

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

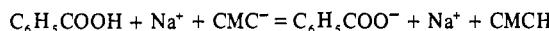
and reproducibility was within $\pm 2\%$.

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

Table I. Normal Boiling Point, Density, and Refractive Index of Ethylene Glycol Disubstituted Derivatives

| Compd | Bp at 101.325 kPa, ($T - 273.15$) K | | Density at 298.15 K, d/g cm ⁻³ | | Refractive index at 298.15 K, n_D^2 | | Molar volume, V/cm ³ mol ⁻¹ | Molar refraction, R/cm ³ mol ⁻¹ |
|---|--|--------------|--|-------------|--|-------------|--|---|
| | Obsd | Lit. | Obsd | Lit. | Obsd | Lit. | Exptl | Calcd |
| CH ₃ OCH ₂ CH ₂ OCH ₃ | 84.50 | 83-85 (7) | 0.86370 | 0.859 (3) | 1.3770 | 1.3771 (2) | 104.34 | 24.00 |
| C ₂ H ₅ OCH ₂ CH ₂ OCH ₃ | 103.5 | 101-102 (13) | 0.84600 | | 1.3843 | | 123.11 | 28.80 |
| C ₃ H ₇ OCH ₂ CH ₂ OCH ₃ | 124.7 | 124.5 (13) | 0.84195 | | 1.3920 | | 140.36 | 33.44 |
| C ₄ H ₉ OCH ₂ CH ₂ OCH ₃ | 147.3 | 146-147 (1) | 0.84085 | | 1.3997 | 1.3988 (16) | 157.22 | 38.09 |
| C ₂ H ₅ OCH ₂ CH ₂ OC ₂ H ₅ | 121.2 | 121.4 (19) | 0.83510 | | 1.3898 | 1.3886 (7) | 141.52 | 33.53 |
| C ₃ H ₇ OCH ₂ CH ₂ OC ₂ H ₅ | 141.8 | 134-136 (12) | 0.83273 | | 1.3960 | | 158.76 | 38.15 |
| C ₄ H ₉ OCH ₂ CH ₂ OC ₂ H ₅ | 163.9 dec | 161-162 (16) | 0.83306 | 0.8325 (16) | 1.4025 | 1.4017 (16) | 175.53 | 42.79 |
| C ₃ H ₇ OCH ₂ CH ₂ OC ₃ H ₇ | 163.2 dec | 162 (12) | 0.83124 | 0.8364 (11) | 1.4013 | 1.3978 (13) | 175.93 | 42.77 |
| C ₄ H ₉ OCH ₂ CH ₂ OC ₃ H ₇ | 185.0 dec | 184.7 (12) | 0.83146 | | 1.4068 | | 192.72 | 47.42 |
| C ₄ H ₉ OCH ₂ CH ₂ OC ₄ H ₉ | 205. ₆ -6. ₃ dec | 200-201 (7) | 0.83189 | 0.8337 (2) | 1.4112 | 1.4120 (12) | 209.49 | 52.50 |
| CH ₃ OCH ₂ CH ₂ OOCOCH ₃ | 143.2 | 141 (8) | 1.00033 | 1.001 (8) | 1.3999 | 1.4025 (8) | 118.08 | 28.62 |
| C ₂ H ₅ OCH ₂ CH ₂ OCOCH ₃ | 156.1 | 153 (8) | 0.96761 | 0.980 (8) | 1.4032 | 1.4030 (5) | 136.53 | 33.34 |
| C ₃ H ₇ OCH ₂ CH ₂ OCOCH ₃ | 173.6 dec | | 0.94767 | | 1.4071 | | 154.15 | 37.95 |
| C ₄ H ₉ OCH ₂ CH ₂ OCOCH ₃ | 193.0 dec | 192 (20) | 0.93517 | 0.933 (20) | 1.4117 | | 171.33 | 42.61 |
| CH ₃ COOCH ₂ CH ₂ OCOCH ₃ | 193.0 dec | | 1.09911 | 1.098 (14) | 1.4139 | | 132.96 | 33.22 |
| | | | | | | | | 33.10 |

distilled under reduced pressure and nitrogen.

The ethylene glycol diacetate was supplied from a commercial source of puris grade. It was further purified by repeated fractionations under the reduced pressure after it was dried over Molecular Sieve Type 4A.

The purity of the compounds was determined by GLC using a 4-m column containing Carbowax 20M, and no impurity peaks were found.

Determination of Normal Boiling Point. Normal boiling points were determined by an ebulliometer equipped with an enclosed scale type mercury thermometer calibrated against a standard platinum resistance thermometer. The measurement accuracies were examined by measuring the boiling points of the standard reference compounds, such as water, chlorobenzene, cyclohexanol, and ethylbenzene. To the thermometer readings stem corrections and corrections due to the deviations of the pressures from the standard atmosphere were always applied. Differences less than 0.1 K were found between the observed values and those reported for the boiling points for the reference compounds.

Refractive Index. The refractive indexes for the sodium D line were measured at 298.15 K by Boush & Lomb's Abbe type refractometer calibrated against redistilled water, the refractive index of which at the same temperature was taken to be 1.33250 (18).

Density Measurement. The densities were measured at 298.15 K by a Lipkin-Davison type pycnometer (inner volume was about 2 cm³) calibrated by degassed redistilled water whose density at that temperature was taken to be 0.99704 g cm⁻³ (15). The temperature of the thermostat was established by the platinum resistance thermometer with an accuracy of 0.01 K and was maintained constant within ± 0.002 K.

Before and after each density measurement, the water contents in the samples were always tested. A little increase in the water content in some of the samples was unavoidable, in spite of the special care taken. In such cases, the observed densities were corrected assuming that each sample makes an ideal solution with the dissolved water, but only small correction factors less than unity appeared in the last significant figures of the densities.

The duplicate measurements of the densities for each compound agreed within 0.00005 g cm⁻³.

Results and Discussion

Results from the experimental determinations both of the densities and of the refractive indexes at 298.15 K, as well as from the normal boiling points, are summarized in Table I.

Boiling Point. In the course of the boiling point determinations, it was observed that the compounds which boil at higher

temperatures than 430 K had a tendency somewhat to decompose. These are denoted by (dec) in Table I.

All boiling point readings were corrected to the values at 101.325 kPa. In order to make the correction, either dP/dT value at the boiling point of the compound (6) was employed or the modified Clausius-Clapeyron equation together with the enthalpy of vaporization value at that temperature (4, 9). When the enthalpy of vaporization value at the boiling point was not available, the value at 298 K (10) was taken with the assumption that no serious errors should be caused without the value at the boiling point being used.

It was difficult to correct the boiling point readings of the compounds which tended more or less to decompose, but, as long as the compounds do not contain any polymerized substances but decomposed fragments only, a lower boiling point can be expected than that of the pure compounds.

The uncertainties of the boiling points listed in Table I were, therefore, less than ± 0.1 K for the compounds with the boiling points below 430 K, about ± 0.3 K for 430-445 K, and up to ± 1.2 K for the substances which boiled at a higher temperature than 445 K.

Density. Most of the density data found in the literature poorly agreed with the present results. The densities of the homologous compounds shown in Table I decrease rapidly for a few initial members as the number of carbon atoms increases in the alkoxy group, and then the rate goes down slowly and finally reverses with the densities increasing, as can be usually seen in the homologous compounds that contain a polar group.

Refractive Index. It was difficult to find the literature values comparable with those of the present results, because most of the literature data were given at other temperatures other than 298 K. For only some compounds could the data be compared, but the agreements were rather poor.

Molar Volume and Molar Refraction. From the data given in Table I, molar volumes and molar refractions were calculated. They are also included in Table I.

The molar volumes of dialkoxyethanes and 2-alkoxyethyl acetates, at first sight, seem to increase linearly as the carbon numbers in the alkoxy group increase. As it is, the CH₂ increments of the molar volumes are large for a few initial members of dialkoxyethanes or alkoxyethyl acetates and then approach to the finite value of 16.4 cm³ mol⁻¹. This phenomenon is contrary to that of hydrocarbons in that the CH₂ increments in a few initial members are small and then progressively attain the above constant value. This fact shows that the intermolecular forces at the liquid state are rather remarkable in the initial members of the present homologues and that the effects of the oxygen atom diminish as the number of carbon atoms in the molecule increases.

Table II. Numerical Constants in Equation $Y = a + bn + cn^2$ for Physical Properties of Ethylene Glycol Disubstituted Derivatives

| Compd | | Bp, ($T - 273$)/K | Refractive index, n_D | Molar volume, V/cm^3 | Molar refraction, R_m/cm^3 |
|---|----------|------------------------|----------------------------|---------------------------|---------------------------------|
| $\text{ROCH}_2\text{CH}_2\text{OCH}_3$ | <i>a</i> | 66.950 | 1.36980 | 84.989 | 19.167 |
| | <i>b</i> | 16.610 | 0.00708 | 19.977 | 4.879 |
| | <i>c</i> | 0.870 | 0.00010 | -0.478 | -0.038 |
| $\text{ROCH}_2\text{CH}_2\text{OC}_2\text{H}_5$ | <i>a</i> | 87.950 | 1.37920 | 104.055 | 24.057 |
| | <i>b</i> | 14.220 | 0.00483 | 19.500 | 4.722 |
| | <i>c</i> | 1.200 | 0.00025 | -0.410 | -0.023 |
| $\text{ROCH}_2\text{CH}_2\text{OC}_3\text{H}_7$ | <i>a</i> | 108.975 | 1.38848 | 121.530 | 28.730 |
| | <i>b</i> | 14.355 | 0.00310 | 19.275 | 4.731 |
| | <i>c</i> | 1.175 | 0.00038 | -0.390 | -0.015 |
| $\text{ROCH}_2\text{CH}_2\text{OC}_4\text{H}_9$ | <i>a</i> | 131.675 | 1.39735 | 137.933 | 33.376 |
| | <i>b</i> | 14.315 | 0.00188 | 19.681 | 4.739 |
| | <i>c</i> | 1.075 | 0.00040 | -0.452 | -0.179 |
| $(\text{ROCH}_2)_2$ | <i>a</i> | 49.950 | 1.36268 | 65.830 | 14.555 |
| | <i>b</i> | 32.660 | 0.01504 | 39.511 | 9.533 |
| | <i>c</i> | 1.600 | -0.00073 | -0.905 | -0.040 |
| $\text{ROCH}_2\text{CH}_2\text{OCOCH}_3$ | <i>a</i> | 132.950 | 1.39728 | 99.078 | 23.910 |
| | <i>b</i> | 8.470 | 0.00231 | 19.367 | 4.733 |
| | <i>c</i> | 1.650 | 0.00033 | -0.328 | -0.015 |

Table III. Difference of Physical Constants between Isomeric Compounds

| Pair of isomers | Bp, $\Delta T/K$ | Density, $\Delta d/g \text{ cm}^{-3}$ | Molar volume, $\Delta V/\text{cm}^3 \text{ mol}^{-1}$ | Refractive index, Δn_D | Molar refraction, $\Delta R_m/\text{cm}^3 \text{ mol}^{-1}$ |
|--|------------------|---------------------------------------|--|-----------------------------------|--|
| $n\text{-C}_3\text{H}_7\text{OCH}_2\text{CH}_2\text{OCH}_3$ $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OC}_2\text{H}_5$ | +3.9 | +0.00685 | -1.17 | +0.0024 | -0.09 |
| $n\text{-C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{OCH}_3$ $n\text{-C}_3\text{H}_7\text{OCH}_2\text{CH}_2\text{OC}_2\text{H}_5$ | +5.5 | +0.00812 | -1.54 | +0.0037 | -0.06 |
| $n\text{-C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{OC}_2\text{H}_5$ $n\text{-C}_3\text{H}_7\text{OCH}_2\text{CH}_2\text{OC}_3\text{H}_7$ | +0.7 | +0.00282 | -0.40 | +0.0012 | +0.02 |

Molar refractions evaluated from the present experimental results and those calculated from both atomic and structural contributions given by Vogel (17) are respectively listed in the last two columns in Table I. The agreements were good but slightly higher values (ca. 0.2%) were observed for dialkoxyethanes, and excellent agreements were obtained for 2-alkoxyethyl acetates and ethylene glycol diacetate.

Smoothed Values. The observed data given in Table I led to calculation of the smoothed values for the series of dialkoxyethanes and alkoxyethyl acetates by means of the following type of equation:

$$Y = a + bn + cn^2$$

where *a*, *b*, and *c* are the empirical constants and *n* is the number of carbon atoms in the alkoxy group.

Throughout the series of dialkoxyethanes, $\text{ROCH}_2\text{CH}_2\text{OR}'$, it can be seen that the CH_2 increments are not strictly monotonous, but it can be seen that the CH_2 increments become monotonous when a series of compounds is considered of which the alkoxy group, R, in one terminal group in the molecule is maintained constant while the number of carbon atoms in the other terminal alkoxy group, R', is successively increased.

The numerical values of the constants in the equation are summarized in Table II, but those for the density were not calculated because the curves of the density vs. the number of carbon atoms were so concaved that it was not possible to make a good fitting by means of such a simple equation. Table II also includes the constants for a series of compounds in which only symmetrical dialkoxyethanes are taken as the elements of the homologue.

Physical Constants of Isomeric Dialkoxyethanes. In the present investigation, three sets of isomeric dialkoxyethanes were included. The differences in the physical constants between the isomers are compiled in Table III. The tabulated values in all cases refer to the values of more symmetrical compounds minus those of less symmetrical ones.

As can be seen in Table III, the difference between 1-methoxy-2-butoxyethane and 1-ethoxy-2-propoxyethane is largest and the one between 1-ethoxy-2-butoxyethane and 1,2-diproxyethane is smallest except the molar refraction.

These facts show that there is some difference of the intermolecular forces between the isomeric compounds in the liquid state and that the intermolecular forces of the less symmetrical compounds are always larger than those of more symmetrical ones. But unfortunately no satisfactory theory can be found at present to explain these experimental facts.

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