

ENTROPIES OF DIPHENYLGLYOXAL SOLUTIONS IN NON-POLAR SOLVENTS

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ABSTRACT

The solubilities of diphenylglyoxal were determined between 15 and 45°C in eight non-polar organic solvents and compared with theoretical values calculated from calorimetric data, following the regular solution theory. Entropy data obtained show that solvent–solute interactions take place in some of the solvents, increasing solubility and resulting in deviations from regular solution behaviour. Solvents can be divided in two groups, one of which gives “regular solutions” of diphenylglyoxal. In all cases the observed solubility approaches that predicted as the temperature rises.

INTRODUCTION

The important role played by some glyoxals in controlling cellular division and their inhibiting behaviour in oxygen capture have recently been pointed out [1]. In consequence we are interested in providing data on the physicochemical parameters of these compounds that would contribute to a better understanding of their structure–activity relationships. Among aryl glyoxals, diphenylglyoxal is the most interesting, since it presents a high liposolubility and because of the importance of its hydrazone derivatives.

It is not possible to predict how much a certain solute will dissolve in a particular solvent, unless we deal with “regular solutions”. In these cases, the mol fraction solubility (x_2) of a solid solute can be calculated from the equation

$$-\ln x_2 = -\ln x_2^i + V_2\phi_1^2(\delta_2 - \delta_1)^2/RT \quad (1)$$

The first term represents ideal solubility and is obtained from calorimetric data by means of the energy required to liquify the solid at temperature T . The second term represents the heat of mixing which is expressed in terms of

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the solubility parameters, δ_2 and δ_1 , the square roots of the cohesive energy densities of solute and solvent, respectively. V_2 is the molar volume of the solute and ϕ_1 , the volume fraction of solvent in the saturated solution.

The presence of the heat term in eqn. (1) decreases the x_2 value and, hence, when $\delta_1 = \delta_2$ this term becomes zero and the solubility reaches its maximum value and equals the ideal solubility. This can be calculated [2] from the equation

$$-\ln x_2^i = \frac{1}{R} \left\{ \left(\Delta H_m - aT_m - \frac{b}{2} T_m^2 \right) \frac{T_m - T}{T_m T} + a \ln \frac{T_m}{T} + \frac{b}{2} (T_m - T) \right\} \quad (2)$$

where ΔH_m , T_m , a and b are calorimetrically determined; ΔH_m is the heat of fusion at the melting point, T_m ; a and b are two constants derived from the expression of ΔC_p as a function of the absolute temperature, T

$$\Delta C_p = a + bT \quad (3)$$

ΔC_p being the difference between the heat capacities of the solid and supercooled liquid.

The use of the eqn. (1), in an attempt to predict the solubilities of diphenylglyoxal [2], led to poor agreement between experimental and predic-

TABLE I

Solubilities and calorimetric data for diphenylglyoxal ^a

Solvent		Mole fraction solubility			
		15°C	25°C	35°C	45°C
Hexane	Obs.	0.0045	0.0070	0.0105	0.0150
	Calc.	0.0227	0.0300	0.0388	0.0497
Heptane	Obs.	0.0064	0.0085	0.0126	0.0176
	Calc.	0.0288	0.0342	0.0442	0.0566
Carbon tetrachloride	Obs.	0.0785	0.1078	0.1480	0.2014
	Calc.	0.1435	0.1851	0.2392	0.3065
Toluene	Obs.	0.1288	0.1762	0.2410	0.3132
	Calc.	0.1503	0.1933	0.2500	0.3205
Benzene	Obs.	0.3205	0.3421	0.3860	0.4477
	Calc.	0.1500	0.1962	0.2533	0.3248
Chloroform	Obs.	0.2767	0.2972	0.3384	0.3916
	Calc.	0.1502	0.1960	0.2535	0.3246
Dichloromethane	Obs.	0.2605	0.2768	0.2950	0.3254
	Calc.	0.1490	0.1922	0.2485	0.3180
1,2 Dichloroethane	Obs.	0.2400	0.2590	0.2818	0.3074
	Calc.	0.1420	0.1898	0.2453	0.3143
Ideal solubility		0.1504	0.1962	0.2536	0.3249
Entropy of fusion		15.50	15.47	15.43	15.39

^a ΔC_p (cal mol⁻¹ K⁻¹) = 17.37 - 0.01 T ; melting point, 368 K; enthalpy of fusion = 5592 cal mol⁻¹.

ted results and it was suggested that this could be due to the difference between molar volumes of solute and solvent preventing random distribution assumed in regular solution theory. In this paper, we are interested in testing this hypothesis by measuring solubilities in the same solvents and in a range of temperatures from 15 to 45°C.

MATERIALS, EXPERIMENTAL METHODS AND RESULTS

Materials and experimental methods on solubility determinations, on the one hand, and calorimetric measurements, on the other, are the same as previously described [2]. The results are shown in Table 1.

DISCUSSION

Provided the solution is diluted, or if the solution is not far from ideal [3], the entropy change of a solid forming a regular solution in a liquid is given by

$$\bar{S} - S^s = R \frac{d \ln x_2}{d \ln T} \quad (4)$$

where x_2 represents mole fraction solubility at temperature T , S^s is the entropy of the solid solute and \bar{S} the partial entropy of the solute in solution. $\bar{S} - S^s$ is therefore the sum of the entropies of fusion and dilution.

Hildebrand [4], showed that in the expression

$$\left(\frac{\partial \ln x}{\partial \ln T} \right)_{\text{sat}} \approx \frac{\bar{H} - H^s}{RT} \quad (5)$$

the heat term changes very slightly with temperature. The result is that the curves representing $\log x_2$ against $\log T$ show long linear regions. Accordingly, entropies of solution of diphenylglyoxal have been investigated by plotting \log mole fraction solubility against \log temperature. Two types of behaviour have been observed: one where entropies of solution are nearly independent of temperature and the other where the entropies increase with increasing temperature (Fig. 1). Entropies of solution are obtained from the slopes of the straight lines, or from the tangents to the curves at the temperatures of interest.

The theoretical entropy change to disperse a liquid solute in a solvent is given by

$$\bar{S} - S^0 = -R \ln x_2 \quad (6)$$

S^0 is the entropy of the liquid solute, so that $\bar{S} - S^0$ represents the entropy of dilution.

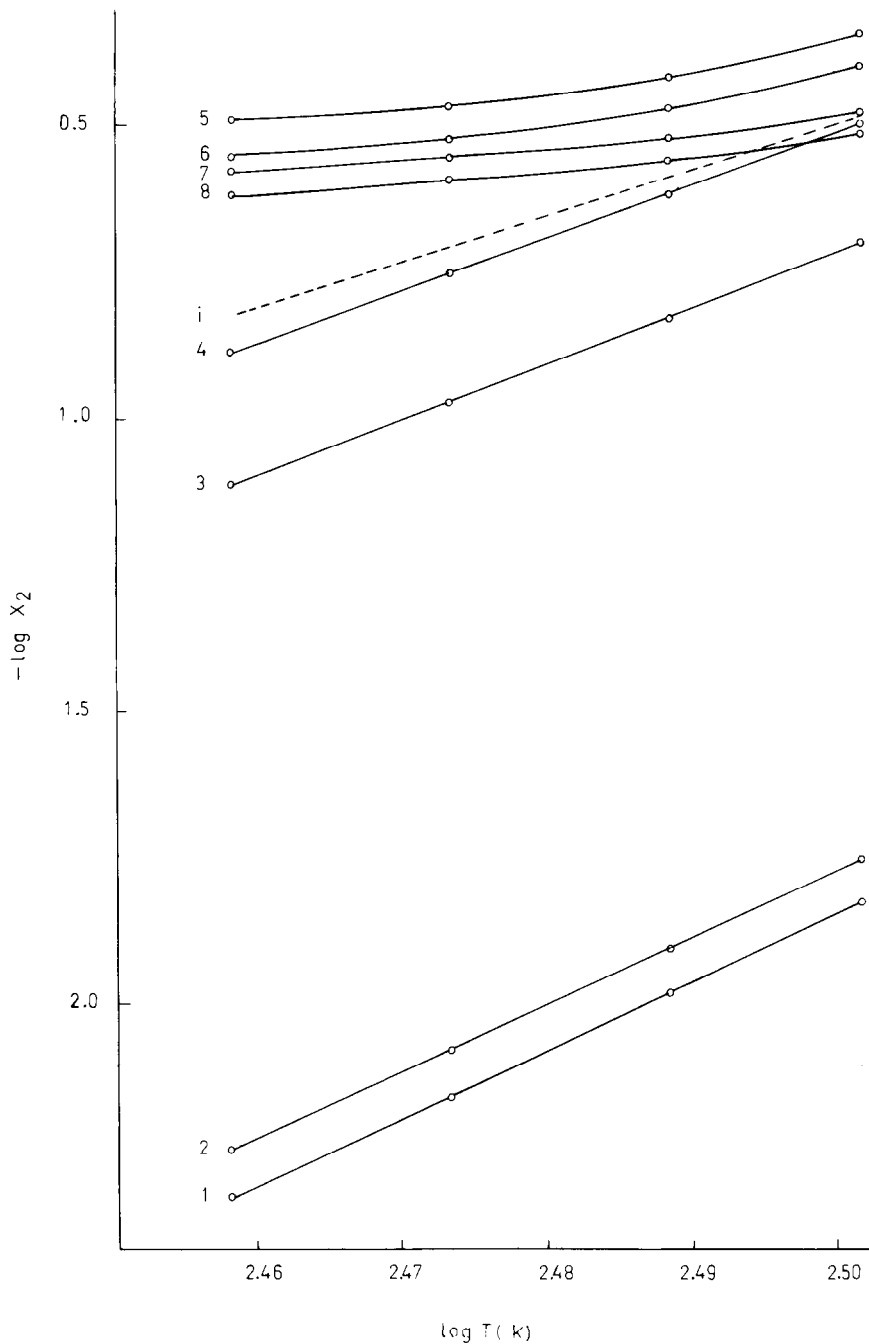


Fig. 1. Determination of entropies of solution of diphenylglyoxal: 1, hexane; 2, heptane; 3, carbon tetrachloride; 4, toluene; 5, benzene; 6, chloroform; 7, dichloromethane; 8, 1,2-dichloroethane; i, ideal.

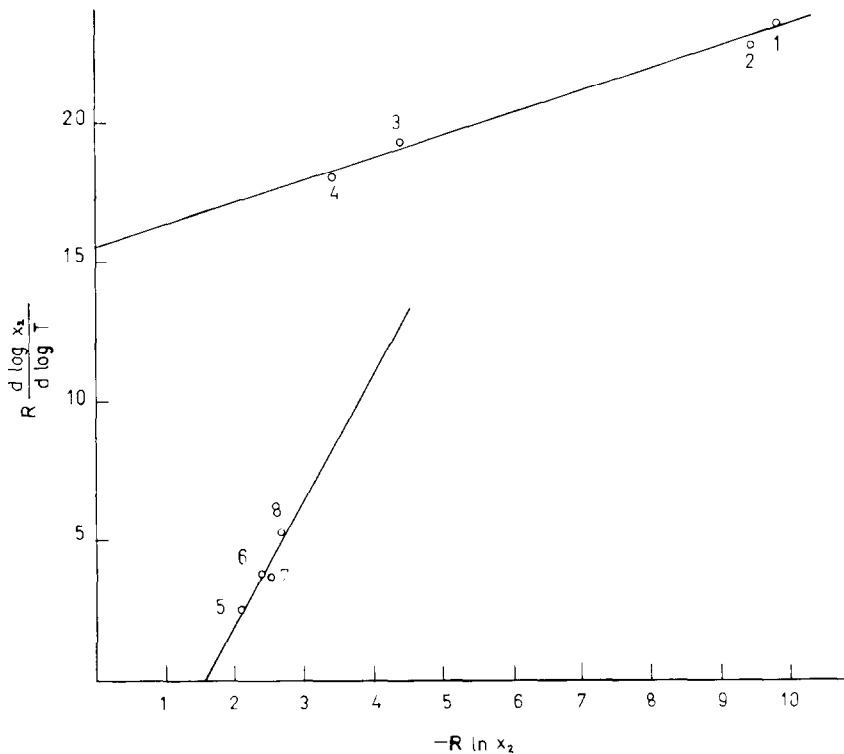


Fig. 2. Entropies of solution of diphenylglyoxal against ideal entropies of dilution at 25°C. Solvent numbers are the same as in Fig. 1.

The effects of molar volumes on entropies of solution have been studied by plotting entropies obtained from eqn. (4) against those calculated from eqn. (6). A typical result is shown in Fig. 2. The points are widely scattered and regression analysis gives low correlation coefficients. However, we can divide these solvents in two groups as before. For the first group, the regression analysis gives an acceptable correlation coefficient (~ 0.995) and a positive intercept on the ordinate axis (~ 15.5), which agree well with entropies of fusion obtained calorimetrically and shown in Table 1.

In the second group of solvents, regression analysis gives a lower correlation coefficient and negative intercept on the $d \log x_2 / d \log T$ axis, indicating negative entropies of fusion.

A similar situation has been observed by Hildebrand and Glew [5], who determined the entropies of solution of iodine in a series of solvents. Their violet iodine solutions, which are known to be regular, followed the same behaviour (straight line) as in our case for the first group of solvents in Fig. 2. All their other points lay below this line, and represented brown solutions, in which iodine is known to be complexed. The analogy suggests that the saturated solutions of diphenylglyoxal are regular in our first group of

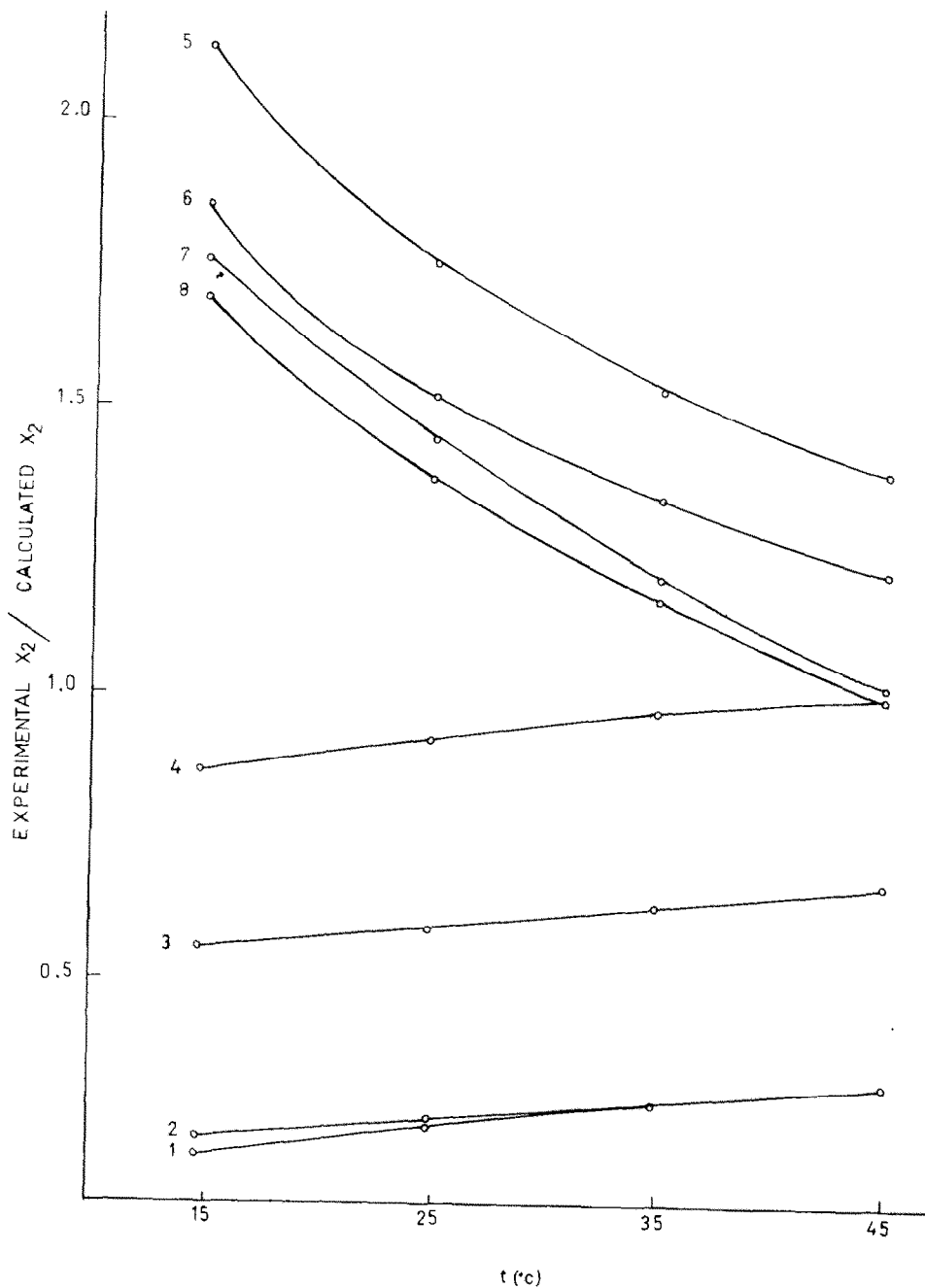


Fig. 3. Variation of experimental/calculated solubilities of diphenylglyoxal with temperature. Solvent numbers are the same as in Fig. 1.

solvents (hexane, heptane, carbon tetrachloride and toluene), and the diminished entropy in the other solvents (benzene, chloroform, dichloromethane and 1,2-dichloroethane) may be due to complex formation.

The variation in the ratio of observed solubility to calculated regular solubility, as a function of temperature is shown in Fig. 3. Calculated solubilities were obtained using the integrated heat of fusion as was indicated in ref. 2. In all solvents examined, the experimental values approach the calculated values as the temperature increases. Solvents can be divided again into the same two groups: in one group, the ratio of the experimental solubility to calculated solubility increases in a nearly linear way, and in the other, the ratio decreases uniformly, but not linearly with increasing temperature.

Although the entropy results indicate that the solvents in the first of the above groups form regular solutions of diphenylglyoxal, this appears to be contradicted by the fact that the observed solubilities are lower than those anticipated for regular solutions. Shinoda and Hildebrand [6] have encountered similar cases and have concluded that sometimes the solubility parameter does not give a correct measure of forces of attraction between solvent and solute. Expansion of the squared term, $(\delta_2 - \delta_1)^2$, in eqn. (1) gives the sum of the cohesive energy densities of solvent and solute minus twice their geometric mean, which represents the energy gained in bringing the unlike molecules into contact. It is probable that the solubilities of diphenylglyoxal, in solvents forming regular solutions, are low because the geometric mean is too high an estimate for the intermolecular attraction between solute and solvent molecules. When the molar volume of the solvent is less than that of the diphenylglyoxal, solvent molecules will be unable to approach solute molecules as closely as their own kind. This can result in a lower cohesive energy between solute and solvent than that predicted by the geometric mean assumption, and a lower solubility than anticipated. This difference will decrease as the molar volume of the solvent approaches that of the solute: the geometric mean will become a better estimate of cohesive energy between solvent and solute, and the observed solubility will approach the calculated value. Figure 3 illustrates this phenomenon since lines 1-4 appear in such a manner that the relative difference between partial molar volumes of solvent and solute in the saturated solution diminishes.

A similar argument can be advanced for the effect of temperature on the regular solutions, shown in Fig. 3. Translational molecular motion increases with temperature and makes close molecular packing more difficult. Steric effects, therefore, become less important as the temperature increases, with a resulting increase in the reliability of the geometric mean and in the observed solubility.

As has been suggested previously, the entropy indicates complex formation between the solvents of the second group and diphenylglyoxal. Complex formation affects the solubility in the opposite way to that outlined above.

Attractive forces between unlike molecules are now greater than those between like molecules and the cohesive energy is greater than that given by the geometric mean. The result is that the solubilities are higher than those calculated for regular solutions as is shown in Fig. 3. Furthermore, complex formation would be expected to decrease with increasing temperature, accounting for the drop in the solubility observed in Fig. 3.

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