Thermochimica Acta, 94 (1985) 85–92
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MICROCALORIMETRIC DETERMINATION OF THE ENTHALPIES OF SOLUTION OF OXIRANE IN BENZENE, TOLUENE, p-XYLENE AND 2,2,4-TRIMETHYLPENTANE AT 298.15 K AND 101.3 kPa

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ABSTRACT

Using a differential microcalorimeter, the enthalpies of solution, ΔH_S (298.15 K, 101.3 kPa), of oxirane in benzene, toluene, p-xylene and 2,2,4-trimethylpentane are determined in the mole fraction range $0.00005 < x < 0.001$ of the solute. ΔH_S exhibits a strong dependence on x in aromatic solvents, becoming more exothermic by 10 to 15 kJ/mol when x falls below 0.0005. This effect is attributed to a short-ranged structure formation of the solvent induced by the dissolved gas molecules. No dependence of ΔH_S on x is found in 2,2,4-trimethylpentane.

INTRODUCTION

In a previous paper (ref.1) microcalorimetric measurements of the enthalpies of solution ΔH_S (298.15 K, 101.3 kPa) of trifluoromethane and chlorotrifluoromethane in several aromatic hydrocarbons in the mole fraction range $5 \times 10^{-5} < x < 2 \times 10^{-3}$ of the solute were reported. The most remarkable result was a strong dependence of ΔH_S on x much below saturation such that ΔH_S becomes more exothermic by 5 to 10 kJ mol^{-1} when x falls below 5×10^{-4}. We attribute this additional exothermic effect to a structure formation of the solvent being induced by the molecules of the dissolved gases (ref.2). If this interpretation is correct, the observed effect should strongly depend both on the structures of the solvent and the solute.

Recently, new papers on the calorimetric determination of the enthalpies of solution of gases in liquids have been published. Battino and Marsh (ref.3) used a modified version of the displacement calorimeter of Marsh, Stokes et al. (ref.4) which was designed for the incrementwise determination of the enthalpies of mixing of liquids. The authors succeeded in performing gas dissolution isothermally and isobarically by introducing the gas into the calorimeter at a rate which equals the rate of its dissolution. They did not find any dependence of ΔH_S on x on dissolving rare gases, nitrogen, carbon dioxide and gaseous al-

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0040-6031/85/$03.30

kanes in cyclohexane, benzene, and tetrachloromethane in the range $10^{-4} < x < 10^{-3}$. The ΔC_p values calculated from the change of ΔH_s between 298.15 K and 318.15 K, which range from 3o to 50 J mol^{-1} K^{-1}, do not indicate any structure formation of the solvent, too. Gill and Wadsö (ref.5) have developed a sophisticated technique for measuring ΔH_s of slightly soluble gases in water. Although this method is very sensitive and yields precise results, it has not been designed by the authors for determining the dependence of ΔH_s on the concentration of the solute. Using this method, Olofsson et al.(ref.6) have recently published ΔH_s data on rare gases, oxygen and gaseous alkanes in water at 288.15 K, 298.15 K and 308.15 K. The anomalous high ΔC_p values, ranging from 200 to 400 J mol^{-1} K^{-1}, reveal a structure formation of water by the dissolved gases.

In this paper we present the results of new measurements of ΔH_s (298.15 K, 101.3 kPa) of oxirane (= ethylene oxide) in benzene, toluene, p-xylene, and 2,2,4-trimethylpentane. Both the compactness of the three-membered ring and the dipole moment $\mu = 6.30 \times 10^{-30}$ Cm of oxirane should favour the structure formation of solvents being susceptible to such an effect.

METHODS

Reagents

Oxirane (Messer, Griesheim, purity 99.9 %) was filled into a glass storage vessel of 250 cm^3 capacity. For degassing, the vessel was repeatedly evacuated after having frozen the oxirane with liquid nitrogen. A number of samples from 5 to 25 microliters were taken with a precision gas-tight syringe for calibrating the integrator scale of the gas chromatograph. The standard deviation of the calibration factor was ± 1.9 %.

The solvents benzene, toluene, p-xylene and 2,2,4-trimethylpentane (Merck, Darmstadt; pro analysi, purity better than 99.7 %) were dehydrated under nitrogen by chromatography on mole sieves 0.4 nm. Toluene and 2,2,4-trimethylpentane were previously rectified on a laboratory column with 75 theoretical plates. Benzene: d_4^{20} 0.87865 n_D^{20} 1.5011; toluene: d_4^{20} 0.86692 n_D^{20} 1.4965; p-xylene: d_4^{20} 0.86105 n_D^{20} 1.4958; 2,2,4-trimethylpentane: d_4^{20} 0.69185 n_D^{20} 1.3914.

Calorimetric Measurements

The calorimetric procedure was similar to that described in ref.1. Measurements were performed in a LKB batch differential microcalorimeter designed by Wadsö (ref.7) being installed in a big air thermostat which was controlled to 298.15 ± 0.05 K. A gas-tight piston syringe was incorporated into the air-bath of the calorimeter allowing the gases to be introduced into the working cell at constant flow rates from 3 to 6×10^{-4} cm^3 s^{-1}. To perform the measurements at constant pressure, the solvents were presaturated and the calorimeter cells were flushed out with helium. This procedure, however, allows only changes with respect to the solvents saturated with helium to be detected. Because helium is only very slightly soluble in liquid hydrocarbons and its enthalpy of solution is moderately endothermic (ref.8), the assumption that it does not much influence the dissolution of oxirane - which is much better soluble - seems to be justified.

4 cm^3 of the solvent saturated with helium was filled into the larger compartment of the working cell previously flushed with helium. The residual nitrogen content of the vapour phase, determined by gas chromatography, was smaller than 2%. After the thermal equilibrium had been attained, dissolution was started by introducing oxirane from a stainless steel capillary of 0.15 mm i.d. at a rate of 6×10^{-4} cm^3 s^{-1}. The total heat evolved was calculated from the integrator readings (see ref.1).

Gas Chromatographical Analysis

An improved technique for the gas chromatographical analysis of small quantities of dissolved gases in liquid samples was adopted, using a Carlo Erba 'Fractovap' Model 4200 dual column gas chromatograph with a thermal conductivity detector and a Spectra Physics Model 4270 integrator. The stainless steel columns filled with 'Porapak Q', a silanized porous polymer, were connected by a 'Bimatic' device in such a way that the solvent - with a retention time of about 30 minutes - is retained in the first section of the column whilst the separation of the gaseous solutes - with a retention time of about 3 minutes - takes place in the second section of the column where no solvent is present. This arrangement allows the solvent to be eluted through a bypass without flowing through the detector.

Each calorimetric measurement was followed by a gas chromatographical analysis of the final solute concentration. For this purpose, 3 to 5 samples of 50 microliters each were taken from different sites in the solution. It follows from the agreement of the gas volume being introduced with the solute mole fraction determined analytically and from the absence of oxirane in the vapour phase that oxirane was virtually completely dissolved in all the solvents which have been studied. Therefore, no correction of the observed heat effect for saturation of non-dissolved gas with solvent vapour is required. Although no solubility data on oxirane in hydrocarbon solvents are given in the literature, there can be no doubt that our ΔH_s measurements have been performed far below saturation. For this reason, oxirane seems to be most suitable for studying the concentration dependence of ΔH_s.

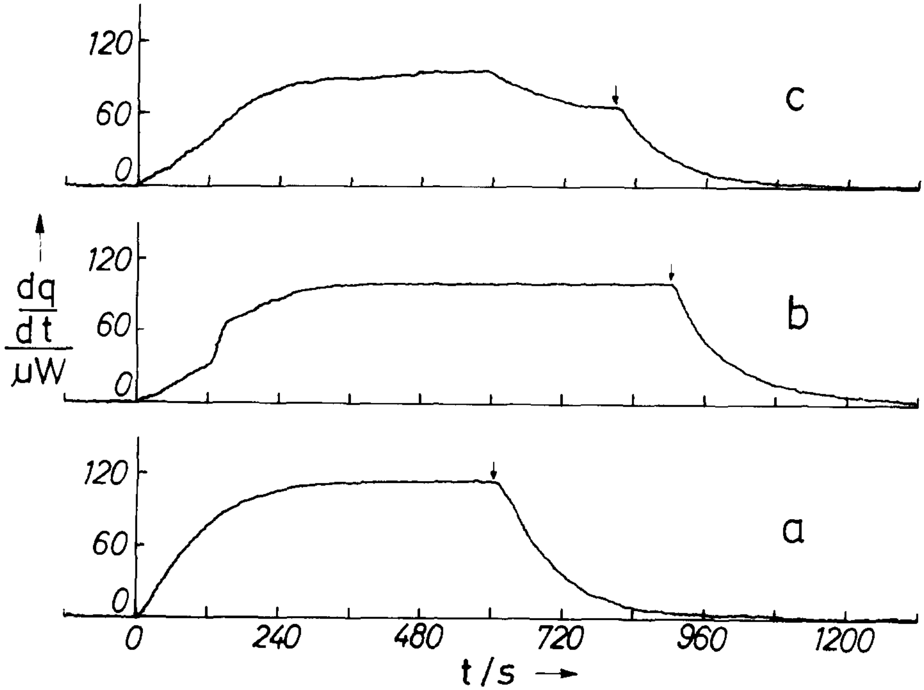

Fig.1. Examples of heat flow curves dq/dt = f(t). (a) Calibration with 112.5 µW during 600 s; 4 cm^3 of 2,2,4-trimethylpentane in the working cell. (b) Dissolution of oxirane in 4 cm^3 of 2,2,4-trimethylpentane during 900 s; final mole fraction $x = 1.15 \times 10^{-4}$. (c) Dissolution of oxirane in 4 cm^3 of p-xylene during 800 s; final mole fraction $x = 1.02 \times 10^{-4}$. Gas flow rate $6 \times 10^{-4}\ cm^3\ s^{-1}$.

Heat flow curves dq/dt = f(t)

Although the total heat evolved on dissolving oxirane was determined from the integrator readings, it is informative to record the heat flow curves, dq/dt = f(t), too. Typical examples are presented in Fig.1. Curve a is a calibration curve obtained on feeding the heater of the working cell, filled with 4 cm^3 of 2,2,4-trimethylpentane, with a constant electric power of 112.5µW during 600 s, without rotating the calorimeter block. Both the rise and the decrease of the dq/dt signal correspond to a simple exponential function being characterized by the half-time $\tau = 70$ s of the heat flow. Curve b was obtained on introducing oxirane at a constant rate of $6 \times 10^{-4}\ cm^3\ s^{-1}$ into 4 cm^3 of 2,2,4-trimethylpentane during 900 s. The fluctuations of the slope of the curve in the first three minutes may be explained by initial concentration differences within the solution which are balanced out by diffusion. After about 7 minutes a plateau is reached which remains constant until the gas flow is stopped. Then the dq/dt signal decreases according to a simple exponential function as in Curve a. Curve c, being obtained on dissolving oxirane at the same rate in 4 cm^3 of p-xylene during 800 s, has a quite different shape which, however, is characteristic for all aromatic solvents. The dq/dt signal, a small positive slope of which persists, exhibits a discontinuity after about 600 s, dropping by about 30% of its value despite of the unchanged inflow rate of the gas. When the gas flow is stopped, the dq/dt signal drops exponentially. It is true that the heat flow curves represent the dissolution process only with a time lag given by the half-time of the heat flow. However, it is reasonable to assume that the discontinuity of Curve c and the drop of the dq/dt signal after about 600 s arises from the breakdown of the structures being established in the solution by the dissolved gas at very low concentrations.

RESULTS AND DISCUSSION

The results obtained on the four systems which have been studied are presented in Figures 2 and 3 and in Table 1. The experimental data may be fitted by the empirical equation (solid curves in Fig.2)

$$\Delta H_s(x) = [\, 2\,\Delta H_s^o - \Delta H_s^\infty(1 - e^{ax})] \,/\, (1 + e^{ax}) \,, \qquad (1)$$

where $\Delta H_s^o = \Delta H_s(x=0)$ is the ordinate intercept and ΔH_s^∞ the plateau which is attained asymptotically at $x > 5x10^{-4}$. The fitting parameter $a \gg 1$ is calculated by minimizing the error square sum. The shape of the curves in Fig.2 resembles that of the curves given in ref.1. The plateau ΔH_s^∞ is shifted from - 6.0 to - 8.35 kJ mol^{-1} in the order benzene > toluene > p-xylene. This effect indicates an increase of the exothermic interaction of oxirane with the aromatic nucleus to which the methyl substituents contribute by hyperconjugation. Despite the uncertainty of ΔH_s which attains ±1.0 to ±2.0 kJ mol^{-1} in very dilute solutions, the decrease of ΔH_s in the range $x < 5 \times 10^{-4}$ is obvious.

From the point of view of structure formation of the solvent the following qualitative interpretation is proposed: Oxirane molecules dissolved in aromatic hydrocarbons act as centers of a short-ranged structure formation. Because no long-ranged order does exist in liquids, the centers disturb each other. From the fact that the plateau of ΔH_s is attained at a molar ratio of solute: solvent = 1 : 2000 follows that the structures are completely distroyed when the average distance among the centers corresponds to eight solvent molecules or less.

For comparison, we have measured ΔH_s of oxirane in a solvent which was expected not to be susceptible to structure formation. For this purpose, 2,2,4-trimethylpentane, a branched aliphatic hydrocarbon the molecular structure of which does not much differ from a sphere, was chosen. As shown in Fig.3 no significant dependence of ΔH_s on x could be detected. This result supports our

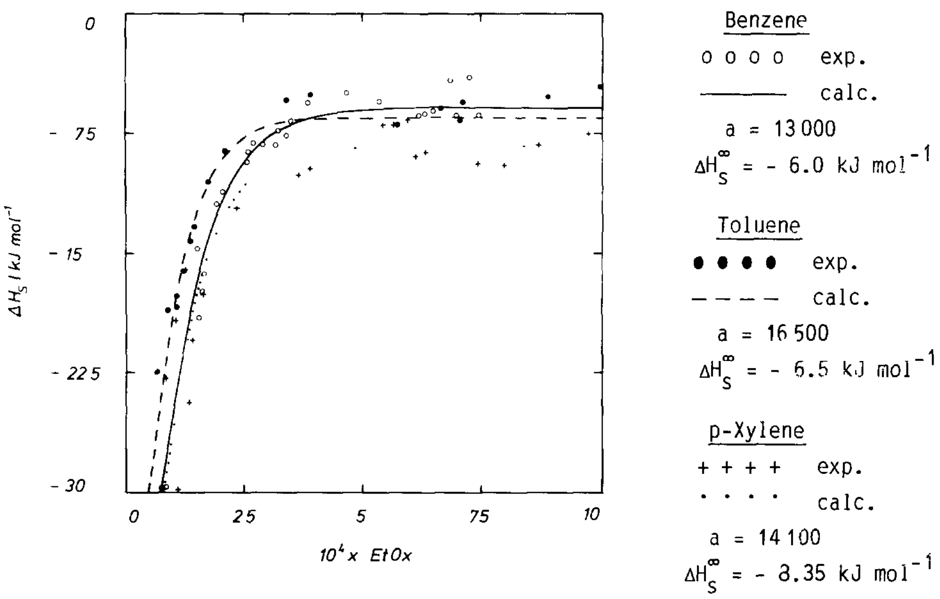

Fig.2. Plots of ΔH_S(298.15 K, 101.3 kPa) of oxirane in aromatic solvents versus mole fraction x of the solute. Experimental values (cf. Table 1) and smoothing curves calculated with eq.(1).

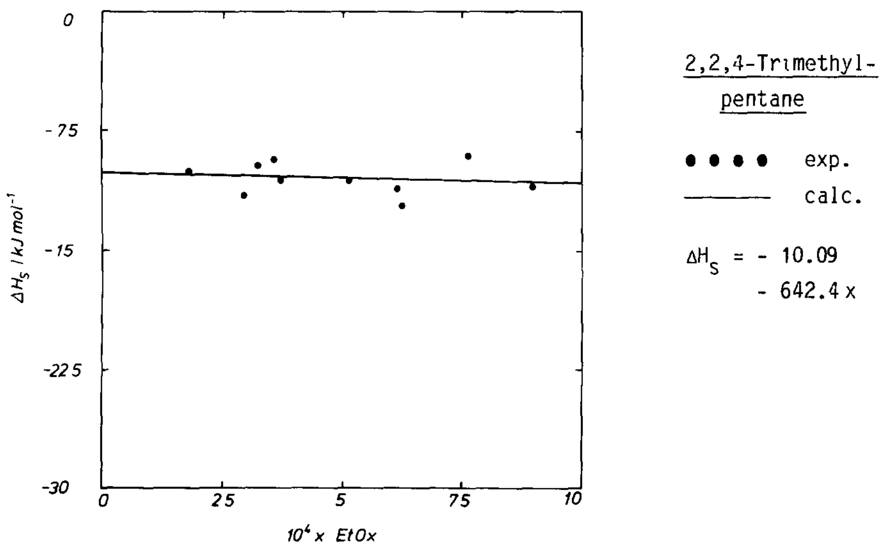

Fig. 3. Plot of ΔH_S(298.15 K, 101.3 kPa) of oxirane in 2,2,4-trimethylpentane versus mole fraction x of the solute. Experimental values (cf. Table 1) and regression line.

TABLE 1

Enthalpies of solution ΔH_s (298.15 K, 101.3 kPa) of oxirane ın benzene, toluene, p-xylene, and 2,2,4-trimethylpentane.

$10^3 x$	$-\Delta H_s$/kJ mol^{-1} exp.	$-\Delta H_s$/kJ mol^{-1} calc.
	Benzene	
0.0798	29.80	29.03
0.1458	14.88	17.50
0.1492	19.21	24.24
0.1564	17.60	16.15
0.1604	16.51	15.73
0.1866	12.11	13.15
0.1988	11.37	12.17
0.2505	9.51	9.26
0.2532	8.92	9.16
0.2634	8.35	8.78
0.2831	8.41	8.16
0.3099	8.44	7.54
0.3156	7.54	7.43
0.3323	7.87	7.16
0.3416	6.97	7.03
0.3765	5.87	6.65
0.4581	5.20	6.23
0.5261	5.74	6.09
0.6119	6.65	6.03
0.6234	6.53	6.03
0.6407	6.35	6.02
0.6764	4.46	6.01
0.6901	6.63	6.01
0.7160	4.21	6.01
0.7363	6.65	6.01
	Toluene	
0.0608	22,56	27.16
0.0729	29.76	24.28
0.0855	18.69	21.60
0.1030	17.79	18.40
0.1033	18.47	18.35
0.1176	16.22	16.17
0.1331	14.33	14.21
0.1416	13.47	13.29
0.1718	10.68	10.77
0.2062	8.74	8.98
0.3343	5.59	6.81
0.3853	5.27	6.63
0.5690	7.15	6.51
0.6598	6.17	6.50
0.6991	6.88	6.50
0.7051	5.77	6.50
0.8829	5.45	6.50
0.9915	4.85	6.50

$10^3 x$	$-\Delta H_s$/kJ mol^{-1} exp.	$-\Delta H_s$/kJ mol^{-1} calc.
	p-Xylene	
0.0790	23.02	-
0.0798	23.02	28.75
0.1024	19.37	24.24
0.1062	29.95	23.56
0.1226	16.18	20.89
0.1299	24.50	19.84
0.1378	20.59	18.77
0.1598	17.76	16.25
0.2306	12.37	11.45
0.3593	10.31	8.87
0.3844	9.89	8.72
0.5361	7.21	8.39
0.5607	7.19	8.38
0.5882	6.85	8.37
0.6074	9.11	8.37
0.6260	8.84	8.36
0.7366	9.60	8.35
0.7922	9.70	8.35
0.8635	8.42	8.35
0.9678	7.71	8.35
1.0197	7.32	8.35
	2,2,4-Trimethylpentane	
0.1789	9.89	10.20
0.2920	11.56	10.28
0.3193	9.55	10.30
0.3524	9.17	10.32
0.3691	10.52	10.33
0.5100	10.55	10.42
0.6135	11.06	10.48
0.6237	12.11	10.49
0.7623	8.80	10.58
0.8969	10.88	10.67

assumption that structure formation of the solvent should be responsible for the dependence of ΔH_S on x.

There is no doubt that water is the solvent with the most pronounced tendency to structure formation. Unfortunately, our calorimetric procedure does not allow to determine ΔH_S of very slightly soluble gases in water. In a recent publication, Dec and Gill(ref.9) used a steady-state microcalorimetric method for determining ΔH_S (298.15 K, 101.3 kPa) of gaseous hydrocarbons in water in order to investigate the hydrophobic effect. No attempt, however, was made for studying the dependence of ΔH_S on the concentration of the solute. On establishing a linear correlation between the number of C-H bonds of the solute and the change of ΔH_S, ΔG_S, ΔS_S, the authors found that this effect depends on special features of the molecular structure of the (nonpolar) solutes, like ring formation or triple bonds.

Financial support of this work by the Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg, and the Fonds der Chemischen Industrie, Frankfurt am Main, is gratefully acknowledged.

REFERENCES

1 F.Becker, G.Braun and A.Steiger, J.Chem.Thermodynamics 13 (1981) 833.
2 G.Braun, F.Becker and A.Steiger, Ber.Bunsenges.Phys.Chem. 85 (1981) 1010.
3 R.Battino and K.N.Marsh, Aust.J.Chem. 33 (1980) 1997.
4 R.H.Stokes, K.N.Marsh and R.P.Tomlins, J.Chem.Thermodynamics 1 (1969) 211.
5 S.J.Gill and I.Wadsö, J.Chem.Thermodynamics 14 (1982) 905.
6 G.Olofsson, A.A.Oshodj, E.Qvarnström and I.Wadsö, J.Chem.Thermodynamics 16 (1984) 1041.
7 I.Wadsö, Acta Chem.Scand. 22 (1968) 927.
8 E.Wilhelm and R.Battino, Chem.Rev. 73 (1973) 1.
9 S.F.Dec and S.J.Gill, J.Solution Chem. 13 (1984) 27.