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THERMODYNAMIC EQUILIBRIUM AND EXCESS PROPERTIES OF ALKYLSULPHATES IN WATER BY VAPOUR PRESSURE OSMOMETRY

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ABSTRACT

In this paper we have studied the thermodynamic behaviour of sodium dodecylsulphate (SDS) and sodium tetradecylsulphate (STS) in aqueous micellar solutions over a wide range of temperatures (298–363 K). From vapour pressure osmometry measurements we have determined the osmotic and activity coefficients, the excess Gibbs free energy, excess enthalpy and excess entropy functions.

Using several association models we have determined the type of association of the two detergents studied. Finally, self-association constants have been calculated in the temperature range 298–363 K, for the different association models.

INTRODUCTION

For the last ten years, vapour pressure osmometry (VPO) has been increasingly applied in the determination, not only of molecular weights, but also of osmotic coefficients and of excess properties [1–3]. This technique allows the calculation of these parameters with relative ease and efficiency. Moreover, through the use of several theoretical models [4,5] the association mechanism of a micellar system can be determined, as well as the parameters associated with the process.

In this work a study has been made of the behaviour of the detergents sodium dodecylsulphate (SDS) and sodium tetradecylsulphate (STS) in aqueous micellar solutions in the temperature range 298–363 K.

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EXPERIMENTAL

Sodium dodecylsulphate (SDS) and sodium tetradecylsulphate (STS) were purified by standard procedures.

The aggregation of SDS and STS was followed by vapour pressure osmometry. The osmometric measurements were carried out in the temperature range 298–363 K, on a Knauer 1974 Model vapour pressure osmometer. A universal probe which had previously been calibrated with sodium chloride in water was used.

The R values for both the standard and alkylsulphates were recorded in a Houston Recorder as a function of time. In all cases a constant resistance was obtained after 2–3 min. At least five ΔR values were measured for each solution and the mean value was taken. The drop size was kept as constant as possible and equal in the two thermistors, so that the precision of the ΔR values ranged between 0.5 and 1.0%.

DISCUSSION

Under appropriate experimental conditions (solvent, temperature, concentration, etc.) there are a great number of molecules or ions which can become associated to form units with a higher molecular weight.

There are two basic types of association mechanism [4,5]; the closed and the open or unlimited. The first can be expressed by

$$nA_1 \overset{k}{\rightleftharpoons} A_n$$

and the second mechanism by

$$A_1 + A_1 \overset{k_2}{\rightleftharpoons} A_2$$

$$A_2 + A_1 \overset{k_3}{\rightleftharpoons} A_3$$

$$A_{n-1} + A_1 \overset{k_n}{\rightleftharpoons} A_n$$

where k_2, $k_3, \ldots, k_n$ are the association constants of the different processes and A_1, $A_2, \ldots, A_n$ are the monomer, dimer,..., n-mer, respectively.

Using these two basic types of association the following models can be proposed [4,5]:

Model 1. In this model we can suppose that the association follows a closed-type mechanism. Calculated osmotic molality, $\overline{m}_{\text{calc}}$, is expressed by

$$\overline{m}_{\text{calc}} = m_1 + km_1^2$$

where $k = m_n/m_1^n$.

Models 2–5 are based on the open mechanism.

Model 2. Here all association equilibrium constants are considered equal, i.e., $k_2 = k_3 = \ldots\ldots = k_n$, k, and the calculated osmotic molality can be evaluated by the equation

$$\overline{m}_{\text{calc}} = m_1 \frac{(km_1)^n - 1}{km_1 - 1}$$

Model 3. In this model the dimerization constant is considered independent of the other association constants. Here $k_3 = k_4 = \ldots\ldots = k_n$ and

$$m_{\text{calc}} = m_1 + \frac{k_2 m_1^2 (km_1)^{n-2} - 1}{km_1 - 1}$$

where $k = \mathrm{k}_2(k_n)^{n-2}$.

Model 4. In this case k_2 is assumed to be independent and other association constants are interrelated by the expression $k_x = q/x$, where q is an empirical parameter. In this model, the association constants decrease when n increases. The total association constant, k, is given by

$$k = k_2 \prod_{3}^{n} (q/x) = 2k_2 q^{n-2}/n!$$

when $n \to \infty$, $k \to 0$.

The calculated osmotic molality is

$$\overline{m}_{\text{calc}} = m_1 + 2k_2 \sum_{2}^{n} (q^{x-2}/x!) m_1^x$$

Model 5. This model is similar to model 4, except that the association constants increase with x; $k_x = q(x-2)/(x-1)$, when $x \to \infty$, $k \to q$.

The product of all association constants can be expressed by

$$k = k_2 \prod_{3}^{n} q \frac{(x-2)}{(x-1)} = k_2 \frac{q^n}{n}$$

To determine which of these models is the best, it is necessary to minimize the function (1) in all models

$$U = \sum_{x=1}^{s} (\overline{m}_{x_{\text{obs}}} - \overline{m}_{x_{\text{calc}}})^2 \tag{1}$$

where s represents the number of experimental values. In order to compare the different models, the following expression must be used

$$\sigma = \frac{|U_{\min}|}{(s-p)}$$

where p is the number of independent association constants. In models 1 and 2, p is equal to one, and to two in models 3–5.

TABLE 1

Values of the degree of association, dimerization constant, multimerization constant and parameters q and σ for SDS at 298 and 318 K

Model	298 K				318 K			
	n	$k_2 \times 10^{-1}$	$k \times 10^{-2}, q$ *	$\pm\sigma \times 10^3$	n	$k_2 \times 10^{-1}$	$k \times 10^{-2}, q$ *	$\pm\sigma \times 10^3$
1	50		0.08	7.25	47		0.06	3.84
2	55		0.12	6.12	53		0.10	7.88
3	62	2.51	2.02	4.28	58	1.80	1.39	1.30
4	65	4.72	1.55 *	1.37	62	3.95	1.23 *	1.12
5	62	1.39	1.65 *	2.88	59	0.81	1.52 *	1.74

* Values of q are indicated by an asterisk.

In Tables 1–4 the values of n, k_2, q and σ for different models are summarized. From Tables 1–4 it is deduced that the theoretical model which best reproduces the experimental results is the model 4 (open mechanism). Consequently, this implies that a heterogeneous distribution of the micellar size is going to be obtained in the system, which is in agreement with the results obtained by Corkill et al. [7] and Elworthy and Mysels [8] for other systems and using other physico-chemical techniques.

The association number values calculated by VPO in this work agree with those given in the literature [9–11].

For SDS and STS the relationship between the multimerization constants calculated by VPO and the association number, $\tilde{n}$ (Figs. 1 and 2), has been studied, finding a dependence of the type $k = A \exp(Bn)$.

In Fig. 3 it can be seen how in these two homologous detergents, the law which relates the multimerization constant, k_n, and the mean number of molecules, $\bar{n}$, which form the micels is the same; i.e., the A and B values for both detergents studied are 1 and $(7.75 \pm 0.05) \times 10^{-2}$, respectively. We consider this result to be important since, on dealing with a general law, it

TABLE 2

Values of the degree of association, dimerization constant, multimerization constant and parameters q and σ for SDS at 333 K and 363 K

Model	333 K				363 K			
	n	$k_2 \times 10^{-1}$	$k \times 10^{-2}, q$ *	$\pm\sigma \times 10^3$	n	$k_2 \times 10^{-1}$	$k \times 10^{-2}, q$ *	$\pm\sigma \times 10^3$
1	42		0.04	3.85	43		0.03	6.01
2	48		0.08	7.79	47		0.05	4.60
3	53	1.56	1.75	1.47	51	1.19	0.53	2.11
4	58	3.48	1.04 *	1.25	55	2.91	0.71 *	1.38
5	52	0.63	1.47 *	1.88	50	0.62	1.35 *	1.75

* Values of q are indicated by an asterisk.

TABLE 3

Values of the degree of association, dimerization constant, multimerization constant and parameters q and σ for STS at 310 K and 318 K

Model	310 K				318 K			
	n	$k_2\times10^{-3}$	$k\times10^{-4}, q^*$	$\pm\sigma\times10^3$	n	$k_2\times10^{-3}$	$k\times10^{-4}, q^*$	$\pm\sigma\times10^3$
1	116		1.23	7.89	113		0.99	9.03
2	117		1.50	5.15	117		1.30	5.27
3	129	2.65	2.01	2.01	124	1.75	1.87	3.77
4	135	3.00	3.54 *	1.16	133	2.66	3.04 *	1.26
5	130	2.17	1.97 *	1.79	127	1.93	2.61 *	2.16

* Values of q are indicated by an asterisk.

TABLE 4

Values of the degree of association, dimerization constant, multimerization constant and parameters q and σ for STS at 333 K and 363 K

Model	333 K				363 K			
	n	$k_2\times10^{-3}$	$k\times10^{-4}, q^*$	$\pm\sigma\times10^3$	n	$k_2\times10^{-3}$	$k\times10^{-4}, q^*$	$\pm\sigma\times10^3$
1	112		0.83	8.17	108		0.60	7.81
2	115		1.02	6.25	112		0.75	5.66
3	123	2.07	1.60	4.13	120	1.53	1.55	3.85
4	131	2.36	2.60 *	0.75	128	1.97	2.06 *	0.97
5	125	1.79	2.39 *	2.26	122	1.61	1.73 *	2.22

* Values of q are indicated by an asterisk.

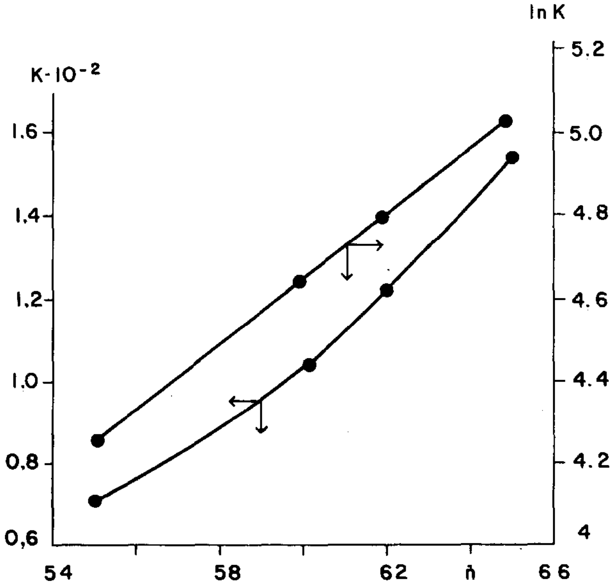

Fig. 1. Plot of k and ln k as a function of association number, $\bar{n}$, for SDS.

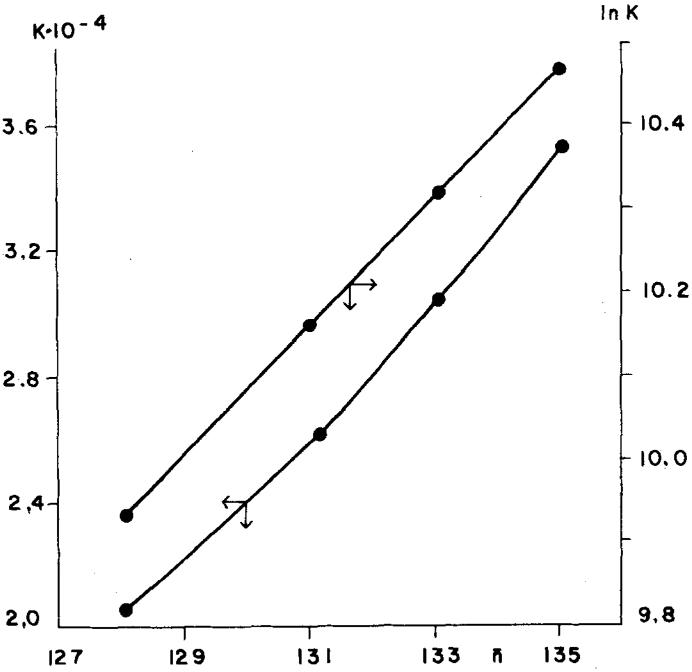

Fig. 2. Plot of k and ln k as a function of association number, $\bar{n}$, for STS.

will permit the calculation of association constants if the mean association number of the detergent is known. This is currently being investigated and the preliminary results obtained are promising.

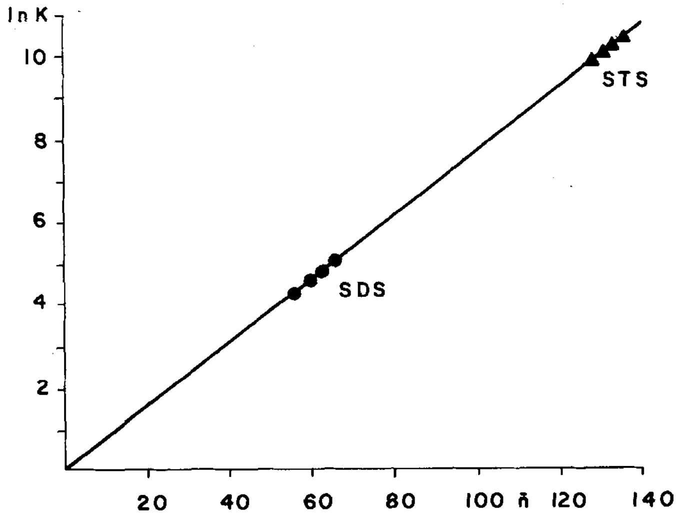

Fig. 3. Variation of ln k as a function of association number, $\bar{n}$, for SDS and STS.

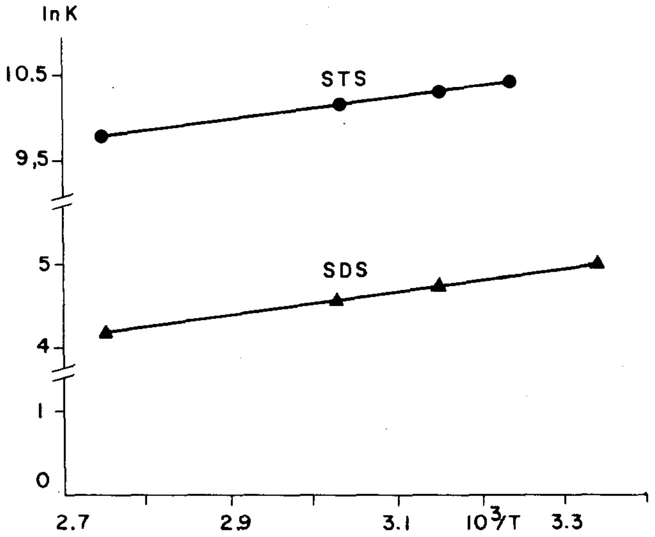

Fig. 4. Arrhenius plot of multimerization constant for SDS and STS.

On the basis of the expressions

$\Delta G = \Delta H - T\Delta S$

and

$\Delta G = -RT \ln k$

the thermodynamic magnitudes ΔG, ΔH and ΔS in the studied temperature range can be calculated (Figs. 4 and 5).

In Table 5 the results obtained are shown. As can be seen, the increment

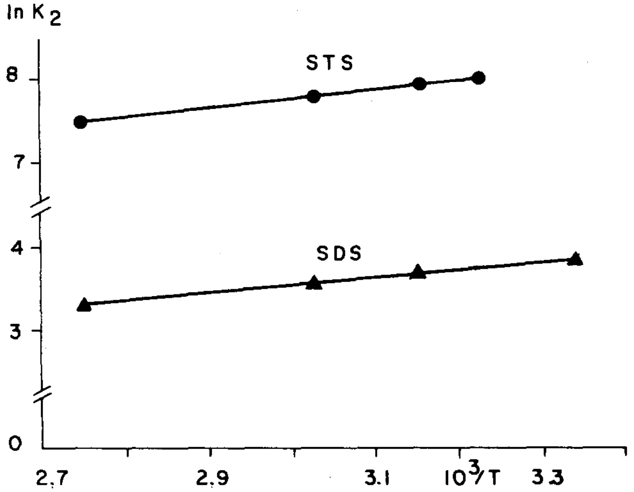

Fig. 5. Arrhenius plot of dimerization constant for SDS and STS.

TABLE 5

Increase of Gibbs free energy, enthalpy and entropy for SDS and STS at 298 K

Detergent	Dimerization			Multimerization		
	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K)
SDS	−9.61	−7.06	8.56	−12.57	−9.32	10.91
STS	−20.17	−7.21	43.49	−26.38	−9.30	57.32

of entropy is very small and positive. This is due to two antagonistic contributions; on the one hand the arrangement of the detergent molecules to form the micels, and on the other the increase in the disorder of the water molecules as a consequence of the formation of micels. Morever, Aranow [12] has shown that it is necessary to take into account the mobility of the alkyl chain inside the micel since this contributes to an increase in the disorder of the system, increasing the entropy.

Another thermodynamic parameter which can be calculated from the experimental results obtained by VPO is the activity coefficient.

In effect, according to the Gibbs–Duhem equation

$$S\mathrm{d}T - V\mathrm{d}p + \Sigma n_i \mathrm{d}\mu_i = 0$$

and at constant T and P

$$\Sigma n_i \mathrm{d}\mu = 0$$

from which, on the basis of some simple relations, the Gibbs–Duhem equation is obtained in its integral form

$$\ln \gamma_2 = (\phi - 1) + \int_0^x (\phi - 1)\mathrm{d}\ln x_2$$

where γ_2 is the mean ionic activity coefficient and ϕ is the osmotic coefficient.

As can be seen in Figs. 6 and 7, the variation of ln γ_2 as a function of molality, m, in the temperature range studied for SDS and STS, shows negative deviations from Raoult's law, as could be expected [13].

The excess functions, G^E, H^E and S^E were also calculated for the two detergents. As can be seen in Figs. 8 and 9, the excess Gibbs free energy is negative at all temperatures. This fact indicates that a great compatibility exists between the detergent and the water, which was only to be expected if the results obtained previously are taken into account. Morever, it confirms that the water molecules are involved in the mechanism of micel formation.

To calculate quantitatively these interactions the Guggenheim and Stokes equation has been used [14]

$$G^E = RTx_1x_2\chi_{12}$$

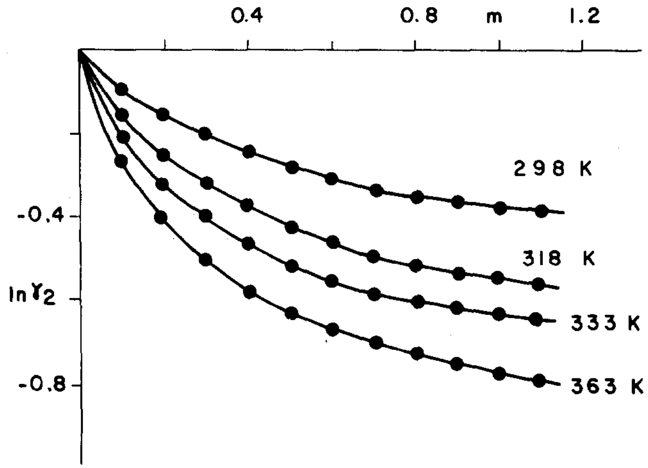

Fig. 6. Variation of ln γ_2 as a function of molality, *m*, in the temperature range 298–363 K, for SDS.

where x_1 and x_2 are the solvent and solute molar fractions, respectively, and χ_{12} the solute–solvent interaction parameter. This parameter, characteristic of the system at a given temperature, depends only on the molecular interactions of the system and its use permits investigation of the thermodynamic quality of a solvent with respect to the detergent. In effect, a bad solvent interacts weakly and χ_{12} will be positive. On the contrary, a good solvent has great affinity for the detergent (as occurs in our systems) and χ_{12} will be negative (Fig. 10).

It is interesting to observe that the extrapolation of the two straight lines

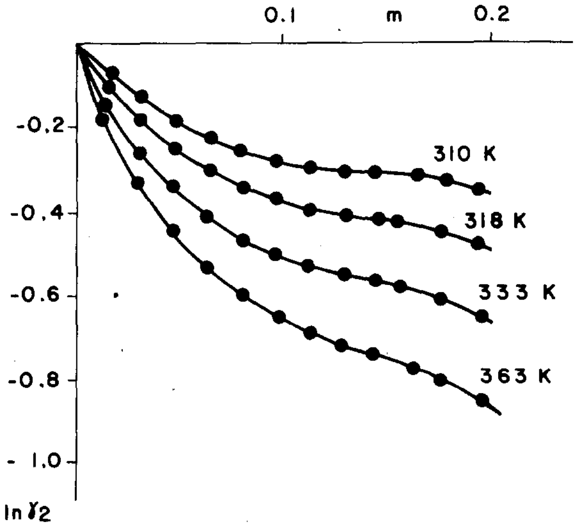

Fig. 7. Variation of ln γ_2 as a function of molality, *m*, in the temperature range 310–363 K, for STS.

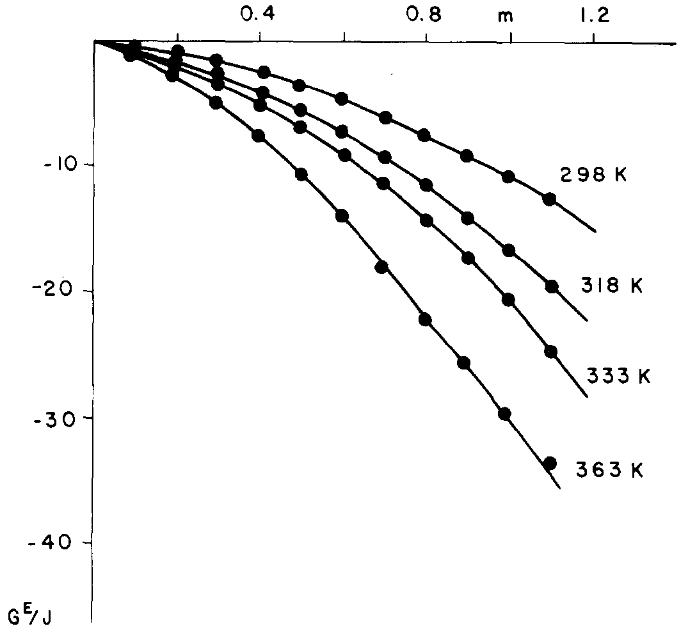

Fig. 8. Variation of excess Gibbs free energy, G^E, as a function of molality, *m*, in the temperature range 298–363 K, for SDS.

converge at point $\chi_{12} = 0.50$. At this point the second virial coefficient vanishes and the system behaves ideally; all the excess functions becomes zero. It has to be pointed out, nevertheless, that this is a hypothetical point.

Knowing the value of G^E and its variation with temperature, it is possible

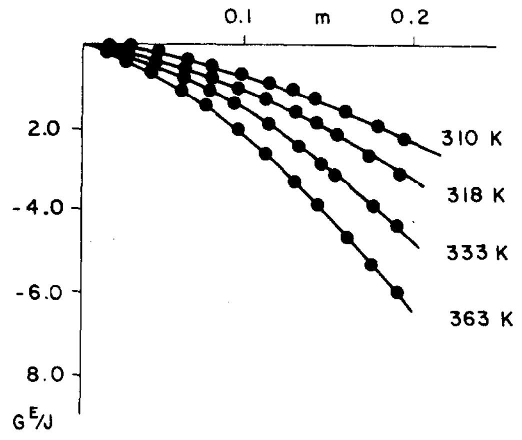

Fig. 9. Variation of excess Gibbs free energy, G^E, as a function of molality, *m*, in the temperature range 310–363 K, for STS.

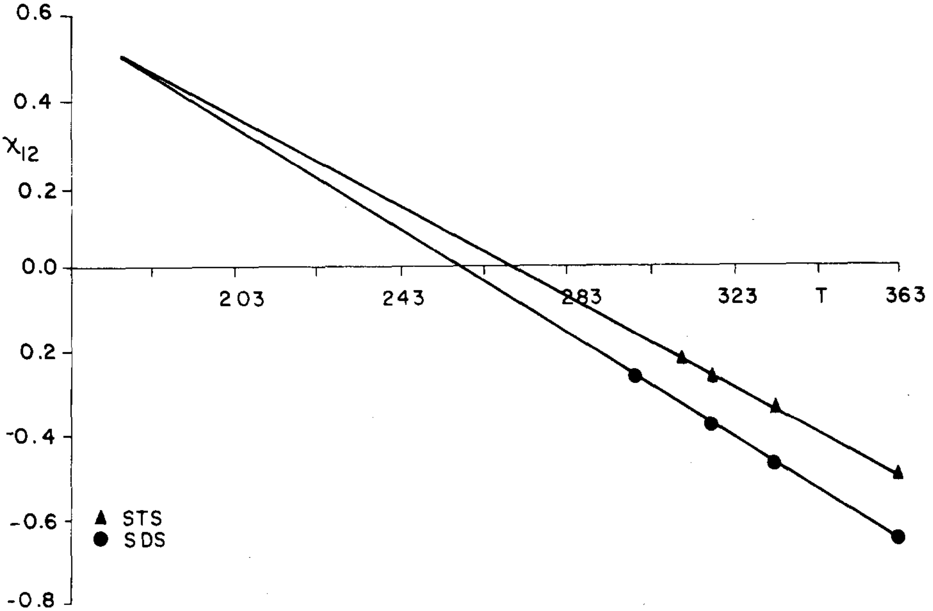

Fig. 10. Plot of solute–solvent interaction parameter, χ_{12}, as a function of temperature for SDS and STS.

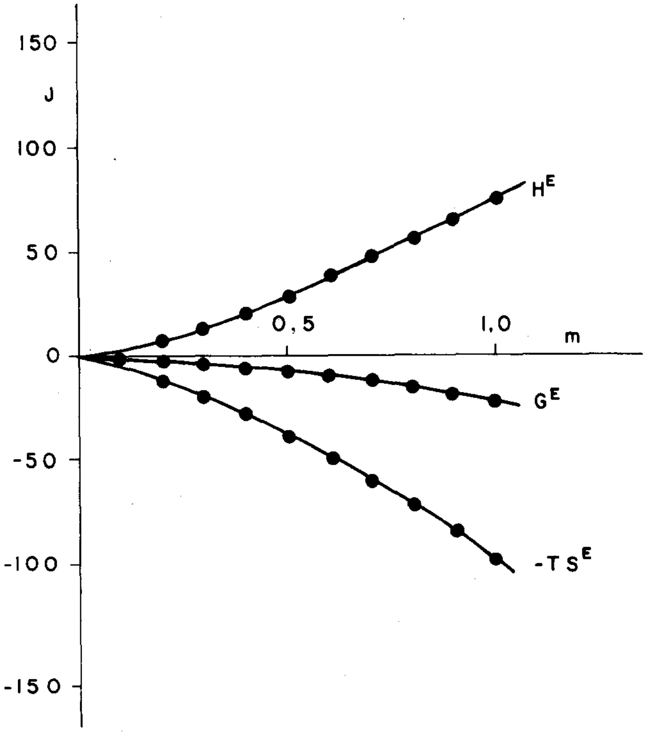

Fig. 11. Plot of excess functions as a function of molality, *m*, for SDS.

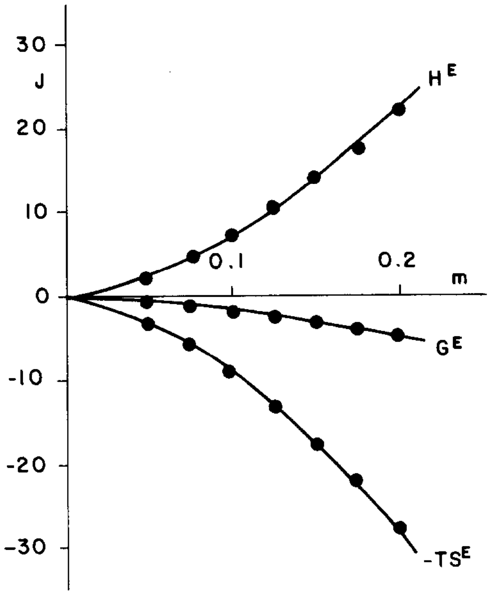

Fig. 12. Plot of excess functions as a function of molality, *m*, for STS.

to calculate S^E and H^E from the equations

$$S^E = -\left(\frac{\partial G^E}{\partial T}\right)_{p,x}$$

and

$$G^E = H^E - TS^E$$

In Figs. 11 and 12 the results at 333 K are shown for SDS and STS, respectively.

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