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THERMODYNAMIC BEHAVIOR OF WATER–ACETONITRILE MIXTURES

EXCESS VOLUMES AND VISCOSITIES

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ABSTRACT

Densities of water+acetonitrile mixture have been measured from 308.15 to 278.15 K over the entire composition range. Partial molal volumes of both components of the mixed system have been calculated and deviations from ideal volumes of mixing have been evaluated. Literature data on viscosity have also been treated by a least square method and activation thermodynamic functions of viscous flow computed. Structural correlations have been made with previous results on acid–base properties; they allow to distinguish several interaction regions between components of binary systems.

INTRODUCTION

We are engaged in a systematic research of physical and thermodynamic properties of mixed solvents water+acetonitrile. In a preliminary work[1], acid–base properties of water–acetonitrile mixtures were investigated over the composition range 0–0.65 in mole fraction of ACN, x_{ACN}. Medium effects relative to hydrogen ion have then been estimated through solvation parameters, $({}^{\mathrm{t}}D_{\mathrm{g}}^{\circ})_{\mathrm{H}}$, whose changes in terms of x_{ACN} show no extremum, contrary to previously studied water–protic solvent mixtures.

This behavior has been explained by considering that no enhancement of tridimensional water-lattice takes place in the water-rich region; hydrogen ion does not undergo a marked preferential solvation compared to aqueous medium. Structural effects have been exhibited quantitatively by computing enthalpic and entropic components of $({}^{\mathrm{t}}D_{\mathrm{g}}^{\circ})_{\mathrm{H}}$, that embody no longer a compensation effect, as regards free enthalpy changes. Several regions can be distinguished.

It seemed worthwhile to support these results by examining deviations from different ideal physical properties. It is the purpose of the present work to report excess properties of water–ACN mixtures, at different temperatures, over the whole composition range to detect possible structural changes. In a first part, volumes of

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mixing have been calculated from density measurements and partial molar volumes of both components estimated. Literature data[2] concerning viscosity of the mixtures considered have been treated to get viscous flow activation thermodynamic functions, in order to complete preliminary conclusions[1]. In a further work, we shall present the results of our own measurements relative to the dielectric behavior of these systems.

EXPERIMENTAL

Solvents

Water was purified from an ion-exchanger. Its specific conductance was always less than $1.0 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$. It was stored under dry nitrogen, previously purified.

Prolabo analysis grade acetonitrile was dried over phosphorus pentoxide and fractionated twice. Then it was stored like water. The final product had a specific conductance less than $1 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$.

All solvent mixtures were made up by weight under nitrogen pressure and vacuum corrected, using Mettler B5 and B6 balances, from thoroughly degassed samples of water and ACN. As indicated by Armitage et al.[3], this precaution was necessary, particularly at low temperature, to avoid air bubbles to appear after mixtures, since nitrogen is less soluble in the mixture than in the two separate solvents.

Method

Measurements have been carried out in a water-bath, whose temperature was kept constant at 308.15±0.02 K and 298.15±0.02 K, using a high precision Colora thermostat. At lower temperatures, 288.15 and 278.15 K, a TUK-30D Lauda Kryostat was used; then, the temperature was kept constant within 0.1 K. In every case, it was checked by means of a calibrated platinum resistance thermometer and a Leeds and Northrup Mueller bridge.

Densities of binary mixtures and of pure acetonitrile have been measured in a Y-shaped pycnometer, where solvent was introduced with a 5 cm^3-syringe. The accuracy is about $2 \times 10^{-4}\ g\ cm^{-3}$ in density and about $0.01\ cm^3\ mol^{-1}$ in volume. The values obtained at 298.15 K have been compared with previous reliable data at this temperature[3,4] and show satisfactory agreement.

Calculations

Except least square fittings, calculations have been performed with an electronic computer Wang 370. As for least square calculations, they have been carried out using the Wang 2200 calculator.

For convenience, water will be identified as component 1 and ACN as component 2. Compositions are stated as mole fractions x_2 of organic solvent rather than temperature-dependent volume fractions ϕ_2.

RESULTS

Excess volumes of mixing

Densities, *d*, of binary mixtures at 308.15, 298.15, 288.15 and 278.15 K are reported in Table 1. Partial molar volumes $\bar{V}_{H_2O}$ and $\bar{V}_{ACN}$ have been computed from subsequent relationship:

$$\bar{V}_i = \left(\frac{1}{d} + (1-w_i)\cdot\frac{\partial\left(\frac{1}{d}\right)}{\partial w_i}\right)\cdot PM_i \tag{1}$$

TABLE 1

DENSITIES, $d^{T}_{277.15}$, OF WATER-ACETONITRILE SYSTEMS AT VARIOUS TEMPERATURES, *T*, FOR DIFFERENT MOLE FRACTIONS, x_2, OF ACETONITRILE

x_2	$d^{308.15}_{277.15}$	$d^{298.15}_{277.15}$	$d^{288.15}_{277.15}$	$d^{278.15}_{277.15}$
0	0.99406	0.99707	0.99913	0.99999
0.0500	0.9744	0.9779	0.9842	0.9881
0.1000	0.9544	0.9586	0.9673	0.9725
0.1500	0.9350	0.9399	0.9498	0.9557
0.2000	0.9167	0.9223	0.9327	0.9390
0.2500	0.8997	0.9062	0.9166	0.9232
0.3000	0.8842	0.8915	0.9018	0.9087
0.3500	0.8702	0.8782	0.8883	0.8957
0.4000	0.8575	0.8662	0.8762	0.8841
0.4500	0.8460	0.8552	0.8653	0.8737
0.5000	0.8355	0.8451	0.8553	0.8642
0.5500	0.8259	0.8357	0.8461	0.8553
0.6000	0.8170	0.8270	0.8376	0.8471
0.6500	0.8087	0.8187	0.8296	0.8392
0.7000	0.8009	0.8111	0.8220	0.8318
0.7500	0.7937	0.8040	0.8150	0.8248
0.8000	0.7870	0.7975	0.8085	0.8184
0.8500	0.7808	0.7916	0.8026	0.8125
0.9000	0.7752	0.7863	0.7972	0.8074
0.9500	0.7702	0.7813	0.7923	0.8026
1	0.7656	0.7767	0.7878	0.7980

w_i : weight fraction of component i
PM_i: molecular weight
d has been developed in a polynomial form $\sum_j a_j \cdot x_2^j$. Therefore, we get for $\bar{V}_i$:

$$\bar{V}_i = \left(\frac{1}{d} + (1-w_i)\cdot\frac{\partial}{\partial w_i}\left(\sum_j a_j \cdot x_2^j\right)\right)\cdot PM_i = \sum_j A_j \cdot x_2^j \tag{2}$$

where A_j coefficients are chosen by the method of least squares. It was found that seven coefficients are requested to give accurate results; with five coefficients, the extremum of $\bar{V}_i$, previously observed[3,5] at 298.15 K, is not observed. For the sake of homogeneity, subsequent treatments by the least square method will also give seven coefficients.

Excess volumes of mixing V^E have been calculated using following equation:

$$V^E = \sum_i x_i(\bar{V}_i - V_i^\circ) = \sum_j A'_j \cdot x_2^j \tag{3}$$

where V_i° holds for the molar volume of component V_i.

They have also been fitted by least square treatment. A_j and A'_j coefficients are summarized in Table 2.

TABLE 2

VALUES OF THE LEAST SQUARES PARAMETERS IN EQNS (2) AND (3)

Variable	*Temp.*	A_0	A_1	A_2	A_3	A_4	A_5	A_6
$\bar{V}_{H_2O}$	308.15	18.13	0.64	−30.39	130.2	−246.6	212.5	−67.00
	298.15	18.09	−1.06	−8.22	41.12	−90.40	87.52	−29.80
	288.15	18.04	0.22	−32.32	146.0	−280.1	241.7	−76.23
	278.15	18.03	−0.73	−27.87	143.2	−291.9	260.2	−83.73
$\bar{V}_{ACN}$	308.15	48.98	16.70	54.17	−410.6	864.8	−776.1	255.7
	298.15	47.42	47.55	−208.2	500.6	−653.4	433.3	−114.5
	288.15	46.56	27.91	5.58	−309.0	753.3	−714.2	242.0
	278.15	44.60	55.22	−172.2	215.3	−27.79	−140.1	76.5
V^E	308.15	0	−5.75	22.57	−47.38	57.54	−35.11	8.12
	298.15	0	−5.02	20.18	−47.99	69.21	−51.02	14.65
	288.15	0	−6.81	29.34	−65.29	81.35	−50.86	12.27
	278.15	0	−7.60	37.08	−93.36	128.5	−88.17	23.58

Viscosities

Viscosities have been obtained by double interpolation at convenient mole fractions and temperatures through a least square treatment, from literature data given by Mato et al.[2]. Values are summarized in Table 3.

The data so obtained have been treated on the basis of Eyring's theory[6] according to the equation:

$$\eta = \frac{hN}{V} e^{\frac{-\Delta S^{*}}{R}} e^{\frac{\Delta H^{*}}{RT}} \tag{4}$$

where h, N and R stand for Planck, Avogadro and ideal gases constants, respectively. V is the molar volume, ΔS^* and ΔH^* are "activation entropy" and "activation enthalpy" of viscous flow. Eqn. (4) may be transformed into:

$$\ln(\eta \cdot V) = \ln(hN) - \frac{\Delta S^*}{R} + \frac{\Delta H^*}{RT} = \frac{a}{T} + b \tag{5}$$

which predicts linear plots of $\ln(\eta V)$ against T^{-1} whatever the considered mixtures.

TABLE 3

VISCOSITIES, η^{T} $(mPa\cdot s)$, OF WATER–ACETONITRILE SYSTEMS AT VARIOUS TEMPERATURES, T, FOR DIFFERENT MOLE FRACTIONS, x_2, OF ACETONITRILE

Least square treatment of data of Mato et al.[2].

x_2	$\eta^{308.15a}$	$\eta^{298.15a}$	$\eta^{288.15}$	$\eta^{278.15b}$
0	0.723	0.895	1.142	1.489
0.0500	0.781	0.980	1.266	1.669
0.1000	0.777	0.971	1.252	1.649
0.1500	0.742	0.919	1.175	1.536
0.2000	0.699	0.856	1.080	1.396
0.2500	0.657	0.795	0.991	1.263
0.3000	0.619	0.743	0.915	1.150
0.3500	0.586	0.699	0.851	1.056
0.4000	0.555	0.658	0.794	0.976
0.4500	0.524	0.616	0.738	0.899
0.5000	0.491	0.572	0.679	0.820
0.5500	0.455	0.524	0.615	0.736
0.6000	0.420	0.476	0.551	0.651
0.6500	0.388	0.433	0.492	0.574
0.7000	0.365	0.401	0.449	0.515
0.7500	0.353	0.386	0.429	0.486
0.8000	0.355	0.391	0.436	0.492
0.8500	0.368	0.413	0.466	0.527
0.9000	0.383	0.436	0.498	0.568
0.9500	0.378	0.432	0.493	0.560
1	0.321	0.349	0.379	0.412

[a] Values interpolated at desired temperature. [b] Extrapolated values.
These values have also been interpolated at convenient mole fractions.

TABLE 4

VALUES OF LEAST SQUARES PARAMETERS IN TYPE (3)-EQN

Variable	*Temp.*	A_0	A_1	A_2	A_3	A_4	A_5	A_6
η^{E}	308.15	0	3.19	−23.68	81.32	−145.0	126.6	−42.46
	298.15	0	4.58	−35.57	124.4	−222.8	194.3	−64.98
	288.15	0	6.52	−51.20	178.4	−316.7	274.1	−91.14
	278.15	0	9.37	−73.62	252.8	−441.0	375.9	−123.5
$\Delta H^{\ddagger}$	—	4,017	12,841	−164,187	683,026	−1,344,719	1,238,652	−428,398
$\Delta S^{\ddagger}$	—	6.12	31.41	−454.1	1,913	−3,773	3,472	−1,199
$\Delta G^{\ddagger}$	308.15	2,131	3,169	−24,313	93,706	−182,513	169,141	−59,011
	298.15	2,192	3,465	−28,707	112,301	−219,313	203,109	−70,774
	288.15	2,253	3,804	−33,446	132,096	−258,100	238,626	−82,994
	278.15	2,314	4,107	−37,854	150,691	−294,861	272,537	−94,730

Therefore, ΔH^{*} and ΔS^{*} will be calculated from the following relationships:

$$\Delta H^{*} = R\cdot a \tag{6}$$

$$\Delta S^{\ddagger} = -R\cdot\{b+\ln(hN)\} \tag{7}$$

while $\Delta G^{\ddagger}$ is derived from equation:

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\cdot\Delta S^{\ddagger} \tag{8}$$

All activation functions have also been fitted by the method of least squares. The parameters selected to obtain the best fit of the experimental results are included in Table 4.

Excess viscous flow activation functions have been plotted in Fig. 1 against x_{ACN}. Deviations from ideality have been estimated using the simplified equation given by Decroocq[7]:

$$X^{\ddagger E} = X^{\ddagger} - (\phi_1\cdot X_1^{\ddagger} + \phi_2\cdot X_2^{\ddagger}) \tag{9}$$

where $X^{\ddagger}$ represents the considered activation function.

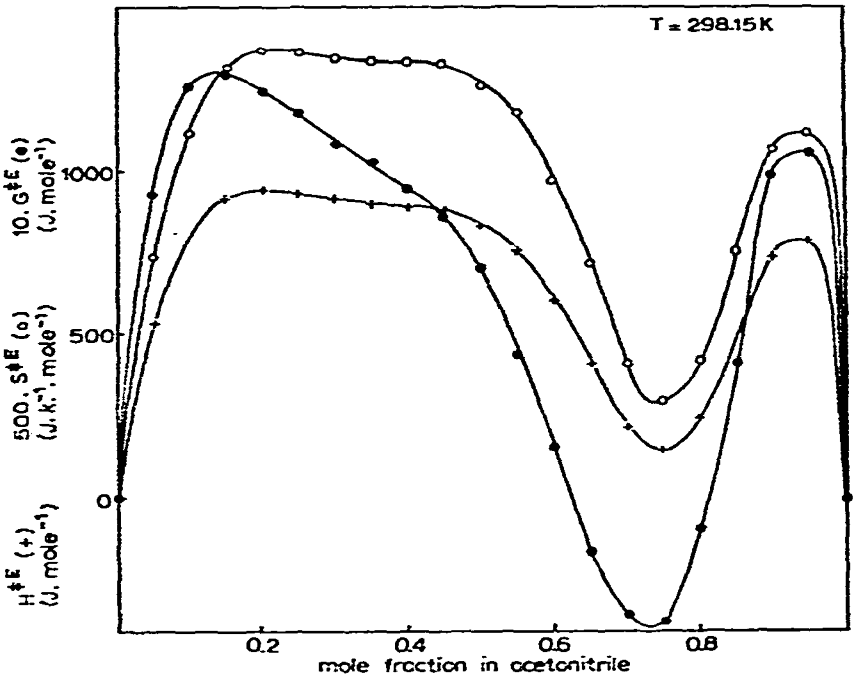

Fig. 1. Excess viscous flow activation functions plotted against mole fraction x_{ACN} for water–acetonitrile mixtures.

ϕ_1 and ϕ_2 are the volume fractions of the components of the mixture and have been defined[5]:

$$\phi_i = \frac{x_i\cdot \bar{V}_i}{x_i\cdot \bar{V}_i + x_j\cdot \bar{V}_j} \tag{10}$$

The excess viscosity, η^{E}, has been calculated in the same way, using eqn (9).

DISCUSSION

Partial molar volumes have been analyzed considering differences $(\bar{V}_i - V_i^\circ)$, i.e., relative partial molar volumes. In both cases, water and acetonitrile, they do not show an appreciable dependence on temperature, concerning extremums. A minimum is observed for $(\bar{V}_{H_2O} - V_{H_2O}^\circ)$ at $x_{ACN} = 0.78$–0.80, while a very small maximum exists for $(\bar{V}_{ACN} - V_{ACN}^\circ)$ at this same mole fraction. On the contrary, an inflection point becomes more and more pronounced in the range 0.3–0.35 in the ACN mole fraction, as the temperature decreases.

Excess volumes curves show negative values over the entire composition range, whatever the temperature. These smooth graphs present a minimum near $x_{ACN} = 0.3$. In connection with the inflection point of relative partial molar volumes, its position is somewhat dependent on the temperature, since it moves to lower values of x_{ACN}, when T is decreasing. For instance, the minimum corresponds to $x_{ACN} = 0.32$ at 308.15 K, whereas it lies at $x_{ACN} = 0.26$ at 278.15 K.

Curves $V^E(x)$ also exhibit a point of inflection at large mole fractions of ACN, corresponding to extrema of $\bar{V}_i$.

On the whole, the behavior of the binary mixtures can well be explained by the occupation of the free volumes, or cavities, of water network, by the other component. It is still difficult to attribute the magnitude of V^E and the asymmetry of the volume contractions to structural effects rather than to specific interactions between unlike molecules.

Supplementary information can be provided by the study of viscosity functions. Plots of excess viscous flow activation functions, $H^{\ddagger E}$, $S^{\ddagger E}$ and $G^{\ddagger E}$ against mole fraction x_{ACN} (Fig. 1) are characterized by a flat maximum at $x_{ACN} = 0.2$. Then follows an inflection point in the range 0.3–0.4. After that, a strong decrease occurs, which leads to a minimum near 0.75, and finally a large increase of the three functions gives rise to another sharp maximum at about 0.95. The same behavior is observed for excess viscosity, η^E, at different temperatures.

The values of $S^{\ddagger E}$ are not low enough to allow classification of water+acetonitrile solvents as "regular" solutions, in the sense of Hildebrand[8]. On the other hand, according to Reed and Taylor[9], and Meyer et al.[10], $G^{\ddagger E}$ is a reliable criterion to detect or to exclude the presence of interactions between unlike molecules. On this basis, one might conclude from positive values of $G^{\ddagger E}$ that interactions do exist between water and acetonitrile molecules, except at $x_{ACN} = 0.7$–0.8, where only structural effects are responsible for the observed deviations from ideality.

Now, it can be worthwhile to compare acid–base properties with previous conclusions, where the explored range was unfortunately limited to $x_{ACN} = 0.65$. From the values of enthalpic and entropic solvation parameters, two regions could be distinguished: the former between water and $x_{ACN} = 0.15$–0.20 with a maximum, the latter beyond this limit including a minimum close by $x_{ACN} = 0.3$–0.35, both extrema are in good agreement with the above-mentioned extrema or inflection point relative to excess volumes, relative partial molal volumes and excess activation functions. A third region was expected to exist, in accordance with spectroscopic data of Sidorova et al.[11], from $x_{ACN} = 0.8$ to the pure organic solvent. This range of composition also corresponds with our results relative to maxima of $(\bar{V}_i - V_i^\circ)$ and successive changes of sign of $G^{\neq E}$.

Consequently, such evidences support previous assumptions about the existence of three interaction regions in water–acetonitrile mixtures. It is now possible to propose some structural description of these mixed solvents.

If we take into account Gurikov's model[12] of liquid water, we can assume that, in the water-rich region $(0 < x_{ACN} \lesssim 0.2)$, the voids of the aqueous structure are progressively filled by the organic molecules, without enhancement of this structure, as shown by relative partial molar volumes. Methyl and cyanide groups are not easily engaged in hydrogen bonding processes. However, the geometry of the acetonitrile molecules cannot fit exactly to the aqueous network; it is likely that, independent of the number of available voids, the network will break beyond a given percentage in organic solvent. Sidorova et al.[11] have shown, from Raman and IR measurements, that the displacement of 5185 cm^{-1} band occurs from $x_{ACN} = 0.16$, which agrees fairly well with extrema of acid–base properties and viscosity activation excess functions.

In an intermediate region $(0.15\text{–}0.2 \leqslant x_{ACN} \leqslant 0.75\text{–}0.80)$, a progressive break of the precedent structure occurs. According to Naberukhin[13], this range of concentration will be called "microheterogeneity region". The size of the remaining aggregates is reduced. It is to emphasize that this range is characterized by extrema near 0.3–0.4 corresponding to excess volumes, enthalpic and entropic solvation parameters, ultrasonic absorption[3] extrema and inflection points of viscosity functions.

The third region $(0.75\text{–}0.80 \leqslant x_{ACN} < 1)$ can be compared to some extent with the water-rich region, since we can consider that the initial structure of organic solvent is progressively disturbed by the addition of water molecules, as demonstrated by a sharp maximum of viscosity excess functions and dielectric properties[14].

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