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# Ultrasonic absorption in aqueous binary mixtures. II. *p*-Dioxane–water at 11 and 25°C

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Ultrasonic absorption has been measured in the *p*-dioxane/water system at 25° and 11°C at nine concentrations over the frequency range 0.3–630 MHz. It is shown that the frequency dependence can be fitted quantitatively by the "fluctuation" theory of Romanov and Solov'ev if NMR determined diffusion data are available. The experimentally determined amplitude of absorption agrees very well with that calculated using experimental thermodynamic data and the R-S theory. The ultrasonic relaxation times show the same concentration dependence as the high frequency dielectric relaxation measured by Garg and Smyth. The discussion considers the ultrasonic fluctuations as a dynamic analog of the clathrate hydrate forming proclivities of such solutes.

## INTRODUCTION

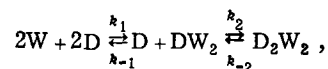
The dynamics of the interaction of simple hydrocarbon derivatives with water has a direct bearing on many problems of practical and theoretical importance. It clearly relates directly to the important conformational changes that occur when biomolecules react. Unfortunately, the high inherent rates of such interactions make most kinetic techniques of little value. Ultrasonic absorption has looked very promising,<sup>1</sup> but the interpretation of ultrasonic data for hydrocarbon–water systems has not been clearcut.

In a recent paper,<sup>2</sup> we reported a detailed study of the *t*-butylamine–water system at 25 °C. In the low amine concentration range, it was possible to fit the small chemical relaxation observed with a single relaxation model. The relaxation could be quantitatively interpreted using the well-characterized amine hydrolysis reaction. In the higher amine concentration range (>0.5 C), the ultrasonic absorption is much larger and cannot be fitted to a single relaxation. After subtracting the absorption due to the hydrolysis reaction, we showed that the excess absorption could be fitted using the fluctuation approach of Solov'ev and his co-workers.<sup>3</sup> However, the fit was not totally convincing for two reasons. First, the need to correct for the amine hydrolysis reaction complicates the interpretation. Second, there is not enough good thermodynamic data available on the system to be able to calculate the amplitude of the absorption from the fluctuation theory.

Therefore, to further test the fluctuation theory we needed a system that was uncomplicated by reactions such as hydrolysis and one where a wide variety of good thermodynamic data was available. *p*-Dioxane–water looked ideal to us. Because of its wide use as a mixed solvent system in electrolyte studies, all of the common thermodynamic parameters of the system had been measured over the whole concentration range. Once purified, this cyclic ether forms quite stable solutions with water. Finally, earlier work showed measurable ultrasonic absorption in the system.

In the most systematic earlier work, Hammes and

Knoche<sup>4</sup> measured ultrasonic absorption over the concentration range  $X_D$  from 0.18 to 0.80 and the frequency range 10–185 MHz. The data obtained at a given concentration could not be fitted to a single relaxation. The two relaxation fit of HK was explained in terms of a two-step hydrogen bonding equilibrium in the form



and the following parameters obtained at 25 °C,

$$k_1 = 1.4 \times 10^9 \text{ sec}^{-1}, \quad \Delta V_1 = \pm 1.5 \text{ cm}^3/\text{mole},$$

$$k_{-1} = 2.8 \times 10^8 \text{ sec}^{-1}, \quad \Delta V_2 = \pm 0.5 \text{ cm}^3/\text{mole},$$

$$k_2 = 1.5 \times 10^8 \text{ sec}^{-1}, \quad \Delta H_1 = \pm 1.0 \text{ kcal/mole},$$

$$k_{-2} = 1.0 \times 10^8 \text{ sec}^{-1}, \quad \Delta H_2 = \pm 0.3 \text{ kcal/mole}.$$

This analysis follows the classical H-bond approach originally suggested by Burton<sup>5</sup> and extensively developed by Andreae<sup>6</sup> and co-workers. There is no question that the ultrasonic data can be fitted quantitatively by such an analysis. However, we feel that there are important questions raised by the results of such an analysis.

Does such a complicated mechanism make any physical sense? The simplest process ( $D + W \rightleftharpoons DW$ ) does not appear and the first step given seems to involve a simultaneous three molecule process.

How are the rate constants obtained related to the known dielectric relaxation times<sup>7</sup> or simple diffusion controlled rates? The rates seem too low for such a concentrated system where molecules merely have to rotate to react.

The  $\Delta V$  and  $\Delta H$  values produced cannot be related to the known thermodynamic properties of the system.

Therefore, we thought we would re-examine this system covering a wider frequency range than was available to Hammes and Knoche.

## EXPERIMENTAL SECTION

The *p*-dioxane was purified by a standard method.<sup>8</sup> Solutions were made up by weight using deionized water and stored in the dark until use.

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## Sound absorption measurements

### High frequency

In the range 5–630 MHz the absorption coefficient  $\alpha$ , defined by  $I_x = I_0 e^{-2\alpha x}$  in terms of intensities and distance, was measured by a standard send–receive pulse apparatus.<sup>9</sup> Three cells of different dimensions using quartz crystals of 1, 10, and 30 MHz were used. The electronic equipment was a Matec 6600 mainframe and 700 series plugins with a 1235B amplitude monitor. Frequencies were measured by the heterodyne beat method using a Hewlett-Packard 610 signal generator and a 5237C frequency meter. The cells are jacketed and the temperature controlled to  $\pm 0.05^\circ$  with a lauda bath.

### Low frequency

In the range from 0.3 to 10 MHz absorption was measured using the cylindrical resonator method of Eggers.<sup>10</sup> A complete description of the apparatus will be published later.<sup>11</sup> It uses a Hewlett-Packard HP 3330B frequency synthesizer and HP 461A amplifiers. The whole measurement is controlled and the data accumulated by a dedicated HP 9815 calculator.

### Sound velocity measurements

The sound velocities were determined by the “sing-around” technique<sup>12</sup> using an NUS Model 6100 laboratory velocimeter with a Hewlett-Packard 5237C digital frequency meter. The temperature was controlled to  $\pm 0.02^\circ$  using a Forma bath.

A complete set of  $(\alpha, f)$  data is available from one of the authors (G. A.) on request.

## RESULTS AND ANALYSIS

Measurements were made at nine *p*-dioxane concentrations ranging from  $X_D = 0.17$  to  $X_D = 0.79$  at both 11 and  $25^\circ\text{C}$ . For each concentration, ultrasonic absorp-

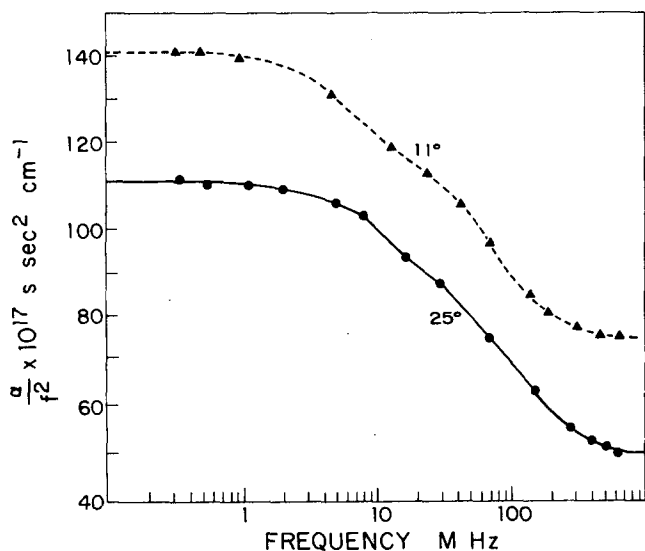


FIG. 1. Ultrasonic absorption for  $X_D = 0.45$  fitted to a double relaxation.

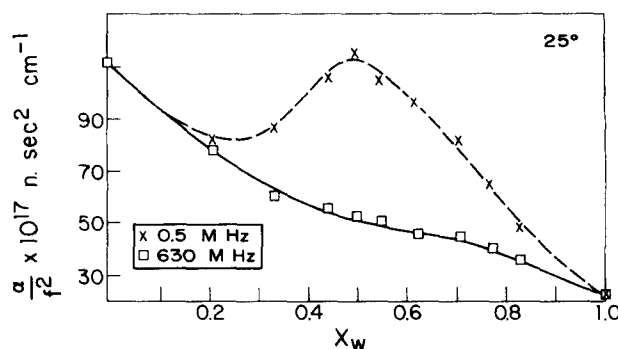


FIG. 2. Effect of concentration on amplitude of ultrasonic absorption at low and high frequency.

tion measurements were made between 0.30 and 630 MHz. Figure 1 shows typical data at  $X_D = 0.45$  at both temperatures. The solid line is a computer fitted double relaxation fit of the data using a nonlinear least squares program (NLSQ):

$$\left(\frac{\alpha}{f^2}\right) = \frac{A_1}{1 + (f/f_{R1})^2} + \frac{A_2}{1 + (f/f_{R2})^2} + B. \quad (1)$$

Figure 2 shows the variation of  $(\alpha/f^2)$  with mole fraction water at two frequencies—one below the primary relaxation region and the other above it.

There is no question that a double relaxation fit can describe the data at all concentrations and at both temperatures. However, one cannot fit the relaxation parameters  $(A_1, A_2, f_{R1}, f_{R2})$  obtained in this way with a unique mechanism such as that proposed in HK. And the rate constants obtained using similar mechanisms still do not make good physical sense in terms of an H-bonding mechanism or the dielectric relaxation results.

Therefore, we decided to attempt to fit the data using the fluctuation approach. Then (see Ref. 13),

$$\left(\frac{\alpha}{f^2}\right) = \frac{Q}{\omega} I(l_m) + B, \quad (2)$$

$$Q = \frac{8\pi^5 \bar{V}^2 kT}{v\beta_s (G'')^2} \left( \frac{V''}{\bar{V}} - \frac{\alpha H''}{C_p} \right)^2, \quad (3)$$

where  $\bar{V}$  is the molar volume of solution,  $v$  is the sound velocity in solution,  $\beta_s$  is the adiabatic compressibility of solution,  $C_p$  is the specific heat of solution,

$$G'' = \left( \frac{\partial^2 G_E}{\partial X_2^2} \right) + \frac{RT}{X_2(1-X_2)},$$

$$V'' = (\partial^2 V_E / \partial X_2^2),$$

$$H'' = (\partial^2 H_E / \partial X_2^2),$$

$Y_E$  is the excess thermodynamic property, and

$$I(l_m) = \omega \left( \frac{1}{D_{12} l_m} - \frac{\omega^{1/2} P}{8 D_{12}^{3/2}} \right), \quad (4)$$

$$P = 2\pi - \ln \left( \frac{a l_m^2 - \sqrt{2a} l_m + 1}{a l_m^2 + \sqrt{2a} l_m + 1} \right) - 2[\tan^{-1}(\sqrt{2a} l_m + 1) - \tan^{-1}(\sqrt{2a} l_m - 1)], \quad (5)$$

where  $a = \omega/2D_{12}$ ,  $\omega = 2\pi f$ ,  $D_{12}$  is the mutual diffusion coefficient, and  $l_m$  is the minimum interaction length.

TABLE I. Diffusion coefficients, *p*-dioxane–water.

$X_2$	$D_1 \times 10^5$ (cm <sup>2</sup> sec <sup>-1</sup> )	$D_2 \times 10^5$ (cm <sup>2</sup> sec <sup>-1</sup> )	$D_{12} \times 10^6$ (cm <sup>2</sup> sec <sup>-1</sup> )
25 °C			
0.17	1.151	0.5695	3.913
0.23	1.108	0.5459	3.096
0.29	1.153	0.5689	2.525
0.38	1.236	0.6549	1.758
0.45	1.300	0.7424	1.296
0.50	1.334	0.8069	1.120
0.56	1.371	0.8808	1.147
0.67	1.423	0.9971	1.930
0.79	1.520	1.098	3.956
11 °C			
0.17	0.7007	0.3363	2.331
0.23	0.6696	0.3211	1.840
0.29	0.7022	0.3357	1.512
0.38	0.7365	0.3912	1.049
0.45	0.7590	0.4473	0.7668
0.50	0.7704	0.4888	0.6586
0.56	0.7945	0.5368	0.6761
0.67	0.8282	0.6152	1.141
0.79	0.8832	0.6924	2.330

Equation (2) is a four parameter fit ( $Q, l_m, D_{12}, B$ ).  $B$  can be estimated from the high frequency limit of the experimental data.  $Q$  can be obtained *in principle* from thermodynamic data on the system.  $D_{12}$  is most readily obtained using NMR techniques. Only  $l_m$  is not clearly related to other available data. In the Solov'ev derivation, a Debye distribution of relaxation times (and fluctuation lengths) is assumed.  $l_m$ , then, is the assumed minimum fluctuation length cutoff.

Equation (2) does not work well as a four parameter fitting equation for data. Even using sophisticated NLSQ strategies, no unique fit can usually be obtained. This is caused by the very close coupling of  $D_{12}$  and  $l_m$  in Eq. (4).

To get around this we have calculated  $D_{12}$  from the NMR data of Clemett.<sup>14</sup> Clemett measured  $D_1$ , the self-

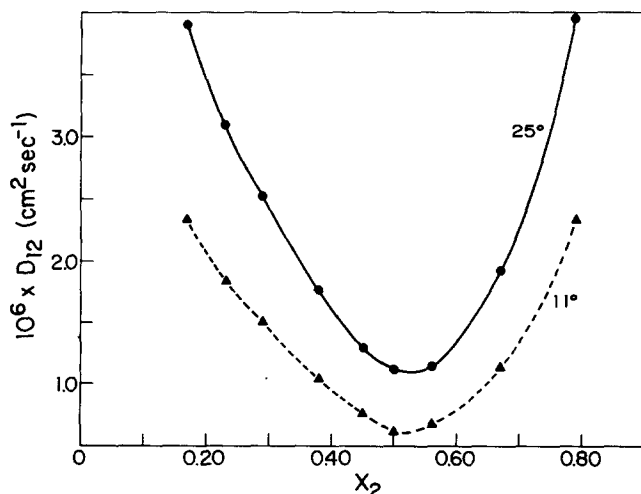


FIG. 3. Mutual diffusion in *p*-dioxane–water mixtures as a function of *p*-dioxane concentration.

diffusion coefficient of H<sub>2</sub>O in deuterodioxane, and  $D_2$ , the self-diffusion coefficient of dioxane in D<sub>2</sub>O, over a fairly wide concentration range and at 10°, 34°, and 54°. Using an HP9815 calculator and plotter in the graphic analyzer mode we could pick off  $D_1$  and  $D_2$  for each concentration and each temperature. We then fitted the ( $D_1, X_1$ ) and ( $D_2, X_2$ ) data sets with polynomials and interpolated the needed  $D_1$  and  $D_2$  values at our concentrations. We then used an Arrhenius fit to obtain the needed values at our temperatures of 11° and 25°.  $D_{12}$  is given by a Hartley–Crank expression:

$$D_{12} = (X_1 D_2 + X_2 D_1) \left( 1 + \frac{\partial \ln \gamma_2}{\partial \ln X_2} \right). \quad (6)$$

Vierk's vapor pressure data<sup>15</sup> were fitted to obtain the thermodynamic term at 25°. The calculated  $D_{12}$ 's and other values are given in Table I and shown in Fig. 3. We have assumed that the thermodynamic term is the same at 11° and 25° since Vierk's data are only at the latter temperature.

Using the  $D_{12}$  values obtained in the above manner all the data could be fitted to Eq. (2) allowing  $Q, l_m$ , and  $B$  to vary arbitrarily. In all cases a unique "best fit" could be obtained. The derived values are given in Table II. The same data sets shown in Fig. 1 are shown in Fig. 4 fitted to the fluctuation equation. Considering that we are fitting with only three parameters ( $Q, l_m, B$ ) instead of the five parameters ( $A_1, A_2, f_{R1}, f_{R2}, B$ ) of Eq. (1), the fits are just as good by normal statistical criteria.

The next problem is to examine whether  $Q$  as calculated from the thermodynamic data bears any resemblance to  $Q$  determined from the experimental data by curve fitting. Equation (3) is usefully rewritten

$$Q = \left( \frac{8\pi^5 kT}{1} \right) \left( \frac{\bar{V}^2}{v\beta_s} \right) \left( \frac{1}{G''} \right)^2 \left( \frac{V''}{\bar{V}} - \frac{\alpha H''}{C_p} \right)^2. \quad (7)$$

TABLE II. Fluctuation parameters, *p*-dioxane–water.

$X_2$	$D_{12} \times 10^6$ (cm <sup>2</sup> sec <sup>-1</sup> )	$Q \times 10^{28}$ (cm <sup>2</sup> sec)	$l_m \times 10^8$ (cm)	$B \times 10^{17}$ (sec <sup>2</sup> cm <sup>-1</sup> )
25 °C				
0.17	3.91	2.58	5.22	35.9
0.23	3.10	4.47	5.17	38.5
0.29	2.53	5.21	5.16	44.1
0.38	1.76	4.43	4.53	45.1
0.45	1.30	3.34	4.32	49.5
0.50	1.12	3.15	4.29	52.0
0.56	1.15	2.64	4.24	55.3
0.67	1.93	2.48	4.48	60.4
0.79	3.96	1.33	6.43	77.7
11 °C				
0.17	2.33	2.65	4.23	51.4
0.23	1.84	4.05	4.61	55.2
0.29	1.51	3.26	4.29	58.2
0.38	1.05	2.46	3.99	63.8
0.45	0.767	2.15	3.94	37.3
0.50	0.659	2.06	3.50	77.2
0.56	0.676	2.06	3.80	80.4
0.67	1.14	2.91	4.63	89.9
0.79	2.33	1.40	5.81	95.5

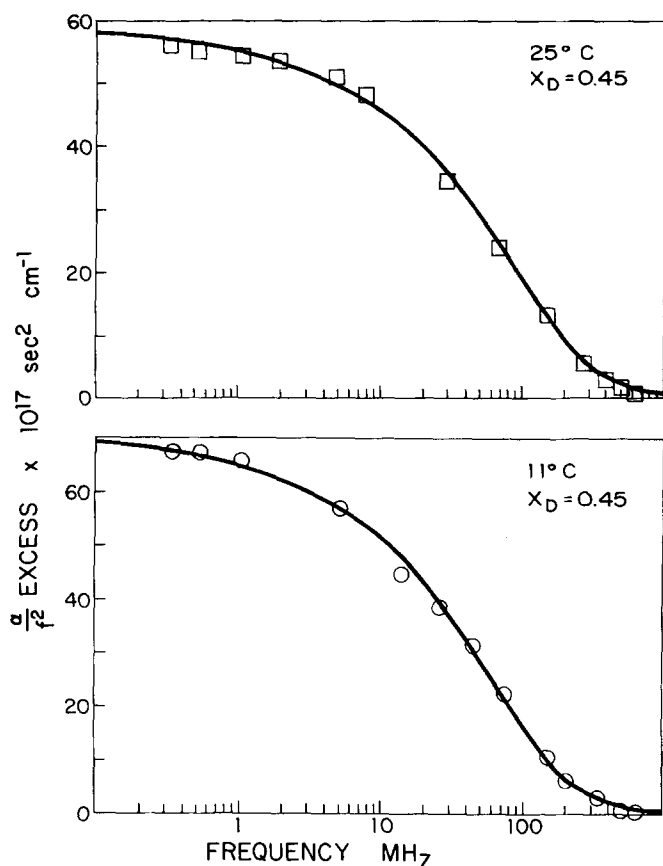


FIG. 4. Ultrasonic absorption for  $X_D = 0.45$  fitted to R-S fluctuation theory.

The density data needed for  $\bar{V}$  and  $\alpha$  were obtained from the work of Tommila<sup>16</sup> as checked against the work of Gliniski.<sup>17</sup>  $v$  was our own work<sup>18</sup> and together with the above described density was used to calculate  $\beta_s$ .  $C_p$  was obtained from the  $C_p(\text{excess})$  given by Morcom and Smith<sup>19</sup> and the known  $C_p$ 's of the pure substances. The interpolated values of the quantities are given in Table III and shown in Fig. 5.

The  $Y''$  calculations present a very severe problem involving as they do the second derivatives of the measured excess functions. For  $G_E$  we have used Vierk's data,<sup>15</sup> checking it against the work of Grunwald *et al.*<sup>20</sup> and the smoothed data of Goates and Sullivan.<sup>22</sup>  $H_E$  values are reported by Goates and Sullivan,<sup>21</sup> Morcom and

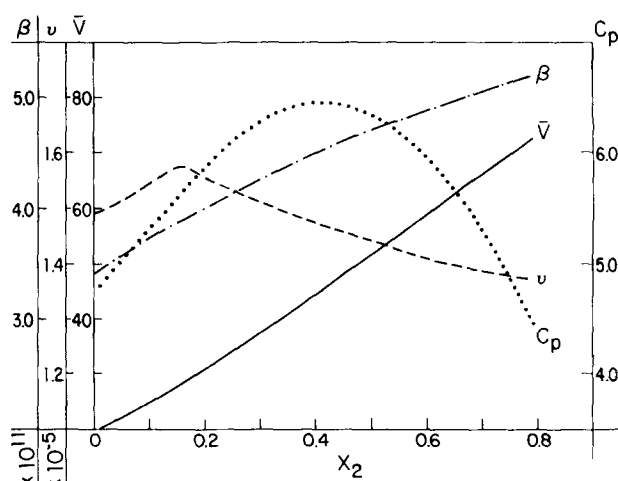


FIG. 5. Some thermodynamic parameters of *p*-dioxane-water mixtures at 25°C.  $\beta$  is adiabatic compressibility,  $\bar{V}$  is molar volume,  $v$  is sound velocity, and  $C_p$  is specific heat.

Smith,<sup>19</sup> and Nakayama.<sup>22</sup> All the excess functions can be fitted using the equation proposed by Barker<sup>23</sup> and used extensively by Copp and Everett<sup>24</sup>:

$$Y_E = (1 - X_2)X_2 \sum_{i=0}^n A_i (1 - 2X_2)^i. \quad (8)$$

Figure 6 shows the excess functions plotted versus mole fraction. The form of the curves is very typical for such systems as discussed by Franks.<sup>25</sup>

The second derivative of Eq. (8) gives quite sensible values of  $G''$  and  $V''$  in the concentration region of interest to us ( $0.17 \leq X_2 \leq 0.79$ ). However, numerous mathematical ploys to obtain  $H''$  gave numerous different nonsensical results. A close examination of *all* three sets of  $H_E$  data in the concentration range of interest ( $0.17 \leq X \leq 0.79$ ) showed that the best and only statistically *honest* mathematical description was given by

$$H_E = A + BX_2,$$

whose second derivative is obviously zero. Therefore, we dropped the  $(\alpha H''/C_p)$  term from  $Q$ . Figure 7 shows the remaining components of  $Q$  in the form

$$Q = \left( \frac{8\pi^5 kT}{1} \right) \left( \frac{\bar{V}^2}{v\beta_s} \right) \left( \frac{1}{G''} \right)^2 \left( \frac{V''}{\bar{V}} \right)^2. \quad (9)$$

TABLE III. Thermodynamic data, *p*-dioxane-water at 25°C.

$X_2$	$d$ (g cm <sup>-3</sup> )	$\bar{V}$ (cm <sup>3</sup> mol <sup>-1</sup> )	$10^{-5} \times v$ (cm sec <sup>-1</sup> )	$10^{11} \times \beta$	$10^4 \times \alpha$ (g cm <sup>-3</sup> deg <sup>-1</sup> )	$10^{-7} \times C_p$ (erg deg <sup>-1</sup> g <sup>-1</sup> )
0.17	0.9970	28.96	1.571	3.91	7.146	5.674
0.23	1.0348	32.87	1.538	4.08	7.923	6.015
0.29	1.0363	36.85	1.517	4.19	8.355	6.258
0.38	1.0361	42.97	1.479	4.44	8.939	6.439
0.45	1.0354	47.86	1.458	4.60	9.341	6.427
0.50	1.0344	51.43	1.441	4.70	9.600	6.338
0.56	1.0327	55.76	1.422	4.80	9.879	6.140
0.67	1.0309	63.78	1.400	5.00	10.30	5.523
0.79	1.0288	72.40	1.374	5.18	10.64	4.475

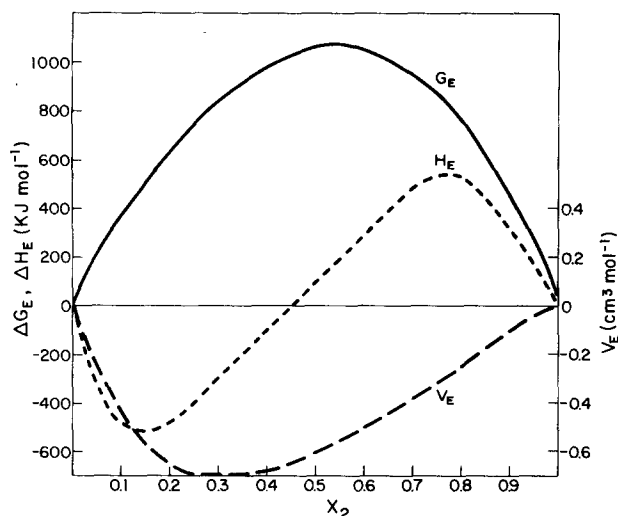


FIG. 6. Excess thermodynamic functions in *p*-dioxane-water mixtures at 25 °C.

Finally, Fig. 8 shows  $Q$  (exptl) contrasted with  $Q$  (theor) for the *p*-dioxane-water system at 25°. The fit is remarkable considering all of the assorted data that went into  $Q$  (theor). It is clear that the maximum in  $Q$  is caused by a counterplay between the  $G''$  and  $V''$  terms and the system is dominated by neither. It is unfortunate that not enough data are available at 11° to permit a detailed  $Q$  analysis at this temperature.

## DISCUSSION AND CONCLUSION

We have shown that the fluctuation approach can be used to fit the ultrasonic absorption in the *p*-dioxane-water system over the full range of frequencies and concentrations. Furthermore, the ultrasonically determined amplitude factor  $Q$  is very close to the  $Q$  calculated *ab initio* from equilibrium thermodynamic data. It is clear that the fluctuation theory fits the ultrasonic data quantitatively without the introduction of any kinetic mechanisms or the derivation of any kinetic parameters that cannot be related to other known properties of this system.

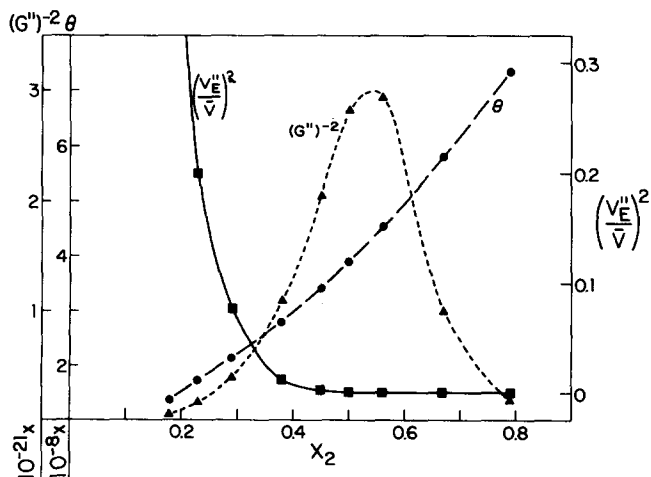


FIG. 7. Components of fluctuation amplitude,  $Q$ , in *p*-dioxane-water mixtures at 25 °C. ( $\theta = \bar{V}^2/\nu\beta_s$ ).

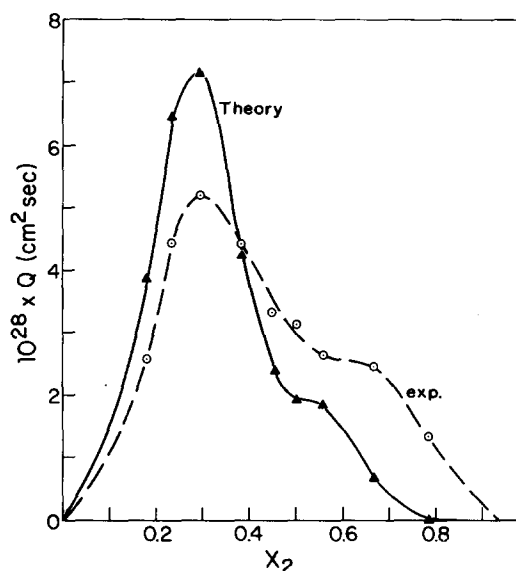
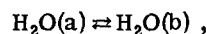


FIG. 8. Comparison of experimental and theoretical fluctuation amplitudes in *p*-dioxane-water mixtures at 25 °C.

At the same time, the fluctuation approach does not give us a model of the process that is occurring. What are these fluctuations and to what do they relate? We feel that an intriguing clue is given by the work of Glew and his co-workers. In a number of papers<sup>28-31</sup> Glew points out that the remarkable thermodynamic and spectroscopic properties of many simple hydrocarbon-water systems can be related to the propensity of these same hydrocarbon derivatives to form clathrate hydrates in the solid state. The translation of this to solution behavior is very difficult to make in a quantitative fashion. However, qualitatively we can consider a typical two-state model for water<sup>32</sup>:



where (a) is a more structured form and (b) less structured. Commonly, (a) was considered to be similar to pieces of an Ice I structure and (b) to be monomeric or interstitial depending on the particular model. An elaborate form of this has been used by Mikhailov<sup>33,34</sup> to explain the thermodynamic properties of ethanol-water systems. However, it is not at all obvious that Ice I fragments are the only sensible choice for the structured component. In fact, a molecular dynamics "experiment" that introduced an Ar atom into an assembly of  $\text{H}_2\text{O}$  molecules seemed to produce fragments that looked like clathrate cage pieces.<sup>35</sup> Therefore, we suggest that in the presence of a hydrophobic moiety the structured water may more resemble clathrate cages than Ice I. The formation of such cages provides larger cavities for the hydrophobic moiety. The formation and breakup of such cage structures can provide the fluctuations in the thermodynamics of the water so useful in explaining the ultrasonic data. It should in principle be possible to take the Mikhailov model, modify it to allow a clathrate-type structured component and thus provide a molecular picture for both the thermodynamic and acoustic data.

Finally, we want to examine the relaxation times used in our interpretation. In the Solov'ev approach

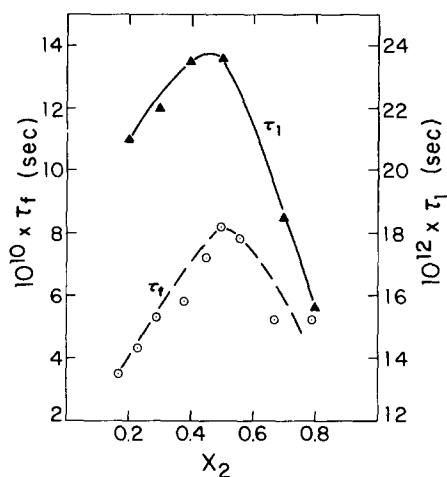


FIG. 9. Comparison of fluctuation relaxation times ( $\tau_f$ ) and high frequency dielectric relaxation times ( $\tau_1$ ) in *p*-dioxane-water mixtures at 25 °C.

$$\tau \equiv l^2/2D_{12}, \quad (10)$$

where  $l$  is allowed to range from  $l_m$ , the minimum interaction length, to infinity. Let us define

$$\tau_m \equiv l_m^2/2D_{12} \quad (11)$$

so that  $\tau_m$  is the relaxation time related to the minimum interaction length. Figure 9 shows  $\tau_m$  at 25 °C plotted against mole fraction *p*-dioxane. On the same plot is the  $\tau_1$  reported by Garg and Smyth<sup>7</sup> from dielectric measurements. The maxima in the two curves correspond quite well but differ from the maxima in  $Q$ . The two relaxation times differ by over 2 orders of magnitude so are clearly describing different aspects of the fluctuation process. One can speculate that the dielectric number describes the molecular level process while the  $\tau_m$  describes the cooperative movement of numerous molecules.

In conclusion, we feel that we have demonstrated the power of the fluctuation approach in the analysis of ultrasonic data in such systems. The frequency dependence can be clearly related to mutual diffusion and dielectric relaxation in the system. The concentration dependence is predictable from the known thermodynamics of the system. No arbitrary reaction mechanisms need be assumed and no unrelated rate constants or thermodynamic parameters are produced. The only weakness of the fluctuation approach is that of any equilibrium thermodynamic technique—no molecular model is needed or produced. However, we have indicated one path that might eventually produce a molecular model for the fluctuation theory. This path is at present being explored experimentally and theoretically in this and other systems.

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