ELSEVIER

Thermochimica Acta 259 (1995) 23-29

thermochimica acta

Excess thermodynamic properties of tetrabutylammonium butyrate aqueous solution[☆]

Gy. Jákli*, L. Markó

Central Research Institute for Physics of the Hungarian Academy of Sciences, H-1525 Budapest, P.O.B. 49, Hungary

Received 14 September 1994; accepted 16 December 1994

Abstract

Based on differential vapour pressure measurements, excess free energies, excess enthalpies and excess entropies of the solvent of n-Bu$_4$N-butyrate aqueous solutions have been determined over wide temperature and molality ranges (20–80°C, 0.5–6.0 m). The minima observed with the excess entropies $\Delta S_1^{ex}/m$ and enthalpies $\Delta H_1^{ex}/m$ at 1.7 m correspond to the solid clathrate composition of the n-Bu$_4$N$^+$, i.e. to 1:33 solute/solvent ratio. This suggest that in the solution at around 1.7 m concentration, a clathrate–hydrate-like arrangement dominates in time average, and this structure results from solute–solute interaction ("structural hydrational interaction") and not from solute–solvent interaction (hydrophobic hydration). Similar minima of $\Delta S_1^{ex}/m$ and $\Delta H_1^{ex}/m$ were observed previously with n-Bu$_4$NBr solution. However, here the structuring effect was only half of that with the butyrate system. This shows that the Br$^-$ ion significantly disturbs the hydrophobic hydration structure, while the butyrate anion fits into this structure.

Keywords: Clathrate-like structure; Hydrophobic interaction; Solution excess properties; Tetrabutylammonium butyrate

---

1. Introduction

Since Frank and Evans in 1945, in their frequently cited paper [1], introduced the concept of "iceberg"-formation for the process of solvent–structure enhancement in aqueous solutions by hydrophobic solutes, a number of experimental techniques have

---

[☆] Presented at the 13th International Symposium on Chemical Thermodynamics, Clermont-Ferrand, France, 17–22 July 1994.

* Corresponding author.

SSDI 0040-6031(95)02269-4

been used to determine what kind of water structure exists in these systems. Despite the large number of investigations, there is no agreement, and different interpretations of the water-structure enhancement are proposed [2]: one is the "ice-like" structure, another is a "clathrate–hydrate-like" structure or, according to a third, a non-tetrahedral water structure exists (consisting of dimers, trimers, tetramers, etc.) around the hydrophobic surface of solute molecules.

Using a differential vapour pressure method, we recently determined the excess free energy ΔG_1^{ex}, excess enthalpy ΔH_1^{ex} and excess entropy ΔS_1^{ex} of the solvent of n-Bu_4NBr normal (and heavy) water solutions in wide temperature and concentration ranges [3]. Among these properties for the degree of solvent structuredness (degree of order), the most direct information can be obtained from the (relative) excess entropy, which compares the entropy of the solvent in the solution with that of the pure solvent at a given temperature. The value $\Delta S_1^{ex}/m$ (m is molality) showed that a maximum of the structural enhancement of the solvent (entropy minimum) due to one mole of solute occurs at 1.7 ± 0.1 mol, i.e. at the same solute–solvent ratio which corresponds to the solid clathrate–hydrate composition (1:33).

To check the influence of anions on the excess thermodynamic properties of n-Bu_4N^+, in the present work we carried out a similar investigation on n-Bu_4N-butyrate aqueous solution, taking into account the opposite hydrational behaviour of Br^- and butyrate, i.e. while Br^- is a well-knonw "structure breaker", butyrate shows a "structure maker" character [4]).

2. Experimental

The n-B_4N-butyrate salt was freshly prepared from analytical grade reagents, using a method given by Simon and Uhlig [5]. It was dried in vacuum at room temperature to constant weight and the aqueous solutions with different concentrations were prepared gravimetrically. The vapour pressure differences between the pure solvent and solutions were measured on an apparatus fully described elsewhere [6]. In this apparatus, the pressure differences are determined by capacitance manometers. Samples are held in a copper block, whose temperature is controlled by a thermostat and measured with a platinum resistance thermometer. The calibration procedures for manometer and thermometer are described elsewhere [7]. Experience with the apparatus has shown that the precision, in the case of aqueous systems, is 0.2–0.3% of $\Delta P/P$ in the range of 5–80°C. Earlier measurements [3] have shown that this precision on the vapour pressure lowering, i.e. on solvent activity, coupled with measurements at small increments (2–3°C) over a wide temperature range (~ 60°C) results in a precision of ΔS_1^{ex} corresponding to an entropy change caused by 1°C with the pure solvent.

3. Results

Osmotic coefficients Φ were obtained from the differential vapour pressure measurements carried out between pure water $P_H^{\ominus}$, and solution P_H^m, at 2–3°C intervals from 20 to 80°C. Altogether, 249 $\Delta P = P_{\mathrm{H}}^{\ominus} - P_{\mathrm{H}}^{m}$ data were taken at six different concentrations between 0.5 and 6.0 molality. The osmotic coefficients were calculated from

$$\Phi = \frac{-55.508}{2m}\left[\ln\frac{P_{\mathrm{H}}^{m}}{P_{\mathrm{H}}^{\ominus}} - \frac{V_{\mathrm{H}}}{RT}(P_{\mathrm{H}}^{m} - P_{\mathrm{H}}^{\ominus}) + b_{\mathrm{H}}(P_{\mathrm{H}}^{m} - P_{\mathrm{H}}^{\ominus})\right] \tag{1}$$

where m is molality, $V_{\mathrm{H}}^{\ominus}$ is the molar volume of liquid water [8] and b_{H} is the second virial coefficient [9]. The temperature dependence of the Φ values could be fitted to an equation of the form

$$\Phi = A_1 + A_2 t + A_3 t^2 \tag{2}$$

The parameters of the least-square fits, the standard deviations and the number of data points measured at the different molalities are collected in Table 1. In view of the large number of experimental data ($\Delta P = P_{\mathrm{H}}^{\ominus} - P_{\mathrm{H}}^{m}$) they are not included in this paper. They are available from the authors on request.

The excess thermodynamic functions of the solvent, ΔG_1^{ex}, ΔH_1^{ex} and ΔS_1^{ex}, were calculated from the osmotic coefficient and from its temperature derivative utilizing the relations [10]

$$\Delta G_1^{\mathrm{ex}} = -55.508\,RT\left[\frac{vm\Phi}{55.508} + \ln\frac{55.508}{vm + 55.508}\right] \tag{3}$$

$$\Delta H_1^{\mathrm{ex}} = vmRT^2\frac{\partial\Phi}{\partial T} \tag{4}$$

$$\Delta S_1^{\mathrm{ex}} = \frac{\Delta H_1^{\mathrm{ex}} - \Delta G_1^{\mathrm{ex}}}{T} \tag{5}$$

The parameters of Table 1 were used to calculate the excess functions at the different experimental molalities and their values at even temperatures are collected in Table 2; the corresponding errors at 25, 40 and 60°C are also given. The relative magnitude of the excess functions at 25°C as a function of the molality are shown in Fig. 1. In Fig. 1 the excess properties of 55.5 mol solvent are divided by the molality m. This is to clarify the changes in the hydrational behaviour of the solvent caused by the solute. The temperature dependence of ΔS_1^{ex} is demonstrated in Fig. 2. Here it can be seen that the structuring effect of the solute, even at 60°C, is significant. From a phenomenological

Table 1
Parameters of Eq. (2)

m/(mol kg^{-1})	A_1	$10^2 A_2$	$10^5 A_3$	$10^2 \sigma$	Data pts.
0.5	1.293	−1.046	5.045	1.20	58
1.0	1.589	−1.948	10.820	1.36	48
1.5	1.717	−2.344	13.500	0.74	25
2.0	1.689	−2.331	13.950	0.66	47
4.0	1.438	−1.114	5.181	0.72	37
6.0	1.538	−1.078	7.494	1.26	35

Table 2
Excess properties of the solvent in aqueous *n*-Bu_4N-butyrate solution as a function of molality *m* and temperature *T*

$m/(\mathrm{mol\ kg^{-1}})$	$T/°\mathrm{C}$	$\Delta G_1^{ex}/(\mathrm{J\ kg^{-1}})$	$\Delta H_1^{ex}(\mathrm{J\ kg^{-1}})$	$T\Delta S_1^{ex}/(\mathrm{J\ kg^{-1}})$
0.5	20	−275	−6033	−5757
	25	−178 ± 80	−5868 ± 600	−5688 ± 800
	30	−84	−5681	−5595
	40	93 ± 100	−5239 ± 900	−5331 ± 1100
	50	255	−4703	−4957
	60	399 ± 200	−4068 ± 1400	−4465 ± 1400
	70	522	−3328	−3848
1.0	20	−1269	−21653	−20384
	25	−928 ± 250	−20798 ± 2800	−19870 ± 2100
	30	−603	−19748	−19245
	40	−3 ± 400	−17650 ± 3000	−17648 ± 2800
	50	521	−15038	−15559
	60	957 ± 600	−11989 ± 4000	−12946 ± 3900
	70	1294	−8482	−9777
1.5	20	−2400	−38670	−36274
	25	−1795 ± 250	−37007 ± 2800	−35216 ± 2100
	30	−1220	−35164	−33948
	40	−167 ± 200	−30918 ± 2000	−30755 ± 2700
	50	738	−25891	−26634
	60	1474 ± 300	−20043 ± 4000	−21523 ± 4400
	70	2023	−13335	−15363
2.0	20	−3051	−50674	−47622
	25	−2259 ± 250	−48293 ± 2000	−46034 ± 2100
	30	−1509	−45662	−44154
	40	−148 ± 400	−39625 ± 3000	−39478 ± 2700
	50	1003	−32510	−33510
	60	1917 ± 800	−24251 ± 4000	−26168 ± 3600
	70	2565	−14803	−17368
4.0	20	−5883	−51831	−45948
	25	−5110 ± 400	−50551 ± 3500	−45441 ± 3700
	30	−4360	−49094	−44734
	40	−2939 ± 600	−45627 ± 5000	−42688 ± 4700
	50	−1641	−41391	−39750
	60	−486 ± 1000	−36342 ± 14000	−35857 ± 6100
	70	504	−30441	−30946
6.0	20	−13075	−66728	−53652
	25	−12197 ± 1400	−62377 ± 1200	−50180 ± 12300
	30	−11397	−57615	−46221
	40	−10041 ± 2100	−46815 ± 16000	−36774 ± 16400
	50	−9061	−34236	−25176
	60	− 8498 ± 3500	−19791 ± 22000	−11293 ± 20000
	70	−8398	−3388	5009

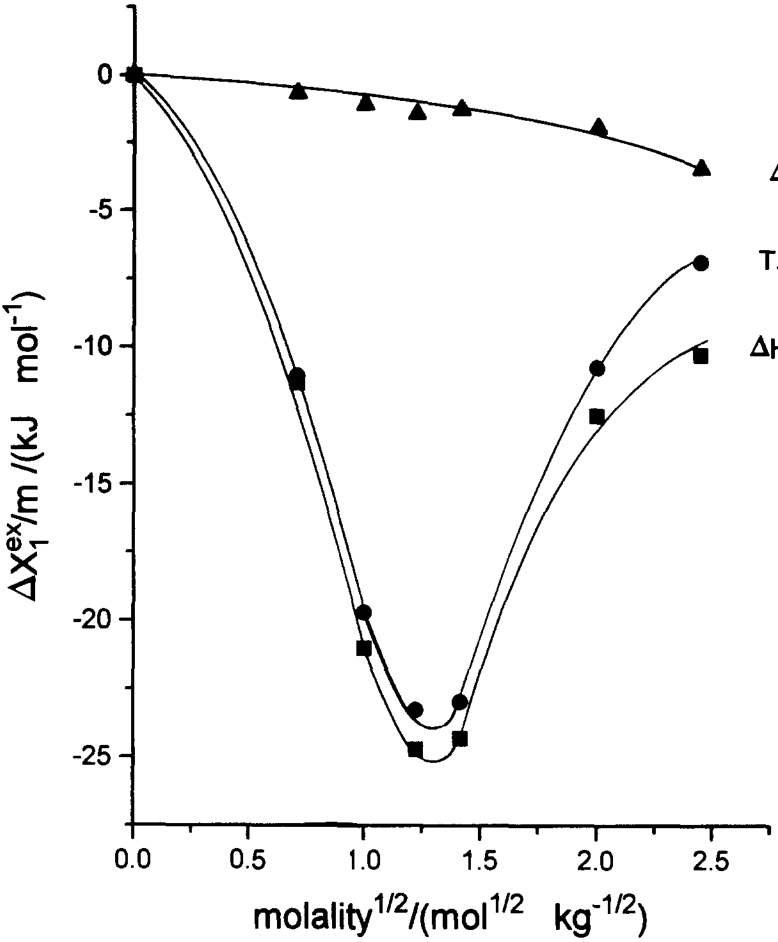

Fig. 1. Excess properties of the solvent in n-Bu_4N-butyrate solution at 25°C.

comparison, the solute influence on the entropy of the solvent (or on some other property) can be compared to the influence of the temperature on the pure solvent, using the "structural temperature" concept of Bernal and Fowler [11]. On the right ordinate of Fig. 2, ΔT_{str} indicates how much the temperature of pure water has to be changed to obtain the entropy decrease corresponding to the influence of the solute.

A check for the temperature derivative of the osmotic coefficients would be of special importance because it was used to determine ΔS_1^{ex} (through ΔH_1^{ex}), which reflects most directly the structural changes of the solvent. There are no data available in the literature for $d\Phi/dT$; however, calorimetric determination of the heat of dilution of n-Bu_4N-butyrate was carried ou by Lindenbaum [12] at 25°C, up to $6m$. The agreements of the ΔH_1^{ex} values are within experimental error, our data being 5–6%

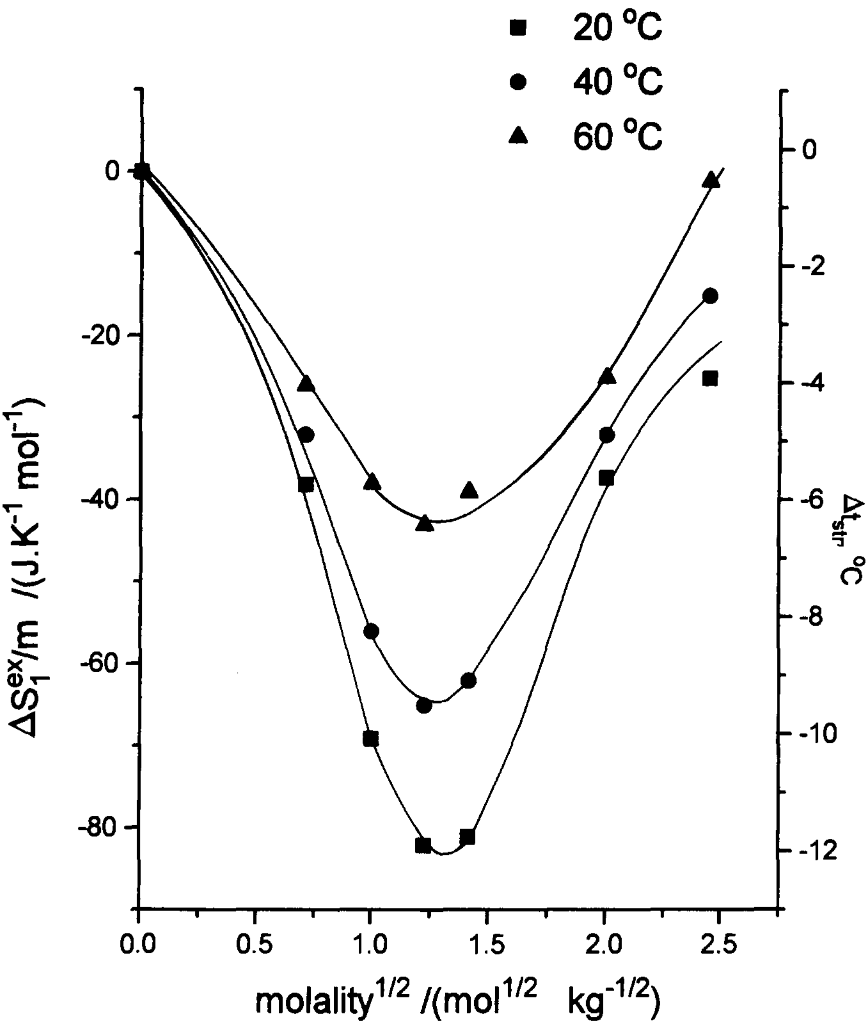

Fig. 2. Temperature dependence of the solvent excess entropy $(\Delta S_1^{ex}/m)/(\mathrm{JK^{-1}\,mol^{-1}})$ in *n*-Bu_4N-butyrate solution.

higher. We believe that this precision holds at other temperatures and in the case of ΔS_1^{ex} as well.

4. Discussion

The large negative values of $T\Delta S_1^{ex}$ and ΔH_1^{ex}, at and around their minima show that the structuredness of the water molecules and their interaction energies are significantly stronger in n-Bu_4N-butyrate solution than in pure water. The influence of the solute (per mole) is the strongest at the molality corresponding to the minimum, which is $1.7(\pm 0.2)\,m$, corresponding to a solute/solvent ratio of 1:33 (± 4). Because this is the composition of the solid clathrate–hydrates of the n-Bu_4N-salts, we believe that the above result supports strong evidence that in the aqueous solution at around $1.7\,m$, a clathrate–hydrate-like geometrical arrangement also dominates in time average. A further consequence of this result is that the "clathrate-like" structure (at least in n-Bu_4N-salt solutions) results from solute–solute interaction ("structural hydrational interaction") and not from solute–solvent interaction (hydrophobic hydration). A comparison with the n-Bu_4NBr solution, measured in our laboratory earlier [3], shows that the extra structuredness of the solvent (as expressed by ΔS_1^{ex}) at $1.7\,m$ and at room temperature is twice as large with the butyrate system as with the bromide system: ΔT_{str} with the butyrate system is -12°C, and only -6°C with the bromide system. A further difference is that ΔG_1^{ex} with the butyrate system is (also) negative, while that with the bromide one was positive. This shows that the Br^- ion significantly disturbs the hydrophobic hydration structure, while the butyrate anion fits into this structure.

Acknowledgement

Financial support from the Hungarian Research Fund under Grant OTKA-1846 is gratefully acknowledged.

References

[1] H.S. Frank and M.W. Evans, J. Chem. Phys., 13 (1945) 507.
[2] J.Y. Hout and C. Jolicoeur, in R.R. Dogonadze (Ed.), The Chemical Physics of Solvation, Part A, Elsevier, New York, 1985, Chap. 11.
[3] Gy. Jákli and L. Markó, A.C.H. Models in Chemistry, in press.
[4] S. Lindenbaum, J. Phys. Chem., 74 (1970) 3027; J. Chem. Thermodyn., 3 (1971) 625.
[5] A. Simon and B. Uhlig, Chem. Ber., 85 (1952) 977.
[6] Gy. Jákli and H. Illy, KFKI Report 80–15 (1980).
[7] G. Jancsó, J. Pupezin and A.W. Van Hook, J. Phys. Chem., 74 (1970) 2984.
[8] E. Whalley, Proc. of the Joint Conference on the Thermodynamic and Transport Properties of Fluids, 1957, Institute of Mechanical Eng., London, 1958, p. 15.
[9] D. Eisenberg and W. Kauzmann, The Structure and Properties of Water, Oxford University Press, London, 1969, p. 48.
[10] J. Pupezin, Gy. Jákli, G. Jancsó and W.A. Van Hook, J. Phys. Chem., 76 (1972) 743.
[11] J.D. Bernal and R.H. Fowler, J. Chem. Phys., 1 (1933) 515.
[12] S. Lindenbaum, J. Phys. Chem., 75 (1971) 3733.