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Link to publication

Download date: 08. Feb. 2024

NOTES

Comparison of Hydrophile–Lipophile Balance of Glycerol, DMGP, and DOP with the Activity Coefficient of Water at Infinite Dilution in the Compound

INTRODUCTION

Characterization of the "polarity" of an organic medium by an exactly measurable quantity is interesting in such fields as the stability of dispersions in organic media, emulsion stability, etc. Very often, a rather crude "rule of thumb" is employed: the hydrophilic/lipophilic balance (HLB) value (1). Szymanowski and Beger (2) define the polarity index of a compound on the basis of gas chromatographic data (retention volumes), as

$$PI = 100 \log(C - 4.7) + 60, \qquad [1]$$

where PI is the polarity index and C is the apparent number of carbon atoms in a standard alkane having the same retention as the compound concerned. Establishing a value for C requires retention data not only of the component under study, but also of n-alkanes.

Although a high correlation between PI and HLB is found we propose that it is much more straightforward to compare the HLB to a thermodynamic quantity, viz., the activity coefficient of water at infinite dilution in the compound, γ° H$_2$O. This activity coefficient can be derived from gas chromatography (3). The choice to use the activity coefficient at infinite, rather than at some intermediate, dilution is based upon the fact that water has very low solubility in many of the components under study.

Alternatively, the HLB of a substance may be related to the distribution constant of the substance between water and a nonpolar solvent, e.g., decane. In this respect the HLB would be determined by the activity coefficient of the substance at infinite dilution in water, as well as by its activity coefficient at infinite dilution in the apolar medium. It is, however, interesting to investigate if a simple correlation with γ° H$_2$O may suffice.

Below we will compare the HLB to γ° H$_2$O at 298 K and other temperatures in glycerol, di(methoxy-glycol)-phthalate (DMGP), and di(2-ethyl-hexyl)-phthalate (DOP). These compounds have been used as media with varying degrees of hydrophility in studies of coagulation (4).

METHODS

Stainless steel columns (2 mm inner diameter, 2 m long) were filled with packings containing various loadings of

glycerol, DMGP, and DOP. It is necessary to vary the liquid loading to be able to rule out concurrent contributions to retention (5). Concurrent retention mechanisms are ruled out by extrapolating retention data to infinite liquid loading, whereupon the activity coefficients of the injected solute follow from (6)

$$\ln \gamma = \ln \frac{RT}{p_i^\circ v_L K_L} - \frac{B_{11} p^\circ}{RT}, \qquad [2]$$

where K_L is the partition coefficient of the solute in the stationary phase, defined as the ratio of molarities of the solute in the gas and the liquid phase, at equilibrium. K_L is equal to the ratio V_N/V_L extrapolated to infinite loading; V_N is the net retention volume; V_L is the stationary phase loading of the column; v_L is the molar volume of the stationary phase; p_i° is the saturated vapor pressure of the solute at column temperature; B_{11} is the second virial coefficient of the solute vapor.
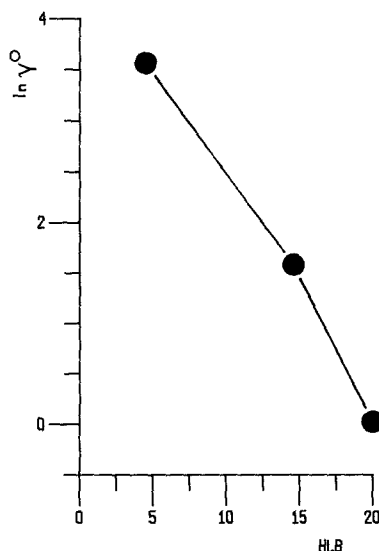

FIG. 1. Plot of the activity coefficient of water at infinite dilution in glycerol, DMGP, and DOP extrapolated to 298 K versus the HLB value of the media.

TABLE I

Partition Coefficients and Activity Coefficients of Water at Infinite Dilution in Glycerol, DMGP, and DOP

Liquid phase	T (°C)	$p°$ (atm)	K_L	B (cm³/mole)	ln $\gamma°$ H₂O
DOP	60	0.199	18.7	−0.690	2.935
DOP	70	0.312	14.5	−0.614	2.776
DOP	80	0.473	12.4	−0.551	2.547
DOP	90	0.701	8.9	−0.496	2.513
DMGP	60	0.199	155.9	−0.690	1.314
DMGP	70	0.312	109.3	−0.614	1.250
DMGP	80	0.473	80.5	−0.551	1.171
DMGP	90	0.701	58.3	−0.496	1.131
GLY	60	0.199	2126.4	−0.690	−0.106
GLY	70	0.312	1400.6	−0.614	−0.107
GLY	80	0.473	1009.7	−0.551	−0.165

Note. For the meaning of the symbols refer to Eq. [2] in the text.

Note that ln γ is based here upon the so-called symmetrical convention, where $\mu = \mu° + RT \ln \gamma$, with μ the chemical potential of the compound, x the mole fraction, and $\mu°$ the chemical potential of the pure compound.

We found that it is not necessary to include a correction term for carrier gas nonideality in Eq. [2].

MATERIALS

Glycerol was obtained from Merck, Darmstadt (grade Wasserfrei, Reinst 98–100.5%), and DMGP and DOP from Fluka, Ag, Buchs, >98 and >99%, respectively. All compounds were used without further purification.

RESULTS AND DISCUSSION

Table I lists the values of the activity coefficients obtained from the GLC measurements. Using the following well-known relationship (7) activity coefficients at 298 K were calculated,

$$\ln \gamma_{i°,T} = \ln \gamma_{i°,T=T_{ref}} + \frac{H_i^E}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right), \quad [3]$$

where $\gamma_{i,T}°$ is the activity coefficient of component i at infinite dilution, temperature T; $H_i^{E,0}$ is the excess partial molar enthalpy of component i at infinite dilution (assumed here to be independent of temperature); T_{ref} is a reference temperature.

Table II lists the activity coefficient of water at infinite dilution at 298 K as well as the HLB values of the media under study (taken from Ref. (4)). Figure 1 is a plot of the activity coefficient versus the HLB value. It is seen that there is a high degree of correlation between the quantities, where ln $\gamma°$ decreases as the HLB increases. This is readily understood by realizing that an increase in HLB indicates a more hydrophilic medium, more compatible with water, and thus yielding an activity coefficient closer to unity. In order to establish the possible existence of a linear relationship between ln $\gamma°$ H₂O and HLB we feel that more data are needed.

CONCLUSIONS

The activity coefficient of water at infinite dilution in a medium may very well serve as a less arbitrary measure of the polarity of the medium than is the HLB, because the activity coefficient is based directly upon measurement. Also, it is more straightforward to use the activity coefficient and less data are required than, e.g., for the polarity index. Preliminary investigations indicate a high degree of correlation between the activity coefficient of water at infinite dilution and the HLB, but more data are needed to establish whether a linear relationship exists.

TABLE II

Activity Coefficients of Water at Infinite Dilution at 298 K and HLB Values

Medium	HLB	ln γ_{298} water
Glycerol	20	0.02
DMGP	14.6	1.58
DOP	4.5	3.56

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