

CALORIMETRIC STUDY OF THE PROXIMITY EFFECT IN ALIPHATIC DIESTERS

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Excess molar enthalpies, H^E , at atmospheric pressure and 303.15 K are reported for binary mixtures of 1-chlorohexane with diethyl oxalate, diethyl malonate, diethyl succinate, diethyl glutarate, diethyl adipate, diethyl pimelate and diethyl sebacate. These experimental results, together with those obtained previously on the excess enthalpies of aliphatic diester + *n*-hexane mixtures, are interpreted in terms of molecular surface interactions between aliphatic, chlorinated and carboxylate groups. Comparison of the enthalpy interchange parameters reveals a decrease of the intermolecular interactions with decreasing intramolecular COO—COO distance in the diester molecule.

One of the most apparent intramolecular effects in non-electrolyte solutions is the "proximity effect", consisting of the mutual interaction between groups in the same molecule, which may considerably alter the values of the interchange parameters in organic mixtures. This has already been well established in acetals, aromatic chlorides, aromatic ethers, disulphides and dichloroalkanes [1–3].

Our aim now is to establish it in aliphatic diesters, by studying the calorimetric behaviour of mixtures containing an aliphatic diester and either *n*-hexane or 1-chlorohexane. The diesters used were diethyl oxalate, diethyl malonate, diethyl succinate, diethyl glutarate, diethyl adipate, diethyl pimelate and diethyl sebacate.

As far as we know, the only previous calorimetric measurements on these mixtures are those of Monzón *et al.* on aliphatic diester + *n*-hexane [4], and those of Manzini *et al.* on mixtures containing dialcohol esters isomeric with our diesters [5].

Materials

The liquids used were Merck–Schuchardt and Fluka products with better than 99 mole per cent purity. Refractive indices, used as purity criterion, agreed satisfactorily with those found in the literature. The liquids were also subjected to g.l.c. analysis, and in all cases but diethyl pimelate and diethyl sebacate the purity was better than 99.5 mole per cent; no purification was attempted, because of the difficulty of distilling the liquids.

Methods

Calorimetric measurements

The calorimeter was isobaric and quasi-isothermic [6]. The mixing cell was an anchor-shaped glass receptacle filled under vacuum with Hg to isolate weighed quantities of the two liquids in the limbs of the cell. Electric energy was measured to better than 0.5%, and the temperature of the water was controlled to within 0.002 K. Test measurements on hexane+cyclohexane were carried out and agreement with the data reported earlier [7] was better than 0.5% over the central range of concentration.

Results

The values obtained for the excess enthalpies were fitted by the least squares procedure to the equation

$$H^E, \text{ J mol}^{-1} = x(1-x) \sum_n A_n (1-2x)^n \quad (1)$$

where x is the mole fraction of 1-chlorohexane, and the standard deviation $s(H^E)$ was obtained in each case. Coefficients A_n and standard deviations are given in Table 1. All the H^E results are plotted in Fig. 1, where the solid lines are those calculated from the smoothing equations.

Discussion

The excess enthalpies of the 1-chlorohexane + diester systems are positive and decrease as the separation between the —COO— groups increases (internal “dilution” effect of carboxylate groups in the diester molecule). Comparison of the H^E values, at the maximum, for these mixtures with those of the corresponding n -hexane + diesters shows that the introduction of a chlorine atom into the n -hexane molecule causes a decrease in the values of H^E for the 1-chlorohexane mixtures, ranging from 900 to 950 J mol^{-1} at the maximum (a little less for mixtures containing diethyl oxalate and diethyl malonate).

In order to establish the proximity effect, we chose a “reference state” in which the two carboxylate groups showed practically no mutual interaction. Definition of such a system comes through an interaction parameter obtained from monoester + n -hexane and monoester + 1-chlorohexane mixtures according to a molecular

Table 1 Coefficients A_n and standard deviations $s(H^E)$ for the representation of the excess molar enthalpies at 303.15 K by equation (1)

$(x)C_6H_{13}Cl+$	A_0	A_1	A_2	$s(H^E), J mol^{-1}$
$(1-x)C_2H_5O_2CCO_2C_2H_5$	3571	-232.0	-913.9	10.7
$(1-x)C_2H_5O_2CCH_2CO_2C_2H_5$	3334	-185.5	-710.8	10.3
$(1-x)C_2H_5O_2C(CH_2)_2CO_2C_2H_5$	2807	-124.9	-314.7	7.0
$(1-x)C_2H_5O_2C(CH_2)_3CO_2C_2H_5$	1886	-215.9	-237.0	5.3
$(1-x)C_2H_5O_2C(CH_2)_4CO_2C_2H_5$	1370	-68.0	-197.5	2.6
$(1-x)C_2H_5O_2C(CH_2)_5CO_2C_2H_5$	976	-274.2	196.5	2.6
$(1-x)C_2H_5O_2C(CH_2)_8CO_2C_2H_5$	1.41	2.86	6.7	1.9

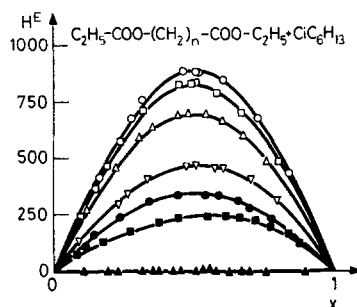


Fig. 1 Excess molar enthalpies H^E at 303.15 K for $x C_6H_{13}Cl +$. \circ , $(1-x)C_2H_5O_2CCO_2C_2H_5$; \square , $(1-x)C_2H_5O_2CCH_2CO_2C_2H_5$; \triangle , $(1-x)C_2H_5O_2C(CH_2)_2CO_2C_2H_5$; \diamond , $(1-x)C_2H_5O_2C(CH_2)_3CO_2C_2H_5$; \bullet , $(1-x)C_2H_5O_2C(CH_2)_4CO_2C_2H_5$; \blacksquare , $(1-x)C_2H_5O_2C(CH_2)_5CO_2C_2H_5$; \blacktriangle , $(1-x)C_2H_5O_2C(CH_2)_8CO_2C_2H_5$

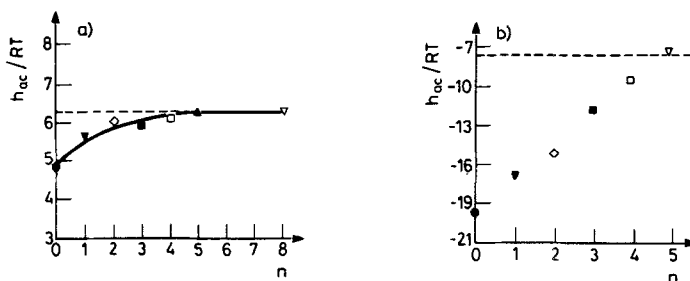


Fig. 2 (a) Aliphatic-carboxylate enthalpy of interchange parameter $C_{ac} = h_{ac}(T)/RT$, in the mixtures $C_6H_{14} + H_5C_2O_2C(CH_2)_nCO_2C_2H_5$ vs. n , the number of CH_2 groups (b) Chlorine-carboxylate enthalpy of interchange parameter in the mixtures containing C_6H_{13} . Symbols as in Fig. 1

surface interaction treatment [2] in its "zero-order" and "quasi-chemical" approximations.

In Fig. 2(a), the reference aliphatic – carboxylate parameters obtained from the monoester + *n*-hexane mixtures is compared with those obtained from the various diester + *n*-hexane mixtures. The close agreement from *n* = 5 up to *n* = 8 (*n* = number of intermediate CH₂ groups between the two COO groups) is consistent with the mutually independent behaviour of the two carboxylate groups in the same molecule.

In Fig. 2(b), the values of the chlorine – carboxylate parameter obtained from the diester + 1-chlorohexane mixtures are compared with the "reference" value. The results are similar to the latter, and there is close agreement between both types of parameters for diethyl pimelate + 1-chlorohexane.

References

- 1 H. V. Kehiaian, IPC Science and Technology Press (1979) 121.
- 2 J. P. Grolier, K. Sonskowska-Kehiaian, H. V. Kehiaian, J. Chim. Phys., 68 (1971), 922. *ibid.* 70 (1973) 367.
- 3 C. Polo, C. Gutiérrez Losa, M.-R. Kechavarz and H. V. Kehiaian, Ber. Bunsenges. Phys. Chem., 84 (1981) 525.
- 4 J. M. Monzón, S. Otin and C. Gutiérrez Losa, J. Chem. Thermodyn., 13 (1981) 385.
- 5 G. Manzini, V. Crescenzi and R. Furlanetto, Macromol., 8 (1975) 198.
- 6 C. Gutiérrez Losa and M. Gracia, Rev. Acad. Ciencias Fis-Quím. Natur. Zaragoza, XXVI (1971) 101.
- 7 A. Amhed, Trans. Faraday Soc., 69 (1973) 387.

Zusammenfassung — Bei Atmosphärendruck und 303,15 K gemessene molare Überschenthalpien (H^E) werden für binäre Gemische von 1-Chlorhexan mit Diäthylloxalat, Diäthylmalonat, Diäthylsuccinat, Diäthylglutarat, Diäthyladipat, Diäthylpimelate bzw. Diäthylsebacat angegeben. Diese experimentellen Ergebnisse werden zusammen mit den früher für Gemische von aliphatischen Diestern und *n*-Hexan erhaltenen Resultaten als molekulare Oberflächenwechselwirkungen zwischen aliphatischen, chlorierten und Carboxylatgruppen interpretiert. Ein Vergleich der Enthalpieaustauschparameter läßt eine Verminderung der intermolekularen Wechselwirkungen mit abnehmendem intramolekularem Abstand zwischen den COO-Gruppen erkennen.

Резюме — Приведены избыточные молярные энтальпии (H^E) при атмосферном давлении и температуре 303,15 К для двойных смесей 1-хлоргексана с диэтиловыми эфирами щавелевой, малоновой, сукциновой, глутаровой, адипиновой, пимелиновой и себадиновой кислот. Полученные экспериментальные результаты, наряду с ранее измеренными для смесей алифатический диэфир + *n*-гексан, интерпретированы на основе молекулярных поверхностных взаимодействий между алифатической, хлорзамещенной и сложноэфирной группами. Сопоставление энтальпийных взаимообменных параметров показывает уменьшение межмолекулярных взаимодействий с одновременным уменьшением внутримолекулярных COO—COO взаимодействий.