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Molar excess enthalpies of binary mixtures of the three glycols ethanediol, 1,2-propanediol and 1,2-butanediol with methanol or ethanol

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Abstract

Excess molar enthalpies h^E of different glycol+methanol and glycol+ethanol mixtures at atmospheric pressure were measured at the temperatures (285.65, 298.15, 308.15, and 323.15 K). Glycol+ethanol mixtures were also measured at the temperature 338.15 K. The glycols were the following: ethanediol, 1,2-propanediol, and 1,2-butanediol. The experimental results are correlated using the Redlich–Kister equation and are qualitatively discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Flow calorimetry; Excess enthalpy; Glycol; Alcohol

1. Introduction

Excess molar enthalpies of different glycol+ methanol and glycol+ethanol mixtures were measured to build up a database for investigations on the parameter optimization of different group contribution methods [1–3] with the help of Evolutionary Algorithms. Since literature data does not provide a sufficient number of excess enthalpy isotherms containing more than two main-groups (i.e. more than one main-group interaction) following the group concept of Wu and Sandler [4,5] or original UNIFAC [6], measurements with substances containing three or more main-groups are carried out.

The data presented here were measured with an LKB 2277 calorimeter at the temperatures 285.65, 298.15, 308.15, and 323.15 K. Glycol+ethanol mixtures were also measured at the temperature 338.15 K. The glycols were the following: ethanediol, 1,2-propanediol, and 1,2-butanediol.

2. Experimental

Ethanediol was supplied by Merck (analytical grade, mass fraction 0.995), 1,2-propanediol and 1,2-butanediol were supplied by Sigma-Aldrich (analytical grade, mass fraction 0.99). Methanol and ethanol were both supplied by Roth (analytical grade, mass fraction 0.999 and 0.998, respectively). Prior to usage, the alcohols were dried using beads of molecular sieve (Dehydrate Fluka). All substances were used without

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Table 1
Molar excess enthalpy data h^E for binary mixtures with ethanol at different temperatures for different mole fractions x

x	h^E (J mol^{-1})	x	h^E(J mol^{-1})	x	h^E (J mol^{-1})
$x(CH_2OH)_2+(1-x)CH_3OH$, T=285.65 K					
0.300	101	0.550	110	0.800	60
0.350	110	0.600	103	0.850	48
0.400	114	0.650	94	0.900	31
0.450	114	0.700	85	0.950	12
0.500	113	0.750	75		
$x(CH_2OH)_2+(1-x)CH_3OH$, T=298.15 K					
0.050	32	0.350	121	0.650	100
0.100	58	0.400	124	0.700	89
0.150	77	0.450	124	0.750	75
0.200	94	0.500	123	0.800	60
0.250	106	0.550	118	0.850	48
0.300	115	0.600	108	0.950	12
$x(CH_2OH)_2+(1-x)CH_3OH$, T=308.15 K					
0.050	36	0.400	129	0.750	77
0.100	63	0.450	128	0.800	61
0.150	85	0.500	126	0.850	45
0.200	101	0.550	120	0.900	31
0.250	113	0.600	112	0.950	10
0.300	122	0.650	101		
0.350	127	0.700	90		
$x(CH_2OH)_2+(1-x)CH_3OH$, T=323.15 K					
0.050	37	0.400	132	0.750	68
0.100	68	0.450	131	0.800	59
0.150	90	0.500	127	0.850	43
0.200	105	0.550	119	0.900	31
0.250	117	0.600	109	0.950	16
0.300	126	0.650	99		
0.350	131	0.700	84		
$xCH_3CH(OH)CH_2OH+(1-x)CH_3OH$, T=285.65 K					
0.050	−13	0.400	−44	0.750	−32
0.100	−20	0.450	−44	0.800	−28
0.150	−27	0.500	−44	0.850	−21
0.200	−34	0.550	−43	0.900	−16
0.250	−38	0.600	−42	0.950	−10
0.300	−41	0.650	−39		
0.350	−43	0.700	−36		
$xCH_3CH(OH)CH_2OH+(1-x)CH_3OH$, T=298.15 K					
0.050	−10	0.350	−47	0.750	−42
0.100	−22	0.400	−50	0.800	−38
0.150	−30	0.550	−54	0.850	−28
0.200	−36	0.600	−53	0.900	−24
0.250	−41	0.650	−49		
0.300	−45	0.700	−47		
$xCH_3CH(OH)CH_2OH+(1-x)CH_3OH$, T=308.15 K					
0.050	−11	0.400	−54	0.750	−45
0.100	−21	0.450	−55	0.800	−40

Table 1 (*Continued*)

x	h^E (J mol^{-1})	x	h^E(J mol^{-1})	x	h^E (J mol^{-1})
0.150	−30	0.500	−55	0.850	−35
0.200	−38	0.550	−55	0.900	−25
0.250	−44	0.600	−53	0.950	−11
0.300	−49	0.650	−51		
0.350	−51	0.700	−48		
xCH$_3$CH(OH)CH$_2$OH+(1−x)CH$_3$OH, T=323.15 K					
0.050	−11	0.350	−63	0.801	−52
0.100	−24	0.400	−64	0.850	−43
0.150	−35	0.600	−73	0.900	−32
0.200	−45	0.650	−70	0.950	−17
0.250	−53	0.700	−68		
0.300	−59	0.750	−61		
xCH$_3$CH$_2$CH(OH)CH$_2$OH+(1−x)CH$_3$OH, T=285.65 K					
0.050	−19	0.350	−42	0.650	−23
0.100	−29	0.400	−41	0.700	−18
0.150	−36	0.450	−38	0.750	−15
0.200	−40	0.500	−36	0.800	−13
0.250	−42	0.550	−31	0.850	−10
0.300	−43	0.600	−29	0.950	−5
xCH$_3$CH$_2$CH(OH)CH$_2$OH+(1−x)CH$_3$OH, T=298.15 K					
0.050	−21	0.350	−50	0.650	−34
0.100	−33	0.400	−48	0.700	−30
0.150	−41	0.450	−46	0.750	−28
0.200	−45	0.500	−44	0.800	−25
0.250	−48	0.550	−41	0.850	−22
0.300	−49	0.600	−37	0.950	−14
xCH$_3$CH$_2$CH(OH)CH$_2$OH+(1−x)CH$_3$OH, T=308.15 K					
0.100	−26	0.400	−57	0.700	−40
0.150	−36	0.450	−55	0.750	−35
0.200	−47	0.500	−52	0.800	−33
0.250	−53	0.550	−49	0.850	−31
0.300	−57	0.600	−47	0.900	−24
0.350	−58	0.650	−43	0.950	−13
xCH$_3$CH$_2$CH(OH)CH$_2$OH+(1−x)CH$_3$OH, T=323.15 K					
0.050	−19	0.400	−73	0.750	−48
0.100	−36	0.450	−73	0.800	−40
0.150	−50	0.500	−72	0.850	−31
0.200	−60	0.550	−69	0.900	−23
0.250	−67	0.600	−67	0.950	−13
0.300	−72	0.650	−63		
0.350	−73	0.700	−58		

further purification and they were partially degassed under vacuum.

The measurements were carried out using an LKB 2277 calorimeter. Microliter syringes, which are driven by a stepping motor, pump the pure substances through the measuring cell, in which the mixing process takes place. Due to the great difference in viscosity of the pure substances a static mixer is

Table 2
Molar excess enthalpy data h^E for binary mixtures with ethanol at different temperatures for different mole fractions x

x	h^E (J mol^{-1})	x	h^E (J mol^{-1})	x	h^E (J mol^{-1})
$x(CH_2OH)_2+(1-x)CH_3CH_2OH$, T=285.65 K					
0.050	89	0.300	359	0.850	154
0.100	169	0.350	377	0.900	114
0.150	223	0.400	387	0.950	64
0.200	283	0.450	387		
0.250	324	0.800	185		
$x(CH_2OH)_2+(1-x)CH_3CH_2OH$, T=298.15 K					
0.050	108	0.400	404	0.750	263
0.100	194	0.450	405	0.800	217
0.150	262	0.500	396	0.850	167
0.200	314	0.550	383	0.900	111
0.250	352	0.600	363	0.950	58
0.300	379	0.650	335		
0.350	395	0.700	304		
$x(CH_2OH)_2+(1-x)CH_3CH_2OH$, T=308.15 K					
0.050	103	0.400	418	0.750	273
0.100	201	0.450	417	0.800	225
0.150	270	0.500	411	0.850	175
0.200	322	0.550	394	0.900	118
0.250	362	0.600	372	0.950	60
0.300	390	0.650	346		
0.350	408	0.700	312		
$x(CH_2OH)_2+(1-x)CH_3CH_2OH$, T=323.15 K					
0.050	83	0.400	450	0.750	290
0.100	184	0.450	449	0.800	240
0.150	265	0.500	441	0.850	184
0.200	327	0.550	424	0.900	124
0.250	385	0.600	400	0.950	62
0.300	422	0.650	371		
0.350	440	0.700	333		
$x(CH_2OH)_2+(1-x)CH_3CH_2OH$, T=338.15 K					
0.050	128	0.400	472	0.750	297
0.100	237	0.450	469	0.800	244
0.150	314	0.500	460	0.850	188
0.200	374	0.550	437	0.900	126
0.250	417	0.600	408	0.950	64
0.300	447	0.650	379		
0.350	468	0.700	343		
$xCH_3CH(OH)CH_2OH+(1-x)CH_3CH_2OH$, T=285.65 K					
0.050	59	0.400	166	0.750	126
0.100	103	0.500	165	0.800	109
0.150	128	0.550	161	0.850	85
0.200	139	0.600	156	0.900	57
0.300	156	0.650	146	0.950	27
0.350	161	0.700	139		
$xCH_3CH(OH)CH_2OH+(1-x)CH_3CH_2OH$, T=298.15 K					
0.050	68	0.350	241	0.650	187
0.100	121	0.400	243	0.700	165

Table 2 (*Continued*)

x	h^E (J mol^{-1})	x	h^E (J mol^{-1})	x	h^E (J mol^{-1})
0.150	164	0.450	240	0.750	133
0.200	195	0.500	232	0.800	109
0.250	220	0.550	222	0.900	56
0.300	233	0.600	206	0.950	29
xCH$_3$CH(OH)CH$_2$OH+(1−x)CH$_3$CH$_2$OH, T=308.15 K					
0.050	76	0.400	269	0.750	159
0.100	135	0.450	266	0.800	129
0.150	179	0.500	258	0.850	97
0.200	214	0.550	245	0.900	64
0.250	240	0.600	228	0.950	29
0.300	257	0.650	208		
0.350	266	0.700	185		
xCH$_3$CH(OH)CH$_2$OH+(1−x)CH$_3$CH$_2$OH, T=323.15 K					
0.050	72	0.400	292	0.750	168
0.100	128	0.450	287	0.800	135
0.150	184	0.500	280	0.850	98
0.200	228	0.550	264	0.900	59
0.250	261	0.600	247	0.950	22
0.300	280	0.650	223		
0.350	289	0.700	198		
xCH$_3$CH(OH)CH$_2$OH+(1−x)CH$_3$CH$_2$OH, T=338.15 K					
0.050	86	0.400	304	0.750	172
0.100	154	0.450	303	0.800	139
0.150	207	0.500	290	0.850	105
0.200	244	0.550	277	0.900	65
0.250	271	0.600	255	0.950	32
0.300	292	0.650	233		
0.350	301	0.700	205		
xCH$_3$CH$_2$CH(OH)CH$_2$OH+(1−x)CH$_3$CH$_2$OH, T=285.65 K					
0.050	54	0.400	143	0.750	120
0.100	87	0.450	147	0.800	99
0.150	106	0.500	151	0.850	76
0.200	119	0.550	154	0.900	49
0.250	128	0.600	155	0.950	20
0.300	134	0.650	147		
0.350	140	0.700	133		
xCH$_3$CH$_2$CH(OH)CH$_2$OH+(1−x)CH$_3$CH$_2$OH, T=298.15 K					
0.050	59	0.400	214	0.750	126
0.100	106	0.450	211	0.800	98
0.150	143	0.500	206	0.850	73
0.200	171	0.550	196	0.900	50
0.250	191	0.600	182	0.950	21
0.300	205	0.650	169		
0.350	211	0.700	150		
xCH$_3$CH$_2$CH(OH)CH$_2$OH+(1−x)CH$_3$CH$_2$OH, T=308.15 K					
0.050	70	0.400	237	0.750	141
0.100	119	0.450	234	0.800	115
0.150	156	0.500	228	0.850	88

Table 2 (*Continued*)

x	h^E (J mol^{-1})	x	h^E (J mol^{-1})	x	h^E (J mol^{-1})
0.200	187	0.550	217	0.900	58
0.250	209	0.600	202	0.950	25
0.300	225	0.650	185		
0.350	233	0.700	165		
$x\mathrm{CH_3CH_2CH(OH)CH_2OH}+(1-x)\mathrm{CH_3CH_2OH}$, T=323.15 K					
0.050	74	0.400	260	0.750	146
0.100	131	0.450	257	0.800	116
0.150	176	0.500	249	0.850	86
0.200	210	0.550	234	0.900	53
0.250	234	0.600	218	0.950	21
0.300	249	0.650	198		
0.350	258	0.700	174		
$x\mathrm{CH_3CH_2CH(OH)CH_2OH}+(1-x)\mathrm{CH_3CH_2OH}$, T=338.15 K					
0.050	96	0.400	283	0.750	157
0.100	161	0.450	279	0.800	128
0.150	201	0.500	265	0.850	97
0.200	229	0.550	251	0.900	66
0.250	253	0.600	232	0.950	31
0.300	270	0.650	207		
0.350	280	0.700	186		

located inside the measuring cell to ensure sufficient mixing of the pure substances. The setup was initially tested with measurements of ethanol+water. They show a very good agreement with literature data. Reproducibility of the measurements proves to be well within 1%. Details about the experimental setup are given elsewhere [7].

3. Results and discussion

The measured excess enthalpies are given in the Tables 1 and 2. Table 3 gives the coefficients for the Redlich–Kister polynomial including their standard deviations σ, which were fitted to the experimental results:

$$h^E\ (\mathrm{J\,mol^{-1}}) = \frac{x(1-x)\sum_i A_i(2x-1)^{i-1}}{1+k(2x-1)}. \qquad (1)$$

Fig. 1 shows the excess enthalpy isotherms of the glycol+methanol mixtures as well as the corresponding Redlich–Kister curves. The plot for ethanediol+methanol shows endothermic, slightly asymmetrical parabolic curves. With increasing temperature, the excess enthalpy values rise slightly, the temperature dependence is small. The isotherms at the temperatures 308.15 and 323.15 K do not differ much. It is interesting to note that, in contrast to ethanediol+methanol, both 1,2-propanediol+methanol and 1,2-butanediol+methanol exhibit exothermic isotherms. Both systems show increasing values with increasing temperatures. All those absolute values lie below 80 J mol^{-1}. These little heat effects and the large difference in viscosity between the glycols and the alcohols may be responsible for the slight scatter of the experimental data points for the two systems. 1,2-propanediol+methanol shows parabolic curves. The curves of 1,2-butanediol+methanol for temperatures up to 308.15 K are flattened for mole fractions above $x \approx 0.4$ and they even show two inflection points in that region. The curvature for T= 323.15 K differs from those at the other temperatures. However, the location of the experimental data points between x=0.75 and x=0.85 may be an indication for inflection points, although a Redlich–Kister fit even

Table 3
Redlich–Kister coefficients A_i and k in Eq. (1) for representing the molar excess enthalpies for binary mixtures

T (K)	A_0	A_1	A_2	A_3	A_4	k	σ (J mol^{-1})
$x(CH_2OH)_2+(1-x)CH_3CH_2OH$							
285.65	453	−101	−30				2
298.15	484	−174	20				2
308.15	500	−217	28				2
323.15	500	−237	72				2
$xCH_3CH(OH)CH_2OH+(1-x)CH_3OH$							
285.65	−176	36	−42				1
298.15	−209	−5	−59				1
308.15	−223	−16	−40				1
323.15	−299	−56	5				2
$xCH_3CH_2CH(OH)CH_2OH+(1-x)CH_3OH$							
285.65	−142	103	48	−3	−164	−0.28	1
298.15	−176	165	−82	33	−204	−0.32	1
308.15	−211	217	−153	−88	8	−0.44	1
323.15	−290	86	−59				1
$x(CH_2OH)_2+(1-x)CH_3CH_3OH$							
285.65	1500	−1924	466			−0.99	5
298.15	1600	−538	150				5
308.15	1651	−515	135				4
323.15	1781	−510	7				7
338.15	1846	−714	217				4
$xCH_3CH(OH)CH_2OH+(1-x)CH_3CH_2OH$							
285.65	660	332	171			0.68	4
298.15	932	−444	90				3
308.15	1029	−458	143				3
323.15	1131	−466	−48				4
338.15	117	−581	45				4
$xCH_3CH_2CH(OH)CH_2OH+(1-x)CH_3CH_2OH$							
285.65	606	106	225	−579			1
298.15	824	81	−72			0.49	3
308.15	914	495	−277			0.93	1
323.15	997	368	−344			0.84	3
338.15	1062	457	−311			0.89	2

with a polynomial grade of five did not reproduce that curvature.

Measurements of 1,2-butanediol+water, which had been carried out previously [7], exhibit curves with the same characteristics. They both resemble the form of ethanol+water with its two inflection points and a strong temperature dependence. Probably, the same principles of clusters of water molecules and a random mixture of water and alcohol [8–10] form the basis for the curvatures of 1,2-butanediol+water and 1,2-butanediol+methanol. It must be noted that despite the great difference in viscosity between the glycols and methanol and the fact that the heat of mixing is quite small, the experimental setup is able to resolve even such complex curvatures.

In Fig. 2 the excess enthalpy isotherms of the glycol+ethanol mixtures including their Redlich-Kister curves are displayed. All systems are endothermic and show increasing values with increasing temperature. The curvatures are mainly slightly asymmetrical parabolas, whereas the systems 1,2-propanediol+ethanol and 1,2-butanediol+ethanol at

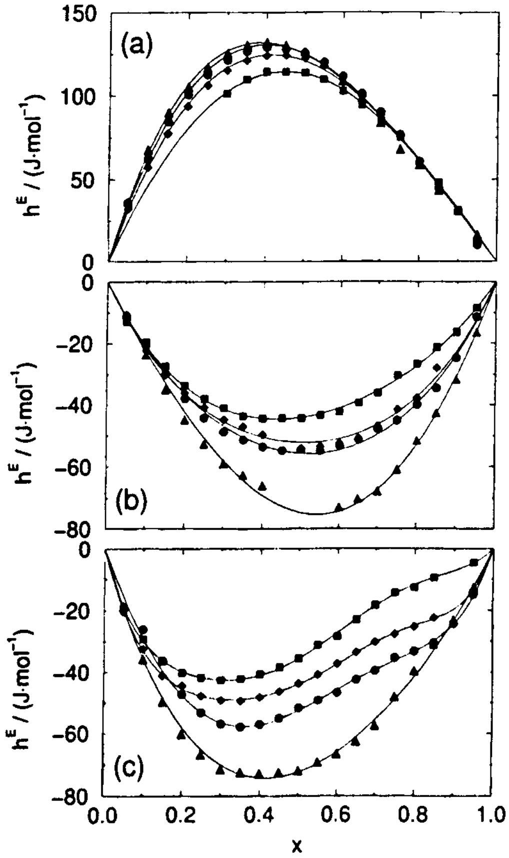

Fig. 1. Experimental excess enthalpies h^E: (a) $x(CH_2OH)_2+(1-x)CH_3OH$; (b) $xCH_3CH(OH)CH_2OH+(1-x)CH_3OH$; and (c) $xCH_3CH_2CH(OH)CH_2OH+(1-x)CH_3OH$; at the temperatures: (■), 285.65; (◆) 298.15; (●) 308.15; (▲) 323.15 K.

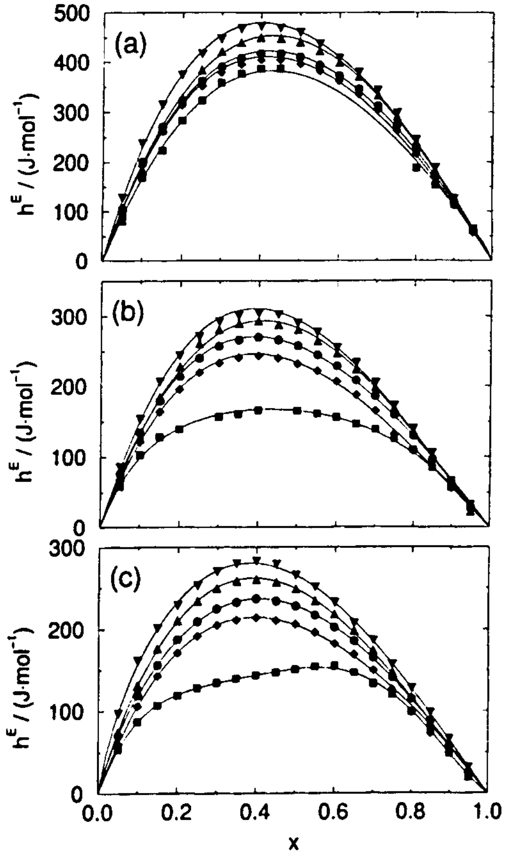

Fig. 2. Experimental excess enthalpies h^E: (a) $x(CH_2OH)_2+(1-x)CH_3CH_2OH$; (b) $xCH_3CH(OH)CH_2OH+(1-x)CH_3CH_2OH$; (c) $xCH_3CH_2CH(OH)CH_2OH+(1-x)CH_3CH_2OH$ at the temperatures: (■) 285.65; (◆) 298.15; (●) 308.15; (▲) 323.15; (▼) 338.15 K.

T=285.65 K differ from the isotherms at the other temperatures. The curve for 1,2-propanediol+ethanol is flattened in the middle of the concentration range compared to the curves at the temperatures above 285.65 K. 1,2-butanediol+ethanol shows an extremely flattened region, it resembles forms originating from miscibility gaps. However, since 1,2-butanediol as well as ethanol are polar substances, this interpretation seems rather unlikely.

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