

Contribution to the Thermodynamics of High Polymer Solutions. V. Solubility of Heterogenous Polymers

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of Lindsay, McElcheran, and Thode³ on the C¹³ isotope effect in the decomposition of oxalic acid into CO2, CO, and H2O are of the order of magnitude predicted for malonic acid. The isotope effects should be comparable in the decarboxylation of oxalic and malonic acids. We have studied the isotope effect in the decarboxylation of malonic acid by following the isotopic composition of the CO2 liberated from ordinary malonic acid.

The decomposition of malonic acid gives C13O2 and C12O2 according to the following equations

$$C^{12}H_2(C^{12}OOH)_2 \xrightarrow{k_1} C^{12}O_2 + C^{12}H_3C^{12}OOH$$
 (1)

$$C^{13}H_2(C^{12}OOH) \xrightarrow{k_2} C^{12}O_2 + C^{13}H_3COOH$$
 (2)

$$C^{12}H_2 \xrightarrow{k_3} C^{13}O_2 + C^{12}H_3COOH$$
 (3)

$$\xrightarrow{k_4} C^{12}O_2 + C^{12}H_3C^{13}OOH.$$
 (4)

Since the reaction is first order, the ratio C13O2/C12O2 is at any

time,
$$t$$
,
$$C^{13}O_{2}/C^{12}O_{2} = \frac{k_{3}M_{3}^{0}(1 - e^{-(k_{3} + k_{4})t})}{(k_{3} + k_{4})\left[M_{1}^{0}(1 - e^{-k_{1}t}) + M_{2}^{0}(1 - e^{-k_{2}t}) + \frac{k_{4}}{k_{3} + k_{4}}M_{3}^{0}(1 - e^{-(k_{3} + k_{4})t})\right]}$$

where M_{10} , M_{20} , and M_{30} are the initial amounts of the malonic acids in Eqs. (1)-(3). If α is the average fraction of C^{13} in natural carbon and if we assume that there is no fractionation in the formation of malonic acid, then we get

$$C^{13}O_2/C^{12}O_2 = \frac{2\alpha k_3}{(1-\alpha)k_1}$$
 at small t

and

$${
m C^{13}O_2/C^{12}O_2} = {2\alpha k_3 \over (1-\alpha)(k_3+k_4)} \ {
m at} \ t = \infty \, .$$

Implicit in these equations are the approximations that $k_2\alpha \simeq k_1\alpha$, $k_4\alpha \simeq k_3\alpha \simeq (k_1/2)\alpha$. These assumptions are justified by our results.

C. P. malonic acid was further purified by fractional crystallization from water at about 20°C. The sample used in experiment 2 (M.P. 137-137.5°C) was 99.2 percent pure by acidimetric titration. Samples of the order of 5 grams were decomposed in a thermostated (137.5±0.5°C) vacuum system. The CO₂ was separated from the acetic acid by cold traps. A sample of the CO2 was collected after a small amount of decomposition and another sample was taken for analysis after completion of the reaction. A portion of the purified malonic acid was oxidized completely to CO₂ by KIO₃ and K₂Cr₂O₇ in a mixture of syrupy H₃PO₄ and 30 percent fuming H₂SO₄. Determination of the ratio of C¹³O₂/ $C^{12}O_2$ from the oxidation gives directly $\alpha/(1-\alpha)$. The samples were analyzed with a Consolidated-Nier isotope ratio mass spectrometer. During the course of analysis frequent determinations were made on samples of tank CO2 to check the precision and reproducibility of the mass spectrometer. The results are given in Table I. The values of $k_1/2k_3$ were corrected back to zero time. For the calculation of k_4/k_3 the values of $t \infty$ were corrected for the amount of sample of different isotopic composition removed at te. Our results for tank CO2 and the CO2 from the combustion of the malonic acid are in good agreement with each other and the results of Nier and Gulbransen⁴ (0.0111±0.0002). The close agreement between tank CO2 and the combustion sample justify our assumption in regard to fractionation in the formation of the two C13 malonic acids. It should be pointed out that malonic acid sample 1 was purified in a different manner and contained some NaCl, which does not take part in the reaction. The discrepancy between the tank CO2 analyses as well as the other samples in the two different sets of experiments resulted from the differences

TABLE I.

Exp.	Sample	$C^{13}O_2/C^{12}O_2$	Av. dev.	$k_1/2k_3$	k_4/k_3
1	$t = \epsilon$	0.010587	0.024%	1.039 ±0.001	
1	Tank CO2	0.010986	0.024%		
- 1	$t = \infty$	0.010902	Single Det.		1.020
2	$t = \epsilon$	0.010918	0.008%	1.035 ± 0.001	
2	Tank CO2	0.011287	0.078%		
2	Combustion	0.011303	0.047%		
2	t = ∞	0.011200	0.10 %		1.019 ± 0.00
heory				1.021	1.0198

in the operating characteristics of the spectrometer over a period of several weeks. In any given experiment the reproducibility was excellent as shown by the average deviations, which were usually taken from three or more independent determinations.

The theoretical values were calculated according to the method previously given for C^{14} . The theoretical value for k_4/k_3 is in excellent agreement with experiment. The discrepancy between the theoretical and experimental values for $k_1/2k_3$ results from the fact that the malonic acid vibrations cannot be completely approximated by an XY2 model. The vibrations within the carboxyl group should be taken into account as both our experiments and those on oxalic acid show. The C14 experiments on malonic acid² measure k_4/k_3 in the above notation. Both theory and the C13 experiments on oxalic and malonic acids are not consistent with the large isotope effects reported2 for C14 substitution in malonic and brom-malonic acids.

* Research carried out under the auspices of the AEC.

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Contribution to the Thermodynamics of High Polymer Solutions. V. Solubility of Heterogenous Polymers

G. GAVORET AND MICHEL MAGAT Laboratoire de Chimie-Physique, Faculté des Sciences, Paris August 19, 1949

N an article in course of publication we give some results on precipitation limits of narrow fractions and mixtures of fractions of GRS, precipitated by ethanol from toluene solutions. We came to the conclusion that the precipitation limit for mixtures was not determined by the number average molecular weight as previously suggested on the basis of a statistical treatment,2 but was dependent on an average of a rather higher order than the weight average.

Lately Stockmayer³ has corrected the results of Scott and has shown that the precipitation limit is determined by the relation

$$2\mu_c = (1 + x_w^{-1/2})^2 - \frac{(x_z^{1/2} - x_w^{1/2})^2}{x_w \cdot x_z^{1/2}},\tag{1}$$

where x_w is the weight average and x_z the z average of the number of segments.4

In the absence of published data Stockmayer could not check his formula experimentally. It was interesting to attempt a verification with our data. To make a rigorous test one would have to determine u-values independently, say from osmotic pressure measurements, and to make all the comparisons at critical concentrations. This is prohibitively long and the precise determination of the precipitation limit at the rather high critical concentrations is difficult. We have hence proceeded in a different way. A calibration curve, molecular weight, viz., concentration of alcohol at the precipitation point, was established from experiments on narrow fractions, for which $\bar{M}_n \approx \bar{M}_w \approx \bar{M}_s$; the real concentration of the polymer at the precipitation point being $\varphi_P = 1.10^{-2}$. From this plot and the experimentally determined amount of alcohol required for precipitation of mixtures of frac-

TABLE I.

No.	Molecular weight of fractions	Composition of the mixture by weight	16-3					
			E.E.	M.W.	M_{St}	M_n	M_{w}	M_z
8	75 20	9.62 90.38	30.0 ± 1		27.8	21.5	25.3	35.7
9	220 1	88.4 11.6	250	±35	207	8.3	194	220
10	220 1	46.0 54.0	170	±15	148	1.8	101	219
11	220 1	13.15 86.85	125	±10	102	1.15	29.9	189.5

tions, one can obtain the experimental equivalent molecular weight of the fraction-mixture (E.E.M.W.). The E.E.M.W. can be then compared to calculated \bar{M}_n , \bar{M}_w , \bar{M}_z values and to the molecular weight of the hypothetical fraction \bar{M}_{St} , that according to (1) would have the same precipitation point as the mixture used.

 \bar{M}_{St} was calculated from:

as calculated from:

$$(1+x_{St}^{-1/2})^2 = 2\mu_c = (1+x_w^{-1/2})^2 - \frac{(x_z^{1/2}-x_w^{1/2})^2}{x_w \cdot x_z^{1/2}}.$$
(2)

Table I gives the results obtained in a few characteristic cases (all the molecular weights in thousands). The agreement between E.E.M.W. and M_{St} without being perfect is much better then between E.E.M.W. and the other averages and can be judged as satisfactory, in view of the unavoidable errors in the molecular weights of fractions.

- ¹ G. Gavoret and M. Magat, J. Chimie Phys. (to be published). ² R. L. Scott, J. Chem. Phys. **13**, 178 (1945). M. Magat, J. Chimie Phys.

- to be published.

 3 W. H. Stockmayer, J. Chem. Phys. 17, 588 (1949).

 4 In the note published by Stockmayer the sign before the second term is given as positive but from the context one can deduce that in reality it should be negative.

A Preferentially Oil Soluble Carrier for Radiocobalt-60

J. R. WHITE Socony-Vacuum Laboratories, Paulsboro, New Jersey August 15, 1949

FREQUENTLY met with industrial problem is the quantitative measurement of the location and flow of liquids through porous media or behind barriers to visibility and access. One attack on this measurement problem is to incorporate a gammaactive material in the liquid and to trace the movement of the liquid with a Geiger counter or other radiation detector located externally to the system barriers. When the flowing liquid consists in mutually little soluble liquid pairs, such as water and oil, it is generally desirable that the gamma-active tracer be confined to only one liquid phase.

The cobaltous salt of the dodecyl ester of tetrahydrophthallic acid, having the structural formula,

is suitable for carrying the gamma-activity of radiocobalt-60 into oils in a highly preferential manner. This salt possesses the following properties as a carrier:

1. Solubility to the extent of 1.5 percent by weight of the salt in acid washed kerosene at 25°C.

- A kerosene over water distribution coefficient in excess of 200 at 25°C provided that the water have a pH of seven and not contain cations exchangeable with cobaltous ion.
 Thermal stability to temperatures in excess of 100°C.
 Hydrolytic stability in contact with water at pH-7.
- 5. Stability toward photolysis provoked by sunlight.

This organic salt has been synthesized from samples of Atomic Energy Commission irradiated cobaltic oxide (Co₂O₃). The oxide has been digested to solution with 12N hydrochloric acid and adjusted to pH-5 with sodium hydroxide solution. A water solution of the sodium salt of the organic acid has been admixed with the cobaltous chloride solution in appropriate mole proportions, whence the cobaltous salt of the organic acid precipitates. The precipitated salt suspended in the water phase has been directly extracted into a desired oil by gentle agitation of contacting phases of oil and water containing suspended salt. Any excess cobaltous chloride has then been removed from the oil phase by repeated water washing. Large samples of oil containing as much as 0.03 mc/ml have been prepared by this procedure.

Condensation Coefficient and Adsorption

HANS M. CASSEL Pittsburgh, Pennsylvania August 15, 1949

HE condensation coefficient, defined as the ratio, α , of the observed rate of evaporation to the gas kinetically computed excess of molecules striking the surface of the condensed phase per unit time, has recently been discussed by G. Wyllie¹ from the standpoint of Volmer's theory of phase transitions.2 Accordingly, evaporation and condensation have to be considered as (at least) two-step processes, the exchanged molecules passing through the adsorbed state at the interface. To describe the rate of transition from the substrate into the adsorbed film Wyllie introduces the simplest possible hypothesis, namely that this is given by $A(\Gamma_0 - \Gamma)$, where A depends on the temperature, and Γ is the superficial concentration, the subscript referring to the state of equilibrium. Regarding the exchange between the film and the vapor phase he assumes that the adsorption isotherm is that of an ideal two-dimensional gas: $\Gamma = \tau bp$. Here, τ is the "verweilzeit" in the adsorbed state, determining the rate of desorption, $b = (2\pi mkT)^{-\frac{1}{2}}$, and p is the vapor pressure. On this basis, Wyllie derives the expression

 $\alpha = A/(1/\tau + A)$.

It is quite obvious that the restriction to low pressure adsorption limits the validity of this theory unnecessarily, and that a better approximation can be obtained on the assumption of a Langmuir type adsorption isotherm

$$\Gamma = \tau b p / (1 + \tau \beta b p). \tag{1}$$

This implies that the occupied fraction of the surface, $\beta\Gamma$, is blocked to impinging molecules, and the condensation efficiency correspondingly reduced. On this basis, the result is

$$\Gamma = (A \Gamma_0 + bp)/(1/\tau + A + \beta bp)$$
 (2)

and

$$\alpha = A/(1/\tau + A + \beta bp)(1 + \tau \beta bp_0). \tag{3}$$

This means that α becomes dependent on the pressure and, therefore, must be smaller for condensation than for evaporation. It should be noticed that the factor $(1+\tau\beta bp_0)$, being always greater than $(1+\beta\Gamma_0)$, may surpass the amount 2 if τ is great enough. Provided that $1/\tau$ can be neglected in comparison to A, the maximum condensation coefficient that may be attained is

$$\alpha_{\text{max}} = 1/(1 + \tau \beta b p_0). \tag{4}$$

One has to be aware that Langmuir type adsorption can be expected only at temperatures higher than the critical temperature of the film which in the case of van der Waals' forces is half the critical temperature of its substance in bulk.4 At lower temperatures the cohesive interaction between adatoms will contribute to