was better than 99·5 mol per cent. The densities of compounds are in good agreement with those reported in the literature (Riddick and Bunger 1970; Timmermans 1950).

2.2 Apparatus and procedure

The VLE data were determined using a modified Jones-Colburn recirculating still (Ammer *et al* 1956). The system pressure was adjusted to the desired value by means of a micrometer needle valve and a vacuum pump. The manometer readings were taken by means of a cathetometer accurate to within $\pm 0\cdot01$ mm. The ultimate system pressure was obtained after applying both the barometric and the gravitational corrections. The

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Table 1. Second virial coefficient (B) and molar liquid volume (V) of pure liquids at 333.15 K.

Compound	$B(\text{cm}^3 \text{mol}^{-1})$	$V(\text{cm}^3 \text{mol}^{-1})$
1-Butanol	-2360(-2364)*	95.2
2-Methyl-1-propanol	-2634(-2642)*	96.4
2-Butanol	-2288	96.0
2-Methyl-2-propanol	-1740	99.7
<i>n</i> -Octane	-3003	170.6

* Berro *et al* 1982.

temperature of the equilibrium chamber was measured accurately upto ± 0.1 K.

The vapour and liquid compositions were determined by the density method at 298.15 K for all the systems except for *n*-octane-2-methyl-2-propanol at 299.15 K. The uncertainty in the density measurements was less than 5×10^{-5} and in the mole fraction was less than 5×10^{-4} respectively.

The liquid phase activity coefficients (γ) were calculated according to the expression:

$$\gamma_i = (Py_i/P_i^s x_i) \exp \{ [(V_i - B_{ii})(P_i^s - P) + \delta_{12}(1 - y_i)^2 P] / RT \}, \quad (1)$$

where $i = 1, 2$; x, y are mole fractions of liquid and vapour respectively; P = solution pressure; P^s = vapour pressure of pure component; and $\delta_{12} = 2B_{12} - B_{11} - B_{22}$.

The δ_{12} term was not taken into the calculations of γ , because of the large uncertainties involved in the calculated and actual values of B_{12} . The second virial coefficients (B) were calculated using Tsonopoulos equation (Tsonopoulos 1974), and are reported in table 1, along with the liquid molar volumes of pure components at 333.15 K. The values of second virial coefficients obtained for 1-butanol and 2-methyl-1-propanol are in agreement with those of Berro *et al* (1982).

The excess free energy was calculated using the equation:

$$G_m^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2). \quad (2)$$

3. Results and discussion

The P - x - y data measured at 333.15 K for the four systems along with the calculated values of γ_1, γ_2 and G_m^E are given in table 2.

The thermodynamic consistency of the experimental data was checked by Herington's (1952) equal area method. Even though the data have not been checked by the other computational methods (Cuncell and Hicks 1980; Christiansen and Fredenslund 1975), our data are thermodynamically consistent, being better than 1.5%, 3.0%, 1.8% and 2.0% for 1-butanol, 2-methyl-1-propanol, 2-butanol and 2-methyl-2-propanol systems respectively.

The excess free energy of mixing, G_m^E , is positive, throughout the concentration range (figure 1) and decreases with the branching of the alcohol. This behaviour may be due to hydrogen-bond breaking, molecular interactions and structural effects. Berro *et al* (1982), Brown *et al* (1969), and Anilkumar and Katti (1980) have also studied excess free

Table 2. Isothermal vapour-liquid equilibrium data for *n*-octane(1) + isomeric butanol (2) systems at 333.15 K.

x_1	y_1	$P(\text{mmHg})$	γ_1	γ_2	G_m^E (J. mol^{-1})
<i>n</i> -Octane (1) + 1-butanol (2)					
0.0000	0.0000	59.20	—	1.000	—
0.0359	0.2075	72.22	5.316	1.001	170
0.0525	0.2601	76.80	4.854	1.010	258
0.1234	0.4159	91.71	3.936	1.028	536
0.1725	0.4800	99.61	3.515	1.052	717
0.2599	0.5226	105.87	2.697	1.147	996
0.3580	0.5534	110.13	2.155	1.286	1209
0.4742	0.5784	112.30	1.734	1.511	1324
0.5877	0.6002	112.72	1.457	1.835	1306
0.6557	0.6117	112.35	1.327	2.127	1233
0.7255	0.6293	110.93	1.218	2.512	1097
0.7883	0.6448	109.64	1.136	3.089	939
0.8297	0.6569	107.40	1.077	3.634	779
0.8802	0.6892	105.50	1.047	4.594	619
0.9266	0.7264	102.10	1.015	6.396	415
0.9450	0.7599	98.83	1.008	7.254	323
0.9670	0.8390	90.48	0.997	7.429	175
1.0000	1.0000	78.60	1.000	—	—
<i>n</i> -Octane (1) + 2-methyl-1-propanol (2)					
0.0000	0.000	92.4	—	1.000	—
0.0093	0.0372	96.61	4.916	1.015	83
0.0305	0.1107	102.07	4.713	1.012	173
0.1394	0.3171	123.0	3.559	1.052	611
0.2250	0.3859	130.64	2.828	1.115	881
0.3000	0.4168	133.74	2.344	1.199	1060
0.4791	0.4695	135.80	1.681	1.490	1231
0.5383	0.4808	135.00	1.555	1.605	1245
0.6405	0.5073	132.68	1.326	1.957	1170
0.6565	0.5127	131.23	1.294	2.003	1130
0.6710	0.5161	130.20	1.264	2.062	1095
0.7096	0.5389	129.60	1.223	2.182	1024
0.8095	0.5835	119.06	1.085	2.807	728
0.8341	0.5983	117.00	1.066	3.056	660
0.8920	0.6602	109.62	1.027	3.724	460
0.9450	0.7574	98.92	1.006	4.718	251
0.9600	0.7879	96.25	1.001	5.521	196
1.0000	1.0000	78.60	1.000	—	—
<i>n</i> -Octane (1) + 2-butanol(2)					
0.0000	0.0000	135.80	—	1.000	—
0.0392	0.0953	149.40	4.541	1.027	236
0.0640	0.1370	151.56	4.082	1.027	319
0.1155	0.2033	155.33	3.438	1.028	463
0.1837	0.2555	159.58	2.789	1.069	672
0.2445	0.2879	162.14	2.398	1.122	833
0.3097	0.3177	162.30	2.091	1.178	946
0.3922	0.3426	162.30	1.781	1.289	1054
0.4808	0.3643	160.82	1.531	1.446	1105
0.5847	0.3864	159.60	1.325	1.732	1088
0.6400	0.4073	158.82	1.270	1.920	1075
0.7421	0.4519	151.30	1.159	2.364	918

Table 2. (Contd.)

x_1	y_1	$P(\text{mmHg})$	γ_1	γ_2	G_m^E (J. mol ⁻¹)
0.7936	0.4737	144.83	1.089	2.717	758
0.8630	0.5228	137.13	1.047	3.517	588
0.9196	0.6187	118.34	1.007	4.141	334
0.8490	0.6931	108.53	1.004	4.824	233
0.9830	0.8441	92.06	1.003	6.244	97
1.0000	1.0000	78.6	1.000	—	—
<i>n</i> -Octane(1) + 2-methyl-2-propanol(2)					
0.0000	0.0000	289.60	—	1.000	—
0.0159	0.0187	290.51	4.208	1.000	64
0.0554	0.0506	289.33	3.256	1.004	192
0.1372	0.1080	284.51	2.761	1.016	424
0.2130	0.1452	280.20	2.356	1.052	616
0.3263	0.1846	273.87	1.913	1.146	841
0.4097	0.2053	266.70	1.652	1.242	925
0.4616	0.2200	261.43	1.542	1.311	957
0.5450	0.2424	249.56	1.374	1.439	938
0.6260	0.2632	236.92	1.237	1.619	868
0.7152	0.2857	224.57	1.116	1.956	747
0.8360	0.3400	200.03	1.016	2.799	504
0.8778	0.3866	182.41	1.006	3.192	407
0.9031	0.4168	172.93	1.001	3.631	348
0.9410	0.5231	142.81	1.000	4.038	229
0.9800	0.7652	101.80	1.007	4.196	100
1.0000	1.0000	78.6	1.000	—	—

energy of mixing of butanols and *n*-hexane, butanols and benzene and butanols and *n*-heptane systems respectively. They also observed that the G_m^E values were positive and decreased with the branching of the alcohol.

3.1 Correlation of data

The G_m^E data were fitted to the Redlich-Kister type polynomial equation:

$$G_m^E = x_1 x_2 \sum_0^2 A_n (x_1 - x_2)^n \quad (\text{J. mol}^{-1}) \quad (3)$$

Table 3. Fitting parameters of (3) along with standard deviations $\sigma(G_m^E)$.

System	A_0	A_1	A_2	$\sigma(G_m^E)$
<i>n</i> -Octane(1) + <i>n</i> -butanol(2)	5305.2	481.2	186.6	12.7
<i>n</i> -Octane(1) + iso-butanol(2)	4952.1	-322.2	328.3	22.1
<i>n</i> -Octane(1) + <i>sec</i> -butanol(2)	4387.9	86.9	827.1	22.7
<i>n</i> -Octane(1) + <i>tert</i> -butanol(2)	3720.3	65.6	211.5	18.7

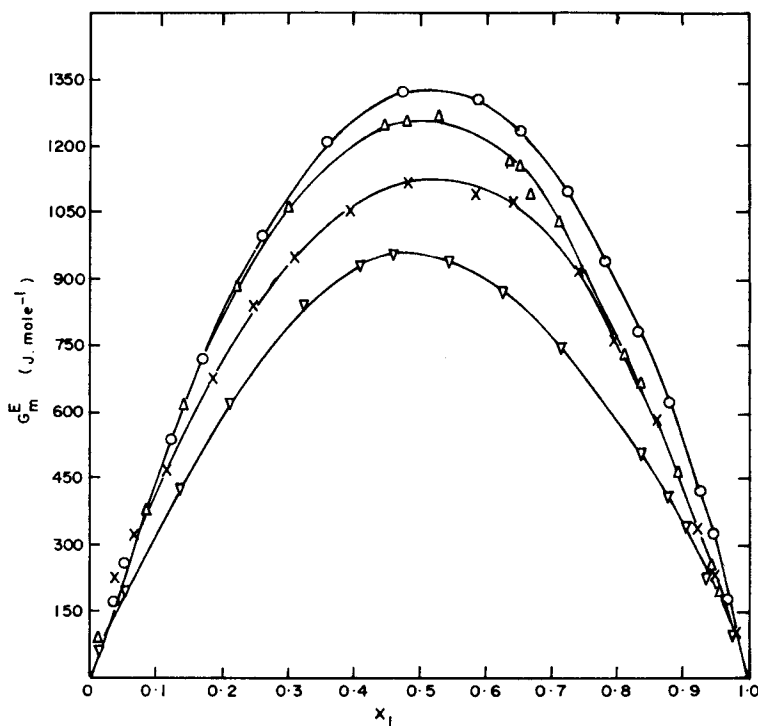


Figure 1. Excess free energy of mixing, G_m^E , at 333.15 K, for (O), *n*-octane (1) + 1-butanol (2); (Δ), *n*-octane (1) + 2-methyl-1-propanol (2); (\times), *n*-octane (1) + 2-butanol (2); (∇), *n*-octane (1) + 2-methyl-2-propanol (2).

The least square constants along with $\sigma(G_m^E)$ are given in table 3. The G_m^E data were also correlated using Wilson's equation (Wilson 1964; Orye and Prausnitz 1965).

$$G_m^E/RT = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1). \quad (4)$$

The values of Λ_{12} and Λ_{21} along with $\sigma(G_m^E)$ are listed in table 4.

Table 4. The parameters of the Wilson equation (4) along with $\sigma(G_m^E)$.

System	Λ_{12}	Λ_{21}	$\sigma(G_m^E)$ (J. mol ⁻¹)
<i>n</i> -Octane(1) + 1-butanol(2)	0.3129	0.1883	20.6
<i>n</i> -Octane(1) + 2-methyl-1-propanol(2)	0.2565	0.3067	26.1
<i>n</i> -Octane(1) + 2-butanol(2)	0.3530	0.3093	26.5
<i>n</i> -Octane(1) + 2-methyl-2-propanol(2)	0.4284	0.4262	17.8

4. Conclusions

From the above study the following conclusions may be drawn:

- (1) For all the four systems the excess free energy is positive due to hydrogen-bond breaking.
- (ii) Branching of the alkyl chain of alcohols makes a significant change in excess free energy.

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