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THERMODYNAMICS OF AQUEOUS MIXTURES OF NONELECTROLYTES. V. ISOBARIC HEAT CAPACITIES AND ULTRASONIC SPEEDS FOR WATER + ETHANENITRILE MIXTURES AT 25°C *

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ABSTRACT

Volumetric heat capacities and ultrasonic speeds were measured at 25°C for water + ethanenitrile mixtures over the entire mole fraction range using a flow microcalorimeter and pulse-echo-overlap equipment, respectively. Excess volumes and coefficients of thermal expansion reported previously were used in conjunction with the present data to yield isobaric and isochoric heat capacities, and isentropic and isothermal compressibilities. The present study supports the view that ethanenitrile acts as a structure breaker.

INTRODUCTION

In Part IV of this series [1] we reported excess volumes as a function of mole fraction at 5° intervals of temperature from 15°C to 35°C for binary mixtures of water with ethanenitrile. From these results the excess coefficient of thermal expansion at 25°C was obtained as a function of mole fraction. The present paper reports measurements of volumetric heat capacities at constant pressure and of ultrasonic speeds for the same system over the entire mole fraction range. Thus the two studies together yield results for isobaric and isochoric heat capacities and for isentropic and isothermal compressibilities at 25°C.

EXPERIMENTAL

The source and purification of ethanenitrile, and its densities at 5° intervals of temperature from 15°C to 35°C were reported in the previous paper [1]. Deionized distilled water was used and its volumetric properties, which were assumed to be those of SMOW (Standard Mean Ocean Water), were calculated from the equation given by Kell [2].

For the heat capacity measurements mixtures were prepared by mass. In

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calculating the mole fraction, corrections were applied for the effect of buoyancy and for the water content of the ethanenitrile. The error of the mole fraction is estimated to be less than 5×10^{-5}. The heat capacities were measured in a Picker flow microcalorimeter using a temperature increment of about 1.5° centred on 25°C. Details of the apparatus and its operational procedure have been described previously [3,4]. The measurement yields the difference of the volumetric heat capacities of the two liquids flowing in the test and reference cells. Water was used as a starting reference and a value of 75.292 J K^{-1} $mole^{-1}$ was adopted for its heat capacity [5]. A stepwise procedure was followed in which each liquid (pure or a mixture) after measurement served as a reference for the subsequent liquid. In order to minimize errors due to mixing effects and the errors inherent in the stepwise procedure, measurements on mixtures with the same mole fractions were repeated with the test and reference liquids interchanged. The results were corrected for power losses. Volumetric heat capacities, $C_{p,m}/V_m$, were converted into molar heat capacities, $C_{p,m}$, using molar volumes, V_m, from our previous study [1]. The error of the molar excess isobaric heat capacities, $C^E_{p,m}$, is estimated to be less than 0.05 J K^{-1} $mole^{-1}$.

A pulse-echo-overlap method [6] was used to measure ultrasonic speeds at atmospheric pressure and a frequency of 3 MHz in a successive dilution mixing cell [7]. Water was used as a reference and a value of 1496.739 m s^{-1} [8] was adopted for the speed of ultrasound in it at 25°C. The error of the relative ultrasonic speeds is estimated to be less than 0.2 m s^{-1}; the reproducibility of the measurement is 10 times better. The error of the composition of the mixture is less than 0.02%.

RESULTS

A value of 91.06 J K^{-1} $mole^{-1}$ at 25°C was measured for the molar heat capacity of ethanenitrile. This agrees reasonably well with the value 91.46 J

TABLE 1

Molar excess isobaric heat capacities for x H_2O + $(1 - x)$ CH_3CN mixtures at 25°C

x	$C^E_{p,m}$ (J K^{-1} $mole^{-1}$)	x	$C^E_{p,m}$ (J K^{-1} $mole^{-1}$)	x	$C^E_{p,m}$ (J K^{-1} $mole^{-1}$)
0.02804	0.31	0.50978	8.30	0.85229	5.14
0.05477	0.94	0.55408	8.26	0.86125	4.98
0.08369	1.73	0.59986	8.05	0.87366	4.90
0.10295	2.28	0.60473	8.09	0.90088	4.53
0.12306	2.88	0.64406	7.68	0.90885	4.44
0.14691	3.66	0.69504	7.06	0.92020	4.24
0.20126	5.15	0.70117	7.06	0.93011	4.04
0.23978	6.06	0.73053	6.69	0.93918	3.79
0.30493	7.13	0.75234	6.37	0.95089	3.39
0.34028	7.54	0.77189	6.08	0.96425	2.77
0.45005	8.29	0.78434	5.93	0.97547	2.07
0.46168	8.18	0.80228	5.73	0.98531	1.31_4
0.49733	8.38	0.83086	5.34	0.99475	0.50_6

TABLE 2

Ultrasonic speeds, u, and excess coefficients of isentropic compressibility, κ_S^E, for $x\ H_2O + (1-x)\ CH_3CN$ mixtures at 25°C

x	u (m s^{-1})	κ_S^E (TPa^{-1})	x	u (m s^{-1})	κ_S^E (TPa^{-1})
0.0	1278.01	0.0	0.7494	1447.48	−187.54
0.0045	1278.59	−1.59	0.7548	1450.61	−187.72
0.0174	1280.25	−6.19	0.7792	1465.51	−187.74
0.0380	1282.89	−13.46	0.7964	1476.54	−186.86
0.0779	1287.81	−27.13	0.8074	1483.68	−185.74
0.1189	1292.73	−40.71	0.8362	1502.72	−180.65
0.1589	1297.64	−53.70	0.8648	1520.98	−171.39
0.1975	1302.64	−66.10	0.8835	1531.98	−162.61
0.2368	1307.92	−78.40	0.9030	1541.47	−150.25
0.2760	1313.51	−90.38	0.9124	1545.10	−142.91
0.3152	1319.38	−101.92	0.9224	1548.23	−134.19
0.3549	1325.73	−113.17	0.9321	1549.23	−123.99
0.3944	1332.43	−123.74	0.9467	1548.42	−106.26
0.4339	1339.60	−133.64	0.9565	1545.26	−92.12
0.4737	1347.62	−143.08	0.9662	1539.47	−75.89
0.5134	1356.49	−151.81	0.9913	1511.25	−22.58
0.5533	1366.69	−160.02	0.9933	1508.23	−17.73
0.5934	1378.49	−167.57	0.9952	1505.20	−12.95
0.6335	1392.35	−174.43	0.9971	1501.85	−7.75
0.6738	1408.78	−180.43	1.0	1496.739 *	0.0
0.7143	1428.17	−185.14			

* Adopted from ref. 8.

K^{-1} $mole^{-1}$ obtained from a linear interpolation of the data reported by Putnam et al. [9] and differs from the value 91.7 J K^{-1} $mole^{-1}$, determined more recently by de Visser et al. [10], by less than its experimental uncertainty. The results for the molar excess heat capacities of $x\ H_2O + (1-x)\ CH_3CN$ mixtures at 25°C are given in Table 1, where x represents the mole fraction of water.

Experimental values of the ultrasonic speed, u, in $x\ H_2O + (1-x)\ CH_3CN$ mixtures are listed in Table 2. Our value for u in ethanenitrile at 25°C is 1278.01 m s^{-1}; some values of u (m s^{-1}) from the literature are: 1290 ± 10 [11], 1284 [12], 1288 [13]. Blandamer et al. [14] have reported in graphical form the ultrasonic speeds in water + ethanenitrile mixtures at 0, 25, and 35°C. Their results at 25°C agree qualitatively with ours.

The coefficient of isentropic compressibility, κ_S, defined by the equation

$$\kappa_S = -V_m^{-1}(\partial V_m/\partial p)_S \tag{1}$$

was calculated from the relation

$$\kappa_S = (\rho u^2)^{-1} \tag{2}$$

where ρ is the density. Values of ρ for the pure components, and the mixtures at 25°C were obtained from our previous work [1]. The excess values, κ_S^E (as defined in ref. 15), are summarized in Table 2.

TABLE 3

Coefficients, a_j, and standard deviations, σ, for representations of $C^E_{p,m}$ and κ^E_S by eqn. (3) *

	$C^E_{p,m}$ (J K^{-1} mole^{-1})	κ^E_S (TPa^{-1})
a_1	33.288	−747.96
a_2	−1.421	63.17
a_3	5.629	−231.74
a_4	20.342	−107.80
a_5	−27.335	
a_6	−68.870	
a_7	45.584	
σ	0.04	0.31

* For $C^E_{p,m}$, $Z = x$; for κ^E_S, $Z = \phi = 18.0686x/[18.0686x + 52.8652(1-x)]$.

The results for $C^E_{p,m}$ and κ^E_S were fitted with the smoothing function

$$X^E = Z(1-Z)\sum_{j=1}^{n} a_j(1-2Z)^{j-1} \tag{3}$$

with Z equal to the mole fraction of water in the case of $C^E_{p,m}$, and Z equal to the volume fraction of water referred to the unmixed state in the case of κ^E_S. Values of the coefficients a_j were determined by the method of least-squares with all points weighted equally, and are given in Table 3 along with the standard deviations for the representations.

The molar isochoric heat capacity, $C_{V,m}$, and the coefficient of isothermal compressibility, κ_T, are related to $C_{p,m}$ and κ_S by the following two equations

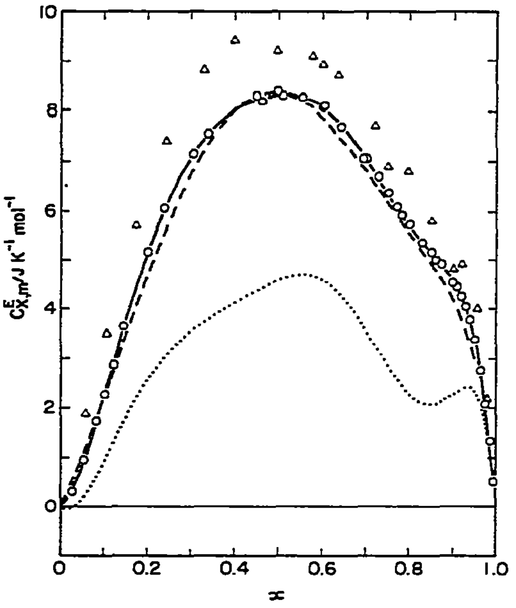
$$\kappa_T = \kappa_S + TV_m\alpha^2/C_{p,m} \tag{4}$$

and

$$C_{V,m} = C_{p,m}\kappa_S/\kappa_T \tag{5}$$

where α is the coefficient of thermal expansion. Smoothed values of $C^E_{p,m}$ and κ^E_S along with α^E reported previously [1] and the values of the properties of the pure components were used to evaluate $C^E_{V,m}$ and κ^E_T by the procedure described elsewhere [15]. Figure 1 shows plots of $C^E_{p,m}$ and $C^E_{V,m}$ against the mole fraction of water. Our values of $C^E_{p,m}$ are smaller than those measured by de Visser et al. [10]; for an equimolar mixture the difference amounts to about 10%. However, our results agree well with the values of $(\partial H^E_m/\partial T)_p$ for 25°C estimated from the excess enthalpies of mixing, H^E_m, at 5, 25 and 45°C reported by Morcom and Smith [16]. This calculation assumed a linear temperature dependence of H^E_m.

Plots of κ^E_S and κ^E_T are shown in Fig. 2. There is little difference in the magnitudes of these properties. Grant-Taylor and Macdonald [17] have derived κ_T from measurements of thermal-pressure coefficients and α. Values of κ^E_T obtained from their results and shown in Fig. 2 are more negative than



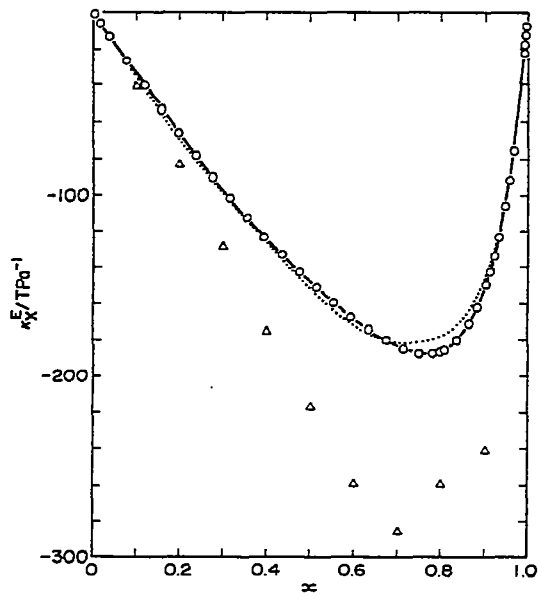
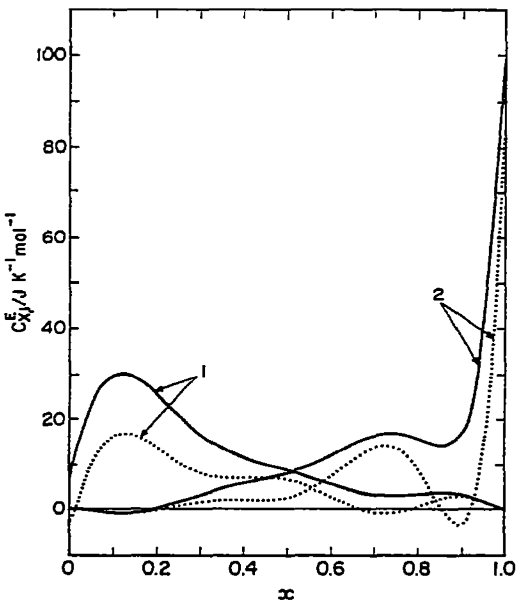


Fig. 1. Molar excess heat capacities of x H$_2$O + (1 — x) CH$_3$CN mixtures at 25°C. ○, Our experimental results for $C^E_{p,m}$; △, results of de Visser et al. [10]. ———, $C^E_{p,m}$; ..., $C^E_{V,m}$; — — —, $(\partial H^E_m/\partial T)_p$ estimated from Morcom and Smith [16].

Fig. 2. Excess coefficients of compressibility of x H$_2$O + (1 — x) CH$_3$CN mixtures at 25°C. ○, Our experimental results for κ^E_S; △, results of Grant-Taylor and Macdonald for κ^E_T [17]. ———, κ^E_S; · · · · · ·, κ^E_T.



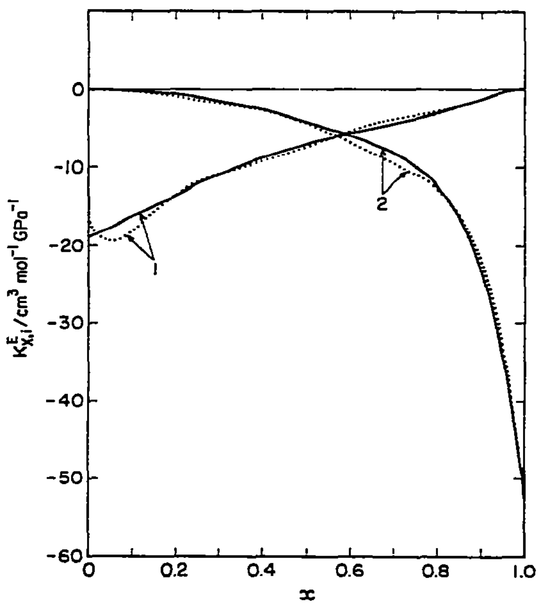


Fig. 3. Partial molar excess heat capacities of x H$_2$O + (1 — x) CH$_3$CN mixtures at 25°C. ———, $C^E_{p,i}$; · · · · · ·, $C^E_{V,i}$. Labels indicate i, the relevant component for the differentiation (1 = water, 2 = ethanenitrile).

Fig. 4. Partial molar excess compressoins of x H$_2$O + (1 — x) CH$_3$CN mixtures at 25°C. ———, $K^E_{S,i}$; · · · · · ·, $K^E_{T,i}$. Labels indicate i, the relevant component for the differentiation (1 = water, 2 = ethanenitrile).

ours though the composition dependence is qualitatively similar.

Partial molar excess isobaric heat capacities, $C_{p,i}^{E}$, were calculated from eqn. (3) with the coefficients from Table 3. It was found that in the region of $x > 0.9$, eqn. (3) does not represent the $C_{p,m}^{E}$ results well enough to allow a meaningful differentiation. The $C_{p,m}^{E}$ data for $x > 0.9$ were fitted separately by eqn. (3) with Z equal to the mole fraction, and the partial molar values derived. Partial molar isochoric heat capacities, $C_{V,i}^{E}$, were calculated in a similar manner. Figure 3 shows plots of $C_{p,i}^{E}$ and $C_{V,i}^{E}$. For ethanenitrile the limiting values of $C_{p,2}^{E}$ and $C_{V,2}^{E}$ are 99.2 and 92.5 J K^{-1} mole^{-1}, respectively.

The molar compressions at constant entropy or at constant temperature are defined by the relation

$$K_m = V_m \kappa_X = -(\partial V_m/\partial p)_X \tag{6}$$

where X is the entropy S or the temperature T. Partial molar excess isentropic compressions, $K_{S,i}^{E}$, and partial molar excess isothermal compressions, $K_{T,i}^{E}$, were obtained by differentiating $K_{S,m}^{E}$ and $K_{T,m}^{E}$ with respect to the amount of component i. Plots of $K_{S,i}^{E}$ and $K_{T,i}^{E}$ are shown in Fig. 4. Again we note that there is little difference in the magnitudes of $K_{S,i}^{E}$ and $K_{T,i}^{E}$. The limiting values for $K_{S,2}^{E}$ and $K_{T,2}^{E}$ are —52 and —51 cm^3 mole^{-1} GPa^{-1}, respectively.

DISCUSSION

There have been a number of thermodynamic and non-thermodynamic studies of water + ethanenitrile mixtures. From the studies by Grant-Taylor and Macdonald [17] (thermal expansion and thermal pressure coefficients), Armitage et al. [18] (V_m^E, ultrasonic and near-IR absorption), and Robertson and Sugamori [19] (temperature dependence of rate of solvolysis of t-butyl chloride in water + ethanenitrile mixtures) one concludes that when ethanenitrile is added to water, it interacts with the free water molecules through weak hydrogen bonding and thus acts as a structure breaker. On the other hand, Moreau and Douhéret [20,21] (V_m^E, viscosity, dielectric constant) and Easteal [22] (salicylic acid luminescence probe study) have suggested that in the region x = 0.85—1.0, ethanenitrile is accommodated in the bulk structure of water, but does not enhance, stabilize, or break the water structure. In a later publication, Easteal [23] (nuclear magnetic resonance) suggested that interstitially accommodated ethanenitrile may interact weakly with water. In our previous paper [1], we reported that in the region x = 0.85—1.0, the partial molar excess volumes indicate the breaking of the water structure by ethanenitrile. In the same region, in Figs. 3 and 4, the steep limiting slope of $C_{p,2}^{E}$ and the absence of minima in $K_{S,2}^{E}$ and $K_{T,2}^{E}$ (as opposed to the behaviour reported previously [24,25] for the structure makers methanol, ethanol, and 1-propanol) support the structure breaking properties of ethanenitrile.

In the mid-region of the mole fraction range, Easteal [23] has postulated that water + ethanenitrile mixtures form a pseudo two-phase system. In such a case one normally observes that the various partial molar excess properties show very little variation with x [24,26,27]. However, we do not observe this for the present heat capacities and compressibilities. The values of the partial molar excess properties are subject to uncertainties because of the number of smoothing steps involved in their calculations. In the case of $K_{T,1}^{E}$, the minimum observed in the ethanenitrile-rich region may be due to the nature of the calculations. However, the rather prominent maxima observed for $C_{p,1}^{E}$ and $C_{V,1}^{E}$ are realistic and can be attributed to the existence of water—ethanenitrile interactions.

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