MICELLE FORMATION AND HYDROPHOBIC BONDING IN DEUTERIUM OXIDE[1]

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ABSTRACT

The critical micelle concentrations of sodium decyl and lauryl sulfates at 25°C have been determined from precise conductance data in water and in heavy water. The critical concentrations in heavy water are slightly lower (by about 2.5%). The solubility of sodium lauryl sulfate at 9°C is also only about 5% lower in heavy water. The conductance of both small ions and micelles approximately follow Walden's rule. The interpretation of the solubility and the critical concentration data lead to somewhat conflicting estimates regarding the relative strength of hydrophobic bonding in the two media: the difference in either case appears to be small. It is suggested that this result may be misleading because of compensating effects of dimerization of the long-chain ions.

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INTRODUCTION

Liquid deuterium oxide (D_2O) has been frequently used in the past to study the solvent isotope effects on various solutes, particularly inorganic electrolytes and those capable of hydrogen bonding or acid-base equilibria. Recently, there has been some interest in the structural aspects of D_2O[3-6] and in the solubility of non-polar solutes.[4,7] This prompts us to report some results obtained several years ago, which deal with the nature of hydrophobic bonding of long-chain compounds in D_2O, and brings out some of the difficulties and complications involved. Since D_2O is often used as a medium for studying biological macromolecules[8-10] or even living cells[10-12], and since hydrophobic bonding is important in most of these systems, the perturbation of hydrophobic bonding in changing the medium from ordinary water to D_2O as revealed by solubility and micellization effects may be of ~~more~~ some general interest.

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(3) C. G. Swain and R. F. W. Bader, Tetrahedron 10, 182, 200 (1960).

(4) C. G. Swain and E. R. Thornton, J. Am. Chem. Soc. 84, 822 (1962).

(5) P. M. Laughton and R. E. Robertson, Canadian J. Chem. 43, 154 (1965).

(6) G. Nemethy and H. A. Scheraga, J. Chem. Phys. 41, 680 (1964).

(7) A. Ben-Naim, J. Chem. Phys. 42, 1512 (1965).

(8) J. Hermans and H. A. Scheraga, Biochim. Biophys. Acta 36, 534 (1959).

(9) D. S. Berns, Biochemistry 2, 1377 (1963).

(10) A. Hattori, H. L. Crespi and J. J. Katz, Biochemistry 4, 1213 (1965).

(11) J. J. Katz, Amer. Scientist 48, 544 (1960).

(12) H. F. DaBoll, H. L. Crespi and J. J. Katz, Biotechnol. Bioeng. 4, 281 (1962).

This work was originally done in the hope that D_2O might prove to be a discriminating probe for the solvent-structure aspects of hydrophobic bonding. H_2O and D_2O are extremely closely matched in all properties except those most sensitive to structure. Thus the surface tension and the dielectric constant[6] of D_2O are lower than those of ordinary water at 25°C by 0.05% and 0.5% only, and it was felt that any interfacial energy effects and the electrical interactions involved in monomer-micelle equilibria should be extremely similar in the two media. On the other hand, the higher viscosity of deuterium oxide (23% higher than water at 25°C), the higher heat capacity (12% higher) and the higher temperature of maximum density (11.2°C compared to 4°C for water),[6] suggest that deuterium oxide is substantially more structured than ordinary water at room temperatures. Indeed, deuterium oxide has been compared to ordinary water at a lower temperature.[11] It was expected, therefore, that the processes like micelle formation in which water structure is widely held to play a predominant role[13] will be materially affected. However, it seems that "A number of competitive processes are involved, involving water-water interactions as well as water-solute or water-interface interactions. Since all of these change when one goes from H_2O to D_2O, a straightforward prediction does not seem easy."[14]

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(13) E. D. Goddard, C. A. J. Hoeve and G. C. Benson, J. Phys. Chem. 61, 593 (1957); P. Mukerjee and A. Ray, ibid. 67, 190 (1963).

(14) H. S. Frank, Personal communication, 1958.

EXPERIMENTAL

Materials

The sample of sodium lauryl sulfate (NaLS) was that of reference (15).

For sodium decyl sulfate, the samples used for H_2O and D_2O were different but they were prepared from the same batch of decyl alcohol in the same manner[16] and their conductivities below the critical micelle concentration (c.m.c.) in H_2O were in good agreement.[16] Similarly good agreement (within about 0.1%) was found for D_2O also.

The D_2O used had an isotopic composition of 99.5+% of deuterium.

Conductance Measurements

The apparatus is described in reference (15). A dilution cell with a doughnut-shaped conductance path, described previously (17) was used.

Solubility Measurements[18]

After long equilibration with the solid, the supernatant solution was filtered and its concentration determined by a spectrophotometric analysis using methylene blue.[19]

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(15) K. J. Mysels, and L. H. Princen, J. Phys. Chem. 63, 1696 (1959).

(16) K. J. Mysels and P. Kapauan, J. Colloid Sci., 16, 481 (1961).

(17) K. J. Mysels, J. Phys. Chem., 65, 1081 (1961).

(18) H. G. Meyers, M. S. Thesis, University of Southern California, 1959.

(19) P. Mukerjee, Anal. Chem., 28, 870 (1956).

RESULTS

The c.m.c.'s were determined from the specific conductance data. It is customary to plot these data against the concentration and to determine the c.m.c. from the intersection of the two straight lines describing the data below and above the c.m.c., neglecting the region of curvature close to the c.m.c.[20] Our conductance data of high relative precision (~ 0.02%) showed evidence of slight curvature in regions well separated from the c.m.c. Since we were primarily interested in the small change in the c.m.c. between H_2O and D_2O, it seemed appropriate to use data over the same concentration range for both media, fit the best straight lines by least squares methods, and obtain the c.m.c. from the calculated intersection point. The precision of the relative values of the c.m.c. was estimated to be about 0.5%. However, the slopes, particularly above the c.m.c., were of greater uncertainty, because of the small concentration range covered.

Table I records the slopes and intercepts of the equation $\chi = \alpha + \beta c$ where χ is the specific conductance, c the molar concentration and α and β are constants determined by least square fits over concentration ranges (in moles/liter) of 1.8 - 2.8 ($\times 10^{-2}$) and 3.8 -4.5 ($\times 10^{-2}$) for NaDS and 3.1 - 6.8 ($\times 10^{-3}$) and 10.2 - 11.6 ($\times 10^{-3}$) for NaLS. The c.m.c. values obtained are also indicated. The c.m.c. decreases by 2.7% and 2.4% for NaLS and NaDS respectively, on passing from H_2O to D_2O.

The difference in the c.m.c.'s, though small, is quite real. This is illustrated in Figure I and II where deviation plots for specific conductance data are shown near the c.m.c. region. The deviation functions were so chosen as to bring the data below the c.m.c. on the same line and the lower

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(20) E. D. Goddard and C. C. Benson, Canad. Jour. Chem., 35, 986 (1957).

portion of this line is not shown. Above the c.m.c., the conductance data show a consistent difference between the two solvents for both systems. The c.m.c's are marked by arrows.

The c.m.c. is not one single concentration but a range of concentrations. As may be seen from the graphs, however, the difference between the concentrations corresponding to the same changes are essentially constant throughout the range. A more objective and quantitative criterion is given by the concentration of micelles at the point selected as the c.m.c. which can be generally obtained from precise data in the transition region.[21] Thus, in our case Figure I and 2 show that the deviation of κ, i.e. $\Delta\kappa$, at the c.m.c., from the κ expected in the absence of micellisation, is very nearly the same for H_2O and D_2O. The $d\kappa/dc$ above the c.m.c. is a measure of conductance of micelles. The fraction that is micellized at the c.m.c. calculated on this basis is 2.4% and 2.3% for H_2O and D_2O for NaDS and 3.4% and 3.3% for H_2O and D_2O for NaLS. This close agreement supports the relative values of the c.m.c.

The solubilities of NaLS were determined at 9.0°C. The values were 7.31 ± 0.05 ($\times 10^{-3}$) in H_2O and 6.97 ± 0.07 ($\times 10^{-3}$) in D_2O, a ratio of $1.05 \pm .02$.

DISCUSSION

Conductance Values

The equivalent conductance (Λ) of inorganic ions like Na^+ or Cl^- in D_2O and H_2O do not follow Walden's rule exactly. Λ_o values (at infinite dilution) in H_2O and D_2O are in the ratio of 1.20 for K^+ and Na^+ and 1.216

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(21) R. J. Williams, J. N. Phillips and K. J. Mysels, Trans. Faraday Soc., 51, 728 (1955).

for Cl^- at 25°C.[22] compared to the fluidity ratio of 1.23.[23] The difference is not large, however. The ratio of the equivalent conductances for NaLS and for NaDS at comparable concentrations below the c.m.c. are 1.22 ± 0.01. The same ratio is shown by the β (= $d\kappa/dc$) values (below the c.m.c.) quoted in Table I, which give an average measure of Λ in the concentration range covered.

The β values above the c.m.c. can be taken to a good approximation as a measure of the conductance of micelles. These are in the ratio 1.29 ± 0.04 and 1.25±0.04 for NaLS and Na DS in H_2O and D_2O, and are not far from the fluidity ratios. The comparatively large uncertainties appear to be due to the presence of some curvature in the κ-c data above the c.m.c. and the relatively narrow range of concentrations available for direct comparison. The data for NaLS in D_2O were somewhat more extensive that those in H_2O for the same sample. If the much more extensive data for other highly similar samples of NaLS in H_2O[20,24] are used for comparison, the ratio of micellar conductances come closer to the fluidity ratio. Thus, to the extent the structural aspects and electrical interactions of micelles are reflected in their conductance, the difference between H_2O and D_2O is small.

Charge Effects and Free Energies of Transfer

The solubilities of inorganic electrolytes in D_2O have been extensively studied.[25] It is found that anhydrous 1:1 electrolytes are less soluble in

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(22) L. G. Longsworth and D. A. Mac Innes, J. Am. Chem. Soc., 59, 1666 (1937).

(23) R. C. Harday and R. L. Cottington, J. Res. Nat. Bur. Stands., 42, 573 (1949).

(24) K. J. Mysels and C. I Dulin, J. Colloid. Sci., 10, 461 (1955).

TABLE I

Constants for the Equation $K = \alpha + \beta c$
and the C.M.C. Data

	below c.m.c.		above c.m.c.		c.m.c.
	$\alpha \times 10^4$	$\beta \times 10$	$\alpha \times 10^4$	$\beta \times 10$	moles/liter
NaLS in H_2O	0.0800	0.6589	3.4663	0.2492	8.27×10^{-3}
NaLS in D_2O	0.0785	0.5399	2.8664	0.1936	8.05×10^{-3}
NaDS in H_2O	0.746	0.6161	11.627	0.2887	3.32×10^{-2}
NaDS in D_2O	0.756	0.5047	9.676	0.2306	3.25×10^{-2}

D_2O by 2 to 20% at 25°C. Most of the salts are highly soluble, so that it is difficult to disentangle the effects due to differences in activity coefficients and purely ion-solvent interactions which appear at infinite dilution. However, Greyson has recently studied the transfer free energies (ΔG) of some alkali metal chlorides from H_2O to D_2O in relatively dilute solutions (0.1M) using ion-exchange membrane potential measurements.[26] The estimated ΔG values at 9°C. from his enthalpy and entropy data are 130, 160, 200 and 200 calories/mole for Li^+, Na^+, K^+, and Cs^+ chlorides. In our case, ΔG, claculated by assuming that NaLS behaves as a 1:1 electrolyte with similar activity coefficients in H_2O and D_2O, is 60 ± 20 calories/mole. Clearly, differences in ion-solvent interactions alone are more than sufficient to explain the solubility difference and the chain contribution to ΔG of NaLS, if any, ~~is likely~~ appears to be negative, the chain being <u>stabilized</u> in D_2O.

For the interpretation of monomer-micelle equilibria, the ion-solvent interactions are irrelevant, since all charges presumably remain in contact with water. This does not preclude some influence of short range forces involving the solvent molecules at the highly charged micelle surface where interionic interactions are very strong. The difference in the free energy of micelle formation per monomer ($\Delta G'$), between H_2O and D_2O, calculated for the mass action model, neglecting dimerization and assuming a 70% binding

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(25) R. D Eddy and A.W.C. Menzies, J. Phys Chem., <u>44</u>, 207 (1940), see also A. H. Kimball "Bibliography of Research on Heavy Hydrogen Compounds", McGraw Hill, New York (1949).

(26) J. Greyson, J. Phys. Chem., <u>66</u>, 2218 (1962).

of the counterions, is about 25 calories/mole for both NaLS and NaDS, $\Delta G'$ being more negative in D_2O.[27] The more elaborate theory of Overbeek and Stigter,[28]

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(27) P. Mukerjee, J. Phys. Chem., 66, 2218 (1962).

(28) J. Th. Overbeek and D. Stigter, Rec. Trav. Chim., 75, 1263 (1956).

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assuming the same size for the micelle, gives about 30 calories/mole for NaLS. If all non-electrostatic interactions involved in the micelles in H_2O and D_2O are assumed to be the same, the $\Delta G'$ calculations indicate that the chain is destabilized in D_2O, i.e. it has a greater hydrophobic character in D_2O, but the difference is small.

Hydrophobic Interactions

The interpretation of the solubility and the c.m.c. values are conflicting, although the over-all solvent isotope effects on the long chains seems to be small. In the absence of any reliable theoretical framework, it is interesting to compare these effects with the relatively scanty results available for non-ionic solutes. Some solubility ratios between H_2O and D_2O, recently determined are, 0.92 for argon, at 25°C[7], ~1.00 for He above 50°C.,[29] and 0.98, 1.04, 1.07, and 1.10 for CH_3F, CH_3Cl,

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(29) E. F. Stephan, W. E. Berry and R. W. Fink, U. S. At. Energy Commission, BMI-1587, 1962, Chem. Abs., 57, 14485 (1962).

CH_3Br, CH_3I at 29.4°C.[4] There is a slight overall trend towards higher ratios with increasing molecular size. Guseva and Parnov have recently determined the solubilities of some hydrocarbons, n-heptane, toluene, and cyclohexane, at relatively high temperatures.[30] The ratios between H_2O and D_2O are about 1.10 - 1.12 between

80-100°C., decreasing slightly with rising temperature. Reasonable extrapolations of these values to room temperatures would give ratios of about 1.11-1.20. For large chains in our case, even larger factors may be reasonably expected.

A possible explanation of the discrepancy between our results and these very rough expectations is ~~not~~ that the c.m.c. or the saturated solution may not truly reflect the monomer-micelle equilibrium or the monomer-solid equilibrium because of pre-c.m.c. association, in particular, dimerisation.[31,32] Since dimerisation depends primarily on the hydrophobic interactions between the chains, if the hydrophobic character of the chains is stronger in D_2O, dimerisation should increase, resulting in an apparent *increase* in the solubility or the c.m.c. and thus compensating, in part, the expected decrease.[32]

We conclude, ~~moreover~~ therefore, that the differences in hydrophobic interactions between H_2O and D_2O are unlikely to be very great, but they may be substantially greater that the small differences estimated from solubility or c.m.c. data neglecting dimerization. Simpler equlibria, such as the distribution of monomers between phases or monomer-dimer equilibria, must be studied before more definitive statements can be made.

Acknowledgement: We are very grateful to Professor Karol J. Mysels for his interest and helpful criticism.

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(30) A. N. Guseva and E. I. Parnov, Radiokhimiya 5, 507 (1964), Chem. Abs. 60, 1174 (1964). The solubility ratios quoted in this paper for 25°C. from the literature appear to be due to a misinterpretation and are in fact ratios of solubilities of H_2O and D_2O in hydrocarbon solvents.

(31) F. Franks and H. T. Smith, J. Phys. Chem., 68, 3581 (1964).

(32) P. Mukerjee, J. Phys. Chem., in press.

LEGENDS FOR FIGURES

Figure 1. -- Plot of deviation function of specific conductance for NaLS at 25°C.

⊙ - in D_2O, $\Delta\kappa = \kappa(\text{exp.}) - 0.05399c$

Δ - in H_2O, $\Delta\kappa = \kappa(\text{exp.}) / 1.220 - 0.05399c + 0.0129 \times 10^{-4}$

Figure 2. -- Plot of deviation function of specific conductance for NaDS at 25°C.

⊙ - in D_2O, $\Delta\kappa = \kappa(\text{exp.}) - 0.05047c$

Δ - in H_2O, $\Delta\kappa = \kappa(\text{exp.}) / 1.221 - 0.05047c + 0.145 \times 10^{-4}$

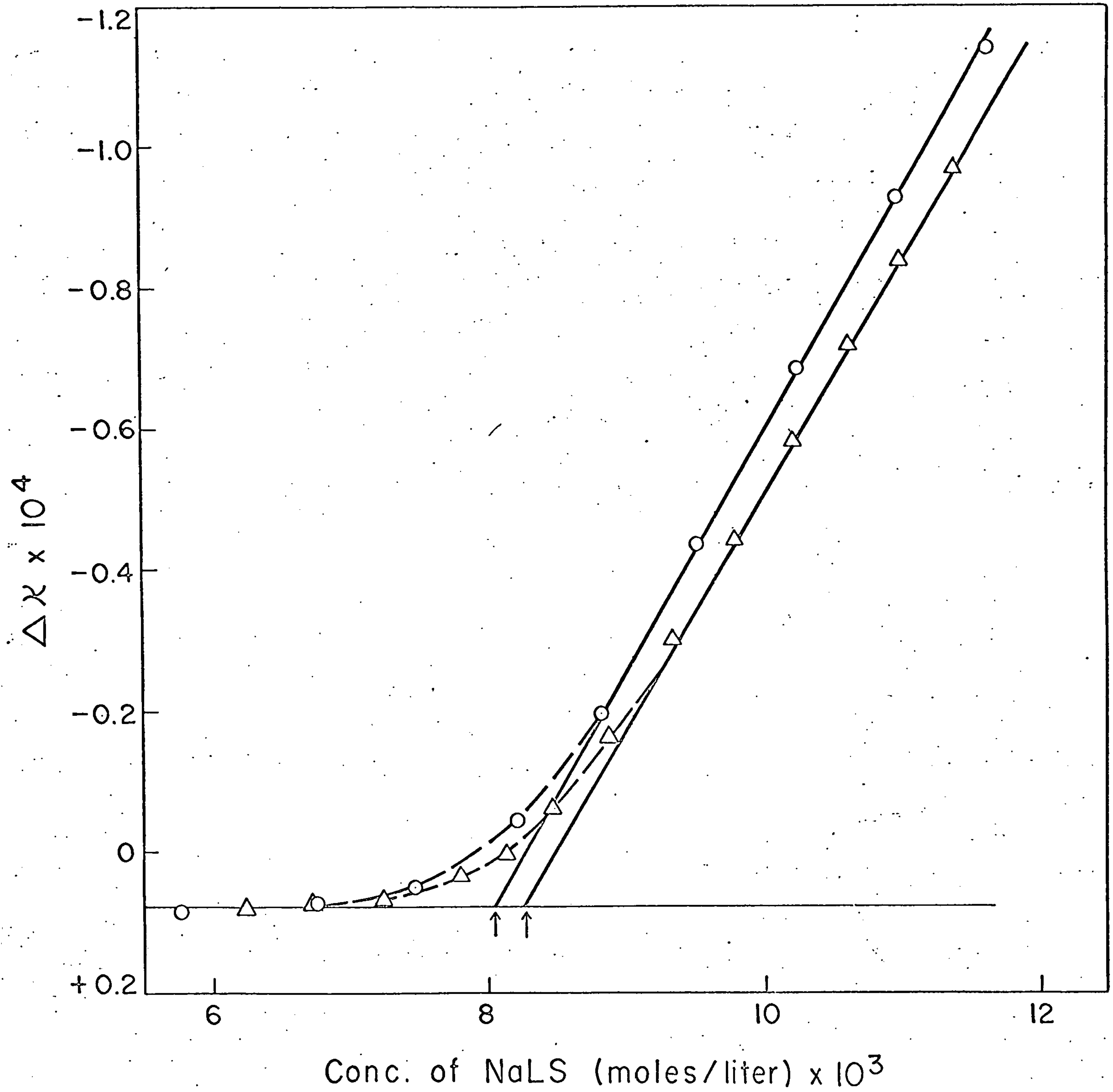
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
0
+0.2
6
8
10
12
$\Delta \varkappa \times 10^4$
Conc. of NaLS (moles/liter) x 10^3

Fig. 1

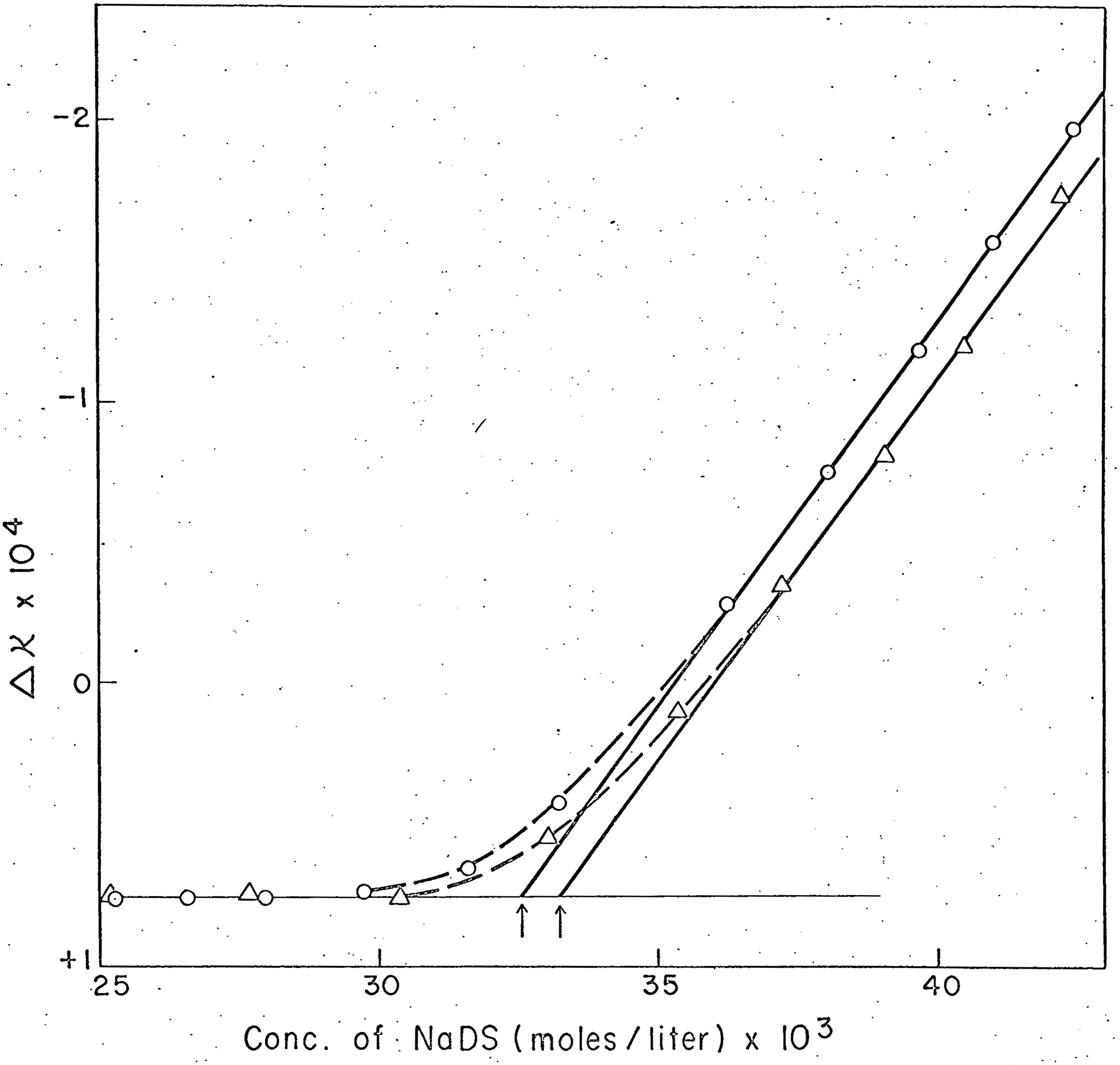

Fig. 2