Insights into solute–solute–solvent interactions from transport property measurements with particular reference to methanol–water mixtures and their constituents

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Abstract - Interactions in methanol-water solutions and in the pure
components are examined using experimental measurements of (a) self-
diffusion of the pure components and isotopic forms of them, (b) diffusion
of both components in the mixture including some measurements for trace
amounts of methanol in water at high pressure, (c) excess thermodynamic
properties and (d) shear viscosities of the mixtures under pressure.

There are indications that the diffusing water particle is, on average,
multi-molecular and that the number of constituent molecules depends on
temperature and pressure. Incorporation of methanol molecules into the
water structure seems to continue to about 25-30 moles percent methanol,
depending on pressure, before the structure is saturated. At higher
compositions the data indicate a progressive disintegration of the water
network. At high methanol compositions the water molecule appears to be
solvated.

INTRODUCTION

Liquid water, at least at temperatures below its normal boiling point, is known to be an
extremely complex fluid with its properties strongly determined by extensive intermolecular
interactions. These are conventionally described as hydrogen bonds and the molecules of
liquid water are thought to be associated by these bonds to varying extents into an
extensive three-dimensional network. The lower alcohols, on the other hand, while also
known to have hydrogen-bonding interactions, are unable to form the three-dimensional
network characterising water but can associate into chains or rings.

Mixtures of a lower alcohol and water therefore provide a particularly complex system
except, perhaps, at the two extremes of the composition range. The situation is complicated
additionally - at least for some properties - by the partial dissociation of both
constituents enabling an exchange of protons between them. Although the transport and
thermodynamic properties of such mixtures have long been known to be anomalous, particularly
from measurements of the shear viscosity, it is now possible to measure the effect of
pressure on some of the transport and thermodynamic properties. The use of pressure as a
variable provides another avenue into the slow process of gaining an insight into the
complex solute-solute and solute-solvent interactions.

This paper principally is concerned with the results of recent measurements made in our
laboratory on methanol-water mixtures and the pure components. These measurements include
the diffusion at atmospheric and higher pressures including isotope effects, the effect of
pressure on the volumes (and derived thermodynamic properties) of the mixtures and some
shear viscosity measurements.

DIFFUSION OF THE PURE COMPONENTS AND ISOTOPE EFFECTS

Water

The diffusion of pure water has been measured usually by either nuclear (proton) magnetic
resonance or the use of isotopic labelling (^3H, ^2H). Measurements (shown in Fig. 1) by our
research group have established that the effect of pressure at temperatures below about
300 K is initially to increase the rate of diffusion up to pressures of about 100 MPa (ref.
1-4). The effect of isotopic substitution of the proton has been shown to be complex since
there is evidence to suggest that there are differences in the strength of intermolecular
hydrogen, deuterium or tritium bonds. There is some indication that rotation of the water
molecule is influential but it is likely that the effect of pressure on the three dimen-
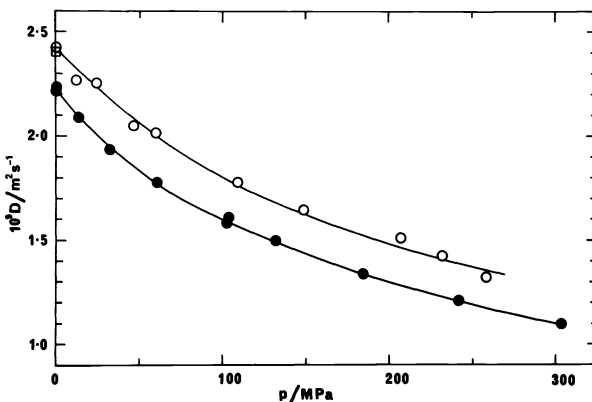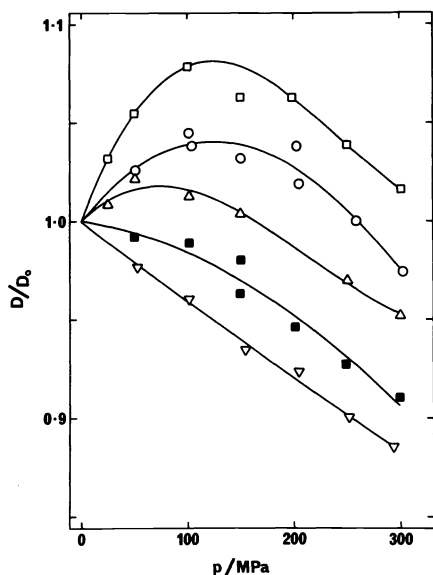sional network is the dominating feature.

Fig. 2. Self-diffusion in methanol (circles) and
methan-d-ol (filled circles) under pressure at
298 K.

← Fig. 1. Self-diffusion coefficient of water under
pressure relative to its value at 0.1 MPa:
squares, 277 K; circles, 283 K; triangles,
298 K; filled squares, 318 K; inverted
triangles, 333 K.

It has been found that the effect of isotopic substitution of ^{18}O on self-diffusion of water
(ref. 4) follows the classical square root of the mass dependence (typical of model hard
sphere fluids) over a wide temperature and pressure range

$$D_S(H_2^{16}O)/D_S(H_2^{18}O) = [m(H_2^{18}O)/m(H_2^{16}O)]^{\frac{1}{2}} = 1.05_5 \qquad (1)$$

The implication of these results is that differences in diffusional behaviour of $H_2^{16}O$ and
$H_2^{18}O$ are due only to the effect of the different masses. That is, there is no effect of
the isotopic substitution on the intermolecular hydrogen bonds. Consequently a true isotope
effect for water can be determined by comparing the tracer diffusion coefficient of $H_2^{18}O$ in
$H_2^{16}O$ with the self-diffusion coefficient of $H_2^{16}O$.
Very recently we have made measurements of the tracer diffusion of $H_2^{18}O$ in ordinary water,
(ref. 5) taken here as $H_2^{16}O$, in which the analysis was made using an extremely precise (1
in 30,000) mass spectrometric isotope ratio technique. These data were combined with
earlier n.m.r. measurements (ref. 4) for self-diffusion of $H_2^{16}O$ to provide numerical values
for the isotope effect. A theoretical estimate of the effect can be obtained from classical
theory in terms of the particle masses m_i

$$D_R = D(H_2^{18}O)/D(H_2^{16}O) = [\mu(H_2^{16}O)/ \mu(H_2^{18}O]^{\frac{1}{2}} \qquad (2)$$

$$\mu(i) = m_i m_j/(m_i + m_j) \qquad (i = H_2^{16}O; \quad j = H_2^{18}O)$$

An assumption that diffusion of water proceeds by movement of single molecules gives $D_R =$
0.9749, about 1% smaller than the experimental result. Easteal, Edge and Woolf (ref. 5)
speculated that the difference between the experimental and predicted values of D_R was due
to the diffusing water particle comprising more than one molecule. Their analysis of the
data is summarised in Table 1.

TABLE 1. Average number of water molecules, n, in diffusing water particles

T/K	n	T/K	p/MPa	n
278.4	1.8	323.1	0.1	1.7
288.2	2.8		51	2.8
298.2	3.0		129	3.1
313.1	2.2		262	1.6
323.1	1.7			

Methanol

Nuclear magnetic resonance and isotope (^{14}C) measurements of diffusion of pure methanol and methan-d-ol (ref. 6) have shown that there is no apparent pressure-induced anomaly in the self-diffusion of methanol. The studies have also shown a pronounced effect on the diffusional behaviour resulting from isotopic substitution of the hydroxyl proton by deuterium (Figure 2). The effect does not follow the classical mass dependence and is closely related to the moment of inertia about the principal axis of the molecule and indicates that rotation of the -OH (or -O^{2}H) group has a major influence on the diffusional behaviour, possibly by affecting the coupling of rotational and translational motion. It is also likely that there are differences in hydrogen and deuterium bond strengths in methanol and methan-d-ol.

To measure isotope effects in methanol separate from (possible) changes in hydrogen bond strengths requires self-diffusion data for ^{18}O-substituted methanol and (should $D_S(CH_3{}^{18}OH)/D_S(CH_3{}^{16}OH)$ follow the classical behaviour represented by equation (1)) tracer diffusion data for $CH_3{}^{18}OH$ in CH_3OH. These data are not yet available but should provide some indication of the number of molecules comprising the average diffusing particle.

Rough Hard Spheres Model

The high pressure self-diffusion data for methanol and water have been examined using a rough hard spheres model based on that of Chandler (ref. 7,8). The model relates the measured self-diffusion coefficient D_S to that of a simulated model hard sphere fluid D_{SHS} by using a factor A_{11} which allows for coupling of translational and rotational momentum; (A_{11} = 1 when there is no coupling)

$$D_S = A_{11} \ D_{SHS} \qquad (0 < A_{11} \leq 1) \tag{3}$$

There is a rapid decrease of $(1-A_{11})$ with increasing temperature for both methanol (ref. 6) and water (ref. 9). In contrast to methanol, for which $(1 - A_{11})$ does not change significantly with pressure at constant temperature, the values for water decrease with increasing pressure, reflecting the effect of pressure on the three dimensional network. (Jonas and Akai (ref. 10) have related such variations in $(1 - A_{11})$ to a decrease in the proportion of hydrogen bonds in the liquid.)

DIFFUSION IN METHANOL-WATER MIXTURES

The diffusion of a tracer amount of methanol in otherwise pure water produces a diffusion coefficient which has a remarkable variation with pressure at temperatures below 298 K (ref. 11) as shown in Fig. 3. At 278 K, particularly, increase in pressure clearly enhances the freedom of movement of the methanol particles. The obvious implication is that the association between the water structure and methanol molecules is not as strong as that between water molecules and consequently distortion of the structure by pressure has a greater effect on the methanol-water interactions. Some authors have suggested that ethanol enhances the open network structure of water and Angell (ref. 12) has proposed that in alcohol-water systems the alcohol molecules are located in the most open, highly structured microregions of the water and these are most effected by increase in pressure. At the other end of the concentration range, in pure methanol, there are also interesting features of the tracer diffusion of pure water and the self-diffusion of methanol (see Table 2).

Although the effective hard sphere diameter (~ 0.284 nm at 298 K) of the water molecule is about 20 percent less than that of methanol (~ 0.364 nm at 298 K) and its mass some 50 percent smaller, the tracer diffusion coefficient of water in pure methanol is substantially smaller than the methanol self-diffusion coefficient. The ratio $D(CH_3OH)/D(H_2{}^{18}O)$ decreases with increasing temperature but remains greater than unity even at 323 K. It seems, therefore, that the effective size of the water particle is substantially larger than that

TABLE 2. Diffusion coefficients in pure methanol at 0.1 MPa[a]

T/K	$D_S(^{14}CH_3OH)$	$D(H_2{}^{18}O)$	$D_S(^{14}CH_3OH)/D(H_2{}^{18}O)$
278.2	1.668	1.462	1.14
298.2	2.369	2.190	1.08
323.2	3.623	3.451	1.05

[a]Units of D: 10^{-9} m^2 s^{-1}

of the methanol particle. Since each water molecule is capable of forming two intermolecular hydrogen bonds there seems little doubt that water diffuses in (pure) methanol as a solvated species. Further knowledge of this aspect is expected to come from our impending studies of diffusion in mixtures under pressure over the complete composition range.

Proton Exchange

Because the hydroxyl proton of methanol is labile and can exchange freely with pure water protons, measurement of diffusion coefficients for water in methanol-water mixtures using n.m.r. or proton labelling (^{3}HHO, ^{2}HHO) techniques has not provided satisfactory results except at high water concentrations. For example, if tritiated water ($H^3HO = HTO$) is used as the tracer then, assuming statistical distribution of the label (T) by proton exchange, the measured diffusion coefficient in a mixture $\{x\ CH_3OH + (1-x)H_2O\}$ is

$$D_T = \frac{1}{1+x} \quad [2(1-x)\ D(HTO) + x\ D(CH_3OT)] \tag{4}$$

The recent application of the $H_2^{18}O$ tracer technique mentioned earlier has, however, enabled simultaneous accurate measurements of the intra-diffusion coefficients of both components (H_2O, CH_3OH) in the mixtures (ref. 13) at 278 and 298 K.

These results, shown in Fig. 4 for 298 K, have a number of interesting features. Notably, in contrast to earlier work (ref. 14) (with tritiated water as the tracer species) there is no coincidence of the two diffusion coefficients in pure methanol; the minimum in $D(CH_3OH)$ occurs at a mol fraction where the molar volume of methanol is also at a minimum; the minimum in $D(H_2^{18}O)$ is at a composition close to where the excess free energy is a maximum (ref. 15).

The diffusion data discussed earlier in this paper have shown clear distinctions between the diffusional behaviour of methanol and water related to differences in solvation of the two species and abilities to participate in the water structure. Consequently there is a question as to whether the proton exchange between methanol and water is truly statistical or favours one component. The intra-diffusion data obtained at 278 K enable a test of this question. Equation (3) can be rewritten

$$D_T = \frac{1}{1+x} \quad [2(1-x)r_2\ D(H_2^{18}O) + x\ r_1\ D(^{14}CH_3OH)] \tag{5}$$

with

$$r_1 = D(CH_3OT)/D(^{14}CH_3OH) \qquad (= 0.9694)$$

$$r_2 = D(HTO)/D(H_2^{18}O) \qquad (= 0.9815) \tag{6}$$

The r_1 represent the $^3H-^1H$ isotope effect and the values in parentheses are based on results in pure water (ref. 1,4,13) and pure methanol (ref. 6); they are assumed to be independent of composition. Use of this equation with measured data for the two diffusion coefficients (ref. 5) provides the predicted values compared with experiment in Table 3.
The agreement of the two sets of D(T) values (for $0 \neq x \neq 1$) is within the experimental error and indicates that the tritium probably is distributed statistically between water and methanol. (The test is not, however, sensitive and can be made to accommodate a $\pm 10\%$ variation in the distribution.)

TABLE 3. Intra-Diffusion Coefficients in $\{x\ CH_3OH + (1-x)\ H_2O\}$ at 278.15 K[a]

x	$D(^{14}CH_3OH)$	$D(H_2^{18}O)$	D_T expt.	eqn.
0	0.881	1.298	1.273	1.273
0.050	0.709	1.254		
0.100	0.624	0.851		
0.200	0.576	0.686		
0.300	0.566	0.659	0.631	0.629
0.400	0.631	0.688		
0.500	0.719	0.741		
0.600	0.825	0.823	0.801	0.804
0.700	0.969	0.918		
0.800	1.152	1.067	1.096	1.094
0.900	1.375	1.186		
1.000	1.668	1.462	1.617	1.617

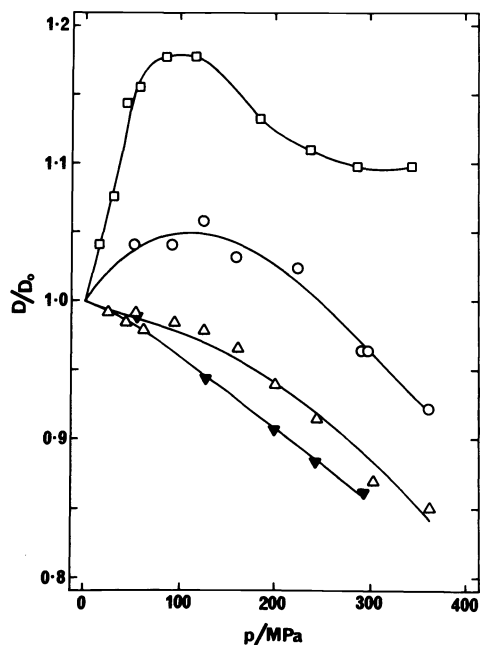[a]Units of D: 10^{-9} m^2 s^{-1}

Fig. 3.   Tracer diffusion of methanol in
   water under pressure: squares, 278 K;
   circles, 288 K; triangles, 298 K;
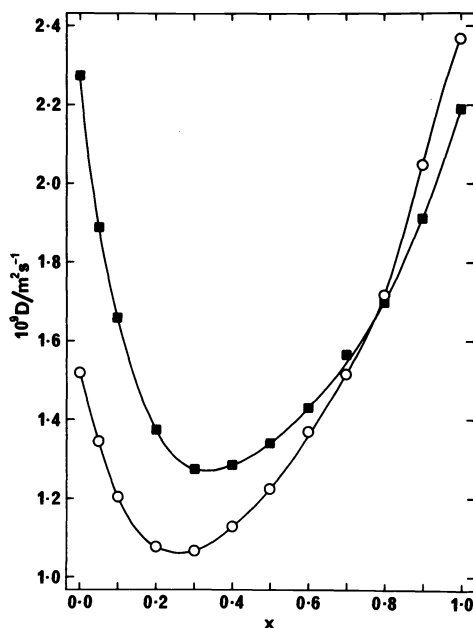   filled inverted triangles, 313 K

Fig. 4.   Diffusion of water (filled
   squares) and methanol (circles) in
   methanol-water mixtures at 298.15 K
   and 0.1 MPa

MUTUAL DIFFUSION;   VELOCITY CORRELATION COEFFICIENTS

Mutual (binary) diffusion coefficients D_{12} and intradiffusion D(1), D(2) coefficients have
been measured recently for methanol(1)-water(2) solutions at 298.15 K using the diaphragm
cell technique (ref. 16).   The results are given in Table 4 with activity coefficient
derivatives $\partial \ln a_i / \partial \ln x_i$ calculated from the data of Butler et al. (ref. 17).   These data
enable calculation of the velocity correlation coefficients for the system.

For a mixture of two non-electrolytes the velocity correlation approach relates the measured
diffusion coefficients to integrals of averages of particular combinations of the velocities
of the diffusing particles and defines velocity correlation coefficients f_{ij} representing,
in the present case, interactions between methanol-methanol (f_{11}), water-water (f_{22}) and
methanol-water (f_{12}).   In principle the velocities can be obtained by computer simulation
should a suitable intermolecular potential function be available.   (The equations used here

TABLE 4.   Tracer and mutual diffusion coefficients in {x CH_3OH + (1-x) H_2O
           at 298.15 K[a]

x	D($^{14}CH_3OH$)	D($H_2^{18}O$)	D_{12}	$\partial \ln a_1 / \partial \ln x_1$
0	1.563	2.275	1.563	1.00
0.05	1.346	1.889	1.369	0.992
0.1	1.205	1.656	1.249	0.972
0.2	1.078	1.374	1.086	0.839
0.3	1.068	1.273	1.002	0.736
0.4	1.129	1.285	0.986	0.677
0.5	1.225	1.341	1.047	0.690
0.6	1.369	1.431	1.190	0.776
0.7	1.517	1.566	1.396	0.889
0.8	1.718	1.698	1.643	0.929
0.9	2.049	1.912	1.913	0.958
1.0	2.369	2.190	2.19	1.00

[a]Units of D: 10^{-9} m^2 s^{-1}

are based on those of Mills and Hertz (ref. 18) converted to refer to mol fractions and using $D(i)$ to represent the intra-diffusion coefficient and f_{ii}^* the corresponding velocity correlation coefficient.)

$$f_{ii}^* = \frac{1000 \, Lx_i}{3} \int_0^\infty \langle v_1^{(i)}(0) \cdot v_1^{(i)}(t) \rangle \, dt = D(i) \qquad (i = 1,2) \qquad (7)$$

$$f_{ii} = \frac{1000 \, Lx_i}{3} \int_0^\infty \langle v_1^{(i)}(0) \cdot v_2^{(i)}(t) \rangle \, dt$$

which gives

$$f_{ii} = \left\{ D_{ij} \bigg/ \frac{(x_1M_1 + x_2M_2)^2}{M_j^2 \, x_j} \quad \frac{\partial \ln a_i}{\partial \ln x_i} \right\} - D(i)$$

$$(i,j = 1,2; \ i \neq j) \qquad (8)$$

$$f_{12} = \frac{1000 \, Lc_2}{3} \int_0^\infty \langle v_1^{(i)}(0) \cdot v_1^{(j)} \rangle \, dt$$

$$= - D_{12} \bigg/ \frac{(x_1M_1 + x_2M_2)^2}{M_1M_2x_2} \quad \frac{\partial \ln a_1}{\partial \ln x_1} \qquad (9)$$

here $v_i^{(j)}(0)$ denotes the velocity of particle i of component j at an arbitrary time t=0.

The velocity correlation coefficients are shown in Fig. 5. The present results are qualitatively similar to the less reliable values of Hertz and Leiter (ref. 19) but near x=1, f_{22} becomes positive. Hertz and Leiter considered that positive f_{22} values indicated water-water association, although this seems unlikely particularly at such high methanol concentrations where the relative values of $D(CH_3OH)$ and $D(H_2O)$ (see Table 2) indicate solvation of the water particles. The interpretation of velocity correlation coefficients is presently in a relatively undeveloped stage (ref. 20) and probably awaits the availability of extensive computer simulation data to provide a set of standard coefficients.

EFFECTS OF PRESSURE

Thermodynamic Properties

Easteal and Woolf (ref. 15) have measured p-V-T properties for methanol-water mixtures between 278.15 and 323.15 K up to 280 MPa. They calculated values for the molar volumes, isothermal compressibility, thermal expansivity, and excess thermodynamic properties (ref. 21). At low temperatures and pressure, the partial molal volume for methanol has a strong minimum which decreases with increasing temperature or pressure up to about 0.25 mol fraction of methanol. The partial molal volume of water has a maximum with increasing pressure at constant temperature and its pressure dependence increases with temperature. The excess molar entropy S_m^E is negative across the composition range and has a minimum between x = 0.25 and x = 0.35; either increase in pressure or temperature or methanol mol fraction (above x = 0.35) increases the S_m^E. The effect of pressure on the excess molar Gibbs energy is shown in Fig. 6 where a comparison is made with acetonitrile-water mixtures. The small pressure dependence for acetonitrile-water is such that the 0.1 MPa values are only slightly greater than at 200 MPa. In the alcohol system pressure clearly has a much stronger influence. On the basis of these results, Easteal and Woolf proposed that at low temperatures and pressures addition of methanol to water up to about 25 to 30 moles percent caused a modification of the hydrogen-bonded water network by accommodation of the alcohol inside cavities accompanied by formation of water-methanol hydrogen bonds. The effect of pressure was considered to cause disruption or distortion of those bonds and hence to explain the major differences observed between similar properties in systems such as acetonitrile-water. An additional effect of pressure (on the thermal expansivity) at 323 K near 80 moles percent methanol was thought to be due to clathrate formation.
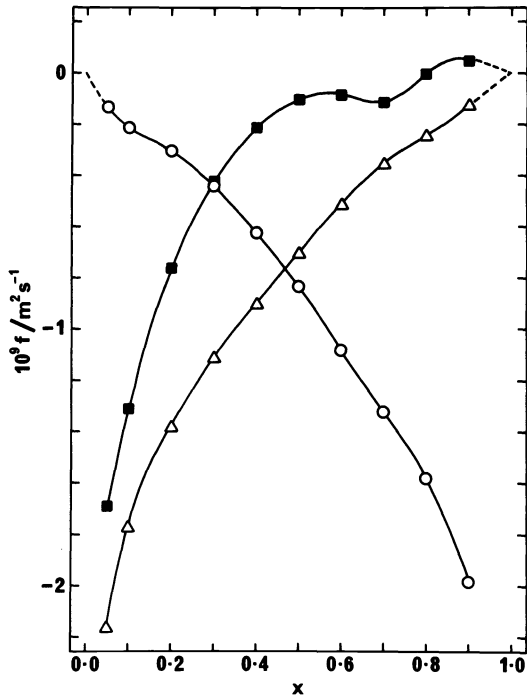
Fig. 5. Velocity correlation coefficients in methanol-water mixtures at 298.15 K and 0.1 MPa: circles, f(methanol-methanol); filled squares, f(water-water); triangles, f(methanol-water).
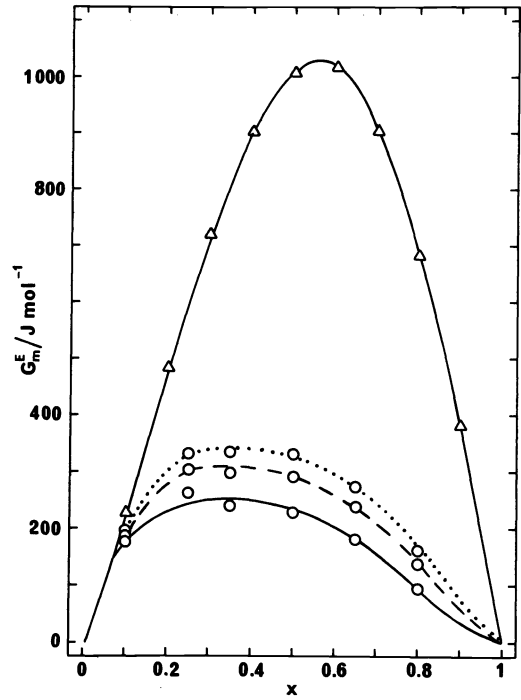

Fig. 6. Excess molar Gibbs energy at 298 K for acetonitrile-water at 250 MPa (triangles) and methanol-water 0.1 MPa (dotted line), 50 MPa (dashed line), 250 MPa (solid line).
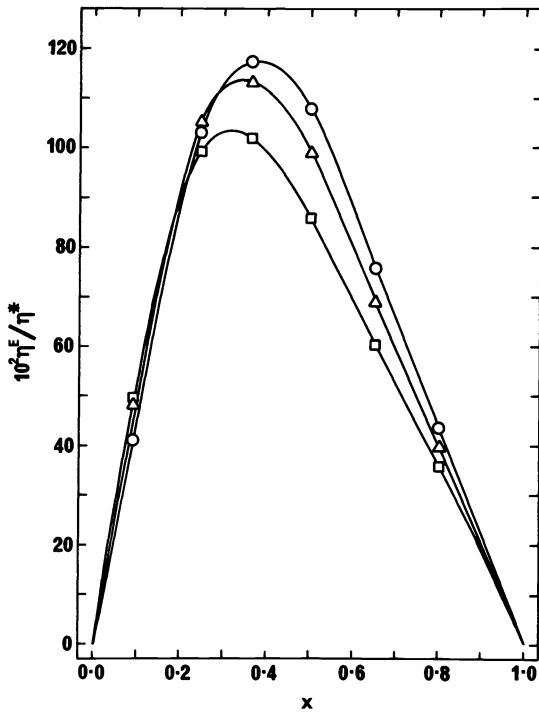

Fig. 7. Excess shear viscosity for methanol-water mixtures at 298.15 K; squares 0.1 MPa; triangles, 100 MPa; circles, 300 MPa (for definition of excess viscosity see eqn. (10)) and (11) and allied text).

Shear Viscosity

Isdale and Woolf (ref. 22) have measured the shear viscosity, η, of methanol-water solutions at 298 K for pressures up to 300 MPa. The principal features of the results are shown in Fig. 7 using excess shear viscosities η^E

$$\eta^E = \eta - \eta^* \tag{10}$$

$$\eta^* = \eta_2 + (\eta_1 - \eta_2)x \tag{11}$$

where η_i (i=1,2) denotes the viscosity of pure i at the same temperature and pressure as the measured η. The maximum in the excess shear viscosity increases slightly with increase in pressure which also shifts the maximum to higher methanol compositions. These results provide additional evidence for the explanations proposed earlier to describe composition dependence of the diffusion results at 0.1 MPa and pressure dependence of thermodynamic properties. The progressive incorporation of the methanol molecules into the water structure up to about 25-30 moles percent is clearly assisted by increase in pressure. Above that composition the results indicate a progressive breakdown of the structure with increasing methanol concentration.

ACKNOWLEDGEMENT

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