Gas Chromatographic Determination of Partition Coefficients of Some Unsaturated Hydrocarbons and Their Deuterated Isomers in Aqueous Silver Nitrate Solutions

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Experiments using aqueous solutions of silver nitrate as a gas chromatographic liquid phase have been carried out. Stability constants for the reaction, $(Ag^+)_{aq} + (\text{Hydrocarbon})_{aq} \rightleftarrows (Ag^+\cdot\text{Hydrocarbon})_{aq}$, where $(\text{Hydrocarbon})_{aq}$ are various light olefins, aromatics, or some of their deuterated isomers have been determined. For the olefins these values are in quantitative agreement with those obtained from conventional static techniques. In the case of ethylene $\Delta H = -23$ kJ/mol and $\Delta S = -38$ J/mol deg. The isotope effect for the solubility of benzene-d_6 (compared to the lightest isomer) in water is 1.05. Aqueous silver nitrate columns should also have interesting analytical applications, particularly in the field of isotopic separations. They appear to be more efficient than the conventional ethylene glycol–silver nitrate columns.

Introduction

This investigation is concerned with the gas chromatographic properties of aqueous silver nitrate solutions. The greater degree of ionization of silver nitrate in water makes such columns more efficient than the more standard solvent phase of silver nitrate in ethylene glycol. Thus the many unique separations[1-4] effected with the latter solvent can be carried out under less severe (near room temperature, 6–12-ft columns) conditions. Furthermore, the gas chromatographic results can now be directly compared with those from static experiments. This provides a test of the reliability of this method as a means of studying reactions in aqueous solutions. Finally, with respect to the silver complexing reaction, thermal and isotope effects can be measured. For such determinations the gas chromatographic method has unique advantages due to the ease of carrying out such experiments at varying temperatures and the handling of small and/or impure samples. It is noteworthy that enthalpies and entropies as well as the extent of the deuterium isotope effect for such processes have not been determined using standard procedures.

Silver nitrate in inert organic solvents has long been used as a substrate in gas chromatography.[1] Due to the formation of silver–olefin complexes such columns are of special interest in olefin analysis. Muhs and Weiss[2] and Cvetanovic and coworkers[3a,b] have made exhaustive chromatographic investigations of the silver nitrate–ethylene glycol system. The former authors derived stability constants for a large number of compounds, while the latter determined the enthalpies and entropies of the complex-forming reaction for several of the smaller olefins. They also found an isotope effect for the corresponding deuterated compounds and were able to make satisfactory separations of the various isotopic isomers from each other.

There is a large volume of stability constant data for silver–olefin complexes in aqueous solution as determined by classical methods.[5] Direct comparison with the earlier gas chromatographic experiments, however, cannot be made since silver nitrate in a medium such as ethylene glycol behaves as a weak salt and is not completely ionized.

Volatile substrates are, in general, unsuitable for gas chromatography since they may affect the sensitivity of the detector and make uncertain the amount of liquid loading. The former is not a problem in this study since a hydrogen flame detector was used and it is completely insensitive to the presence of water. The latter can be minimized by presaturating the helium carrier gas. The ideal situation is of course to have exactly the same amount of water coming in as leaving. This is not easily achieved with the usual techniques. Nevertheless, even with a variation of 5% in inlet and outlet water vapor concentration, at room temperature and usual flow rates (23° and 50 cm^3/min) the total change of liquid loading will be less than 0.004 g/hr. Thus with a liquid loading of 5–15 g one can anticipate at steady state at least several weeks of steady opera-

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(1) B. W. Bradford, D. Harvey, and D. E. Chalkley, *J. Inst. Petrol., London*, **41**, 80 (1955).

(2) M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, **84**, 4697 (1962).

(3) (a) R. J. Cvetanovic, F. J. Duncan, and W. E. Falconer, *Can. J. Chem.*, **41**, 2095 (1963); (b) R. J. Cvetanovic, F. J. Duncan, W. E. Falconer, and R. S. Irwin, *J. Amer. Chem. Soc.*, **87**, 1827 (1965).

(4) J. G. Atkinson, A. A. Russell, and R. S. Stuart, *Can. J. Chem.*, **45**, 1963 (1967).

(5) L. G. Sillen and A. E. Martell, "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964.

tion. The situation will be more favorable at lower temperatures and less favorable at higher temperatures. Finally, and most important to the present study, the actual substance that is responsible for the retention of the hydrocarbons used in this work is the silver ion. It is involatile and the water may almost be regarded as an inert matrix. As a result, the concentration of water on the packing will have slight effect on the measured retention times. Thus, the limits set above can be relaxed considerably for this type of experiment.

There have been several previous gas chromatographic studies in which water was used as the stationary phase.[6-8] Due to its extraordinary solvent properties, rather unusual separations were obtained. In all these cases the volatility of the water did not appear to be an insurmountable problem. There have not been any studies in which aqueous solutions of a strong electrolyte were used as the stationary phase.

Experimental Section

A sketch of the experimental setup is given in Figure 1. Water is introduced into the carrier gas stream by bubbling helium through an aqueous $AgNO_3$ solution of the same concentration as that in the column. The side arm in the saturator permits the replenishment of the evaporated water. In principle, the presence of the salt in the saturation should stabilize the concentration of water present on the packing. If pure water is used, the failure to saturate or to supersaturate the helium stream will ultimately result in a column that is either empty or filled with water. With the presence of the salt, if the departure from equilibrium is small there will be instead an adjustment of the water concentration to a level that is consistent with its partial pressure in the carrier gas stream. In other words, the salt acts as a buffer maintaining constant water content. As noted earlier, these factors are not of prime importance for experiments at or below room temperature (range of present experiments), but they must be considered as the vapor pressure of the solvent increases. Furthermore, since at steady state there will be a gradient in salt concentration along the column (due to the pressure drop), thermal measurements may be more difficult.

The packings were made by mixing the desired amounts of silver nitrate and Chromosorb P(AW) (15–30 g) with an excess of water. The mixture was heated to about 70° while constantly shaken until only the desired amount of water (by weight) was left. It was then poured into $^1/_4$-in. o.d. stainless steel columns. They ranged in length from 5 to 12 ft and contained from 5 to 12 g of water. The silver nitrate concentrations were approximately 0, 0.21, 0.4, 0.98, 1.8, and 3.5 M. It is estimated that these concentrations are accurate to ±2–5%. The columns with high silver nitrate concentration were somewhat unstable. The 3.5 M column has a half-life of about a month. All thermodynamic measurements were made within 1 or 2 days after packing and were therefore not affected by this problem. Ethylene, propylene, the four C_4 olefins, benzene, toluene, and xylenes were used as the solutes. They were injected onto the column with 10- or 100-μl syringes. The effluent was monitored by a GC-5 Beckman hydrogen flame detector. Helium was used as the carrier gas. Retention times, from many runs, over the period of several days were accurate to ±0.5%.

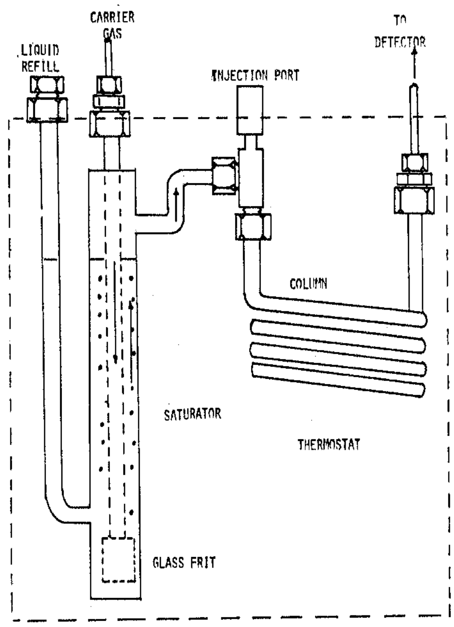

Figure 1. Experimental apparatus.

Results and Discussion

I. Chromatographic Separations. A typical chromatogram for the separation of the olefins is given in Figure 2. The novel feature is the elution of *trans*-butene-2, isobutene, and propylene before ethylene. Column efficiencies for a given quantity of silver nitrate decrease with increasing water loading and temperature. For the 3.5 M $AgNO_3$ columns at 0°, the efficiencies are about 100–200 theoretical plates per foot. Figures 3, 4, and 5 illustrate the isotopic separations that may be effected with a 12-ft 3.5 M $AgNO_3$ column at 0°. The chromatograms of the olefin separations are comparable to that published by Cvetanovic and coworkers.[3a,b] Their separations were carried out on a 40-ft $AgNO_3$–ethylene glycol column at −14° and required a much longer retention time. This is apparently the first report of a separation of C_6D_6 from C_6H_6 with a silver nitrate column. Previously,[9,10] these

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(6) L. H. Phifer and H. K. Plumer, *Anal. Chem.*, **38**, 1652 (1966).

(7) R. E. Pecsar and J. J. Martin, *ibid.*, **38**, 1661 (1966).

(8) B. Karger and A. Hartkopf, *ibid.*, **40**, 215 (1968).

(9) M. Possanzini, A. Pela, A. Liberti, and G. P. Cartoni, *J. Chromatogr.*, **38**, 492 (1968).

(10) A. Liberti, G. P. Cartoni, and F. Bruner, "Gas Chromatography," A. Goldup, Ed., Institute of Petroleum, London, 1965, p 301.

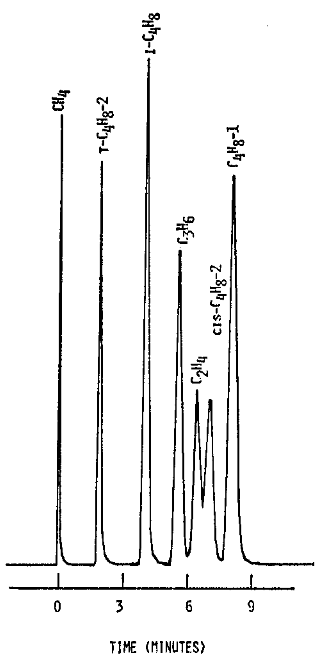

Figure 2. Separation of olefins on a 12-ft aqueous 3.5 *M* $AgNO_3$ column at 23°. Helium carrier gas ~60 cm³/min.

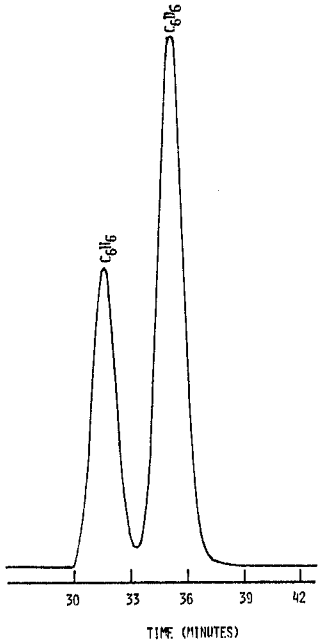

Figure 3. Separation of deuterated and normal benzene on 12-ft 3.5 *M* $AgNO_3$ column at 0°. Helium carrier gas ~60 cm³/min.

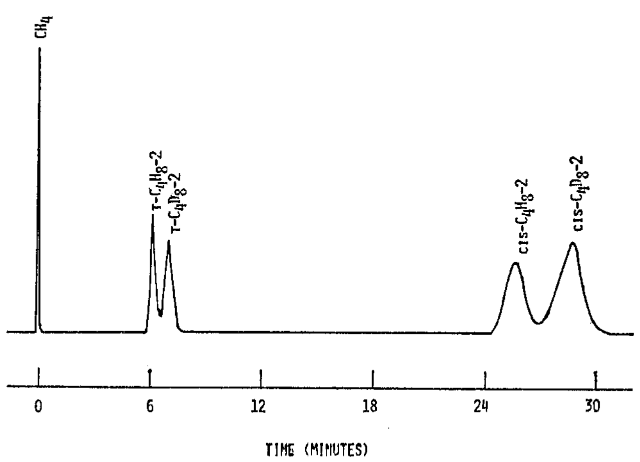

Figure 4. Separation of deuterated 2-butenes from isomers on 12-ft 3.5 *M* $AgNO_3$ column at 0°. Helium carrier gas ~60 cm³/min.

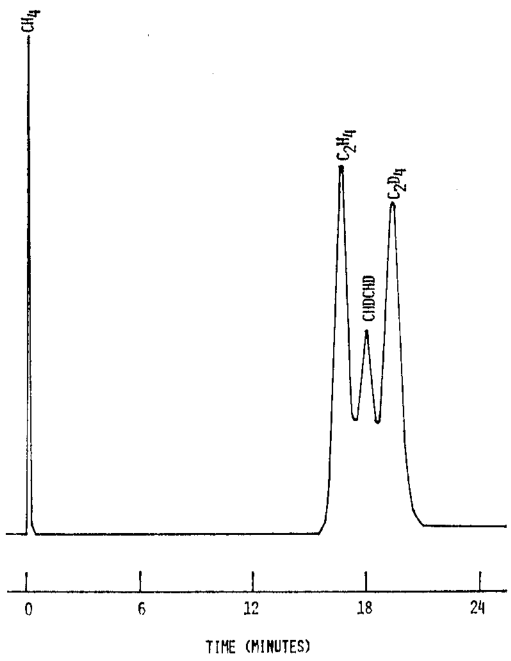

Figure 5. Separation of C_2H_4, CHDCHD, and C_2D_4 isomers on 12-ft 3.5 *M* $AgNO_3$ column at 0°. Helium carrier gas ~60 cm³/min.

compounds have been separated *via* adsorption chromatography on graphitized carbon black, etched glass, and Porapak, and by liquid partition chromatography using squalane. In all cases the isotope effect was much smaller than that found here. Thus, longer columns were required.

These results illustrate the analytical possibilites of using aqueous columns. In the present case use has been made of the strong ionizing properties of water, thus increasing the silver ion activity. It is clear that whenever metal ions are to be used in gas chromatography water is probably the preferred solvent. Furthermore, the enormous volume of data in the literature on chemical complexation in volatile solvents can be quantitatively used for the design of columns. These will be capable of making extremely specific separations since chemical interactions are now involved and effects due to volatility will be minimized. This of course assumes that equilibrium constants derived from standard techniques can be carried over to gas chromtography. This will be demonstrated to be the case in the subsequent section.

Table I: Partition Coefficients (Concn, Liquid Phase/Concn, Gas Phase), K_{obsd}, at Various Concentrations of $AgNO_3$ in Water as a Function of Temperature

	Pure water				0.21 *M* $AgNO_3$				0.40 *M* $AgNO_3$			0.98 *M* $AgNO_3$				1.8 *M* $AgNO_3$			3.5 *M* $AgNO_3$			
	0.0°	13.0°	23.0°	$-\Delta H$, kJ/mol	0°	13.2°	23.2°	$-\Delta H$, kJ/mol	15°	22.7°	$-\Delta H$, kJ/mol	15.0°	20.0°	25.0°	$-\Delta H$, kJ/mol	13.2°	23.2°	$-\Delta H$, kJ/mol	0.0°	13.2°	23.2°	$-\Delta H$, kJ/mol
Ethylene					8.9	3.94	2.27	39	7.0	4.8	36	14.4	10.5	8.5	37	24.3	16.6	28	64.9	35.8	26.7	27
Propylene					10.4	4.0	2.12	46	7.0	4.43	43	14.7	9.9	7.1	45	23.2	14.8	31	65.6	32.9	23.1	29
Isobutene					8.6	3.0	1.52	51	5.1	3.10	46	10.3	7.2	5.2	47	17.2	10.2	34	60.8	26.8	16.7	35
Butene-1					18.7	6.2	2.94	54	10.6	6.27	46	21.4	14.3	10.8	50	36.0	20.8	38	127	54.5	33.2	39
cis-Butene-2					16.3	5.4	2.22	54	9.2	5.50	46	18.5	12.3	9.3	50	31.0	18.0	41	112	47.6	28.9	39
trans-Butene-2					4.6	1.59	0.80	52	2.6	1.59	47	5.1	3.5	2.6	50	8.2	4.8	35	29.5	12.3	7.8	38
Benzene	14.3	7.0	4.3	35	20.0	9.2	5.8	39											134.2	63.8	39.7	34
Toluene	23.2	9.2	4.7	46	25.4	10.2	6.0	43												96.0		
p-Xylene	27.0	11.4	6.4	43			6.5													175		
o-Xylene	35.5	15.0	8.2	43			9.7													270		
Benzene-d_6	15.0	7.4	4.5	35															145.7	68.8	42.9	34

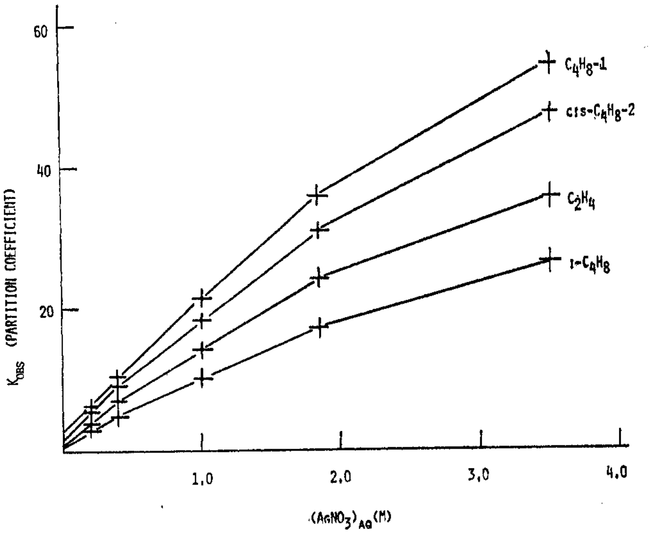

Figure 6. Variation of partition coefficients with $AgNO_3$ concentration at 13°.

II. Data Analysis. Quantitative results, expressed in terms of partition coefficients, K_{obsd} (concentration of sample in liquid phase/concentration of sample in gas phase), are summarized in Table I. They are derived from the well-known relation[11]

$$K_{obsd} = \frac{3}{2}\left[\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1}\right]\frac{Ft_rT_c}{V_LT_f} \quad (1)$$

where p_i = inlet pressure, p_o = outlet pressure, F = flow rate, t_r = retention time (in this study, the time between the elution of methane and the peak of interest), T_c = column temperature, T_f = temperature of the flow meter, and V_L = volume occupied by the liquid phase. The dependence of the partition coefficient on silver nitrate concentration for various olefins is shown in Figure 6. It is similar to that found by Muhs and Weiss[2] in their studies using ethylene glycol as a solvent. They attribute the departure from linearity at high silver nitrate concentrations to a salting out effect. Also included in Table I are the heat quantities (from ln K_{obsd} *vs.* $1/T$ plots and represents the enthalpy for solute going into $AgNO_3$ solutions). For the olefins, these are much larger than usually encountered in chromatographic studies and are a reflection of the involvement of chemical interactions in the solution process. There is a noticeable increase in the negative heat of solution with decreasing silver nitrate concentration. This may be due to the incomplete ionization of silver nitrate at higher concentrations and/or a temperature dependence of the salting out effect.

It was not possible to calculate partition coefficients from retention data of the olefins in the absence of silver nitrate due to their low solubility in water. From

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(11) H. Purnell, "Gas Chromatography," Wiley, New York, N. Y., 1962.

literature values[12] it is estimated that for accurate determinations impractically long columns, several hundred meters, must be used.

For the aromatic compounds direct gas chromatographic determinations have been carried out. Of some interest is the presence of a rather significant isotope effect for the solubility of benzene in water. This has apparently never been reported before and demonstrates the special advantage of the gas chromatographic method since more conventional techniques will require vastly larger quantities of the deuterated benzene isomer.

The partition coefficients are directly related to the equilibrium constants for the various processes that occur in the chromatographic column. The procedure and relevant equations have been given by Muhs and Weiss.[2] This involves the assumption that during the course of the experiment two equilibria

$$(\text{hydrocarbon})_g \overset{K_s}{\longleftrightarrow} (\text{hydrocarbon})_{aq}$$

$$(\text{hydrocarbon})_{aq} + (\text{AgNO}_3)_{aq} \overset{K_c}{\longleftrightarrow} (\text{hydrocarbon–AgNO}_3)_{aq}$$

are set up and lead to the relationship

$$H(\text{partition coefficient}) = K_s + K_sK_c(\text{AgNO}_3)_{aq} \quad (2)$$

Thus in the absence of silver nitrate the partition coefficient is equal to the solubility constant (as defined here it is essentially the inverse of the Henry's law constant). In the present study, as noted earlier, K_s for the olefins that are considered here cannot be directly determined. Furthermore, the experimental scatter is sufficiently large so as to render meaningless any attempt to determine K_s by extrapolating data such as given in Figure 6 to zero $AgNO_3$ concentration. Literature values must then be used.[12-15] The available data are summarized in Table II.[16-18] Unfortunately, data on this subject are extraordinarily scarce. Except for ethylene, the solubilities of small olefins have apparently never been studied over a range of temperatures. Also included in Table II are solubility data for the aromatic compounds.

Calculated values of the equilibrium constant of the complexing reaction at the temperature for which solubility data are available are given in Table III. For the aromatic compounds complexing constants are determined using the gas chromatographic values for the solubility constant. With regard to ethylene, the data in Table III yield an enthalpy and entropy for the complex-forming reaction of $\Delta H = -23$ kJ/mol and $\Delta S = -38$ J/mol deg. As noted earlier, the lack of solubility data prevents similar determinations for the other olefins. However, a rough estimate can be made if it is assumed that the excess energy of solution for these compounds is the same as that for ethylene. On this basis the enthalpies and entropies of reaction turn out to be very similar to those given here for ethylene. Complexing constants for the aromatic compounds are more than an order of magnitude smaller than for the olefins. For reasons that will be dealt with subsequently, the quality of these data is probably inadequate for an accurate determination of enthalpies and entropies of reaction. Also included in Table III are the results from static experiments.[16-18]

Table II: Data on the Solubility of Olefins and Aromatics, K_s (in Terms of Partition Coefficients: Concn in Liquid Phase/Concn in Gas Phase)

	Temp, °C			
	0	13	23	25
Ethylene	0.20^{13}	0.14^{13}	0.11^{13}	$0.107^{12,13}$
Propylene				0.125^{12}
Isobutene				0.112^{12}
Butene-1				0.105^{12}
cis-Butene-2				0.106^{15}
trans-Butene-2				0.109^{15}
Benzene	16.6	8.4	4.9	4.48^{14}
Toluene	19.2	8.8	5.0	4.52^{14} 3.87^{12}
p-Xylene	20.0	9.0	4.6	4.05^{12} 4.15^{14}
o-Xylene				4.62^{12} 5.39^{12}

Table III: Summary of Experimental Results on Complexing Constants (M^{-1}), K_c, and Literature Values

	Temp, °C				
	0	13.2	23.2[a]	25[a]	Lit values, 25
Ethylene	203	127	92	85	85^{17}
Propylene			85	79	87^{17}
Isobutene			55	51	71^{18}
1-Butene			120	110	118^{18}
cis-Butene-2			90	83	62^{18}
trans-Butene-2			29	27	25^{18}
Benzene	1.86	1.45	1.58		2.41^{16}
Toluene	0.43	0.52	1.19		2.95^{16}

[a] Values for olefins at 25° have been extrapolated assuming temperature dependence similar to that of ethylene.

Data on isotope effects, expressed as the ratio of retention time of the deuterated species with respect to

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(12) C. McAuliffe, presented before the Division of Petroleum Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1964.

(13) T. J. Morrison and F. Biller, *J. Chem. Soc.*, 3019 (1952).

(14) R. J. Bohon and W. F. Clauson, *J. Amer. Chem. Soc.*, **73**, 1572 (1951).

(15) F. Irrmann, *Chem.-Ing.-Tech.*, **37**, 789 (1965).

(16) L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, **71**, 3644 (1949).

(17) K. N. Trueblood and H. J. Lucas, *ibid.*, **74**, 1338 (1952).

(18) F. R. Hepner, K. N. Trueblood, and H. J. Lucas, *ibid.*, **74**, 1333 (1952).

Table IV: Data on Isotope Effects in 3.5 M $AgNO_3$

	Temp, °C	Present work	Cvetanovic, *et al.*,[3a,b,4] (in ethylene glycol)
C_2D_4–C_2H_4	0	1.168[a]	1.14 (1.161)
	23.2	1.142	1.113 (1.129)
CHDCHD–C_2H_4	0	1.086	1.07 (1.085)
cis-C_4D_8-2–*cis*-C_4H_8-2	0	1.119	1.08 (1.133)
trans-C_4D_8-2–*trans*-C_4H_8-2	0	1.144	1.09 (1.157)
C_6D_6–C_6H_6	0	1.086 (1.032)[b]	
	13.2	1.079 (1.027)	
	23.2	1.080 (1.028)	

[a] Values are from ratio of retention times. [b] Values in parentheses have been corrected for isotope effect on solubility. They represent K_c(deuterated compound)/K_c(light compound).

its light isomer, are summarized in Table IV. Also included are the results of Cvetanovic and coworkers from studies in ethylene glycol.[4] In their studies they were able to determine the isotope effect for the solubility of the olefins in ethylene glycol. Thus, the isotope effect appropriate to the complexing reaction can be calculated. These numbers are the values in parentheses. In the present study a similar correction could not be applied due to the low solubility of the olefins in water. There is, however, extremely good correspondence between the corrected ethylene glycol values and the uncorrected results of the present investigation. This suggests that there is almost no isotope effect for the solution of the smaller olefins in water. With regard to benzene a complete set of data is available. As could have been expected from the relatively weak silver–benzene complex, the isotope effect for this reaction is small. Indeed, it is even smaller than that for the solubility of benzene in water.

III. Comparisons and Limitations. From an examination of the data summarized in Tables II, III, and IV it can be seen, in general, that there is satisfactory agreement between gas chromatographic and static determinations. For the olefins the agreement with respect to the stability constants can be regarded as quantitative. In the case of aromatic compounds the larger discrepancies between literature and experimental values are undoubtedly due to the fact that the contribution to the retention time of these compounds arises largely from insolubility in water rather than from the complex-forming reaction (as is the case of the olefins). See eq 2. Thus, small errors in the two measured quantities will result in large errors in the stability constant. One source of such error is the neglect of the salting out effect at the 0.214 M $AgNO_3$ concentration.

Another source of error is the possibility of surface effects. Conder, Locke, and Purnell[19] have recently published a series of papers on the importance of surface effects in gas–liquid partition chromatography. This has also been mentioned by Karger[8] in his study of the separation of high molecular weight hydrocarbons by a water column. These considerations are not applicable to the aqueous silver nitrate columns when used with the olefins since surface effects are probably vastly smaller than the contribution to the retention time from the complexing reaction. For the aromatic compounds, even a small manifestation of this effect can cause serious errors. The increasing divergence of the solubility of the aromatics from the literature values for the xylenes as compared to the very good agreement for benzene and toluene may be caused by this sort of phenomenon. On the other hand, a factor that is of special importance here is the very heavy loading of the columns (up to 52% by weight). This will minimize surface effects not only by increasing the total volume but by decreasing the surface area. Water, with its high surface tension, should be particularly effective in this regard.

Finally, some comment should also be made on the correspondence between solubility determinations from static determinations and gas chromatography. In the former the values are appropriate to a particular pressure (1 atm for the olefins and saturation vapor pressure for the aromatics), while the latter are in principle at least for infinite dilution. Thus, in general, exact agreement for the two cases is not expected, although it appears to be a good approximation in the present case. (See, for example, the benzene results.) This may be due that even at the higher pressures the concentration of solute still obeys Henry's law.

IV. Conclusions. Bearing in mind the considerations outlined above, the general trends in the present study do establish the validity of the gas chromatographic method for the determination of physicochemical parameters involving volatile stationary liquid phases. The usefulness and reliability of this method for the generation of thermodynamic data involving nonvolatile solvents is fairly well established.[20] Unfortunately, since most solution chemistry is carried out in solvents of some volatility (water, acetone, methanol, etc.) the systems that have been studied chromatographically are of restricted interest to other fields of chemistry. The present study demonstrates that there are no additional problems when a volatile solvent is used. It is clear that the gas chromatographic method is applicable to a much larger variety of problems than has hitherto been thought possible.

With regard to complex formation by silver ions in water all of the past studies on this subject have been carried out at a single temperature. It is interesting

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(19) J. R. Conder, D. C. Locke, and J. H. Purnell, *J. Phys. Chem.*, **73**, 700, 708 (1969).

(20) J. H. Purnell in "Gas Chromatography," A. B. Littlewood, Ed., Institute of Petroleum, London, 1966.

to note, however, that the thermal quantities (ΔH and ΔS) for the ethylene silver complex forming reaction are in the same range as those found by Denning, Hartley, and Venanzi[21] on the formation of (allyl $NR_3)^+$ $PtCl_3^-$ complexes where R is either an H atom or an ethyl group. In comparison with the results of Cvetanovic and coworkers[3a,b,4] using ethylene glycol, the thermal parameters and the stability constants in water are all larger. One rather surprising feature of the present study is that in contrast to the situation in ethylene glycol and in conformity with static experiments, the substitution of alkyl groups adjacent (compare propylene and 1-butene to ethylene) to the double bond does not cause any large decrease in stability constants. Thus, the earlier gas chromatographic results would seem to be due to the medium, ethylene glycol, rather than any specific property of the complexing reaction.

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[21] R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 324 (1967).

Activity Coefficients and Ion Pairs in the Systems Sodium Chloride–Sodium Bicarbonate–Water and Sodium Chloride–Sodium Carbonate–Water[1]

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The mean activity coefficient of NaCl in electrolytes containing $NaHCO_3$ and Na_2CO_3 has been measured by the potentiometric method, employing both sodium amalgam electrodes and sodium-selective glass electrodes in cells without liquid junction. Harned's rule is obeyed over the ionic strength range from 0.5 to 3.0 with a coefficient $\alpha_{12} = 0.047 \pm 0.003$, independent of ionic strength or whether the anion is CO_3^{2-} or HCO_3^-. These results, as well as the equilibrium constants for protonation equilibria, are discussed in terms of a model where Na^+ forms ion pairs with the carbonate anions. Association constants (at $I = 1.0$) $\log K_1' = 0.96 \pm 0.13$ (for the formation of $NaCO_3^-$) and $\log K_1'' = -0.30 \pm 0.13$ (for the formation of $NaHCO_3$) are derived. Constants obtained at other ionic strengths and corrections to $I = 0$ are given. The relation of ion pairing to the salt effect on the carbonate protonation equilibria is discussed. Systematic deviations of several millivolts observed in the glass electrode data at pH 8 to 9 and ionic strengths below 1 indicate that caution must be exercised in interpreting such measurements.

Introduction

Despite the critical importance of bicarbonate and carbonate ions in natural water systems, little is known about the activity coefficients and ion-pairing equilibria of these species in the presence of alkali metal cations. One indirect study has been made[2] of the activity coefficients of $NaHCO_3$ and Na_2CO_3 alone in aqueous solutions, but no direct measurements have been made of multicomponent activity coefficients, either of NaCl in the presence of carbonate species, or of carbonates in the presence of substantial concentrations of NaCl.

On the other hand, a large body of data has been collected on the protonation equilibria of carbonates,[3,4] mostly in media where extrapolation to infinite dilution is possible. Attempts[4,5] have been made to obtain quantitative information about ion-pairing equilibria from such data, but these rest on a number of *ad hoc* assumptions regarding single-ion activities and the

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[1] Presented at the Symposium on Metal Ions in the Aqueous Environment, 158th National Meeting of the American Chemical Society (Division of Water, Air, and Waste Chemistry), New York, N. Y., Sept 1969.

[2] A. C. Walker, U. B. Bray, and J. W. Johnson, *J. Amer. Chem. Soc.*, **49**, 1235 (1927).

[3] (a) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, Special Publication No. 17, 1964; (b) C. Culberson, D. R. Kester, and R. M. Pytkowicz, *Science*, **157**, 59 (1967); A. Distèche and S. Distèche, *J. Electrochem. Soc.*, **114**, 330 (1967); C. Culberson and R. M. Pytkowicz, *Limnol. Oceanogr.*, **13**, 403 (1968).

[4] F. S. Nakayama, private communication (submitted to *J. Phys. Chem.*).

[5] R. M. Garrels, M. E. Thompson, and R. Siever, *Amer. J. Sci.*, **259**, 24 (1961).