Solubilization of Benzene in Aqueous Solutions of *n*-Alkylammonium Bromide, *n*-Alkanols, Acetic Acid, and Perchloric Acid Measured by Differential Spectroscopy

Selwyn J. Rehfeld

Contribution from the Department of Clinical Pathology and Laboratory Medicine, Division of Hematology, University of California, San Francisco, California 94122.
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Abstract: The differential ultraviolet spectra are reported for aqueous solutions of tetramethyl- and tetrabutylammonium bromide, methanol, butanol, *N*,*N*-dimethylethanolamine, acetic acid, and perchloric acid saturated with benzene at 25°. A critical concentration of $\sim 0.015\ M$ is found for aqueous solutions of tetrabutylammonium bromide. A quantitative comparison of these differential spectra with the spectrum of benzene dissolved in solvents containing molecular groups or environments similar to those which might occur in these aqueous nondetergent solutions is reported. With the exception of perchloric acid, this spectral analysis indicated that benzene is solubilized in a region having solvent properties similar to polyhydric alcohols. These spectral results support the proposal of Arnett and coworkers that hydrophobic interactions are responsible for the salting in of benzene in these aqueous systems. In aqueous perchloric acid solutions the mechanism by which benzene is salted in may involve the formation of a water-soluble complex between benzene and perchloric acid. The activity coefficients for benzene dissolved in these aqueous nondetergent systems are computed and discussed.

Aqueous solutions of quaternary ammonium salts[1–5] and perchloric acid[1,2] exhibit the property of increasing the solubility of benzene in water. This phenomenon is commonly referred to as salting in.[6] With the exception of perchloric acid all these salts possess an alkyl moiety. Various theories[6] have been proposed to explain the salting in of nonelectrolytes by these aqueous salt solutions. Recently it was reported by Arnett, Ho, and Schaleger[5] that none of these theories satisfactorily explained the results of a thermodynamic analysis of the salting in of benzene by aqueous solutions of tetrabutylammonium bromide. They reported[5] that the thermodynamic analysis was exactly analogous to the behavior of nonpolar solutes in mixed aqueous binary solutions which indicated a similarity to hydrophobic bonding. The possibility of micelle formation[3,4] in these systems would be consistent with their results. Lindenbaum and Boyd[7] have cited unpublished measurements which indicate a critical micelle concentration (cmc) of 0.039 *M* for aqueous tetrabutylammonium bromide solutions. The cmc reported was determined using the dye-absorption method.[8] The use of the dye-absorption method to determine the critical micelle concentration (cmc) of surfactant solutions is a well-established technique.[9,10] Values determined for the cmc spectrally are in excellent agreement with values obtained using other methods.[9,10] However, Arnett and coworkers[5] ruled out micelle formation on the basis of not finding an inflection in the plot of surface tension *vs.* tetrabutylammonium bromide concentration. This result does not necessarily rule out the possibility of micelle formation.[11] In the case where the number of monomer units aggregating to form a micelle is less than ~10, one would not expect to find a well-defined inflection in plots of the various colligative properties *vs.* solute concentration.[12,13]

We have further explored the possibility of micelle-like structures existing in aqueous nondetergent solutions using the differential-spectral method recently described in the literature.[14–19] Our objectives are to use quantitative differential spectroscopy[14,19] to measure the amount of benzene solubilized by aqueous solutions of nonelectrolytes and electrolytes, to obtain information about the environment of solubilized benzene in these aqueous solutions and to determine if a critical concentration can be detected. The following aqueous solutions of electrolytes and nonelectrolytes known to salt-in benzene were included in this study: tetramethyl- and tetrabutylammonium bromide,[1–6] perchloric acid,[1,2] methanol, butanol, *N*,*N*-dimethylethanolamine, and acetic acid.

Experimental Section

Materials. The chemicals used were obtained from the following

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[1] F. A. Long and W. F. McDevit, *J. Amer. Chem. Soc.*, **74**, 1778 (1952).

[2] F. A. Long and W. F. McDevit, *Chem. Rev.*, **51**, 119 (1952).

[3] J. E. Desnoyers, G. E. Pelletier, and C. Jolicoeur, *Can. J. Chem.*, **43**, 3232 (1965).

[4] H. E. Wirth and A. Lo Surdo, *J. Phys. Chem.*, **72**, 751 (1968).

[5] E. M. Arnett, M. Ho, and L. L. Schaleger, *J. Amer. Chem. Soc.*, **92**, 7039 (1970).

[6] H. Schneider in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritche, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 5. This reference contains a detailed review of the salting-in phenomenon and current theories proposed to explain the salting in of nonelectrolytes by aqueous salt solutions.

[7] S. Lindenbaum and G. E. Boyd, *J. Phys. Chem.*, **68**, 911 (1964).

[8] M. L. Corrin and W. D. Harkins, *J. Amer. Chem. Soc.*, **69**, 670 (1947).

[9] K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, "Colloidal Surfactants," Academic Press, New York, N. Y., 1963, Chapter I.

[10] E. Hutchinson in "Solvent Properties of Surfactant Solutions," K. Shinoda, Ed., Marcel Dekker, New York, N. Y., 1967.

[11] The use of the term micelle probably does not apply to aggregates which might form in these nondetergent solutions. This topic is covered in more detail in the discussion section of this paper.

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[14] S. J. Rehfeld, *J. Phys. Chem.*, **74**, 117 (1970).

[15] S. J. Rehfeld, *J. Colloid Interface Sci.*, **34**, 518 (1970).

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[18] A. Ray and G. Némethy, *J. Phys. Chem.*, **75**, 809 (1971).

[19] S. J. Rehfeld, *J. Phys. Chem.*, **75**, 3905 (1971).

Table I. Position of Second Maximum in the Progression of the Ultraviolet Vibrationally Allowed Transition (2600 Å System), the Half-Widths ($\Delta\nu_{1/2}$), the Molar Absorptivities ($\epsilon_{\max(2)}$), and the Solute–Solvent Interaction Parameters (ϵ_s/ϵ_ν) in the Benzene Spectra (25°)

Solvent system	Reference	C_6H_6 concn, ±0.0003 mol l.$^{-1}$	$\lambda_{\max(2)}$, ±1 Å	$\epsilon_{\max(2)}$, ±4 l. mol^{-1} cm^{-1}	$\Delta\nu_{1/2}$, ±30 cm^{-1}	ϵ'_s/ϵ_ν, ±0.1
CH_3OH	CH_3OH	0–0.030	2543	268	350	0.19
CH_3OH	CH_3OH	6.23	2548	218	400	0.25
CH_3OH	CH_3OH	10.11	2550	211	420	0.26
C_6H_6	Quartz cell	11.06	2552	201	400	0.26
$CH_3(CH_2)_3OH$	$CH_3(CH_2)_3OH$	0–0.030	2544	254	380	0.19
$CH_3(CH_2)_3OH$	$CH_3(CH_2)_3OH$	3.87	2548	211	410	0.23
$CH_3(CH_2)_3OH$	$CH_3(CH_2)_3OH$	4.11	2548	206	410	0.23
$CH_3(CH_2)_3OH$	$CH_3(CH_2)_3OH$	8.16	2551	204	430	0.27
$HOCH_2CH_2OH$	$HOCH_2CH_2OH$	0–0.030	2547	192	430	0.26
$CH_3CH(OH)CH_2OH$	$CH_3CH(OH)CH_2OH$	0–0.030	2547	206	430	0.27
$HOCH_3CH(OH)CH_2OH$	$HOCH_3CH(OH)CH_2OH$	0–0.030	2549	197	450	0.31
CH_3COOH	CH_3COOH	0–0.030	2543	245	320	0.23
H_2O	H_2O	0.0240	2539	190	530	0.32
Aqueous Solutions Saturated with Benzene (C_6H_6)						
0.51 M $(CH_3)_4NBr$	(A)[a]	0.0043	2543	215	430	0.31
$[CH_3(CH_2)_3]NBr$	(A)[a]					
0.060 M		0.0015	2543	215	410	0.31
0.120 M		0.0030	2543	215	410	0.31
0.166 M		0.0041	2544	215	420	0.31
0.283 M		0.0075	2545	215	430	0.31
0.330		0.0087	2547	215	420	0.31
0.541 M		0.0157	2548	215	420	0.31
0.742 M		0.0345	2550	215	430	0.31
0.59 M $[(CH_3)_2N(CH_2)_2OH$	(A)[a]	0.032	2543	215	430	0.30
CH_3OH	(A)[a]					
0.50 M		0.0033	2543	215	430	0.30
4.68 M		0.0116	2543	215	420	0.27
9.63 M		0.0658	2544	215	450	0.25
4.0 M $HClO_4$	(A)[a]	0.0050	2539	190	>600	0.50

[a] (A) Reference cell contained water saturated with C_6H_6.

sources: tetramethylammonium bromide from Eastman Organic Chemical Co.; the tetrabutylammonium bromide and acetic acid from J. T. Baker Co.; methanol and butanol were spectroquality solvents from Matheson Coleman and Bell; the *N,N*-dimethylethylethanolamine from Aldrich Chemical Co.; the sources of the benzene, polyhydric alcohols, and water are disclosed in previous publications.[14,20] Both salts were recrystallized before using and the *N,N*-dimethylethanolamine was redistilled just before using in these experiments.

Apparatus. A Cary 14 spectrophotometer made available to the author by Dr. I. M. Kuntz, of the Department of Pharmaceutical Chemistry, was employed in all experiments described in this paper.

Results

Differential Spectra. The differential spectra were measured by placing in the reference compartment of the Cary 14 spectrophotometer a cell containing water saturated with benzene, 24.0 mmol/l.$^{-1}$, at 25°.[14] The ultraviolet (uv) differential spectra of benzene in tetrabutylammonium bromide solutions below 0.015 M indicated no increase in benzene solubility in excess of the spectrum measured for benzene in water. In this case, the differential spectrum is simply the instrument base line. This suggests that at lower salt concentrations no micelle-like structures exist.[11,12,14–18] Between 0.015 and 0.7 M tetrabutylammonium bromide a linear increase in benzene concentration is observed. Absorbance of all bands in the differential spectrum increased linearly in this concentration range. No salting in of benzene was observed for the other aqueous electrolyte or nonelectrolyte solutions below a concentration of ~0.3 M.

The spectral analysis of the differential spectra for these aqueous systems and the values obtained for benzene dissolved in methanol, butanol, 1,2-propanediol, 1,2-ethanediol, 1,2,3-propanetriol, acetic acid, and water are presented in Table I. Note that the integrated intensities are the same, 4.1 ± 0.2 × 10^5 l. mol^{-1} cm^{-1}, for all systems with the exception of perchloric acid. In this case, the spectrum was not integrated, but we estimated the value to be greater than 5 × 10^5 l. mol^{-1} cm^{-1}. The values reported in Table I for line position, molar absorptivity, line width, and the solute–solvent interaction parameter[20] for benzene dissolved in these aqueous electrolyte and nonelectrolyte solutions, with the exception of perchloric acid, correspond to those observed for benzene dissolved in various organic solvents.[20]

Amount of Benzene Solubilized. The solubility of benzene in these aqueous systems was measured by the titration method previously described.[14] The sum of the benzene concentration solubilized in water (24.0 mmol^{-1} l.) plus the amount calculated from the differential spectra using a molar absorptivity of 215 l. mol^{-1} cm^{-1} was found to be within 2% of the titration values. In no case did we find more than 0.1 mole fraction of benzene solubilized in these aqueous systems.

Spectral Measurements of Benzene in Various Polar and Nonpolar Solvents. In order to obtain information about the region of solubilization of benzene in the above aqueous electrolyte and nonelectrolyte solutions, the uv spectra of benzene in various polar and nonpolar solvents were compared with its differential

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(20) J. W. Eastman and S. J. Rehfeld, *J. Phys. Chem.*, 74, 1438 (1970). The solvent-induced intensity at the (0–0) frequency, ϵ_s, relative to the normal vibronically allowed intensity at [γ_{00} −530] cm^{-1}, ϵ_ν, is defined as the solute–solvent interaction parameter, ϵ_s/ϵ_ν. The term ϵ_s/ϵ_ν is not comparable to the activity coefficient, α.

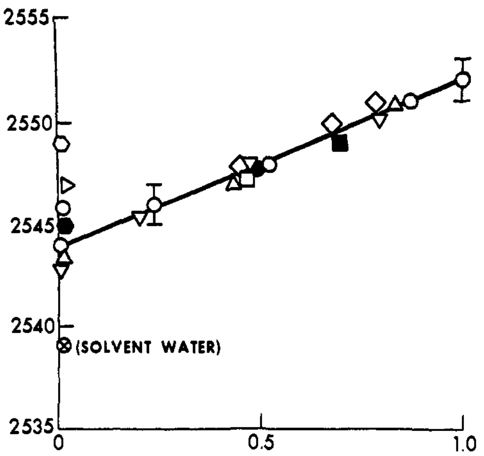

Figure 1. The position of the second maxima [$\lambda_{\max(2)}$] in angströms *vs.* benzene concentration expressed as mole fraction in the following solvents: methanol (▽), 1-butanol (△), 1-dodecanol (◇), *n*-hexane (○), *n*-hexadecane (□), 1,2-propanediol (▷), 1,2,3-propanetriol (○), micelles of NaDDS (●), micelles of CTAB (■), and acetic acid (●).

spectrum in the aqueous solutions. These solvents represented possible environments in which benzene could be solubilized in these aqueous systems.

Position of $\lambda_{\max(2)}$. Plotting the position of the second maxima [$\lambda_{\max(2)}$] *vs.* benzene concentration in polar and nonpolar solvents, an approximately linear relationship is found for benzene dissolved in *n*-alkanes and *n*-alkanols, as shown in Figure 1.[21] Benzene dissolved in solvents such as water and the polyhydric alcohols did not follow this relationship. At low-benzene concentrations, less than 0.03 *M*, the position of $\lambda_{\max(2)}$ was either less or greater than those observed for the *n*-alkanes or *n*-alkanols, as shown in Figure 1.

The amount of benzene solubilized by the quaternary ammonium salts and nonelectrolytes reported in Table I was less than $\sim$0.05 *M*. And the position of $\lambda_{\max(2)}$ varied from 2543 to 2549 Å. At these low-benzene concentrations the values of $\lambda_{\max(2)}$ agree with those found for benzene dissolved in solvents such as *n*-alkanes, *n*-alkanols, acetic acid, or the polyhydric alcohols shown in Figure 1. Thus, using these results we cannot clearly determine the solubilization site of benzene in these aqueous nondetergent solutions.

Molar Absorptivities. The molar absorptivities of benzene dissolved in various solvents *vs.* benzene concentration are shown in Figure 2. Note the values of the molar absorptivities found for dilute benzene solutions (less than 0.1 mol fraction) in solvents such as the alkanes, alkanols, and acetic acid. However, much lower values are found for dilute solutions of benzene in the polyhydric alcohols, as shown in Figure 2.

The molar absorptivities determined for benzene solubilized in the aqueous nondetergent solutions are less than those obtained for benzene dissolved in alkanes, alkanols, and acetic acid at benzene concentrations of less than 0.1 mol fraction, as shown in Figure 2 and Table I. Thus the possibility exists that the benzene is solubilized in a region structured in a manner similar to solvents such as the polyhydric alcohols.

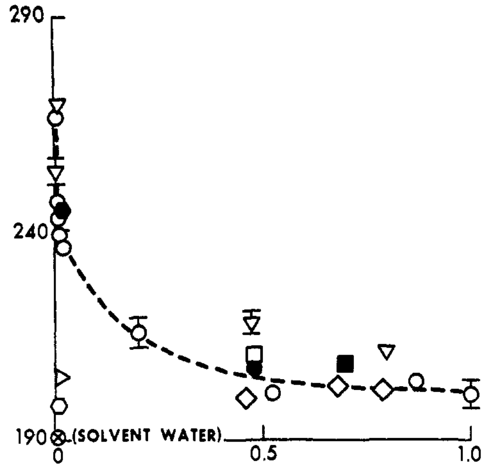

Figure 2. Molar absorptivities (l. mol^{-1} cm^{-1}) *vs.* benzene concentration expressed as mole fraction in the same solvents shown in Figure 1.

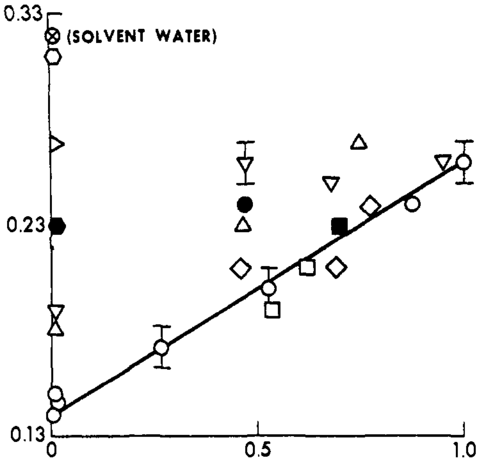

Figure 3. The solvent–solute parameter (ϵ_s/ϵ_ν) *vs.* benzene concentration expressed as mole fraction in same solvents shown in Figure 1.

Solute–Solvent Interaction Parameter. A linear relationship between the solute–solvent interaction parameter (ϵ_s/ϵ_ν) and benzene concentration is found only for solutions of benzene in alkanes as shown in Figure 3. As the carbon number of the alcohol increased the values of ϵ_s/ϵ_ν approached those found for the alkanes.[14,20] The values of ϵ_s/ϵ_ν found for dilute ($\sim$0.05 *M* or less) solutions of benzene dissolved in the polyhydric alcohols corresponded to those found for benzene solubilized in the aqueous nondetergent solutions, as shown in Table I and Figure 3.

Plotting ϵ_s/ϵ_ν *vs.* the dielectric constants of the solvents revealed a relationship within solvent groups as shown in Figure 4. The dielectric constants were obtained from the literature.[22] Note the lack of correction between the values of $\lambda_{\max(2)}$ and the dielectric constants.

Comparing the values of ϵ_s/ϵ_ν found for benzene solubilized in the aqueous nondetergent systems reported in Table I with those shown in Figure 1, it was concluded that benzene is solubilized in a region of high-dielectric constant, >30. This again indicates

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[21] Values shown for $\lambda_{\max(2)}$, molar absorptivities and ϵ_s/ϵ_ν for benzene dissolved in *n*-alkanes and 1-dodecanol were obtained from previous publications.[14,20]

[22] J. A. Riddick and W. B. Bunger, "Techniques of Chemistry," Vol. II, "Organic Solvents," Wiley-Interscience, New York, N. Y., 1970.

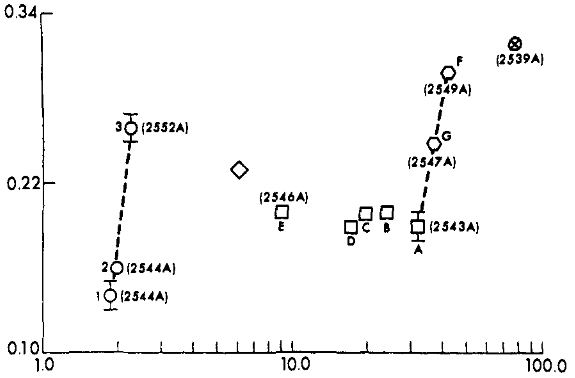

Figure 4. The solute–solvent interaction parameter (ϵ_s/ϵ_ν) *vs.* solvent dielectric constants (at 25°) in the following solvents (benzene concentrations less than 0.03 *M*): water (⊗), 1,2,3-propanetriol (○, F), 1,2-propanediol (○, G), methanol (□, A), ethanol (□, B), 1-propanol (□, C), 1-butanol (□, D), octanol (□, E), 1-hexane (○, 1), 1-octane (○, 2), benzene (○, 3), and acetic acid (◇). Values of $\lambda_{\max(2)}$ are given in parentheses.

that the region in which benzene is solubilized is ordered in a fashion similar to the polyhydric alcohols.

Discussion

As stated in the introduction Arnett and coworkers[5] concluded from thermodynamic considerations that benzene dissolved in aqueous tetrabutylammonium bromide and nonelectrolyte solutions indicated a similarity to hydrophobic bonding. Our spectral results, which indicate that the solubilization sites of benzene in aqueous tetrabutylammonium bromide and nonelectrolytes are the same, support this conclusion.

However, unlike benzene solubilized in micelles $\lambda_{\max(2)}$[14,19] in the differential spectra reported in Table I did not remain constant as the quaternary ammonium salts or nonelectrolyte concentrations were increased. The fact that no bathochromic shift was reported for the differential spectra of benzene-saturated micellar solutions[14,19] suggested that the structure of the micelles in which benzene was solubilized remained unchanged with increasing surfactant concentration. Values of $\lambda_{\max(2)}$ previously reported for the differential spectra of benzene-saturated micellar solutions are shown in Figure 1. The bathochromic shifts, observed in the differential spectra of benzene dissolved in aqueous quaternary ammonium salts and nonelectrolytes reported in Table I, indicate that the refractive indices[20] of the domains in which benzene is solubilized have changed, signifying an alteration in domain structure. These domains appear to have solvent properties similar to the polyhydric alcohols. However, as noted above, none of the differential spectra of benzene dissolved in aqueous quaternary ammonium bromides and nonelectrolytes are exactly the same as those observed for benzene dissolved in the polyhydric alcohols. Indeed, this is to be expected, since these domains are small bodies of nonuniform composition. The solubilized molecules of benzene will then lie at different distances from the hydrated polar region at the surface of the domain. The absorption spectrum observed for benzene will then be a weighted average over a distribution of benzene molecules which do not occupy identical environments within the domains. For this reason only a general description of the solubilization site can be deduced.

Another point of interest is the fact that a critical concentration is observed for aqueous tetrabutylammonium bromide solutions. As shown above, the domains in which benzene is solubilized are not similar to those observed in micellar systems.[14,19] However, no information as to the size of the solubilization sites is available from this spectral study. It is of interest to point out that as a domain increases in size, by increasing the size of the alkyl moiety, a decrease in the ratio of surface to volume occurs and because of hydrophobic interactions between the alkyl moieties the spectral values should tend to approach those observed for benzene dissolved in micelles.[14,19] Thus it may be correct to refer to the domains in the nondetergent solutions as pseudomicelles or premicelles.

The comparison of the differential spectra of benzene solubilized in aqueous perchloric acid with the spectrum of benzene dissolved in water are found to be very similar, as shown in Table I. However, the line width and the value obtained for the solute–solvent parameter are much larger for benzene in the perchloric acid solvent. These results indicate that the salting in of benzene in aqueous perchloric acid solution is not by the same mechanism as in aqueous quaternary ammonium salts or nonelectrolyte solutions. Further, it suggests that a benzene–perchloric acid complex forms which is water soluble.

In conclusion the activity coefficients were calculated from the experimental solubility of benzene dissolved in domains of these aqueous nondetergent solutions. The method of calculating the activity coefficients of benzene solubilized in detergent systems previously described was employed.[14,19] At saturation, $x\gamma = 1.00$ by definition, x is the equilibrium mole fraction of benzene solubilized and γ is the activity coefficient. This leads to the following activity coefficients for benzene dissolved in the domains in the nondetergent solutions: ~35 for tetrabutylammonium bromide, ~90 for tetramethylammonium bromide, ~100–400 for the alcohols, ~300 for acetic acid. The activity coefficients of infinitely dilute benzene in the following solvents are as follows:[23] 110 for 1,2,3-propanetriol, 31 for 1,2-propanediol, 7.5 for methanol, 6.5 for ethanol, and 2300 for water.[14,23] Values of γ greater than 2300 were obtained for benzene dissolved in such solvents as aqueous sodium sulfate.[14] In this type of solvent benzene is salted out.[6,14] This comparison of activity coefficients supports the contention that there is a similarity of the domain in which benzene is solubilized to solvents such as the polyhydric alcohols.

Acknowledgment. This investigation was supported in part by a National Institutes of Health, Grant No. AM 16095.

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[23] C. H. Deal and E. L. Derr, *Ind. Eng. Chem.*, 3, 394 (1964), and by private communication.