Ultrasonic Properties of Ethanol-Water Mixtures

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Measurements have been made of the ultrasonic absorption and velocity in ethanol-water mixtures at 25 °C. Two relaxation processes are observed in the frequency range 12 − 350 MHz, and for both these relaxations a pronounced maximum of the relaxation parameters as a function of concentration is observed in the water-rich concentration range. These relaxation phenomena, as well as a maximum of the ultrasonic velocity, are tentatively taken as reflections of the formation of ice-like water structures around the nonpolar group of the alcohol.

The properties of binary mixtures of water with substances containing nonpolar groups are known to be atypical of other binary liquid mixtures. For example, the ultrasonic absorption and relaxation properties exhibit pronounced maxima as functions of concentration in dilute aqueous solutions of alcohols and alkylamines.[1-4] An inflection point is observed on the curves representing the specific volume as a function of concentration for aqueous solutions of alcohol, ketones, and ethers.[5] Such inflection points, which correspond to extrema of the partial specific volumes of the components of the mixtures, are absent in aqueous solutions of urea or formamide, in which no nonpolar groups are present.[5] They have tentatively been ascribed to interactions between nonpolar groups and solvent water,[5] and the effects observed are in qualitative accordance with the formation of the so-called Frank-Evans structures ("icebergs") in water surrounding the nonpolar groups.[6] The Frank-Evans water structures are characterized by a larger specific volume than that of pure water, and by a lower enthalpy and entropy content;[6-8] the maximum of the heat of mixing of alcohols and water in the water rich concentration range,[1,7] as well as

the positive excess free energy of mixing,[7] may be taken as suggestive experimental evidence of their existence.

The importance of the contribution from structural changes of the solvent to the thermodynamic and kinetic properties of aqueous solutions of biological macromolecules, in particular protein solutions, has often been stressed.[8,9] It is the aim of the present investigation of the ultrasonic properties of ethanol-water mixtures to contribute to the elucidation of the nature of the interactions between nonpolar groups and water. Extensive ultrasonic studies of aqueous solutions of tertiary butyl alcohol are available,[3] but since the nonpolar part of this alcohol is considerably more bulky than most nonpolar groups present in protein molecules, we consider it of interest to supplement the existing data on this alcohol with measurements on ethanol-water mixtures.

Measurements on ethanol-water mixtures at the frequencies 22.5, 37.5, and 52.5 MHz are available in the literature,[1] and data at 70 MHz are mentioned in Ref. 4. We have measured the absorption in ethanol-water mixtures at 25 °C in the frequency range 12 − 350 MHz, and observed at least two relaxation processes in this range.

The experimental data are discussed on the assumption that the relaxations observed reflect interactions between the ethyl group of the alcohol and water. This assumption is based on the observation that the concentration dependence of the ultrasonic properties of the ethanol-water mixtures − characterized by a maximum in the water rich concentration range − is qualitatively similar to the concentration dependence of the ultrasonic prop-

erties of other aqueous solutions containing alkyl groups,[1-4] but strikingly different from that of the ultrasonic properties of aqueous solutions of urea and of formamide.

THEORETICAL

For a system described by a series of reactions:

$$a_{i1}A_{i1} + a_{i2}A_{i2} + \cdots \rightleftharpoons b_{i1}B_{i1} + b_{i2}B_{i2} + \cdots \quad (1)$$
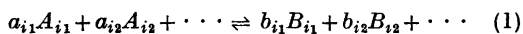
the changes of the equilibrium, caused by the propagation of an ultrasonic wave, may be expressed by the changes of the equilibrium constants $K_i = K_i(P,T)$ of the system

$$dK_i = K_i \left[\left(\frac{\Delta H_i^0}{RT^2} \right)_P dT - \left(\frac{\Delta V_i^0}{RT} \right)_T dP \right] \quad (2)$$

ΔH_i^0 and ΔV_i^0 are the corresponding changes of standard enthalpy and volume, respectively.

The rates at which the equilibria are reestablished (or the relaxation times of the reactions involved) determine the frequency dependence of the absorption coefficient α, usually expressed as [10]

$$\alpha/\nu^2 = \sum_i \frac{A_i}{(1 + (2\pi\tau_i\nu)^2)} + B \quad (3)$$

In this expression ν is the frequency, A_i is the relaxation amplitude, and τ_i the relaxation time of the i'th relaxation process; B is the so-called background absorption parameter, $B = \lim_{\nu \to \infty} (\alpha/\nu^2)$.

The absorption per wavelength at the relaxation frequency, $\mu_{\max,i} = UA_i/4\pi\tau_i$, may be expressed as

$$\mu_{\max,i} = \frac{\pi}{2} \varrho \frac{U^2 V^2}{RT} \Gamma_i \left[\frac{l\Delta H_i}{C_p} - \frac{\Delta V_i}{V} \right]^2 \quad (4)$$

where ϱ is the density, V the molar volume, l the thermal expansion coefficient, U the sound velocity, and C_P the specific heat at constant pressure. Γ_i is given as

$$\Gamma_i = \left[\sum_i \left(\frac{a_{ij}^2}{[A_{ij}]} + \frac{b_{ij}^2}{[B_{ij}]} \right) \right]^{-1} \quad (5)$$

ΔH_i and ΔV_i denote the changes in molar enthalpy and volume for the normal modes of the reactions.[10]

MATERIALS

Water was purified by distillation from aqueous potassium permanganate. α/ν^2 was measured to be 21×10^{-17} s^2 cm^{-1} at 25 °C in agreement with the value reported in the literature.[11]

Ethanol was Absolut Alkohol, ph.d., from De Danske Spritfabrikker, used without further purification. α/ν^2 was measured to be 52×10^{-17} s^2 cm^{-1}, to be compared with the value of 55×10^{-17} s^2 cm^{-1}, reported in the literature.[11] The difference is ascribed to impurities other than water, and was considered to be of no importance in the experiments performed.

Urea and formamide were analytically pure reagents.

EXPERIMENTAL METHODS

The ultrasonic absorption was measured in the frequency range $12 - 350$ MHz by means of a pulse technique.[12] The experimental error of α/ν^2 is 3 %. The amount of liquid required for the measurements is approximately 50 cm^3 at the frequencies $12 - 52$ MHz, and 10 cm^3 at the higher frequencies.

The ultrasonic velocity at 3.6 MHz was measured by means of a sing-around equipment from NUS Corporation, New Jersey, used in connection with a differential cell. The velocities in the mixtures are measured relative to the velocity in pure water, 1497 ms^{-1}.[11] The experimental error is less than ± 0.5 ms^{-1}. The amount of liquid necessary for the velocity measurements is about 15 cm^3.

Densities were measured with a digital densimeter, DMA02, available from Anton Paar, Austria. The temperature control was ± 0.005 °C, which allows the densities to be measured with an accuracy of $\pm 10^{-5}$ gcm^{-3}.

Shear viscosities at 25 °C were measured with a capillary viscometer.

All measurements were made at 25 ± 0.1 °C.

NUMERICAL METHODS

We assume that the measurements of α/ν^2 can be described by two relaxation processes:

$$f(\nu) = \frac{\alpha}{\nu^2} = \frac{A_1}{1 + (2\pi\nu\tau_1)^2} + \frac{A_2}{1 + (2\pi\nu\tau_2)^2} + B \quad (6)$$

This expression contains five parameters, namely the background absorption B, the relaxation amplitudes A_1 and A_2, and the relaxation times τ_1 and τ_2. These parameters are estimated by minimizing the least squares expression

$$s^2(A_1,A_2,\tau_1,\tau_2,B) = \sum_{i=1}^{n} \left(f(\nu_i) - \frac{\alpha_i}{\nu_i^2} \right)^2$$

where n is the number of experimental measurements, and α_i is the measured absorption coefficient for the frequency ν_i.

The minimum is determined by guessing values of the nonlinear parameters τ_1 and τ_2, and, for each guess, determining the values of the linear parameters A_1, A_2 and of B which minimize s^2. The method is described in Ref. 13, section 27.5. The minimum of s^2 with respect to the two nonlinear parameters is found by a random search strategy. This method is not as efficient as a Newton-like iteration, but to our experience much more robust. The values of the parameters in the minimum are called $A_1,^*$ $A_2,^*$ $B,^*$ $\tau_1,^*$ and $\tau_2.^*$ In order to test the reliability of the results, we estimate the variances and covariances of the estimated parameters. The moment matrix is computed as follows [14]

$$\mathbf{M}_{k,l} = \sum_{i=1}^{n} \left(\frac{\partial f(\nu_i)}{\partial \beta_k} \bigg|_{\beta=\beta^*} \right) \times \left(\frac{\partial f(\nu_i)}{\partial \beta_l} \bigg|_{\beta=\beta^*} \right)$$

where

$\beta = (A_1,A_2,\tau_1,\tau_2,B)$ and
$\beta^* = (A_1^*,A_2^*,\tau_1^*,\tau_2^*,B^*)$,

and the variance of the parameters β_k estimated by

$$V(\beta_k) = \frac{\delta^2(\beta^*)}{n-r} C_{k,k}$$

where r is the number of parameters, in the present case 5. $C_{k,k}$ are the diagonal elements of the covariance matrix $C_{i,j}$, which is the inverse of $M_{k,l}.$ [15] The covariance of the parameters β_k β_l is given by

$$\text{Cov}(\beta_k\beta_l) = \frac{S^2(\beta^*)}{n-r} C_{k,l}$$

where $C_{k,l}$ are the off diagonal elements of the covariance matrix.

Because of the covariance between the parameters, it is inconsistent to use the square roots of the estimated variances as reliability interval for more than one parameter. The small number of measurements implies that the estimated variances indicate no more than order of magnitude.

The computer program has been satisfactorily tested on simulated data with a normally distributed pseudorandom noise.[16]

RESULTS

The frequency dependence of α/ν^2 is shown in Figs. 1 and 2 for five concentrations of
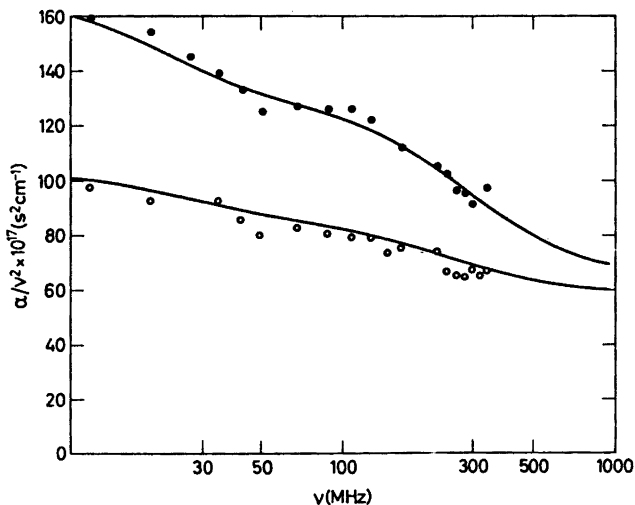

Fig. 1. Relaxation spectra of ethanol−water mixtures. ○, $w=0.3$; ●, $w=0.4$. w is the weight fraction of ethanol.
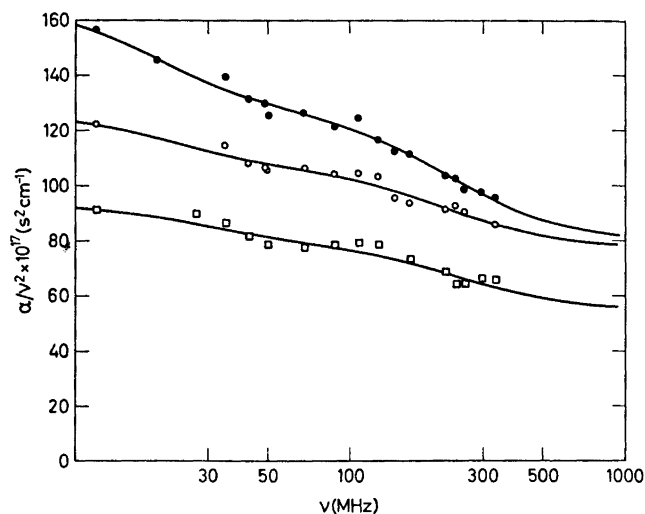
Fig. 2. Relaxation spectra of ethanol—water mixtures. ●, $w=0.5$; ○, $w=0.6$; □, $w=0.7$. w is the weight fraction of ethanol.

alcohol in water. The curves shown on the figures are calculated by fitting the experimental data to eqn. (6).

The values determined of A_i, $\mu_{max,i}$, τ_i, and B are given in Table 1, and presented as functions of concentration in Figs. 3 and 5.

From the ultrasonic velocity at the frequency 3.6 MHz, U, and the density ϱ the isentropic compressibility β_s is calculated as

$$\beta_s = (\varrho U^2)^{-1} \tag{7}$$

Values of U and β_s for a series of ethanol-water mixtures are shown in Fig. 4.

The background parameter B and the classical absorption $(\alpha/\nu^2)_{class}$, calculated as [10]

$$(\alpha/\nu^2)_{class} = \frac{8\pi^2}{3\varrho \overline{U^3}} \eta_s \tag{8}$$

where η_s is the shear viscosity, are shown in Fig. 5 as functions of concentration. This figure also includes the graphs of α/ν^2, measured at the frequencies 12 and 350 MHz. From this figure it is seen that the values of $(\alpha/\nu^2)_{class}$ do not account for the values obtained for B. The observation that B exhibits a distinct maximum at $w=0.4$ suggests that more than two relaxation processes are involved. The data do not, however, allow any analysis in terms of more than two relaxation times.

The thermodynamic data, measured for the alcohol-water mixtures, are summarized] in Table 2.

Fig. 6 presents supplementary measurements of α/ν^2, made on aqueous solutions of urea and formamide, and mentioned in the discussion.

Table 1a. Relaxation parameters of ethanol-water mixtures at 25°C. V denotes the variances of the parameters.

x	w	$\tau_1 10^9$ (s)	$V(\tau_1) 10^9$ (s)	$\tau_2 10^9$ (s)	$V(\tau_2) 10^9$ (s)	$A_1 10^{17}$ (s² cm⁻¹)	$V(A_1) 10^{17}$ (s² cm⁻¹)	$A_2 10^{17}$ (s² cm⁻¹)	$V(A_2) 10^{17}$ (s² cm⁻¹)
0.48	0.70	5.4	4.1	0.6	0.5	15	24	24	47
0.37	0.60	7.1	5.4	0.7	0.4	21	32	29	37
0.28	0.50	8.0	2.7	0.7	0.2	40	23	47	29
0.21	0.40	7.2	2.6	0.5	0.2	43	28	63	75
0.14	0.30	5.9	3.7	0.6	0.4	19	25	26	43

Table 1b. Values of μ_{max} and B for ethanol-water mixtures at 25 °C. V denotes the variances of the parameters.

x	w	$\mu_{max, 1}10^4$	$\mu_{max, 2}10^4$	$B\ 10^{17}$ (s^2cm^{-1})	$V(B)\ 10^{17}$ (s^2cm^{-1})
0.48	0.70	3.0	41.9	55	14
0.37	0.60	3.3	49.2	77	10
0.28	0.50	5.9	82.5	79	8
0.21	0.40	7.3	147.1	64	24
0.14	0.30	4.1	55.3	58	8

DISCUSSION

The concentration dependence of α/ν^2, measured for ethanol-water mixtures (Figs. 1, 2, and 5), is qualitatively similar to the one observed for tertiary butanol-water mixtures,[3] characterized by a maximum in the water-rich concentration range. A similar behavior is observed for alkylamines,[4] and in some cases

it has been ascribed to the protolysis of the amino group.[17] Our reasons for suggesting that these relaxation phenomena reflect interactions between the nonpolar groups and water are the following: *1.* A maximum of α/ν^2 is generally observed in aqueous solutions of substances containing nonpolar groups,[1-4,18,19] but it is absent in aqueous solutions of urea [20,21] and formamide (Fig. 6). The maximum is more
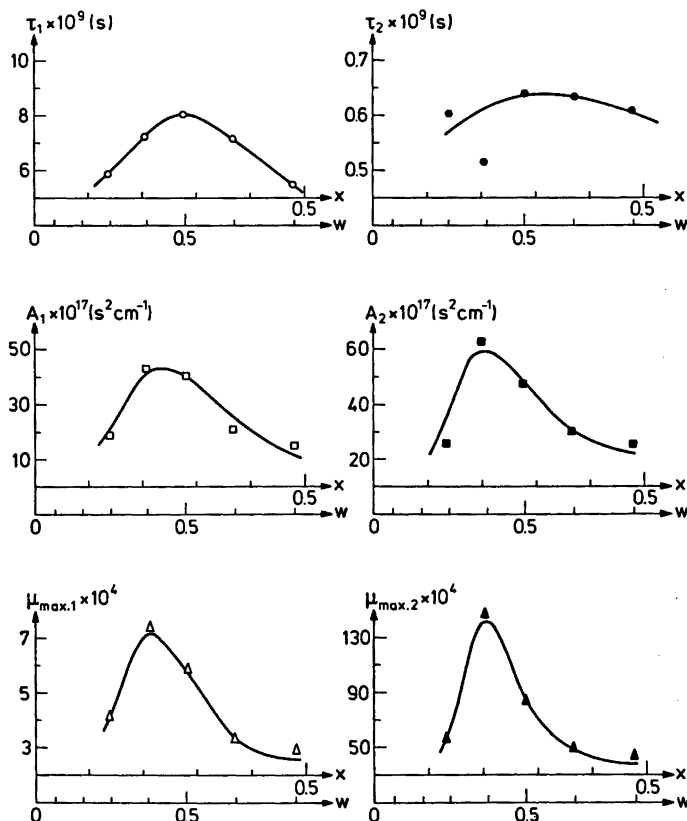

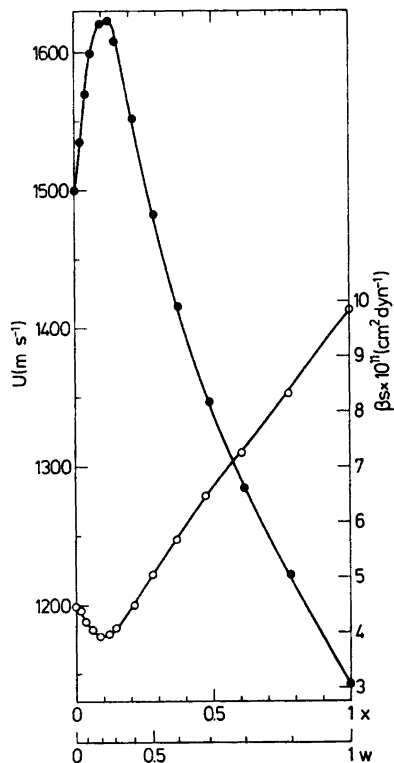*Fig. 3.* The dependence of the relaxation parameters on the mol and weight fraction of ethanol.

Fig. 4. Ultrasonic velocities and compressibilities of various ethanol-water mixtures. $\bullet, U$; $\bigcirc, \beta_s$.

Fig. 5. Ultrasonic absorption properties of ethanol-water mixtures as functions of the ethanol concentration. $\blacksquare$, α/ν^2 at 350 MHz; $\square$, α/ν^2 at 12 MHz; $\bigcirc$, B; $\bullet$, $(\alpha/\nu^2)_{\mathrm{class}}$.

pronounced the larger the nonpolar part of the nonaqueous component.[4] 2. The maximum is located in the water-rich concentration range, and at lower concentrations, the larger the nonpolar group.[4] This observation is in qualitative accordance with the conclusion reached elsewhere,[5,6,8] that interactions between nonpolar groups and water are cooperative, involving a rather large number of water molecules per methyl group. 3. The intensity of the absorption per wavelength a the relaxation frequency, $\mu_{\max}$, is, most likely, a consequence of the rather unique feature of the formation of icelike water structures, that *the changes in standard enthalpy and volume of this process are of opposite sign, $\Delta H° < 0$ and $\Delta V° > 0$*; it is seen from eqn. (2) that in this case the enthalpy and the volume effect of the ultrasonic wave reinforce each other, causing changes of K in the same direction.

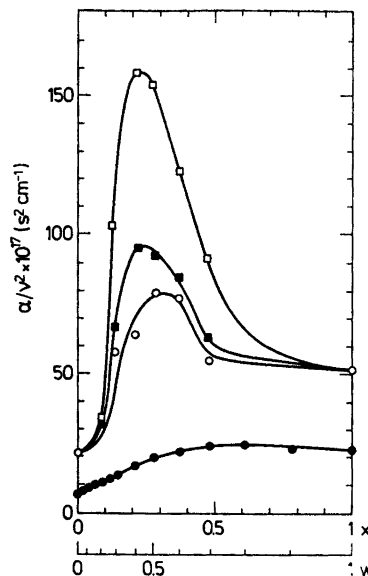The relaxations observed might tentatively

be ascribed to reactions of the type

$$A(H_2O_n) \rightleftharpoons A + nH_2O \qquad (9)$$

where A is the ethyl group of the alcohol, and $A(H_2O)_n$ denotes this group surrounded by n molecules of "icely" structured water. In this case the location of the maximum of the relaxation strength, and the corresponding maximum of the relaxation time at the mol fraction $x = 0.2 - 0.3$ should be taken as evidence, that $n = 3 - 4$.[2] This value of n is in accordance with the formation of the linear or cyclic water structures discussed in Ref. 22, but it is smaller than the number of water molecules (some ten or twenty, possibly more) interacting with a methyl group, estimated by measurements of enthalpy, entropy,[7,8] and volume[5] effects. Possible reaction mechanisms which are consistent with the available thermodynamic data as well as with the kinetic data here presented are
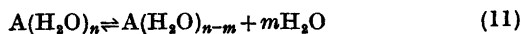
$$A(H_2O)_n + A \rightleftharpoons A + nH_2O + A \qquad (10)$$

and

$$A(H_2O)_n \rightleftharpoons A(H_2O)_{n-m} + mH_2O \qquad (11)$$

Table 2. Thermodynamic data for ethanol-water mixtures at 25 °C.

x	w	ϱ(g cm^{-3})	U(ms^{-1})	η(cP)	$(\alpha/\nu^2)_{\text{class}}10^{17}$ (s^2 cm^{-1})	$\beta_s\,10^{11}$ (cm^2 dyn^{-1})
1.00	1.00	.78515	1144	1.03	23.1	9.7
0.78	0.90	.81399	1221		23.8	8.2
0.61	0.80	.83916	1284		24.7	7.2
0.48	0.70	.86339	1345		24.1	6.4
0.37	0.60	.89011	1416	2.14	22.3	5.6
0.28	0.50	.90983	1481	2.25	20.1	5.0
0.21	0.40	.93252	1549	2.28	17.4	4.5
0.14	0.30	.95090	1604	2.10	14.1	4.1
0.12	0.25	.95966	1619		12.5	4.0
0.09	0.20	.96660	1615	1.74	11.3	3.9
0.06	0.15	.97352	1596		10.0	4.0
0.04	0.10	.98053	1566	1.27	8.9	4.2
0.02	0.05	.98812	1533		7.9	4.4
0.00	0.00	.99705	1497	0.89	7.0	4.5

In (10) it is assumed that the relaxations observed, with relaxation times of the order of $10^{-9}-10^{-8}$ s, are due to reactions of the type (9), catalyzed by non-solvated alcohol molecules. If so, the maximum of the relaxation parameters shall be located at mol fractions of alcohol larger than $1/(n+1)$, and the experimental data thus corresponds to a value of n larger than 4.

The reaction (11) suggests that the formation of icelike water structures around the nonpolar groups proceeds in several distinguishable steps.

A comparison between Figs. 3, 4, and 5 shows that the maximum of the ultrasonic velocity (and the corresponding minimum of the compressibility) is located at a mol fraction of alcohol, which is lower than that of the maximum of the ultrasonic absorption. A similar observation, made for aqueous solutions of acetone, has been taken as evidence that the velocity peak could be used as a measure of the breakdown of a water structure, while the absorption peak could be used as a measure of a complex formation.[2] We wish to point out that different locations of these extrema do not necessarily involve that they shall be ascribed to different kinds of reactions. The location of the velocity peak is determined, not only by the number of moles of the reac-
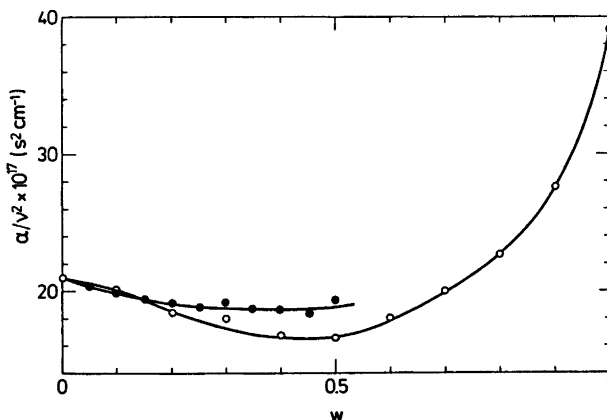

Fig. 6. The concentration dependence of α/ν^2 at 36 MHz for formamide-water (O) and urea-water (●) mixtures.

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tants involved in the reaction reflected, but also by the absolute values of the ultrasonic velocity in the different structures, and by differences of the molar volumes. In the case of the ethanol water mixtures studied here, we tentatively suggest that the relaxation phenomena observed in the frequency range 12 – 350 MHz are all due to the same reaction, namely the formation of ice-like water structures around the nonpolar groups.

REFERENCES

1. Storey, L. R. O. *Proc. Phys. Soc. 65* (1952) 943.
2. Andreae, J. H., Edmonds, P. D. and McKellar, J. F. *Acustica 15* (1965) 74.
3. Blandamer, M. J., Clarke, D. E., Hidden, N. J. and Symons, M. C. R. *Trans. Faraday Soc. 64* (1968) 2691.
4. Blandamer, M. J. In Franks, F., Ed., *Water, A Comprehensive Treatise*, Plenum, New York 1973, p. 495.
5. Bøje, L. and Hvidt, Aa. *J. Chem. Thermodyn. 3* (1971) 663.
6. Frank, H. S. and Evans, M. J. *J. Chem. Phys. 13* (1945) 507.
7. Franks, F. and Ives, D. J. G. *Quart. Rev. Chem. Soc. 20* (1966) 1.
8. Kauzmann, W. *Advan. Protein Chem. 14* (1959) 1.
9. Lumry, R. and Rajender, S. *Biopolymers 9* (1970) 1125.
10. Eigen, M. and de Mayer, L. In Weissberger, A. *Technique of Organic Chemistry*, Interscience, New York – London 1963, p. 895.
11. Schaaffs, W. In Landolt-Börnstein, Group II, Vol. 5, *Molecular Acoustics*, Springer, Berlin 1967.
12. Rassing, J. *Hydrogenbindingskinetik og relaksationsspektrometri*, Thesis, University of Copenhagen, Copenhagen 1971.
13. Hamming, R. W. *Numerical Methods for Scientists and Engineers*, 2nd Ed., McGraw, New York 1973.
14. Cramér, H. *Mathematical Methods of Statistics*, Princeton University Press, Princeton 1946.
15. Rao, C. R. *Linear Statistical Inference and its Applications*, Wiley, New York 1965.
16. Abramowitz, M. and Stegun, A. *Handbook of Mathematical Functions*, Dover, New York 1965.
17. Nishikawa, S. *Bull. Chem. Soc. Jap. 46* (1973) 1657.
18. Hammes, G. G. and Knoche, W. *J. Chem. Phys. 45* (1966) 4041.
19. Sasaki, K. and Arakawa, K. *Bull. Chem. Soc. Jap. 46* (1973) 2738.
20. Hammes, G. G. and Schimmel, P. R. *J. Amer. Chem. Soc. 89* (1967) 442.
21. Arakawa, K. *Bull. Chem. Soc. Jap. 43* (1970) 636.
22. Symons, M. C. R. *Nature (London) 239* (1972) 257.