Both results illustrate the particular interest in using methanol as a molecular probe, in order to detect by chromatography, small effects on the surface of PVC. The method will be extended to other polymers.

One of us (*C.J.*) is indebted to *Fabriques de Tabac Réunies* (Serrières) for financial support. We also wish to thank Mr. *P. Ghiste* for measuring the static isotherms for methanol on PVC.

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257. Thermodynamics of Mixtures

Excess Volumes and Energies of Mixing of Cycloalkane Mixtures (Cyclopentane to Cyclooctane)

by **Luong Minh Duc, Z. Abdellah** and **H. F. Stoeckli**[1])
Institut de chimie, University of Neuchâtel, Switzerland

(3. IX. 73)

Summary. The volumes of mixing for the systems cyclopentane + cyclohexane, cyclopentane + cycloheptane, cyclohexane + cycloheptane (at 20 °C), and cyclopentane + cyclooctane, cyclohexane + cyclooctane, cycloheptane + cyclooctane (at 30 °C) have been measured with a dilatometer. All systems show volume contractions, except the first. The energies of mixing are also given. They vary from 7 to 55 J/mol for equimolar solutions.

1. Introduction. – In earlier investigations in this laboratory, the heats of mixing of several cycloalkane systems were determined [1–2]. In order to allow a further interpretation of the results, the excess volumes of mixing have now been determined. We wish to report here the results for binary systems containing the cycloalkanes from cyclopentane to cyclooctane.

2. Experimental. – The measurements were carried out in a dilatometer described earlier [3], and similar to the model of *Duncan et al.* [4].

The hydrocarbons were all supplied by *Fluka AG*, with a stated purity of better than 99%. Olefinic and aromatic hydrocarbons were eliminated by treatment with H_2SO_4 conc., and after neutralisation (NaOH), washing (H_2O deionized), and drying over $CaSO_4$ anh., the cycloalkanes were distilled. In the case of cycloheptane, it was not possible to prevent a slight reaction with mercury, in spite of repeated shaking with mercury.

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[1]) Author to whom communications should be sent.

3. Results and discussion. – The excess volumes of mixing are shown in Fig. 1 and 2. The results were fitted to an analytical expression of the type

$$V^e = x(1-x)\,[A + B(1-2x)] \tag{1}$$

where x represents the mol fraction of the heavier compound.

The values of A and B, and the mean deviations σ for the systems are given in Table 1.

The results for the system cyclopentane + cyclooctane at 30 °C are compatible with the results of *Ewing et al.* [5] at 15, 25 and 35 °C. (It must be pointed out, that their results are more accurate, owing to the more advanced equipment used for the determination of V^e.)

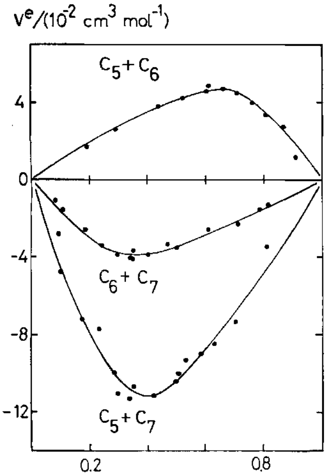

Fig. 1. *The volumes of mixing V^e at 20 °C, for the systems C_5+C_6, C_6+C_7 and C_5+C_7*

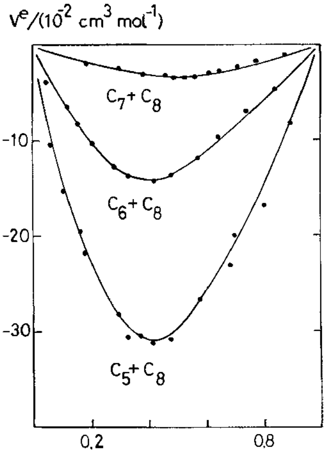

Fig. 2. *The volumes of mixing V^e at 30 °C, for the systems C_5+C_8, C_6+C_8 and C_7+C_8*

Table 1. *Parameters A* (cm³ mol⁻¹) *and B* (cm³ mol⁻¹) *for* V^e *of eq. (1) and* σ (cm³ mol⁻¹)

System	Temp. (°C)	—A	—B	σ
c-C_5 + c-C_6	20	—0.170	0.104	0.001
c-C_5 + c-C_7	20	0.413	0.180	0.005
c-C_6 + c-C_7	20	0.141	0.086	0.002
c-C_5 + c-C_8	30	1.204	0.435	0.010
c-C_6 + c-C_8	30	0.518	0.242	0.005
c-C_7 + c-C_8	30	0.121	0.010	0.002

Using the combined results, which include earlier results for V^e at 298 K [1], it is found that the temperature gradient $(\partial V^e/\partial T) = -0.0045\ \text{cm}^3\,\text{mol}^{-1}\,\text{K}^{-1}$ for $x = 0.4$, near the maximum of all curves.

All the volumes of mixing are negative, except for the system cyclopentane + cyclohexane, which corresponds to the smallest cycloalkanes investigated.

This system shows a complete inversion with respect to the other systems, the maximum of the positive curve being near $x = 0.6$.

The result seems to be in contradiction with the behaviour of the other mixtures of cycloalkanes, and with the general pattern for the mixtures of *n*-alkanes, another class with negative volumes of mixing [6]. However, for this system, a relatively large and positive enthalpy of mixing was found [1–2], and consequently the internal energy of mixing U^e (at constant volume) is again consistent with the results obtained for the different systems, as shown below.

The quantity U^e is given by the relation (2) [6–8]

$$U^e = H^e - T\,(\alpha/\beta_T)\,V^e, \tag{2}$$

where $$\alpha = V^{-1}\,(\partial V/\partial T)_P \quad \text{and} \quad \beta_T = -V^{-1}\,(\partial V/\partial P)_T.$$

Experimental values of U^e, for different mol fractions, are given in Table 2. They were calculated by using the calorimetric values of H^e [1–2], and values of α and β_T from the literature [9–11].

Table 2. *Excess volumes* ($cm^3\ mol^{-1}$), *enthalpies* ($J \cdot mol^{-1}$) *and energies* ($J \cdot mol^{-1}$) *of mixing*

x	$-V^e$	H^e	U^e
cyclopentane + cyclohexane (20 °C)			
0.3	−0.027	17.4	9
0.4	−0.035	22.3	11
0.5	−0.042	26	13
0.6	−0.046	28	13
0.7	−0.045	27	12
cyclopentane + cycloheptane (20 °C)			
0.3	0.105	− 1.7	30
0.4	0.112	− 1.8	32
0.5	0.102	− 1.5	29
0.6	0.087	− 0.8	25
cyclohexane + cycloheptane (20 °C)			
0.3	0.038	2.7	10
0.4	0.038	4.8	15
0.5	0.034	7	18
0.6	0.029	9	20
cyclopentane + cyclooctane (30 °C)			
0.3	0.288	−43	47
0.4	0.309	−45.6	53
0.5	0.300	−42.2	55
0.7	0.216	−22.5	50
cyclohexane + cyclooctane (30 °C)			
0.3	0.127	− 2	40
0.4	0.134	+ 2	47
0.5	0.128	+ 7	50
0.7	0.087	+13	44
cycloheptane + cyclooctane (30 °C)			
0.3	0.026	− 2	6
0.4	0.029	− 3	6
0.5	0.030	− 3	7
0.7	0.024	− 1	7

The energy of mixing is the *difference* of two experimental quantities, and in the present calculation, it was found that the error on U^e was about ± 2 J/mol, for all systems.

The results of Table 2 show a trend in the behaviour of the different systems, similar to earlier observations made for the mixtures of *n*-alkanes [12]: U^e is positive and it increases with the difference in size of the molecules.

The extension of an earlier theory [12] to the present case, was also attempted. It was assumed that the constants a_1 and a_2 in the *Van Laar-Lorentz* equation [8] could be written as $a_1 \approx n_1^2$ and $a_2 \approx n_2^2$, in the case of cycloalkanes. The calculated values of U^e showed only a semi-quantitative agreement with the experimental values for the 6 systems considered.

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258. Zur Kontrolle von Solid-phase Peptidsynthesen durch Eluat-Chloridbestimmung

von **Peter Fankhauser, Peter Fries** und **Max Brenner**
Institut für Organische Chemie, Universität Basel

(10. IX. 73)

Summary. The origin of chloride ion in chloroform and methylene chloride solutions of tertiary amines is studied. The applicability of such solutions in the analytical control of solid-phase peptide synthesis must be seriously questioned. An alternative procedure, amenable to automation, is suggested.

Zur quantitativen Analyse auf freie Aminogruppen harzfixierter Peptide (Resinopeptide[1]) wird oft die Titration des basisch aus den Resinopeptid-hydrochloriden eluierbaren Chlorids herangezogen. Die Methode erlaubt einerseits die direkte Erfassung der bei Deblockierung gebildeten Hydrochloride, anderseits allgemein nach dem

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[1] Als Resinopeptid bezeichnen wir die Gesamtheit des harzfixierten Peptidmaterials [2].