

### Appendix. *K* Values for the Methane–Carbon Dioxide System at Low Temperatures

The linear relationships between the system pressure and compositions can be expressed as

$$P = m^L x_{\text{CO}_2} + b^L \quad (1)$$

and

$$P = m^V y_{\text{CO}_2} + b^V \quad (2)$$

where  $P$  = system pressure,  $x_{\text{CO}_2}$  = mole fraction of  $\text{CO}_2$  in the liquid phase,  $y_{\text{CO}_2}$  = mole fraction of  $\text{CO}_2$  in the vapor phase,  $m^L, m^V$  = slopes of the  $P$ - $x_{\text{CO}_2}$  and  $P$ - $y_{\text{CO}_2}$  curves, respectively, and  $b^L, b^V$  = intercepts of eq 1 and 2 at  $x_{\text{CO}_2} = y_{\text{CO}_2} = 0$ .

When  $x_{\text{CO}_2} = y_{\text{CO}_2} = 0$ , the system pressure will be equal to the vapor pressure of pure methane ( $P^*_{\text{CH}_4}$ ) at system temperature. Thus

$$b^L = b^V = P^*_{\text{CH}_4}$$

Therefore, eq 1 and 2 become

$$P = m^L x_{\text{CO}_2} + P^*_{\text{CH}_4} \quad (3)$$

$$P = m^V y_{\text{CO}_2} + P^*_{\text{CH}_4} \quad (4)$$

then

$$\begin{aligned} K_{\text{CO}_2} &\equiv y_{\text{CO}_2}/x_{\text{CO}_2} \\ &= \frac{(P - P^*_{\text{CH}_4})/m^V}{(P - P^*_{\text{CH}_4})/m^L} \\ &= \frac{m^L}{m^V} \\ &= \frac{\text{slope of } P\text{-}x_{\text{CO}_2} \text{ curve}}{\text{slope of } P\text{-}y_{\text{CO}_2} \text{ curve}} \end{aligned}$$

= function of system temperature only

and

$$\begin{aligned} K_{\text{CH}_4} &\equiv y_{\text{CH}_4}/x_{\text{CH}_4} \\ &= (1 - y_{\text{CO}_2})/(1 - x_{\text{CO}_2}) \\ &= \frac{m^L(m^V - P + P^*_{\text{CH}_4})}{m^V(m^L - P + P^*_{\text{CH}_4})} \end{aligned}$$

= function of system temperature and pressure

A least-squares linear regression method was used to fit the experimental  $P$ - $x_{\text{CO}_2}$  and  $P$ - $y_{\text{CO}_2}$  data and obtain the slopes for each isotherm. Results are as follows:

$T, ^\circ\text{F}$	$10^{-3} m^L$	$10^{-4} m^V$	$K_{\text{CO}_2} = m^L/m^V$
-130.00	-0.625 71	-0.176 77	0.3540
-148.00	-0.407 69	-0.193 02	0.2112
-184.00	-0.185 57	-0.106 00	0.1751

The smoothed vapor–liquid equilibrium data can be calculated from the following equations at different system pressures:

$$x_{\text{CO}_2} = (P - P^*_{\text{CH}_4})/m^L \quad (5)$$

$$y_{\text{CO}_2} = (P - P^*_{\text{CH}_4})/m^V \quad (6)$$

and

$$K_{\text{CH}_4} = (1 - y_{\text{CO}_2})/(1 - x_{\text{CO}_2}) \quad (7)$$

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## On the Solubility of Benzoic Acid in Aqueous Carboxymethylcellulose Solutions

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**Solubility of benzoic acid in distilled and demineralized water and aqueous CMC solutions containing 0.5, 1.0, 1.5, and 2.0% polymer by weight has been determined in the temperature range of 15–45 °C. At any given temperature, the solubility in the polymer solution increases with polymer concentration and seems to approach a constant value at higher concentrations.**

#### Introduction

Dissolution rate studies of low-solubility organic compounds such as benzoic acid, 2-naphthol, etc., have been frequently used as a technique in mass transfer investigations with Newtonian fluids. Such solutes have many inherent advantages. They can be easily molded and pelletized into various shapes. Their solubilities are of moderate range and the analytical procedures are simple. Above all, the dissolution of these

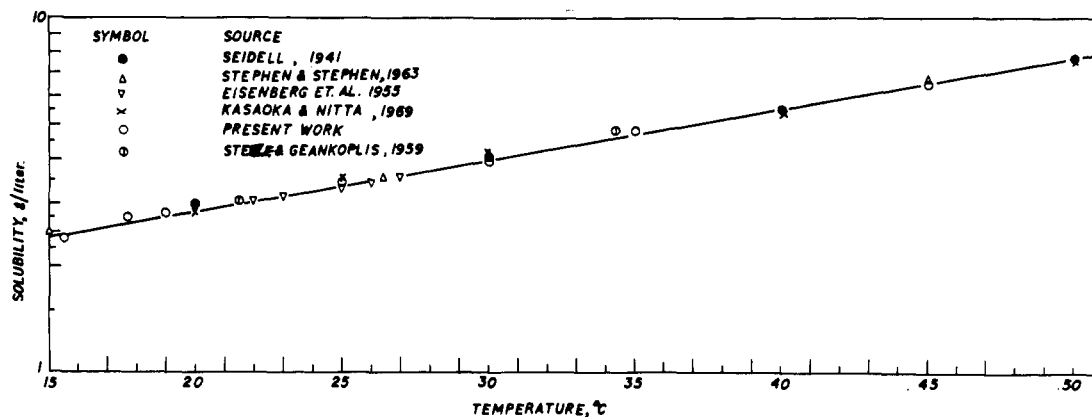


Figure 1. Solubility of benzoic acid in water.

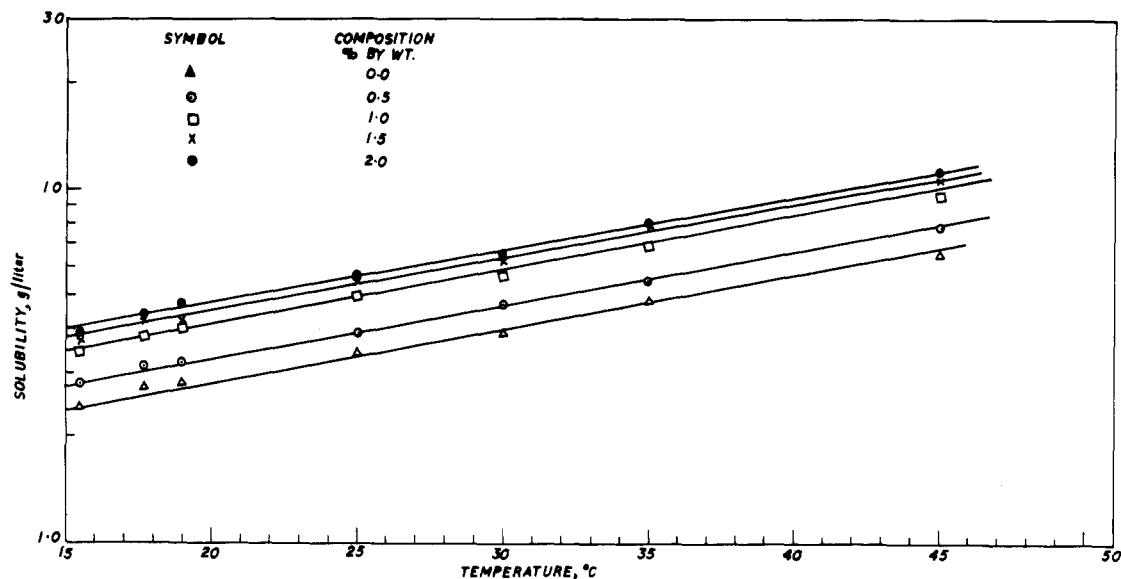


Figure 2. Measured solubility of benzoic acid in demineralized water and aqueous CMC solutions.

Their solubilities are of moderate range and the analytical procedures are simple. Above all, the dissolution of these compounds is a mass transfer controlled phenomenon with little interfacial resistance.

These solutes are also being used in mass transfer studies with non-Newtonian fluids which are currently being studied. The present communication, an adjunct to mass transfer studies undertaken by Kumar (4), reports the solubility of benzoic acid in carbon dioxide free distilled water, demineralized water, and a number of aqueous solutions of carboxymethylcellulose (CMC) containing 0.5, 1.0, 1.5, and 2.0 wt % CMC.

### Experimental Section

**Materials.** Conductivity grade distilled water was prepared in the laboratory. Demineralized water (conductivity less than  $1 \mu\Omega^{-1}$ ) was obtained from the laboratory water supply by treating the latter in an Industrial & Agricultural Engineering Co. (Bombay) Pvt. Ltd., Bombay, India, laboratory demineralizing plant. Aqueous carboxymethylcellulose solutions were prepared from "CELPRO" grade medium-viscosity carboxymethylcellulose supplied by Cellulose Products, Ltd., Ahmedabad, India. A known amount of CMC was initially mixed thoroughly with a small amount of demineralized water. The solution-cum-suspension thus formed was thoroughly mixed with the help of a stirrer and a recirculation pump, until all the CMC dissolved and the mass became completely homogeneous. An appropriate amount of demineralized water was then added to get the desired concentration of polymer and the recirculation and mixing were

Table I. Solubility Data of Benzoic Acid

Soln no.	Temp, °C	Solubility, g/L					
		Water		Aqueous CMC solution, wt %			
		Distilled	Demineralized	0.5	1.0	1.5	2.0
1	15.5		2.421	2.825	3.452	3.712	3.915
2	17.7		2.732	3.140	3.812	4.191	4.431
3	19.0	2.818	2.821	3.235	4.023	4.236	4.726
4	25.0	3.392	3.401	3.908	4.968	5.412	5.677
5	30.0	3.926	3.928	4.731	5.681	6.204	6.592
6	35.0		4.836	5.521	6.872	7.873	8.002
7	45.0		6.502	7.821	9.691	10.602	11.276

resumed for a few more hours. The solutions were allowed to stand for 24 h before use in the actual experiments. Benzoic acid (LR Grade) used was obtained from Sarabhai Merck (Baroda, India).

**Procedure.** Solubilities were determined by equilibrating the solute with the solvent in a 1000-mL flask shaken in a carefully controlled ( $\pm 0.05$  °C) thermostat. Twelve-fifteen-hour periods were allowed for equilibration at any given temperature. In special experiments, in which samples were withdrawn at various time intervals, it was found that no detectable concentration change occurred after 6–8 h. After equilibration, a 25-mL aliquot of solution was pipetted out through a glass wool filled small glass tube having a sintered glass plate cap at the tip and was titrated against standard 0.05 N NaOH solution using phenol red as indicator. All the solubility determinations were made in triplicate

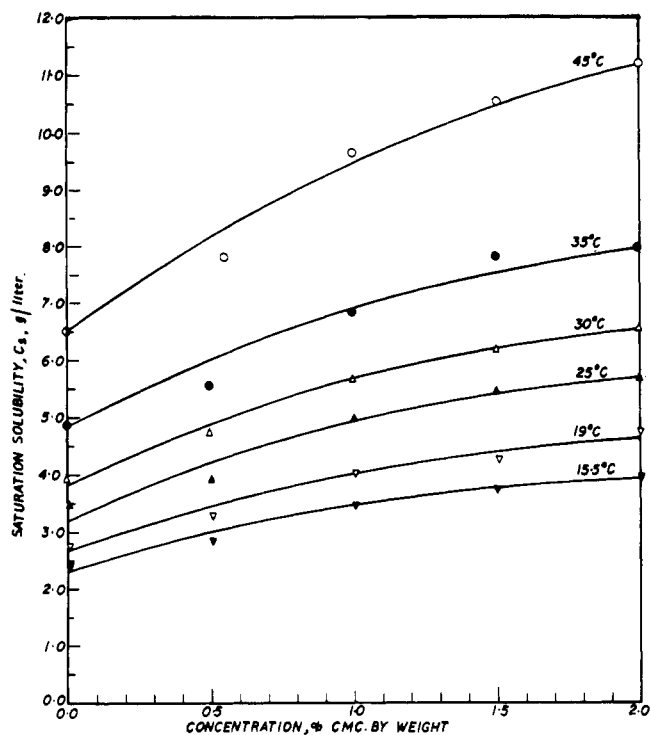


Figure 3. Solubility of benzoic acid in aqueous CMC solutions, effect of CMC concentration.

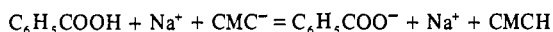
and reproducibility was within  $\pm 2\%$ .

### Results and Discussion

The solubility values for distilled and demineralized water and aqueous CMC solutions are listed in Table I. Present experimental values for distilled and demineralized water are compared with the literature data in Figure 1 which clearly show the close agreement between the present and published results.

No difference between the values for distilled and demineralized water is evident.

The solubility values of benzoic acid in aqueous CMC solutions and demineralized water are plotted against temperature on a semilogarithmic graph in Figure 2. At a particular temperature, the solubility in aqueous CMC solutions is observed to be always higher than that in water and increases with increasing polymer concentration. Figure 3 presents a plot of solubility against polymer concentration with temperature as the parameter. This figure shows that the solubility of benzoic acid in aqueous CMC solutions increases with increasing polymer concentration and it seems that solubility approaches a constant value at higher concentrations. Similar effect of concentration has been observed by Hansford and Litt (2). They believed that the increase in solubility is due to an acid-base type chemical reaction given by



occurring in the polymer solution. The approach of solubility toward a constant value at higher polymer concentration may be due to the following reason. As the polymer concentration increases, the degree of ionization of NaCMC approaches a constant value. This results in the availability of only a fixed number of ions for the above reaction and hence the constant solubility of the acid.

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## Densities, Refractive Indexes, and Normal Boiling Points of 1,2-Disubstituted Ethylene Glycol Derivatives

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Measurements were carried out on densities, refractive indexes at 298.15 K, and boiling points at 101.325 kPa for the purified ethylene glycol diethers, 2-alkoxyethyl acetates and ethylene glycol diacetate. Molar volumes and molar refractions were calculated from the experimental results. The data were smoothed by the equation of  $Y = a + bn + cn^2$ , where  $a$ ,  $b$ , and  $c$  are the empirical constants and  $n$  is the number of carbon atoms in the alkoxy group. The differences of the physical properties of isomeric diethers were also given.

An accurate knowledge of the physical properties of ethylene glycol derivatives is very important, since they are extensively used as industrial solvents. Most data reported as yet, however, are unsatisfactory, even as to their normal boiling points. Here we report an experimental result on some physical properties

determined as accurately as possible for 1,2-disubstituted ethylene glycol derivatives.

### Experimental Section

**Materials.** The 1,2-dialkoxyethanes, except symmetrical compounds, were synthesized at our laboratory by the Williamson method from the corresponding 1-alkoxyethanol and alkyl halide. The reaction products as well as the commercial compounds were repeatedly fractionated over a sodium wire until no impurity peaks were found on the GLC. During the fractionations, the distilling pressures were so regulated that the distillation temperature did not exceed 330 K.

The 2-alkoxyethyl acetates were synthesized by esterifying 2-alkoxyethanol with glacial acetic acid. After the water was removed, the reaction product was distilled off to correct the main fraction. Then it was dried over Drierite and fractionally