Partial Molar Excess Properties of Water and the Lower Alkanols in Organic Solvents at High Dilution

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G_i^E, H_i^E, and TS_i^E values (with i = water, methanol, ethanol, or propanol) at infinite dilution in three organic solvents together encompassing a wide range of hydrophility are reported: glycerol, phthalic acid bis(methylglycolyl ester), and phthalic acid bis(2-ethylhexyl ester). Values were measured by means of gas–liquid chromatography, correcting for the influence of slow mass transfer in the column and for the occurrence of concurrent retention mechanisms. It is shown that there is good correlation between H_i^E and TS_i^E for methanol, ethanol, and 1-propanol in at least two of the organic media investigated but that water does not respond to the correlation. This is explained by the much more pronounced influence of network formation in pure water on thermodynamic properties than in the alkanols. As a result, the use of alkanols as experimental probe to determine hydrophility, a property that typically pertains to interactions with water, is questionable.

1. Introduction

Excess properties have been measured for water, methanol, ethanol, and 1-propanol in organic solvents of strongly different hydrophility. As organic solvents we employed glycerol, phthalic acid bis(2-ethylhexyl ester) (=dioctyl phthalate, abbreviated to DOP), and phthalic acid bis(methylglycolyl ester) (=di(methoxyglycol) phthalate, abbreviated to DMGP). We restricted our measurements to the properties at high dilution ($x_i \rightarrow 0$), since one of our goals was to establish if such properties are sufficient to characterize the hydrophility of the media concerned.

G_i^E was measured by gas chromatography (1) at different temperatures. From the temperature dependence of G_i^E/RT, H_i^E and TS_i^E could be calculated. These data in turn enabled us to calculate G_i^E at 298.15 K.

2. Experimental Section

2.1. Materials. Water was twice distilled. Methanol and ethanol were from Merck and >99.8% pure. Propanol was from Merck, >99.5%. Glycerol was from Merck, "wasserfrei reinst" 98–100%. DMGP and DOP, from Fluka, had >98% purity. Diatomaceous earth was 100–120 mesh.

2.2. Apparatus. A Packard Model 417 gas chromatograph with two parallel columns was used in the measurements. The detector was a katharometer; more sensitive detectors do not detect water. The output of the chromatograph was registered on a recorder, and parallel to that was digitized with an Apple Europlus microcomputer. The signal was amplified prior to digitization using an in-house built amplifier and was filtered by the software. Digitization was performed in order to be able to employ the first statistical moment of the chromatographic peaks rather than the peak maximum to determine retention time. This serves to rule out the influence of slow mass transfer in the column.

3. Procedure

3.1. Packing of the Columns. Various quantities of diatomaceous earth and of the organic solvents concerned were weighed and dissolved in 50 mL of acetone. The acetone was then slowly evaporated in a film evaporator. After the acetone had been removed nearly completely, the packing was transferred to a vacuum stove operating at pressures of 2000–2300 Pa, at 313 K, to remove the rest of the acetone. In this way, packings with a liquid to solid ratio up to 39% (m/m) could be prepared.

The packing was then introduced into a column with an internal diameter of 2 mm, using both vibration and vacuum suction. The column had been rinsed beforehand with acetone to remove any lubricants introduced in the manufacturing process. The amount of packing in the column was determined by weighing.

The stationary liquid phase volumn was varied in order to check influences of retention at SG and SL interfaces (so-called concurrent retention mechanisms (2)). Helium was used as carrier gas, at inlet pressures varying from 150 to 270 kPa.

3.2. Operation. The amount of water or alkanol injected was limited to less than 0.1 μL to prevent nonlinearity of the partition isotherm. The injector was held at a temperature of 453 K, in order to obtain rapid vaporization of the sample. The detector was held at 433 K, in order to avoid condensation.

The retention volume of the samples (V_N) was measured in the usual way (1), using the first statistical moment of the peaks. The retention volumes thus calculated were extrapolated to infinite loading in order to nullify the contribution of concurrent retention mechanisms (2).

In order to establish the extent to which variations in mean column pressure influence the retention volumes, experiments were performed with a column containing DOP, using water, methanol, and ethanol as sample, by varying column inlet pressure between 189 and 279 kPa. No systematic pressure influence was detected. Variations in activity coefficients were 0.5% (water), 0.7% (methanol), and 2.3% (ethanol), which is of the same order of magnitude as measurement reproducibility.

Absence of column bleeding (i.e., evaporation of a significant part of the stationary liquid during prolonged operation) was shown by good reproducibility of retention volumes, after long operation times.

4. Results

From the net retention volume of the sample (V_N) and the volume of stationary liquid in the column (V_L), the distribution coefficient K_L was calculated by (3)

$$K_L = \frac{V_N}{V_L} + (K_I A_I + K_S A_S)\frac{1}{V_L} \qquad (1)$$

where K_L is the partition coefficient, defined as molarity of solute in vapor phase divided by molarity in liquid phase; K_I is the interfacial adsorption coefficient; A_I is the area of LG interface; K_S is the solid adsorption coefficient; and A_S is the exposed area of solid support material. From relation 1, K_L can be obtained by plotting V_N/V_L versus $1/V_L$ and extrapolating to $1/V_L = 0$. The error that results from extrapolation was kept low (<3%) by using high liquid loadings, up to 39% w/w, resulting in low $1/V_L$ values. Errors in V_N and V_L contributed less than 1% to the uncertainty in K_L. From K_L, the activity coefficient can be calculated by (4)

$$\ln \gamma_i = \ln \frac{RT}{p^\circ_i v_L K_L} - \frac{B_{ii} p^\circ_i}{RT} + \frac{p}{RT}(2B_{ij} - B_{jj}) \qquad (2)$$

Table I. Partition Coefficients, Saturated Vapor Pressures, Second Virial Coefficients, and Activity Coefficients at Different Temperatures for Systems with DOP Stationary Phase

sample	T, °C	$p°$, bar	K_L	B, cm^3/mol	ln γ
water	60	0.199	18.7	−0.690	2.94
	70	0.312	14.5	−0.614	2.78
	80	0.473	12.4	−0.551	2.55
	90	0.701	8.9	−0.496	2.51
methanol	60	0.833	31.8	−1.260	1.01
	70	1.222	24.3	−1.104	0.93
	80	1.788	18.8	−0.973	0.85
	90	2.529	14.2	−0.864	0.83
ethanol	60	0.484	58.7	−1.661	0.93
	70	0.731	43.4	−1.607	0.86
	80	1.079	34.6	−1.577	0.74
	90	1.560	25.6	−1.560	0.72
propanol	60	0.196	169.4	−0.774	0.75
	70	0.319	118.3	−0.723	0.65
	80	0.501	85.5	−0.677	0.56

Table II. Partition Coefficients, Saturated Vapor Pressures, Second Virial Coefficients, and Activity Coefficients at Different Temperatures for Systems with DMGP Stationary Phase

sample	T, °C	$p°$, bar	K_L	B, cm^3/mol	ln γ
water	60	0.199	155.9	−0.690	1.31
	70	0.312	109.3	−0.614	1.25
	80	0.473	80.5	−0.551	1.17
	90	0.701	58.3	−0.496	1.13
methanol	60	0.833	81.8	−1.260	0.56
	70	1.222	61.5	−1.104	0.50
	80	1.788	46.6	−0.973	0.44
	90	2.529	35.1	−0.864	0.42
ethanol	60	0.484	136.0	−1.661	0.59
	70	0.731	94.2	−1.607	0.58
	80	1.079	71.7	−1.577	0.51
	90	1.560	55.5	−1.560	0.45
propanol	60	0.196	300.1	−0.774	0.68
	70	0.319	205.6	−0.723	0.60
	80	0.501	148.4	−0.677	0.50
	90	0.765	106.3	−0.635	0.45

Table III. Partition Coefficients, Saturated Vapor Pressures, Second Virial Coefficients, and Activity Coefficients at Different Temperatures for Systems with Glycerol Stationary Phase

sample	T, °C	$p°$, bar	K_L	B, cm^3/mol	ln γ
water	60	0.199	2126.4	−0.690	−0.11
	70	0.312	1400.6	−0.614	−0.11
	80	0.473	1009.7	−0.551	−0.17
methanol	60	0.833	222.4	−1.260	0.75
	70	1.222	158.5	−1.104	0.75
	80	1.788	113.3	−0.973	0.74
ethanol	60	0.484	193.2	−1.661	1.43
	70	0.731	136.8	−1.607	1.40
	80	1.079	96.4	−1.577	1.41
propanol	60	0.196	229.1	−0.774	2.14
	70	0.319	151.0	−0.723	2.10
	80	0.501	103.1	−0.677	2.06

Table IV. Excess Functions of Water, Methanol, Ethanol, and 1-Propanol in Glycerol, DMGP, and DOP

dissolved substance	medium	G_i^E(298.15 K), kJ·mol^{-1}	H_i^E, kJ·mol^{-1}	S_i^E(298.15 K), J·mol^{-1}·K^{-1}
water	glycerol	0.1[a]	2.9	9.26
	DMGP	3.9	6.3	8.08
	DOP	8.8	15.1	2.10
methanol	glycerol	1.9	0.48	−4.80
	DMGP	1.9	5.0	1.04
	DOP	3.1	6.3	1.07
ethanol	glycerol	3.6[a]	1.0	−8.82
	DMGP	2.0	4.8	9.26
	DOP	3.1	7.3	1.43
propanol	glycerol	5.7	3.7	−6.64
	DMGP	3.1	7.8	1.79
	DOP	2.8	9.4	2.19

[a] Values have reduced accuracy.

In carrying out the integration, the temperature dependence of H_i^E was neglected. This is in agreement with the experimental data which showed no distinct deviations from a linear dependence of ln γ_i versus $1/T$.

The results are listed in Table IV. The experimental error in $G_i^E \simeq 200$ J/mol, corresponding to an error of 0.05 in ln γ, except where otherwise indicated. In those cases the extrapolation of G_i^E to 298.15 K was inaccurate due to scattering of $G_i^E(T)$.

5. Discussion

Earlier data about the thermodynamic properties studied here are those reported by Martire (11) on the activity coefficients of methanol, ethanol, and propanol in glycerol. The trend of these data is similar to that of our data; nevertheless there are marked differences in absolute value between Martire's data and those found by us. These discrepancies are partly explained by the fact that the values calculated for ln γ_i are very sensitive to inaccuracies in the saturated vapor pressures of the pure dissolved substances; Martire used an inaccurate interpolation algorithm to calculate these quantities at the temperature of his measurements (62.4 °C).

A widely adopted means of analyzing excess functions of a compound is to plot its H^E versus TS^E. A pronounced complex formation of the sample with solvent molecules leads to negative H_i^E and TS_i^E values, while disruption of a network that is present in either the pure substance or solvent, where the network is not or only partially reformed in the mixture, leads to positive H_i^E and TS_i^E values.

Figure 1a and Figure 1b show the H_i^E versus TS_i^E plots for excess properties of water and low alkanols in DOP and DMGP, respectively. It is seen that, particularly in the case of DOP, there is good correlation between H_i^E and TS_i^E values for the alkanols but that water deviates from the linear relationship in that TS_i^E is lower than expected on the basis of the H_i^E value.
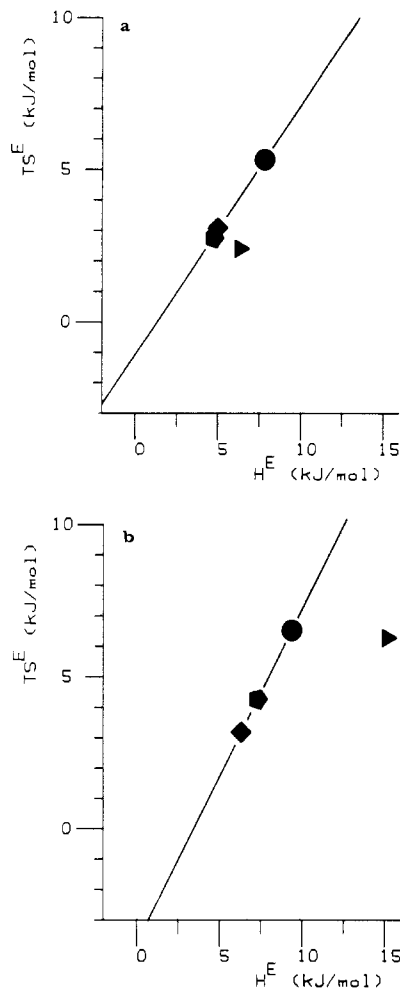
In this relation, $p°_i$ is the saturated vapor pressure of the dissolved substance i at the temperature T; v_L is the molar volume of the stationary liquid; B_{ii} and B_{jj} are the second virial coefficients of the pure dissolved substance and carrier gas, respectively; B_{ij} is the interaction coefficient between sample i and carrier gas; p is the mean column pressure; and R and T have their usual meaning.

Since our results showed no significant dependence of the gas pressure p, we neglected the third term in relation 2. For $p°_i$ we employed values from the literature (5–8). The second virial coefficients were calculated from equations mentioned in the references (9–11). Tables I–III list the values of K_L obtained by extrapolating experimental values to infinite liquid loading, as well as values of $p°_i$ and B_{ii} taken from the literature. Finally, the ln γ values calculated from these data are listed.

From the ln γ_i values thus found, we calculated H_i^E by

$$H_i^E(T) = -T^2 \left(\frac{\partial G_i^E / T}{\partial T} \right)_p \quad (3)$$

where $G_i^E = RT$ ln γ_i and

$$S_i^E(T) = (H_i^E - G_i^E)/T \quad (4)$$

From these data, G_i at 298.15 K was calculated by

$$G_i^E (298.15) = 298.15 \left(\frac{G_i^E(T')}{T'} - \int_{T'}^{298.15} \frac{H_i^E}{T^2} \, dT \right) \quad (5)$$

Figure 1. (a, b) Plot of H^E versus TS^E for water, methanol, ethanol, and 1-propanol at 298.15 K at infinite dilution in DMGP and DOP, respectively. Excess functions of the alkanols show good correlation, but the excess properties of water deviate from the correlation. (▲) water; (◆) methanol; (⬢) ethanol; (●) 1-propanol.

A possible explanation of this fact is the presence of a more pronounced network in water than is present in the alkanols. If this is the case, keeping in mind that hydrophility is a property that typically pertains to water, the use of alkanols as an experimental probe to determine hydrophility (as described in ref 4) is questionable, a point that has also been made on the grounds of comparing G_i^E of water and the alkanols with hydrophility (13).

Glossary

A	area, m^2
B	second virial coefficient, cm^3/mol
G	Gibbs free energy, kJ/mol
H	enthalpy, kJ/mol
K	partition coefficient, no unit or m^{-2}
p	pressure, Pa
R	gas constant, J/(mol·K)
S	entropy, kJ/(mol·K)
T	absolute temperature, K
v	molar volume, m^3/mol
V	retention volume, m^3
γ	activity coefficient, defined so that it equals unity in the pure substance

Subscripts

i	denotes the sample (water, alkanol)
I	interface between gas and liquid phases in chromatographic column
j	carrier gas
L	liquid phase in column
N	net retention
S	surface of solid support in column

Superscripts

o	pure substance
E	excess property

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