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Excess molar enthalpies of eight binary mixtures containing 1,2-epoxybutane + ethyl alkanoates at 298.15 K

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Abstract

Excess molar enthalpies, H_m^E, have been measured using a flow microcalorimeter at 298.15 K and at atmospheric pressure for the eight mixtures containing 1,2-epoxybutane with ethyl acetate, ethyl propanoate, ethyl butyrate, ethyl pentanoate, ethyl hexanoate, ethyl heptanoate, ethyl octanoate and ethyl decanoate. Excess heats of mixing, H_m^E, are positive for all the mixtures and increase with the chain length of the alkanoate, with the exception of ethyl acetate whose H_m^E values were between those of ethyl pentanoate and ethyl hexanoate. Results have been correlated in terms of the Redlich–Kister equation and qualitatively discussed in terms of molecular interactions. © 1998 Elsevier Science B.V.

Keywords: Excess molar enthalpies; Calorimeter; Data correlation

1. Introduction

The current paper is concerned with exploring the composition dependence of excess molar enthalpies, H_m^E, of binary mixtures. In earlier papers [1,2], the measurements of the thermodynamic properties of mixtures containing esters of carbonic acid + a series of alkanoates were reported.

Continuing with this research programme, the excess molar enthalpies of binary mixtures containing 1,2-epoxybutane, a strong proton acceptor monoether used as a solubilizing agent, with eight ethyl alkanoates, namely ethyl acetate, ethyl propanoate, ethyl butyrate, ethyl pentanoate, ethyl hexanoate, ethyl heptanoate, ethyl octanoate and ethyl decanoate have been determined.

The aim of this paper is to characterize the molecular interactions from the excess molar enthalpies.

To our knowledge, no literature data can be found for these mixtures.

2. Experimental

2.1. Chemicals

The chemicals were purchased from Aldrich with the exception of ethyl acetate, which was obtained from Fluka.

The purities of each compound varied from a minimum of 99.0 mol % for 1,2-epoxybutane to a maximum of 99.9 mol % for ethyl acetate. They were

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Table 1
A comparison of measured and literature densities, ρ, for each component at 298.15 K

Component	$\rho/(\mathrm{g{\cdot}cm^{-3}})$	
	measured	literature (Ref.)
1,2-Epoxybutane	0.82463	0.8240 [3]
Ethyl acetate	0.89438	0.89455 [3]
Ethyl propanoate	0.88333	0.8831 [3]
Ethyl butyrate	0.87356	0.87394 [3]
Ethyl pentanoate	0.86938	0.8690 [4]
Ethyl hexanoate	0.87301	0.8730 [5]
Ethyl heptanoate	0.88151	0.8815 [5]
Ethyl octanoate	0.86232	0.8624 [4]
Ethyl decanoate	0.86501	0.8650 [5]

used without further purification, since GLC analysis did not detect any appreciable impurity peaks. The purities were also checked by comparing the densities of pure compounds, measured by an Anton Paar vibrating tube densimeter (DMA 60/602) at 293.15 or 298.15 K, with those found in literature [3–5], as reported in Table 1.

Before measurements, all liquids were kept in dark bottles, dried over molecular sieves (Union Carbide, type 4A, 1/16in. pellets) and degassed by ultrasound using an ultrasonic bath, Hellma, type 460, Milan, Italy.

2.2. Calorimetric measurements

An LKB flow microcalorimeter (LKB Produkter, model 2107, Bromma, Sweden) was used to determine the excess molar enthalpies H_m^E. Measurements were made at 298.15±0.01 K and the temperature controlled by calibrated transistors inside the apparatus.

The electrical calibration and operating procedure have been described elsewhere [6,7]. Two automatic burettes (ABU, Radiometer, Copenhagen, Denmark) were used to pump pure liquids into the mixing cell of the calorimeter. Mole fractions x_1 of 1,2-epoxybutane (component 1) were calculated from the calibrated-flow rates with a precision of 1×10^{-4}, which lead to an error in H_m^E of 0.5–1 J mol^{-1}.

Two duplicate measurements of H_m^E were made for each determination.

The performance of the apparatus was periodically checked by measuring H_m^E of a test mixture of cyclohexane and n-hexane at 298.15 K. The agreement with the literature values of the heat of mixing [8] was ±0.5%, over the central range of mole fraction of cyclohexane.

3. Results

3.1. Correlation of the experimental values

The experimental results obtained from the excess molar enthalpies for the eight mixtures are listed in Table 2 and shown graphically in Fig. 1.

The heat of mixing were fitted by the method of least-squares analysis to the Redlich–Kister equation

$$H_m^E = x_1 x_2 \sum_{k\geq 0} a_k (x_1 - x_2)^k \tag{1}$$

where a_k were adjustable parameters and in each case the optimum number of coefficients was determined by examing the variation in the standard deviation $\sigma(Q_m^E)$ as given by:

$$\sigma(H_m^E) = |\Phi/(N-n)|^{0.5} \tag{2}$$

where N is the number of experimental points, n the number of adjustable parameters, and Φ is a function defined as:

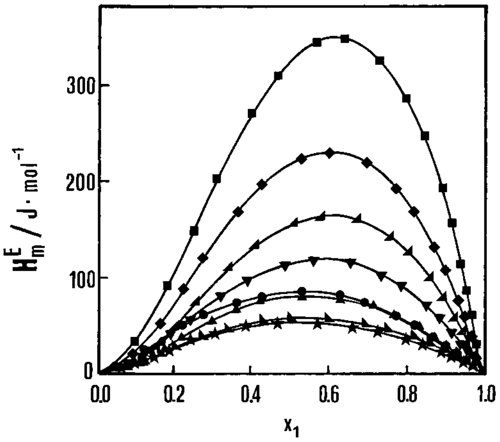

Fig. 1. Excess molar enthalpies, H_m^E, of 1,2-epoxybutane(1) + ethyl alkanoates(2): (●) ethyl acetate, (★) ethyl propanoate, (◣) ethyl butyrate, (▲) ethyl pentanoate, (▼) ethyl hexanoate, (◢) ethyl heptanoate, (◆) ethyl octanoate, (■) ethyl decanoate. Solid lines, Eq. (1).

Table 2
Excess molar enthalpies, H^E_m, of 1,2-epoxybutane(1) + ethyl alkanoates(2) at 298.15 K

x_1	$H^E_m/(J \cdot mol^{-1})$	x_1	$H^E_m/(J \cdot mol^{-1})$
1,2-Epoxybutane(1) + ethyl acetate(2)			
0.0448	9	0.6282	80
0.0858	17	0.6926	72
0.1234	25	0.7717	59
0.1581	34	0.8184	51
0.2198	47	0.8711	38
0.2730	60	0.9001	27
0.3603	74	0.9311	20
0.4288	78	0.9643	10
0.5297	84		
1,2-Epoxybutane(1) + ethyl propanoate(2)			
0.0521	6	0.6646	50
0.0991	12	0.7254	45
0.1417	17	0.7985	36
0.1804	24	0.8408	29
0.2482	34	0.8880	21
0.3057	40	0.9135	16
0.3977	50	0.9407	11
0.4681	53	0.9694	6
0.5690	53		
1,2-Epoxybutane(1) + ethyl butyrate(2)			
0.0596	6	0.6953	52
0.1125	13	0.7526	47
0.1597	19	0.8202	37
0.2022	26	0.8588	30
0.2754	37	0.9012	22
0.3364	45	0.9240	16
0.4319	54	0.9481	11
0.5033	57	0.9733	6
0.6033	58		
1,2-Epoxybutane(1) + ethyl pentanoate(2)			
0.0666	4	0.7198	70
0.1249	14	0.7740	62
0.1763	25	0.8371	49
0.2220	36	0.8726	39
0.2998	54	0.9113	27
0.3634	65	0.9320	21
0.4213	73	0.9536	16
0.5330	79	0.9763	8
0.6313	78		
1,2-Epoxybutane(1) + ethylhexanoate(2)			
0.0735	8	0.7407	104
0.1369	22	0.7920	91
0.1922	38	0.8510	71
0.2408	56	0.8839	58
0.3224	81	0.9195	41
0.3882	95	0.9384	32
0.4876	112	0.9581	23
0.5592	118	0.9786	12
0.6556	115		
1,2-Epoxybutane(1) + ethyl heptanoate(2)			
0.0802	5	0.7585	142
0.1485	26	0.8072	123
0.2074	50	0.8627	96
0.2587	74	0.8933	78
0.3436	110	0.9263	55
0.4110	133	0.9437	45
0.5114	154	0.9617	31
0.5825	163	0.9805	16
0.6767	157		
1,2-Epoxybutane(1) + ethyl octanoate(2)			
0.0896	19	0.7742	192
0.1599	53	0.8204	167
0.2221	87	0.8727	130
0.2758	121	0.9014	108
0.3635	166	0.9320	74
0.4323	194	0.9481	58
0.5332	223	0.9648	42
0.6036	227	0.9821	22
0.6956	218		
1,2-Epoxybutane(1) + ethyl decanoate(2)			
0.0999	33	0.7998	283
0.1816	92	0.8420	245
0.2498	148	0.8888	190
0.3075	201	0.9142	155
0.3998	269	0.9411	112
0.4703	309	0.9552	86
0.5712	342	0.9697	61
0.6397	345	0.9846	30
0.7270	323		

$$\Phi = \sum_{k \geq 0}^{N} \eta_k^2 \tag{3}$$

where $\eta = H^E_{m,calc} - H^E_m$, $H^E_{m,calc}$ being determined from the right-hand side of Eq. (1). The values of adjustable parameters a_k and the standard deviation σ, are listed in Table 3. Fig. 2 shows $H^E_m(x_1 = 0.5)$, the equimolar excess enthalpy of H^E_m, vs. the number n of the CH_2 groups in the ethyl alkanoate molecule $H(CH_2)_nCO_2C_2H_5$.

4. Conclusions

Figs. 1 and 2 show a gradual increase of H^E_m with the increase in the chain length of the ethyl alkanoate, with the exception of the first member of the alkanoate series, ethylacetate. This behaviour was also observed

Table 3
Adjustable parameters, a_k, Eq. (1), and standard deviation, $\sigma(H_m{}^E)$, Eq. (2), of 1,2-epoxybutane + ethyl alkanoates at 298.15 K

Mixture	a_0	a_1	a_2	a_3	$\sigma(H_m^E)/(\mathrm{J{\cdot}mol^{-1}})$
1,2-Epoxybutane					
+ ethyl acetate	336.0	53.2	−88.8		1.1
+ ethyl propanoate	216.5	44.3	−65.2		0.7
+ ethyl butyrate	232.6	71.8	−73.3		0.7
+ ethyl pentanoate	319.2	99.1	−138.7	83.2	1.1
+ ethyl hexanoate	459.4	209.7	−153.0	79.1	1.3
+ ethyl heptanoate	619.4	355.5	−229.3	137.1	1.4
+ ethyl octanoate	864.3	480.1	−206.4	148.6	1.7
+ ethyl decanoate	1284.4	794.0	−205.6	297.2	1.5

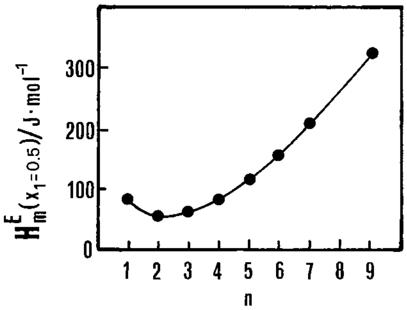

Fig. 2. Values of equimolar excess enthalpy, $H_m^E(x_1=0.5)$, at 298.15 K as a function of the number n of the CH_2 groups in the molecule of ethyl alkanoates $H(CH_2)_nCO_2C_2H_5$, in mixtures with 1,2-epoxybutane.

for mixtures of the same alkanoates with diethyl carbonate [2] and was due, most probably, to a different type of packing of the ethyl acetate molecules during mixing with 1,2-epoxybutane.

In fact, strong interaction energies between molecules can be excluded, even if 1,2-epoxybutane is a good proton acceptor, owing to the availability of H atoms only from CH_2 groups. In this event, steric effects may play a dominant role in the packing of the molecules and the smallest molecule may show an anomalous behaviour.

We have tried to describe the experimental dependence of H_m^E on x_1 through the cell-model, proposed by Prigogine et al. [9,10] and discussed in a previous paper [11]. However, when the H_m^E values are larger than 100 J mol^{-1}, the plots of H_m^E vs. x_1 are increasingly skewed and the theory fails in the prediction of calculated H_m^E values.

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