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Note

Excess enthalpies of *n*-butanol + ethyl esters

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Abstract

Excess molar enthalpies of *n*-butanol + ethyl acetate, +ethyl propionate, +ethyl *n*-butyrate, +ethyl *n*-valerate, +ethyl *n*-caproate have been measured at 308.15 K with a Martin-type isothermal displacement calorimeter. The UNIQUAC model is successfully used to correlate the H_m^E of the five binary systems.

INTRODUCTION

The excess molar enthalpies of *n*-butanol with methyl acetate, ethyl acetate, propyl acetate and *n*-butyl acetate were investigated at 308.15 K [1]. In order to obtain more information on the influence of the chain length of the ester, we measured H_m^E calorimetrically for the five binary mixtures *n*-butanol + ethyl acetate, +ethyl propionate, +ethyl *n*-butyrate, +ethyl *n*-valerate, +ethyl *n*-caproate at 308.15 K at atmospheric pressure.

EXPERIMENTAL

Materials

All liquids were dried with molecular sieves before being carefully distilled using 1.5-m-long packed columns. The densities ρ of the final products of fractional distillation were determined with a DMA45 Anton Paar K.G., and are summarized in Table 1, where values of their refractive indices n_D are also listed. Agreement with reliable literature values [2] is satisfactory for all substances.

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TABLE 1

Densities $\rho/(g\,cm^{-3})$ and refractive indices n_D of component liquids at 20°C

Component	ρ		n_D	
	Exptl.	Ref. 2	Exptl.	Ref. 2
n-Butanol	0.8100	0.8098	1.3994	1.39931
Ethyl acetate	0.9006	0.9003	1.3722	1.3723
Ethyl propionate	0.8920	0.8917	1.3839	1.3839
Ethyl *n*-butyrate	0.8783	0.8785	1.4001	1.4000
Ethyl *n*-valerate	0.8774	0.8770	1.4120	1.4120
Ethyl *n*-caproate	0.8714	0.8710	1.4073	1.4073

Calorimeter

Excess molar enthalpies were determined as described previously [1] with a Martin-type isothermal displacement calorimeter [3] which was constructed in our laboratory [4]. Studies of the test systems indicated that the precision of the results is 1% or better over most of the mole fraction range.

Results

The measured values of H_m^E at 308.15 K are given in Table 2. Numerical equations were established for H_m^E for each binary system with the empirical constants calculated being listed in Table 3.

CORRELATION

The UNIQUAC model [5] represents the excess Gibbs energy as the sum of the combinatorial and residual terms, G^E_{comb} and G^E_{res}

$$G^E = G^E_{comb} + G^E_{res} \tag{1}$$

The excess enthalpy H_m^E is given by applying the Gibbs–Helmholtz equation to eqn. (1)

$$H_m^E = \left[\frac{\partial(G^E/T)}{\partial(1/T)}\right]$$

We assume that the temperature dependences of the energy parameters α_{12} and α_{21} are expressed by a linear function of temperature [6]

$$\alpha_{ji} = C_{ji} + D_{ji}(T - 273.15) \tag{2}$$

Table 4 shows values of the structural parameters r, q and q'. Table 5 presents the UNIQUAC parameters and the standard deviations (SD) of the calculated values based on the experimental results.

TABLE 2

Experimental results for excess enthalpies/(J mol^{-1}) of binary mixtures at 308.15 K

X_1	H_m^E	X_1	H_m^E	X_1	H_m^E
$X_1C_4H_9OH + (1 - X_1)CH_3COOC_2H_5$					
0.0209	159.74	0.3394	1627.88	0.7575	1258.57
0.0445	338.54	0.3654	1669.60	0.7943	1120.63
0.0625	465.91	0.4017	1714.65	0.8280	973.73
0.0845	609.17	0.4369	1742.47	0.8593	828.26
0.1123	777.97	0.4741	1754.50	0.8980	635.03
0.1509	989.26	0.5619	1705.15	0.9288	455.72
0.1859	1151.41	0.6014	1653.33	0.9525	309.34
0.2233	1305.45	0.6400	1584.23	0.9761	155.47
0.2613	1433.36	0.6806	1491.72		
0.2991	1539.14	0.7196	1382.82		
$X_1C_4H_9OH + (1 - X_1)CH_3CH_2COOC_2H_5$					
0.0229	178.02	0.3859	1549.63	0.7504	1088.38
0.0459	346.13	0.4175	1577.36	0.7782	994.52
0.0736	532.70	0.4449	1590.54	0.8052	895.19
0.0985	679.91	0.4776	1596.35	0.8326	795.60
0.1204	800.96	0.5150	1590.72	0.8588	682.50
0.2270	1232.59	0.6076	1459.02	0.8812	585.64
0.2673	1343.73	0.6497	1370.52	0.9576	223.44
0.3035	1429.91	0.6952	1270.84	0.9783	111.18
0.3439	1502.21	0.7226	1175.31		
$X_1C_4H_9OH + (1 - X_1)CH_3CH_2CH_2COOC_2H_5$					
0.0306	229.93	0.4408	1545.27	0.7678	1018.86
0.0637	456.71	0.4752	1547.27	0.7964	918.09
0.0889	613.31	0.5134	1547.91	0.8248	813.70
0.2058	1138.94	0.5505	1522.73	0.8516	707.51
0.2518	1279.77	0.6311	1387.03	0.8746	610.15
0.2971	1390.58	0.6695	1298.63	0.9507	260.98
0.3452	1471.19	0.7041	1217.97	0.9756	125.25
0.3930	1524.71	0.7361	1112.21		
$X_1C_4H_9OH + (1 - X_1)CH_3CH_2CH_2CH_2COOC_2H_5$					
0.0304	222.83	0.4748	1493.41	0.7510	1060.21
0.0650	455.62	0.5088	1479.93	0.7754	982.19
0.0994	661.77	0.5435	1457.12	0.7974	906.12
0.1373	853.13	0.5760	1424.08	0.8217	818.99
0.2549	1249.14	0.6579	1316.16	0.8450	733.75
0.3021	1358.90	0.6740	1273.74	0.8671	649.01
0.3562	1435.71	0.6878	1212.58	0.9550	236.30
0.3961	1471.58	0.7249	1137.81	0.9768	121.63
0.4387	1494.04				
$X_1C_4H_9OH + (1 - X_1)CH_3CH_2CH_2CH_2CH_2COOC_2H_5$					
0.0308	218.79	0.4791	1437.46	0.7832	962.25
0.0645	427.97	0.5218	1414.65	0.8015	890.73
0.0982	620.56	0.5581	1390.74	0.8246	812.86
0.1410	816.99	0.5878	1357.78	0.8463	733.03
0.2832	1273.00	0.6894	1205.33	0.8689	644.43
0.3299	1355.22	0.7199	1131.75	0.8899	550.58
0.3808	1410.12	0.7461	1074.52	0.9612	208.38
0.4302	1439.32	0.7637	1016.77	0.9799	108.55

TABLE 3

Coefficient A_i and standard deviations SD for the representation of $H_m^E/(J\,mol^{-1})$ for five binary mixtures at 308.15 K by the numerical equations, $H^E = x_1x_2\sum A_i(x_2 - x_1)^i$

Ester	A_0	A_1	A_2	A_3	A_4	A_5	SD
Ethyl acetate	6993.0	606.20	701.33	0.9817	−220.13	−5.643	2.0
Ethyl propionate	6342.6	915.23	31.44	902.85	587.49	−471.52	4.9
Ethyl *n*-butyrate	6190.6	854.58	212.51	988.32	446.30	−667.70	4.8
Ethyl *n*-valerate	5949.2	688.58	930.19	1259.7	−238.50	−862.50	5.0
Ethyl *n*-caproate	5718.6	808.42	1351.7	−412.67	−724.48	706.60	3.4

TABLE 4

Structural parameters r, q and q'

Component	r	q	q'
n-Butanol	3.45	3.05	0.88
Ethyl acetate	3.48	3.12	
Ethyl propionate	4.15	3.66	
Ethyl *n*-butyrate	4.83	4.20	
Ethyl *n*-valerate	5.50	4.74	
Ethyl *n*-caproate	6.18	5.28	

TABLE 5

Correlation results of H_m^E of *n*-butanol mixtures with five esters

Ester	C_{21}	D_{21}	C_{12}	D_{12}	SD
Ethyl acetate	590.7063	−1.1914	−143.8895	−0.9481	2.703
Ethyl propionate	5631.071	−71.1554	−460.4404	−2.3330	8.217
Ethyl *n*-butyrate	9.3423	−81.5357	−494.2531	−2.3667	7.697
Ethyl *n*-valerate	741.8184	−0.8241	−148.5360	−0.7405	10.111
Ethyl *n*-caproate	814.3367	−0.0789	−268.6333	−1.2567	7.186

DISCUSSION

The numerical equations for five liquid pairs were solved for excess enthalpies and mole fractions of the mixtures at their maxima. Maximum excess enthalpies and their corresponding mole fractions of the mixtures are listed in Table 6. Comparing the mixing of *n*-butanol with the five ethyl esters, the maximum excess enthalpies decrease with increasing chain length of the esters. The excess enthalpy–mole fraction curves of the

TABLE 6

Excess enthalpies/(J mol^{-1}) and mole fractions of five binary mixtures at maxima

Ester	H_m^E	X_1
Ethyl acetate	1755.4	0.490
Ethyl propionate	1595.5	0.478
Ethyl *n*-butyrate	1551.1	0.467
Ethyl *n*-valerate	1494.4	0.458
Ethyl *n*-caproate	1440.0	0.451

mixtures show regular increases on ascending the ester series. This phenomenon can reasonably be explained by the lengthening of the ester chain tending to weaken the association between the molecules of *n*-butanol and the esters.

REFERENCES

1 W. Yan, R. Lin and W. Yen, Thermochim. Acta, 169 (1990) 171–184.
2 CRC Handbook of Chemistry and Physics., 58th edn., Boca Raton, FL, 1977–1978.
3 R.S. Murray and M.L. Martin, J. Chem. Thermodyn., 10 (1978) 711.
4 W. Yan, R. Lin and W. Yen, Acta Chim. Sinica, 50 (1992) 16–21.
5 D.S. Abrams and J.M. Prausnitz, AICHE J., 21 (1975) 11.
6 I. Nagata and K. Tamura, Thermochim. Acta, 121 (1987) 447–462.