ELSEVIER

Thermochimica Acta 327 (1999) 145–149

thermochimica acta

Excess molar enthalpies of diethyl carbonate + seven pentanol isomers at 298.15 K. Use of the extended cell model of Prigogine

Romolo Francesconi[a,*], Fabio Comelli[b], Carlo Castellari

[a] *Dipartimento di Chimica "G. Ciamician", Università degli Studi, via Selmi 2, I-40126, Bologna, Italy*

[b] *Centro di Studio per la Fisica delle Macromolecole del CNR, via Selmi 2, I-40126, Bologna, Italy*

Received 6 October 1998; accepted 6 November 1998

Abstract

Excess molar enthalpies, H_m^E, of binary mixtures containing diethyl carbonate (common component) + seven pentanol isomers, namely 1-, 2-, and 3-pentanol, 2-methyl-1-butanol, 2-methyl-2-butanol, 3-methyl-1-butanol, and 3-methyl-2-butanol have been determined at 298.15 K using an LKB flow microcalorimeter. All the experimental H_m^E are positive, showing symmetrical trends and maximum values ranging from 2020 (1-pentanol and 3-methyl-1-butanol) to 2400 J mol^{-1} (2- and 3-pentanol). Results have been correlated using the Redlich–Kister equation and interpreted by an extended modified cell model.

Keywords: Calorimeter; Enthalpies; Correlation data; Cell model

1. Introduction

Continuing our research program involving a systematic study of the thermodynamic excess properties of binary mixtures containing dialkyl carbonates + several series of organic compounds [1–3], we report the excess molar enthalpies, H_m^E, of diethyl carbonate (common component, component 1) + seven pentanol isomers, namely 1-, 2-, ad 3-pentanol, 2-methyl-1-butanol, 2-methyl-2-butanol, 3-methyl-1butanol, and 3-methyl-2-butanol, respectively.

Dialkyl carbonates are used as solvents for a variety of extractions of industrial importance, in the synthesis of pharmaceuticals, and in agricultural chemistry [4–6]. The aim of this paper is to verify the capability of the predictive expression developed by Redlich–Kister [7] and to investigate the relative influence of the isomer chain on molecular interactions of these mixtures.

To our knowledge no enthalpic literature data have been reported for the mixtures studied in this paper.

2. Experimental

2.1. Chemicals

Chemicals were Aldrich and Fluka products showing stated purities from suppliers, ≥98 mol%. Diethyl carbonate and pentanol isomers have been purified by refluxing over CaO, then distilled in a 30-plate column, out of which only the middle fraction of the distillate has been considered. Liquids were stored in

---

*Corresponding author. Tel.: +33-51-354325; fax: +33-51-259456; e-mail: Romolo@ciam.unibo.it

PII: S0040-6031(98)00600-5

Table 1
Purities, sources, densities, ρ, of pure chemicals and comparison with literature values at 298.15 K

Component	Purity(mol%)	Source	ρ/(g cm^{-3})	
			experimental	literature
Diethyl carbonate	99.8	Aldrich	0.96923	0.96926[8]
1-Pentanol	99.7	Fluka	0.81086	0.81080[8]
2-Pentanol	99.8	Aldrich	0.80504	0.805[8]
3-Pentanol	99.7	Fluka	0.81718	0.8160[8]
2-Methyl-1-butanol	99.9	Aldrich	0.81502	0.8150[8]
2-Methyl-2-butanol	99.8	Aldrich	0.80461	0.8050[8]
3-Methyl-1-butanol	99.9	Fluka	0.80133 [a]	0.80182 [a][9]
3-Methyl-2-butanol	99.8	Fluka	0.81524	0.81412[10]

[a] At 303.15 K.

dark bottles over molecular sieves (Union Carbide, type 4A, 1/16″ pellets) to remove water and degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy) to avoid bubble formation.

The GLC analysis was conducted on a gas chromatograph, Hewlett–Packard Model 5890 supplied by an HP (cross-linked 5% ME siloxane) capillary column. Mole percent purities, sources, density values in comparison with literature findings [8–10] are reported in Table 1.

2.2. *Enthalpy measurements*

Excess molar enthalpies have been determined using an LKB microcalorimeter (LKB producer, model 2107, Bromma, Sweden) operating under constant flow conditions [11]. Details of the experimental procedure have been described in a previous paper [12]. Two ABU automatic burets (ABU, Radiometer, Copenhagen, Denmark) have been used to pump continuously the required flow of each pure liquid into the mixing cell of the calorimeter.

Mole fractions have been determined from fluxes, and the flow rates have been selected to cover the entire mole fraction range. The errors in the excess molar enthalpies, H_m^E, and the mole fraction, x_1, of diethyl carbonate are estimated to be <1% and 2.10^{-4}, respectively.

The temperature of the apparatus has been electronically controlled and held constant at ±0.01 K.

Prior to measurements, the apparatus with its equipment, has been tested with the standard mixture cyclohexane + hexane and our results have been found in good agreement when compared with those of literature [13], showing an accuracy better than 0.5% at the maximum of the thermal effect.

3. Correlation of the calorimetric data

The experimental H_m^E values of the seven binary mixtures at 298.15 K are given in Table 2. Values for H_m^E have been fitted to the Redlich–Kister equation

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

where a_k are the adjustable parameters, x_1 and x_2 the mole fractions of diethyl carbonate and pentanol isomers, respectively.

The values of a_k, obtained from the least-squares analysis, are reported in Table 3, together with the standard deviations $\sigma(H_m^E)$ defined as

$$\sigma(H_m^E) = [\Phi/(N-n)]^{0.5} \qquad (2)$$

where N is the number of experimental points and n the number of a_ks.

Φ is the objective function defined as

$$\Phi = \sum_{k\geq 0}^{N} \eta_k^2 \qquad (3)$$

with $\eta_k = H_{m,cal}^E - H_m^E$, where $H_{m,cal}^E$ has been determined from the right-hand side of Eq. (1).

Figs. 1 and 2 show the plots of experimental and calculated excess molar enthalpies derived from Eq. (1) as a function of the molar fraction x_1 of diethyl carbonate.

Table 2
Excess molar enthalpies, H_m^E, of diethyl carbonate+pentanol isomers at 298.15 K

x_1	H_m^E/(J mol^{-1})	x_1	H_m^E/(J mol^{-1})
Diethyl carbonate(1)+1-pentanol(2)			
0.0358	254	0.5724	2001
0.0692	474	0.6408	1936
0.1003	692	0.7280	1754
0.1294	866	0.7811	1578
0.1823	1166	0.8426	1276
0.2292	1384	0.8771	1068
0.3084	1651	0.9146	791
0.3728	1817	0.9554	447
0.4714	1964		
Diethyl carbonate(1)+2-pentanol(2)			
0.0361	342	0.5741	2376
0.0696	644	0.6424	2282
0.1010	905	0.7294	2008
0.1302	1153	0.7823	1759
0.1834	1537	0.8435	1409
0.2304	1795	0.8779	1153
0.3100	2115	0.9151	845
0.3745	2294	0.9557	469
0.4732	2418		
Diethyl carbonate(1)+3-pentanol(2)			
0.0356	271	0.5707	2369
0.0687	534	0.6390	2286
0.0996	792	0.7264	2021
0.1285	1030	0.7797	1789
0.1822	1429	0.8415	1436
0.2278	1717	0.8762	1179
0.3068	2068	0.9139	855
0.3700	2238	0.9550	470
0.4695	2383		
Diethyl carbonate(1)+2-methyl-1-butanol(2)			
0.0356	342	0.5711	2232
0.0688	637	0.6396	2147
0.0998	865	0.7269	1901
0.1288	1074	0.7802	1679
0.1812	1411	0.8419	1339
0.2283	1637	0.8765	1120
0.3073	1963	0.9142	825
0.3716	2124	0.9552	458
0.4702	2253		
Diethyl carbonate(1)+2-methyl-2-butanol(2)			
0.0361	307	0.5743	2132
0.0697	569	0.6424	2026
0.1010	794	0.7295	1781
0.1303	978	0.7824	1543
0.1835	1301	0.8436	1229
0.2305	1546	0.8779	996
0.3101	1836	0.9152	737
0.3746	2000	0.9557	407
0.4734	2135		
Diethyl carbonate(1)+3-methyl-1-butanol(2)			
0.0327	277	0.5743	2002
0.0697	569	0.6426	1959
0.1010	772	0.7295	1748
0.1303	966	0.7824	1548
0.1835	1234	0.8436	1254
0.2306	1443	0.8779	1055
0.3101	1723	0.9152	762
0.3747	1870	0.9557	431
0.4734	2012		
Diethyl carbonate(1)+3-methyl-2-butanol(2)			
0.0356	327	0.5710	2216
0.0688	603	0.6395	2137
0.0988	837	0.7269	1898
0.1288	1036	0.7801	1669
0.1815	1357	0.8419	1351
0.2282	1597	0.8765	1119
0.3073	1916	0.9141	802
0.3715	2084	0.9551	458
0.4701	2234		

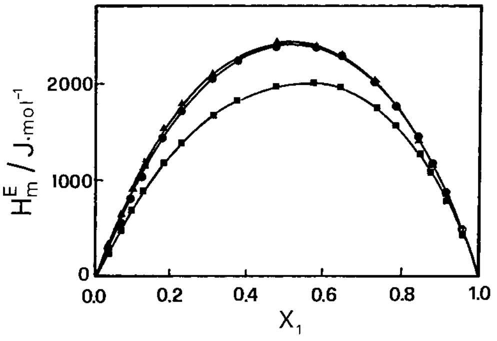

Fig. 1. Excess molar enthalpies, H_m^E, of diethyl carbonate(1) + 1-pentanol(2)(■), diethyl carbonate(1) + 2-pentanol(2)(▲), and diethyl carbonate(1) + 3-pentanol(2)(●) at 298.15 K. Solid curves represent values obtained from Eq. (1).

4. The cell model

The model used to describe the system studied in this paper was elaborated by Prigogine et al. [14–16], Salsburg and Kirkwood [17] and Rowlinson [18,19]

Table 3
Least-squares parameters, a_k, Eq. (1), and standard deviations, $\sigma(H_m^E)$, Eq. (2), of diethyl carbonate+pentanol isomers at 298.15 K

Mixture	a_0	a_1	a_2	a_3	a_4	$\sigma(H_m^E)$/(J mol^{-1})
Diethyl carbonate						
+ 1-pentanol	7935.3	1055.7	2188.8	701.6	−1222.2	6.6
+ 2-pentanol	9677.2	20.7	2416.5	687.6	−1849.7	8.5
+ 3-pentanol	9571.8	191.0	2705.9	1643.3	−3462.1	8.4
+ 2-methyl-1-butanol	9074.2	398.4	1570.6			7.6
+ 2-methyl-2-butanol	8627.1	22.9	746.3			7.9
+ 3-methyl-1-butanol	8091.4	830.0	1764.6			8.8
+ 3-methyl-2-butanol	8989.0	623.0	1357.5			8.7

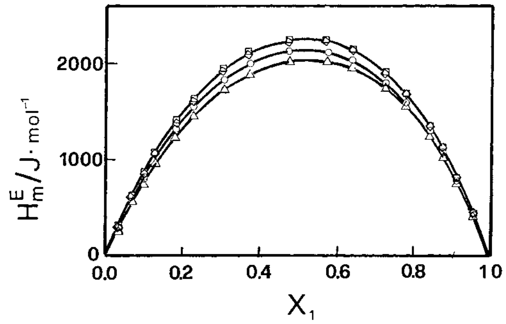

Fig. 2. Excess molar enthalpies, H_m^E, of diethyl carbonate(1) + 2-methyl-1-butanol(2)(□), diethyl carbonate(1) + 2-methyl-2-butanol(2)(○), diethyl carbonate(1) + 3-methyl-1-butanol(2)(△), and diethyl carbonate(1) + 3-methyl-2-butanol(2)(◇) at 298.15 K. Solid lines represent values obtained from Eq. (1).

and leads to the following expression for H_m^E:

$$H_m^E = x_1 x_1 E_{11} z[-1.44q + 10.76(RT/zE_{11})^2 \times (-2\theta - \delta^2 + 4\delta\theta x_2 + 4x_1 x_2 \theta^2)] \quad (4)$$

where

$$\delta = (E_{22} - E_{11})/E_{11} \quad (5)$$

$$\theta = (E_{12} - (E_{11} + E_{22})/2)/E_{11} \quad (6)$$

$$E = E_{11} + E_{22} - E_{12} \quad (7)$$

z is the number of nearest neighbors in the quasi-lattice model, E_{ij} the interaction energy between molecules i and j, and δ, θ the normalized parameters.

Values of δ have been calculated from Eq. (5) with E_{11} and E_{22} evaluated from the heats of vaporization reported in literature [8].

Values for z in the 8–12 range lead to a negligible variation of calculated parameters.

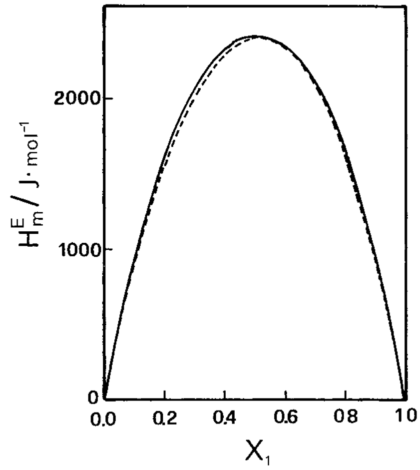

Fig. 3. Comparison between the Redlich–Kister fit (———), Eq. (1), and the cell model (- - -), Eq. (4), of diethyl carbonate + 2-propanol at 298.15 K.

Values of parameters (interaction energies) obtained by the cell model theory at 298.15 K are reported in Table 5.

Fig. 3 shows, as an example, the comparison between the Redlich–Kister fit and the cell-model curve for the diethyl carbonate + 2-pentanol mixture. For all other mixtures, similar discrepancies between best fit and calculated curve are observed.

5. Conclusions

Figs. 1 and 2 show large and positive values of H_m^E for all the mixtures, in agreement with the hydrogen bonding of alkanols. Values of H_m^E are of the same

Table 4
Interaction energies, E_{ij} (in kJ mol^{-1}), Eqs. (5)–(7), obtained by Eq. (4) with z=8 of diethyl carbonate+pentanol isomers at 298.15 K

Mixture	E_{11}	E_{22}	E_{12}	$E_{11}+E_{22}-2E_{12}$
Diethyl carbonate				
+1-pentanol	43.61	56.96	49.59	1.39
+2-pentanol	43.61	53.16	47.55	1.67
+3-pentanol	43.61	53.16	47.55	1.67
+2-methyl-1-butanol	43.61	54.41	48.23	1.56
+2-methyl-2-butanol	43.61	50.22	46.18	1.47
+3-methyl-1-butanol	43.61	55.67	48.94	1.40
+3-methyl-2-butanol	43.61	51.90	46.98	1.55

order of magnitude as the mixtures containing the same alkanols but with propylene carbonate as the second component [20]. However, the mixtures containing diethyl carbonate + 2-pentanol and diethyl carbonate+3-pentanol have practically coincident values of H_m^E.

On the contrary, the H_m^E values of mixtures containing propylene carbonate are spread over a range of 200 J mol^{-1}.

Analogously, the mixtures containing methyl alkanols+diethyl carbonate and methyl alkanols+ propylene carbonate have curves in the same range of H_m^E but with the maximum values increasing in the following order: 3-methyl-1-butanol<2methyl-1-butanol< 2-methyl-2-butanol<3-methyl-2-butanol, respectively.

It is very difficult to estimate the individual contributions of the alkyl groups for these systems owing to the complexity of the molecular interactions which involve hydrogen bonding alkanol-alkanol, alkanol-diethyl carbonate and the hindrance effects due to branching of alkyl groups. This conclusion is also reflected by the values of the calculated energy interaction parameters E_{ij} reported in Table 4.

Only one remarkable feature can be inferred by analysis of Figs. 1 and 2, namely that the values of H_m^E being minimum for the less branched alkanols, that is 1-pentanol and 3-methyl-1-butanol.

As can be seen from Table 4, mixtures of these alkanols with diethyl carbonate show the highest values of E_{22} and E_{12} prevailing over E_{22} with $H_m^E \cong E_{11} + E_{22} - 2E_{12}$ smaller than those of the other mixtures.

References

[1] R. Francesconi, F. Comelli, J. Chem. Eng. Data 42 (1997) 45.
[2] F. Comelli, S. Ottani, R. Francesconi, J. Chem. Eng. Data 42 (1997) 1208.
[3] R. Francesconi, C. Castellari, F. Comelli, Thermochim. Acta 306 (1997) 99.
[4] W. Martindale, The Extra Pharmacopoeia, Pharmaceutical Press, London, 1989.
[5] M.C. Annesini, R. De Sanctis, I. Kikic, J. Chem. Eng. Data 29 (1984) 39.
[6] The Merck Index, Merck Co. Inc., Rahwaj, NJ, 1989.
[7] O. Redlich, A. Kister, Ind. Eng. Chem. 40 (1948) 345.
[8] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents, fourth edn., Wiley–Interscience, New York, 1986.
[9] B. Sreenivasulu, P. Naidu, J. Chem. Eng. Data 38 (1993) 622.
[10] B.D. Smith, R. Srivastava, Thermodynamic Data for Pure Compound, Part B, Elsevier, Amsterdam, 1986.
[11] P. Monk, I. Wasdö, Acta Chem. Scand. 22 (1968) 1842.
[12] R. Francesconi, F. Comelli, J. Chem. Eng. Data 31 (1986) 250.
[13] I. Gmehling, J. Chem. Eng. Data 38 (1993) 143.
[14] I. Prigogine, G. Garikian, Physica 16 (1950) 239.
[15] I. Prigogine, The Molecular Theory of Solutions, North-Holland, Amsterdam, 1957.
[16] I. Prigogine, V. Mathot, J. Chem. Phys. 20 (1952) 49.
[17] Z.W. Salsburg, J.K. Kirwood, J. Chem. Phys. 20 (1952) 1538.
[18] J.S. Rowlinson, Proc. R. Soc. London 214 (1952) 192.
[19] J.S. Rowlinson, J. Chem. Phys. 20 (1952) 337.
[20] F. Comelli, R. Francesconi, C. Castellari, J. Chem. Eng. Data, submitted.