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SOLUBILITY IN AMIDE-WATER COSOLVENT SYSTEMS IV: AMIDE ADSORPTION TO THE AIR/WATER INTERFACE

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INTRODUCTION

It has been suggested that alkylated amides which are used in aqueous cosolvent systems tend to accumulate at the solvent-hydrophobic solute interface (1). Indeed, the possibility that the solute may reside at or within some form of aggregated amide system in those cosolvents has been offered as well (2). In the least, such proposals would require the amides to possess surface or interfacial activity. The present study was undertaken to measure that activity.

EXPERIMENTAL

The procedure involved the determination of the surface tension of several pure amides and their 0.01 mole fraction amide-in-water systems. The latter were

TABLE 1. Surface tension, γ , of several pure amide and 0.01 mole fraction amide-in-water systems at 25°C.

	AMIDE SYSTEM			
	Pure	0.01 Mole Fraction Amide		
AMIDE	γ^o dyne/cm	fa[c]	γ(obs)	γ_c(Calc)
Formamide	57.4[a]	.021	71.1	71.7
N-Methylformamide	38.8[b]	.031	78.8	71.0
N-Ethylformamide	34.3	.039	64.7	70.5
N-Methylacetamide	34.4[b]	.039	68.0	70.5
N,N-Dimethylformamide	34.1[b]	.041	65.3	70.4
N-Ethylacetamide	33.1	.048	63.2	70.1
N-Methylpropionamide	31.7[b]	.047	63.9	70.1
N,N-Dimethylacetamide	33.2[b]	.047	63.8	70.2
N,N-Dimethylpropionamide	31.4	.055	59.0	69.8
N,N-Diethylformamide	28.1[b]	.056	52.8	69.5
N,N-Diethylacetamide	- -	.063	52.5	- -
N,N-Diethylpropionamide	27.7	.070	47.0	68.9
N,N-Dipropylacetamide	38.2	.079	36.6	69.3

a. R. L. Eissler and K. E. VanHolde, Illinois Geol Circ. No. 333, 20 (1962) and F. H. Getman, Rec. Trav. Chem. 55, 231 (1936)

b. R. Gopal and S. A. Rizvi, Jour. Indian Chem. Soc. 43 (3) 179 (1966)

c. Volume Fraction Amide-in-water, Reference 2.

studied since they corresponded to the cosolvent systems used in the previous work (1,2). A Rosanno surface tension balance (Biolar Corporation, North Grafton, Mass.), the operation of which is based on the Wilhelmy plate principle, was used for the measurements. A jacketed cell connected to a thermostated bath ensured a liquid temperature of 25.0 ± 0.1°C. Based on measured temperature coefficients, the uncertainty in the surface tension values obtained using this system was estimated to be within 0.04 dynes/cm. The uncertainties in the literature values cited in Table 1 were reported to be at least this good.

RESULTS AND DISCUSSION

Data from the present work and from the literature are shown in Table 1. Surface tension values, γc, were calculated for the various aqueous solutions according to the expression

$$\gamma_c = f_a \gamma_a^o + f_w \gamma_w^o \qquad (1)$$

Where f_a and f_w are the volume fractions of amide and water respectively; γ_a^o is the surface tension of the pure amide; and γ_w^o is the surface tension of pure water, taken as 72.0 dynes/cm at 25°C.

It is apparent from these data that calculated values are far from the mark in predicting the surface tension of even dilute aqueous solutions of alkylated amides. With the observed found to be lower than the calculated values, one must assume that the solution at the surface is richer in amides than is the bulk.

It is equally apparent that the cosolvents reflect significant surface activity for the amides which increases, not surprisingly, with their degree of alkylation. One should note, particularly, the reduction in the surface tension of the solutions when N,N-diethylpropionamide and N,N-dipropylacetamide are the cosolvents. The surface tension of the latter solution, in fact, is lower than that of the pure amide. Moreover, the data given in Table 1 for the solutions suggests that the surface tensions would drop precipitously if the amide volume fraction was increased further through the use of more highly alkylated amides in the cosolvents. The material at the air/water interface would of course set a lower limit on the surface tension decrease.

The surface phenomena observed in this study correspond with observations made with respect to the solubility of methyl p-hydroxybenzoate (1,2), in that the solubility of the ester increases as the surface tension of the respective cosolvents decrease. This follows the behavior suggested by Yalkowsky et al (3). More to the point, however, the present data demonstrate that even simple amides partition to an interface in proportion to their degree of alkylation.

Accordingly, it seems possible that the partitioning, with the resulting accumulation of amide at the solute surface, is an important aspect of the cosolvency mechanism in amide-water system. It remains unclear, however, whether or not amide aggregation compliments partitioning as a means of minimizing the energy in these cosolvent systems. One might anticipate that such a tendency to aggregate, coupled with a strong drive to partition to an interface would lead to phase separation. The latter has in fact been observed in these systems (2).

REFERENCES

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2. Giaquinto, A. R., Lindstrom, R. E., Swarbrick, J., LoSurdo, A., Jour. Solution Chem. 6, 687 (1977)
3. Yalkowsky, S. H., Amidon, G. L., Zografi, G. and Flynn, G. L., Jour. Pharm. Sci. 64, 48 (1975)